ADDIS ABABA UNIVERSITY
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL AND BIO ENGINEERING

Performance of Synthesized NaOH/Bentonite Catalyst for Production of Biodiesel from Cottonseed Oil

By Lamesign Desta

A Thesis

Submitted in Partial Fulfillment of the Requirement for the Degree of Master of Science in Chemical and Bio Engineering under Environmental Engineering Stream

Addis Ababa University
Addis Ababa, Ethiopia
June 2019

Addis Ababa University

Addis Ababa Institute of Technology

School of Chemical and Bio Engineering

This is to certify that the thesis prepared by Lamesign Desta, entitled: *Performance of Synthesized NaOH/Bentonite Catalyst for Production of Biodiesel from Cottonseed Oil* and submitted in partial fulfillment of the requirements for the degree of Masters of Science in Chemical and Bio Engineering complies with the regulation of the university and meets the accepted standards with respect to originality and quality.

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Declaration

I declare that this thesis entitled "*Performance of Synthesized NaOH/Bentonite Catalyst for Production of Biodiesel from Cottonseed Oil*" for the degree of Masters of Science at Addis Ababa institute of Technology is my own original work. The work has not been presented elsewhere for assessment. Where reference material has been used from other published and unpublished sources it has been properly acknowledged or referred.

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Abstract

In this study, NaOH/bentonite catalyst was synthesized and its performance was evaluated for biodiesel production from cottonseed oil. Impregnation method was used for the synthesis of NaOH/bentonite catalyst and the best catalyst was selected based on the yield of transesterification reactio. The highest yield of biodiesel was obtained by using the catalyst synthesized at 500 ^{0}C of calcination temperature, 5 hr. of calcination time, and NaOH to bentonite ratio of 0.20. The result of the XRD and FTIR characterization showed that the impregnation of NaOH was successful and the active and basic component Na_2O was obtained during calcination process. The optimization result showed that the optimum condition for the transesterification reaction by using the selected catalyst was a temperature of 64.45^{0}C, a catalyst loading of 2%w/w of cottonseed oil, and methanol to oil molar ratio of 6 which resulted in 89.7423% biodiesel yield. Different physicochemical properties of biodiesel produced at the optimum parameters were determined and it was in the range of international standards. The FAME content of the produced biodiesel was 95.8%, which was above the minimum requirement.

Key words: NaOH/*Bentonite, Impregnation, Transesterification, Biodiesel, Cottonseed Oil*

Acknowledgment

First and foremost I would like to express my deepest gratitude to my advisor Dr. Anteneh Marilign for his unwavering guidance, advice, critic, encouragement and insights throughout the study. I wish to express my thanks to Dr. Beteley T. for his support by providing bentonite for my laboratory work. I also thank all of the lab assistants for their valuable technical support, especially to Mr. Hentsa, and Mr. Alene.

I would like to thank Addis Mojo edible oil share company laboratory workers for their willingness to give information, encouragement, technical support and material assistance for the fulfillment of this study. I am grateful for my family and friends for their encouragement, assistance and for their endless moral support.

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Acronyms

ANOVA	Analysis Of Variance
ASTM	American Society of Testing and Material
BBD	Box Behnken Design
CN	Cetane Number
CSB	Cottonseed Biodiesel
CSO	Cottonseed Oil
FAEE	Fatty Acid Ethyl Ester
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
FID	Flame Ionization Detector
FTIR	Fourier Transform Infrared Spectroscopy
GCMS	Gas Chromatography Mass spectroscopy
GHG	Greenhouse Gas
HC	Hydrocarbon
ICCD	International Center for Diffraction Data
IV	Iodine Value
NO_X	Nitrogen Oxides
PAH	Polycyclic Aromatic Hydrocarbons
RSM	Response Surface Methodology
SG	Specific Gravity
SO_X	Sulfur Oxides
WCO	Waste Cooking Oil
XRD	X- Ray Diffraction

Chapter 1

1. Introduction

1.1. Background

Recently heterogeneous catalysts such as solid catalysts and enzyme catalysts are employed to catalyze transesterification reaction for producing biodiesel. Heterogeneous catalysts offers many advantages over homogeneous catalysts such as; simple catalyst recovery, catalyst reusability, simple product purification, less energy and water consumption, less added cost of purification, and simple glycerol recovery etc. Besides, most of the heterogeneous catalysts used especially solid alkaline catalysts have provided high yields, though faced with problem of leaching *(Riadi, Purwanto, Kurniawan, & Oktaviana, 2014*). Also, the stability of enzymes catalysts in non-aqueous media is significant to its excellent catalytic activity, this improves tranessterification and esterification during biodiesel production, and providing high biodiesel yield (95wt%) *(Watanabe, Shimada, Sugihara, & Noda, 2000).* However, the problem mostly associated with enzymes catalysts is the cost of the enzymes, but immobilization of the catalyst could mitigate the cost *(Shah, Sharma, & Gupta, 2004).*

Solid heterogeneous catalysts are noncorrosive, non-toxic, and easily-separated for recycling. Reusability of heterogeneous catalysts makes continuous fixed-bed operation possible. Such continuous process can minimize product separation and purification costs, make it economically viable to compete with commercial petroleum-based diesel fuel. Therefore, to achieve biodiesel that is economically feasible, development of active and cheap catalysts for effective transesterification of different kinds of feedstock's is necessary *(Chew & Bhatia, 2008).*

Sodium hydroxide (NaOH) has been manufactured by activating sodium carbonate with calcium hydroxide in a metathesis reaction. Calcium carbonate which is not soluble in solution is allowed to settle down and separated. The aqueous sodium hydroxide is heated to recover as a white solid substance. The process has later been superseded by the chloralkali process which is an electrolytic process using sodium chloride as the reactant material. Nowadays, sodium hydroxide is industrially produced by this chloralkali process using brine solution available in abundance.

Bentonite is a rock composed essentially of a crystalline clay-like mineral formed by devitrification and the accompanying chemical alteration of a glassy igneous material, usually a tuff or volcanic ash; and it often contains variable proportions of accessory crystal grains that were originally phenocrysts i n the volcanic glass. These are feldspar (commonly orthoclase and oligoclase), biotite, quartz, pyroxenes, zircon and various other minerals typical of volcanic rocks. The characteristic clay-like mineral has a micaceous habit and facile cleavage, high birefringence and a texture inherited from volcanic tuff or ash, and it is usually the mineral montmorillonite, but less often beide1lite (Clarence s. Ross and Earl v. Snannon, 1925).

Bentonites often contain detrital material from various sources in addition to the igneous rock phenocrysts, and sands may be mixed with bentonitic material in all proportions. I t is probably best to confine the name bentonite to material with a t least 75% of the bentonitic clay minerals and less than 25%, of sandlike or other impurities. If it contains between 25 and 75% of sandy impurities it may be called an arkosic bentonite and with less than 25% of the bentonitic clay minerals it may be called a bentonitic arkose. ‘Shales may also contain admixed bentonitic material, but in these its certain identification is very difficult or even quite impossible.

Recently, more than 95% of commercial biodiesel is produced from cotton seed, rapeseed, palm, and sunflower and soybean oil (Okechukwu, Nwanneka, Nonso, Ogechukwu, & Chukwudi, 2016). Out of these cotton seed is cheap in cost and non-edible nature so using it as feed stock will decrease the production cost of biodiesel. Cotton is a warm-weather shrub or tree of the Malvaceae family, the tribe Gossypieae, and the genus Gossypium that grows naturally as a perennial, but for commercial purposes it is grown as an annual crop. It is grown throughout Ethiopia at elevations above 1000 meters and below 1400 meters. Most of the cotton grown in the country is in and around the Awash Valley, in Gambella, in Omo Valley, Humera and Metema. The majority of the cotton is grown on large farms, some of which are irrigated, and is mostly picked by hand (Adelola & Ndudi, 2012). The cotton from these larger operations is ginned locally. As the seed is a waste of textile industry utilizing it for biodiesel production has an advantage in terms of economic development as well as environmental concern. In addition the prior existence of the seed reduces the land required for cultivation and initial cost of biodiesel, due to this the seed could has a potential to manufacture biodiesel commercially in Ethiopia. This could motivate the interest of investors employing on such project area.

1.2. Problem Statement

Replacement of diesel fuel by biodiesel is receiving considerable attention nowadays. Recently the commercialized biodiesel production was used homogeneous catalysts which have purification difficulties which makes the production cost too high. Contaminated effluent from processing of homogeneous catalysts has often caused environmental problems because large amounts of water are needed to remove the catalyst from the product.

To overcome the problems associated with homogeneous catalyzed transesterification process utilization of heterogeneous catalyst is necessary. Heterogeneous catalyzed biodiesel production processes have less number of unit operations; with simple product separation and purification steps, less environmental pollution and no neutralization process is required. The effectiveness of the heterogeneous catalytic conversion depends on the activity of the solid catalyst selected.

Recently, many researchers were performing experimentations with the aim to find solutions of the problems encountered by using homogeneous catalyst for transesterification reaction. As a result of exploration many of the solid catalysts have been explored with better catalytic performances. Different materials have been used previously as solid heterogeneous catalysts such as La_2O_3/ZrO_2, CaO, WO_3/ZrO_2, ZnO-La_2O_3 but the use of clay materials as solid catalyst is rarely been found. Although this process is good with respect to conversion of the reactants but not so economical because of the expensiveness of the elements employed.

Therefore developing of heterogeneous catalyst which has low price, simple preparation process, high stability and highly efficient lead to decrease the production cost and make the price of biodiesel in acceptable value. Clay materials are pervasive in nature as well as heterogeneous in its composition, particle size and also serve as good adsorbents Due to their great abundance, low cost, environmental compatibility, high selectivity, and unique physical and chemical properties bentonite can be used as a catalyst support. Bentonite is clay generated frequently from the alteration of volcanic ash, consisting predominantly of smectite minerals, usually montmorillonite.

In this study synthesis of NaOH/bentonite heterogeneous catalyst and its performance evaluation was carried out as a replacement of homogeneous catalyst for the transesterfication of cottonseed oil.

1.3. Objectives

1.3.1. General Objective

The general objective of this thesis was to synthesize, characterize and evaluate the performance NaOH/Bentonite catalyst for biodiesel production from cottonseed oil using trans-esterification process.

1.3.2. Specific Objective

- To study the effect of NaOH to bentonite proportion on the catalyst performance for transesterification reaction,
- To study the effect of calcination time during catalyst preparation on catalyst performance for transesterification reaction,
- To study the effect of calcination temperature during catalyst preparation on catalyst performance for transesterification reaction,
- To characterize the physicochemical properties of biodiesel,
- To study the catalyst reusability,
- To optimize reaction temperature, time and methanol to oil molar ratio for trans-esterification reaction.

1.4. Significance of the Study

This study was an experimental study on the synthesis and performance evaluation of NaOH/bentonite catalyst for production of biodiesel from cottonseed oil which have the following contribution such as;

- It gives a clear information on the synthesis of NaOH/bentonite catalyst
- It gives an additional alternative heterogeneous catalyst for production of biodiesel
- Motivates researchers to study further on this topic
- It utilizes locally available natural resources for the synthesis of catalyst

- Initiates investors to invest on renewable energy productions,
- Reduces the amount of contaminated effluents produced during the purification of homogeneous catalyzed reactions

Chapter 2

2. Literature Review

Recently, many researchers were performing experimentations with the aim to find solutions of the problems encountered by using homogeneous catalyst for transesterification reaction. As a result of exploration many of the solid catalysts have been explored with better catalytic performances. (Chen, Peng, Wang, & Wang, 2007) studied the transesterification of cottonseed oil with methanol in the presence of solid acids as heterogeneous catalysts. The solid acids were prepared by mounting H_2SO_4 on $TiO_2 \cdot nH_2O$ and $Zr(OH)_4$, respectively, followed by calcining at 823K. $TiO_2\text{-}SO_4{}^{2-}$ and $ZrO_2\text{-}SO_4{}^{2-}$ showed high activity for the transesterification. The yield of methyl esters was over 90% under the reaction conditions of temperature at 230°C, methanol/oil molar ratio of 12:1, reaction time 8 h and catalyst amount relative to oil amount (catalyst/oil) of 2% (w).

(Ali et al., 2016) studied the pre-blended palm and rubber seed oil as a viable feedstock for biodiesel production after pretreatment. The optimum conditions for acid catalyzed pre-treatment were obtained by using sulfuric acid as an acid catalyst at 1 wt. %, alcohol-to-oil ratio of 6:1 and reaction temperature of 62 ºC. The optimum conditions were validated and FFA % was reduced from 20% to less than 2 %. NaOH/bentonite was also investigated as a solid heterogeneous catalyst for transesterification using rapeseed oil as a model feedstock. The catalyst showed promising results by giving 92 wt. % yields at 62 °C and reaction time of 3 hours. These results revealed that NaOH/bentonite catalyst is feasible to use for the transestertification of pre-blended palm and rubber seed oil after pretreatment.

(Lingfeng, Guomin, Bo, & Guangyuan, 2007) investigated the possibility of using KF/γ-Al2O3 as heterogeneous catalysts for the transesterification of cottonseed oil with methanol. The operation variables used were methanol/oil molar ratio (6:1–18:1), catalyst concentration (1–5 wt %), temperature (50–68 °C), and catalyst type. The biodiesel with the best properties was obtained using a methanol/oil molar ratio of 12:1, catalyst (4%), and 65 °C temperature with the catalyst KF/γ-Al2O3. The strongest basic sites (superbasic) promote the transesterification reaction also at very low temperature (65 °C), while the basic sites of medium strength require higher temperatures to promote the same reaction.

(Flávia et al., 2015) studied the feasibility of using bentonite clays in their natural form, acidified and impregnated with CuO, ZnO and CeO_2 by a microwave-assisted solvothermal method, for use in the production of biodiesel. Characterization of the materials confirmed impregnation on the bentonite. Transesterification reactions were performed using the ethylic route at 200 ^{0}C in a Parr reactor for 1, 2 and 4 h. The results indicated that acidified bentonite led to the conversion of triacylglycerides into esters in addition to small amounts of diacylglycerides and monoacylglycerides. However, this material does not lead to the homogeneous impregnation of the oxides on its surface. For the natural bentonite, almost no conversion was obtained for the pure material, but a homogeneous impregnation with zinc oxide was attained, leading to 88% conversion after 4 h of a catalytic test.

As studied by (Sinha & Murugavelh, 2016) Production of fatty acid methyl esters from waste cotton seed oil through transesterification was reported. The GCMS analysis of WCCO oil was studied and the major fatty acids were found to be palmitic acid (27.76%) and linoleic acid (42.84%). The molecular weight of the oil was 881.039 g/mol. A maximum yield of 92% biodiesel was reported when the reaction temperature, time, methanol/oil ratio and catalyst loading rate were 60 ^{0}C, 50 min, 12:1 and 3% (wt.%), respectively. The calcined egg shell catalyst was prepared and characterized. Partial purification of the fatty acid methyl esters was proposed for increasing the purity of the biodiesel and better engine performance. The flash point and the fire point of the biodiesel were found to be 128 ^{O}C and 136 ^{O}C, respectively.

(Towards, Cotton, & Oil, 2010) studied biodiesel production in a cationic environment, at 338 K reaction temperature, the yield of biodiesel was observed to be high within 3 h at the molar ratio of 6:1, when the weight of cation-resin catalyst was 1.5 wt %, for reaction the yield of the biodiesel conversion was 80 %. Since the number of acidic sites of the catalyst and their contacting chances are high, the yield of biodiesel reaches higher value.

Liu et al. (2008) studied transesterification of soybean oil to biodiesel using CaO as a solid catalyst. The BET surface area of the catalyst was 0.56 m^2/g. The reaction was carried out using 12:1 M ratio of methanol to oil, 8 wt.% catalyst concentration at 65^{0}C. Biodiesel yield (95%) was obtained when reaction was carried out for 3 h. The authors also reported comparative activity of CaO with $K_2CO_3/\gamma Al_2O_3$ and $KF/\gamma Al_2O_3$ catalysts. Preparation of these catalysts was carried out by an impregnation method with the help of aqueous solution of potassium carbonate/potassium fluoride and then calcination of impregnated catalysts at 550^0C for 5 h. It was observed that CaO maintained sustained activity for longer time (20 cycles) after repeated use and biodiesel yield was also not affected, while $K_2CO_3/\gamma Al2O3$ and $KF/\gamma Al_2O_3$ catalysts were not able to maintain activity and biodiesel yield also got affected after every use. This was because that the alkali metal compounds dissolved in methanol, which reduced the active ingredients and thereby decreasing biodiesel yield in the subsequent experiments. It was also observed in this study that the presence of water, if in small amount of about 2.8 by wt.% of soybean oil, act as promoter, but if amount of water increases (more than 2.8 by wt.% of soybean oil) it hydrolyzed FAME under basic conditions and also induced soap formation.

The production of fatty acid esters from stearic, oleic, and palmitic acids and polyols (ethylene glycol and glycerol) was studied by (Chaari, Neji, & Frikha, 2017). A series of montmorillonite-based clays catalysts (KSF, KSF/0, KP10, and K10), having different physicochemical properties, were used as acidic catalysts. The influence of the specific surface area and the acidity of the catalysts on the esterification rate were explored. The best catalytic activities were obtained with KSF catalyst. The optimization of various factors on the reaction was also studied, including catalyst concentration, reaction temperature and molar ratio (polyol /fatty acid). The yield rate reached 94% under the optimum conditions and the recovery rate maintained more than 96% after 5 batches.

In the present study an investigation of NaOH/bentonite heterogeneous catalyst for production of biodiesel from cottonseed oil was conducted. As the preparation conditions have a significant effect on the activity of the catalyst; different preparation conditions were taken and their effects are investigated in this study. In addition to this parameters that affect transesterification reaction were studied at different values and the optimum value was proposed for further studies.

2.1. Energy

The world relies on fuel supply for its growth of population and its desire for a higher standard of living. The annual global primary energy consumption of 12 billion tons with the soaring surge of the population, it will increase the crude oil price and directly affects the global economic activity *(Y. He, Wang, & Lai, 2010)*. At present, fossil fuels have made up 80% of the primary energy consumption, which 58% of it is applied in the transportation sector *(Escobar et al., 2009)*. The mass-consumption of fossil fuels has raised concern for the alternative of renewable energy due to the negative effects towards environment, which includes severe climate changes, global warming and increase of sea levels. Among the four common renewable energy alternatives (hydrogen, natural gas, syngas and biofuel), the latter is most sustainable, effective, environment-friendly and ready to be used for automotive engine without further modification. Biofuels are liquid fuels made from plants and residues such as agricultural crops, municipal wastes, or agricultural and forestry by-products *(Balat & Balat, 2009)*. Consequently, research on biofuel production is continuously studied and developed in order to improve its sustainability and reliability as a source of green energy.

The attractiveness of biodiesel as an alternative to conventional fuel includes its engine compatibility and higher engine wear, high portability, ready availability, renewability, higher combustion efficiency, higher energy return, lower sulfur and aromatic content, higher cetane number and higher biodegradability *(Balat, 2011)*. Compared to the use of fossil fuels, combustion of biodiesel results in 490% decrease of total unburned hydrocarbons (HC), and a 75–90% reduce in polycyclic aromatic hydrocarbons (PAHs). Biodiesel also display a noteworthy decrease in particulates and carbon monoxide (CO) as compared to petroleum diesel fuel *(Demirbas, 2007)*. However, biodiesel is not exempted from its shortcomings, which include its higher viscosity, lower energy content, higher cloud point and pour point, higher nitrogen oxide (NOx) emission, lower engine speed and power and injector coking.

Although all of the above can be overcome by efforts of research and technology, the issue of “Food vs. fuel” remains to be a major setback as more than 95% of biodiesel is currently produced from conventionally grown edible oils such as rapeseed, soybean, sunflower and palm. In 2007, approximately 7% of global vegetable oil supplies were employed for biodiesel production. Until the year 2017, the usage is expected to reach up to a third of the edible oil production *(Wiebe et al., 2008)*.

Thus, the usage of non-edible oil as potential feedstock was proposed. Since non-edible oil is lower in cost as compared to edible oil, especially in developing countries where demand for edible oil as food is high, thus the biodiesel production capital is estimated to be lower *(Balat, 2011; Pramanik, 2003).*

2.2. Biodiesel Production Technologies

The direct use of vegetable oils and its blends as fuel in diesel engines had been considered both unsatisfactory and impractical, primarily due to high viscosity, acid composition and free fatty acid content of such oils, as well as gum formation due to oxidation and polymerization during storage and combustion. Carbon deposits and lubricating oil thickening are two of the more obvious problems. As a result of these problems, efforts have been undertaken to convert these vegetable oils to suitable and viable biodiesel fuels. Among the methods used to reduce viscosity and for biodiesel production are micro-emulsion, thermal cracking and transesterification (Ma & Hanna, 2003).

2.2.1. Micro-emulsion

The formation of micro emulsion is one of the potential solutions for solving the problem of vegetable oil viscosity. Micro-emulsions are defined as transparent, thermodynamically stable colloidal dispersion. The droplet diameters in micro-emulsions range from 100 to 1000 Å. Microemulsion can be made of vegetable oils with an ester and dispersant (co-solvent), or of vegetable oils, and alcohol and a surfactant and a cetane improver, with or without diesel fuels. All micro-emulsions with butanol, hexanol and octanol met the maximum viscosity requirement for diesel fuel. The 2-octanol was found to be an effective amphiphile in the micellar solubilization of methanol in triolein and soybean oil. Microemulsions can improve spray properties by explosive vaporization of the low boiling constituents in the micelles. Micro-emulsion results in reduction in viscosity increase in cetane number and good spray characters in the biodiesel.

2.2.2. Pyrolysis

Pyrolysis, strictly defined as the conversion of one substance into another by means of heat or by heat with the aid of a catalyst. Pyrolysis involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules. The pyrolysis of vegetable oil to produce biofuels has been studied and found to produce alkanes, alkenes, alkadienes, aromatics and carboxylic acids in various proportions. The equipment for thermal cracking and pyrolysis is expensive for modest biodiesel production particularly in developing countries. Furthermore, the removal of oxygen during the thermal processing also removes any environmental benefits of using an oxygenated fuel. Another disadvantage of pyrolysis is the need for separate distillation equipment for separation of the various fractions. Also the product obtained is similar to gasoline containing sulphur which makes it less ecofriendly (Abdulla, Chan, & Ravindra, 2011).

Pyrolytic chemistry is difficult to characterize because of the variety of reaction path and the variety of reaction products that may be obtained from the reaction occur. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The first pyrolysis of vegetable oil was conducted in an attempt to synthesize petroleum from vegetable (Gashaw & Teshita, 2014).

2.2.3. Trans-esterification

The most common way to produce biodiesel is the transesterification method, which refers to a catalyzed chemical reaction involving vegetable oil and alcohol to yield fatty acid alkyl esters (biodiesel) and glycerol. The reaction may be facilitated by catalyst using primary or secondary monohydric aliphatic alcohols having 1-8 carbon atoms. It should be noted that this equilibrium reaction needs greater amounts of alcohol to shift the reaction equilibrium forward to produce more methyl esters as the desired product. Although methanol and ethanol are most frequently used, ethanol is the preferred alcohol as it can be derived from agricultural products and is renewable and biologically less objectionable within the environment. However, methanol is mainly employed because of its low cost and its physical and chemical advantages (Demirbas, 2005). The transesterification reaction can be catalyzed by alkali, acid and enzyme catalysts.

a. Homogeneous acid catalyzed esterification reaction

Waste oils contain free fatty acids which cannot be converted to biodiesel using an alkaline catalyst. These FFAs will produce soap that inhibit the separation of the ester, glycerin, and wash water when react with an alkaline catalyst. Hence, liquid acid-catalyzed transesterification is proposed in order to overcome lots of conundrum caused by liquid base catalysts. Sulfuric acid, sulfonic acid, hydrochloric acid, organic sulfonic acid, and ferric sulphate are most commonly acids used as catalysts in transesterification *(Atadashi et al., 2012).*

In the production of biodiesel, hydrochloric acid and sulfuric acid are favored as catalyst. Despite of its insensitivity to FFA in the feedstock and can catalyzes esterification and transesterification simultaneously, acid catalyst has been less popular in transesterification reaction because it has relatively slower reaction rate (Arzamendi et al., 2007; Kouzu et al., 2008). Thus, alcohol to oil molar ratio is the main factor influencing the reaction. Addition of excess alcohol can speeds up the reaction and favors the formation biodiesel product. The steps involve during acid-catalyzed transesterification are initial protonation of the acid to give an oxonium ion followed by the oxonium ion and an alcohol undergo exchange reaction to give the intermediate which later loses a proton to become an ester (Atadashi et al., 2013).

b. Homogeneous Alkali-catalyzed transesterification process

Homogeneous alkaline catalysts are more preferable and commonly used since transesterification reaction using its acid counterpart has slower rate. The most common basic catalysts are potassium hydroxide (KOH), potassium methoxide ($KOCH_3$), sodium hydroxide (NaOH), sodium methoxide ($NaOCH_3$), and sodium ethoxide ($NaOCH_2CH_3$) (Atadashi et al., 2013; Halder, Paul, & Beg, 2014; Lam, Lee, & Mohamed, 2010). These catalysts are commonly used because of several advantages such as able to catalyze reaction at low reaction temperature and atmospheric pressure, high conversion in shorter time, and economically available. Sodium methoxide ($NaOCH_3$) and potassium methoxide ($KOCH_3$) are better catalyst than sodium hydroxide (NaOH) and potassium hydroxide (KOH) due to the ability to dissociate into CH_3O^- and Na^+ and CH_3O^- and K^+ respectively when comparing on biodiesel yield. Alkaline catalyst is more commonly used in commercial biodiesel production because it does not form water during transesterification reaction *(Halder et al., 2014).*

NaOH and KOH are the most common homogeneous base catalyst in biodiesel production. The highest biodiesel yield produced by Calophyllum inophyllum was reported by Silitonga et al. (2014) with 98.53% by using 1 wt% KOH and 9:1 methanol to oil ratio. Silva, Camargo, and Ferreira (2011) reported 95% of biodiesel yield from soybean oil by using NaOH with 1.3 wt% catalysts loading and ethanol to oil ratio of 9:1

c. Two step transesterification process

This method is useful when dealing with feedstocks containing high free fatty acids (FFAs). It has been shown that alkaline catalysts cannot directly catalyze the transesterification of oils containing high FFAs safe for FFA levels ranging from a mass fraction of 0.5% to less than 3% of the oil (Atadashi, Aroua, Abdul Aziz, & Sulaiman, 2012). The transesterification of high FFA oils can be achieved by employing a two-step transesterification process. In this technique, the first step is an acid catalyzed process which involves esterification of the FFAs to FAMEs as described in Section a, followed by a second step, alkali catalyzed transesterification, as described in Section b. Various studies have been conducted using this technique with reported high yields of biodiesel (Berchmans & Hirata, 2008). Although a limit of <3% FFA level in oils has been reported as acceptable for homogeneous alkaline catalysis for biodiesel production without pretreatment, the FFA contents may extend beyond this limit, as it has been reported that a two-step process can also be achieved using alkaline catalysis in both steps to maximize overall yield at room temperature. Ten percent increase in percentage yield was recorded using a two-step alkaline catalysis for a feedstock containing 4% FFAs (Wang, Ou, Liu, Xue, & Tang, 2006).

d. Heterogeneous base-catalyzed transesterification

Numbers of research have been conducted on heterogeneous catalysts to overcome the problems caused by homogeneous catalyst in biodiesel production. Most of the heterogeneous catalysts developed for production of biodiesel are either alkaline oxide or alkaline earth metal oxide supported over large surface area. Heterogeneous basic catalysts are more active than heterogeneous acid catalyst, similar to their homogeneous counterparts *(Arzamendi et al., 2007).* In addition, solid alkaline catalysts, for instance, calcium oxide (CaO) provide many advantages such as higher activity, long catalyst life times, and could run in moderate reaction condition. Nonetheless, CaO as catalyst can also slow down the reaction rate of biodiesel production. Notwithstanding, reaction of CaO with glycerol can leach out calcium diglyceroxide during transesterification which result in necessity of an extra purification step such as ion exchange resin to remove the soluble content in the biodiesel *(Talha & Sulaiman, 2016).*

The highest biodiesel yield was reported by *(Wong, 2009)* with 96.5% obtained from soybean oil by using oyster shells as catalyst. The transesterification was done in 65˚C using methanol as alcohol with ratio of 6:1 and 25 wt% catalysts loading for 5 hours reaction. *(Viriya-Empikul,* *Krasae, Nualpaeng, Yoosuk, & Faungnawakij, 2012*) obtained 94.1% biodiesel yield from palm olein oil when the transesterification was done in 60˚C for 2 hours with methanol to oil ratio of 15:1 and 10 wt% catalysts loading. Whilst Wei et al. (2009) reported 95% biodiesel yield on soybean oil. The reaction was conducted in 65˚C for 3 hours and the methanol to oil ratio was 9:1 with 3 wt% catalysts loading.

Most of the literature reported on heterogeneous base catalyst used lower reaction temperature (<65˚C). As a matter of fact, temperature above 70˚C will result in lower yield as methanol evaporates at 65˚C. Furthermore, base-catalyzed transesterification was proved to have higher reaction rate as compared to acid-catalyzed transesterification which need more vigorous reaction condition including higher temperature during transesterification *(Lam et al., 2010).*

e. Heterogeneous acid catalyzed transesterification

Despite of the effectiveness of homogeneous acid catalyst, it can lead to absolute contamination problems which require good separation and product purification processes. This will be resulted in higher production cost. It is believed that heterogeneous acid catalysts have the potential as alternative to homogeneous acid catalysts. Some of advantages of heterogeneous acid catalyst are insensitive to FFA content, can simultaneously conduct esterification and transesterification, eliminate the washing step of biodiesel, simpler separation process of catalyst from product, regenerating and reusing the catalyst is possible and also reduce the corrosion problems *(Halder et al., 2014; Lam et al., 2010).*

In addition, solid acid catalysts are preferred over liquid acid catalysts due the fact that they contain a multiple sites with different strength of Bronsted or Lewis acidity (Atadashi et al., 2013; Helwani, Othman, Aziz, Kim, & Fernando, 2009). Bronsted acid catalysts have the advantage of promoting simultaneous esterification and transesterification with the use of cheaper feedstock containing high concentration of free fatty acids. A Lewis acid site is more active as compared to Bronsted but is at risk to poisoning from water and/or free fatty acids. Generally said, the low activity of acid catalysts relative to the counterpart basic ones is due to different reaction mechanism. However, efforts to utilizing heterogeneous acid catalyst for transesterification of triglycerides are limited due to daunting point of view for its low reaction rates and possible adverse side reaction *(Helwani et al., 2009)*. Consequently, the mechanisms and factors influence the reactivity of the solid acid catalysts have not fully understood.

f. Supercritical transesterification

While the catalyzed route of production of biodiesel is the most common route used industrially, the major drawbacks of this method include the necessity of treating the free fatty acids and the triglycerides in different reaction stages, the negative effects of any water present in the mixture, catalyst consumption, the necessity of removing traces of the catalyst from the product mixture, the wastes produced, low glycerin purity, and generation of waste water. Any non-catalyzed route bears an inherent attraction associated with the absence of most of these disadvantages due to the absence of the catalyst. Production of biodiesel at supercritical conditions is one such method, where the reaction is carried out at supercritical conditions. Under such conditions, the mixture becomes homogeneous where both the esterification of free fatty acids and the transesterification of triglycerides occur without the need for a catalyst, rendering this method suitable for any type of raw material, especially those that are otherwise difficult to treat using conventional methods, such as animal fats and oils high in free fatty acids (Al-Zuhair, Hussein, Al-Marzouqi, & Hashim, 2012).

Most studies have focused on methanol and ethanol as the alcohols of choice. The key operating parameters, then, have been identified as the temperature, pressure, and methanolto-oil ratio (Marulanda, Anitescu, & Tavlarides, 2010). The typical range of operating conditions over the last decade have been temperatures of 280-400 ^{0}C and pressures of 10-30 MPa (Sawangkeaw, Bunyakiat, & Ngamprasertsith, 2010). Earlier studies investigated pressures up to 45 MPa. Though attractive for many reasons, the challenges regarding this method include the high alcohol-to-triglycerides molar ratios necessary to 42:1 in the case of methanol, and high operating temperatures and pressures.

Table 2.1: Comparison of homogeneous and heterogeneous catalysis for biodiesel production

Type	Advantage	Disadvantages
Homogeneous catalysts	• Modest operation conditions • Base catalyst give favorable kinetics, high activity and give high yield in short time • Base catalysts are 4000 times faster reaction than acid catalyzed transesterifcation • Basic methoxides are more effective than hydroxides • Acid catalysts can be used for both esterification and transesterification simultaneously • Acid catalysts are preferred for low grade oils and are insensitive to FFA and water	• Separation of waste problem after reaction • Saponification, emulsion formation • Catalyst reuse not possible • Limited to batch type of reactors • Basic catalysts are sensitive to the presence of FFA and water • High production cost compared with heterogeneous type • Acid catalysts are corrosive and give very small reaction rate • Acid catalysts require higher molar ratio of methanol to oil, higher temperature, concentration acid and more waste from neutralization reaction
Heterogeneous catalysts	• Environmentally benign, noncorrosive, recyclable, fewer disposal problems • Ease separation of products, higher selectivity, longer catalyst life • Acid heterogeneous catalyze both esterification and transesterification simultaneously and insensitive to FFA and water • Comparatively cheap • Can be used in continuous fixed bed reactors	• Currently moderate conversion compare to high active basic homogeneous • Mass transfer limitation due to the presence of three phase and need well mixing • Basic catalysts require low FFA and anhydrous condition and pretreatments is required for high FFA feedstock • High alcohol to oil ratio required, high temperature and pressure • Acidic catalysts: low acid site concentration, low microporosity, and high cost compared with basic types

g. Enzyme-catalyzed transesterification process

The search for a truly environmentally-friendly approach for biodiesel production has intensified research into the use of enzymes as catalysts. The challenges faced when conventional catalysts are employed are feedstock pretreatment, catalyst removal, waste water treatment and high energy requirement are alleviated in enzyme-catalyzed transesterification reactions. Biocatalysis is mediated by a group of enzymes called lipases, produced by microorganisms, animals and plants (Gog, Roman, Toşa, Paizs, & Irimie, 2012). There are two main groups of lipases: extracellular lipases and intracellular lipases. Intracellular lipases are usually employed in the whole-cell form, eliminating enzyme purification and separation processes. In order to improve enzyme stability and reusability, lipases can be immobilized on several materials.

Biocatalysis is characterized by high selectivity and efficiency, consequent absence of side reactions, and high yield of methyl esters. Further, glycerol recovery is easier and of high grade as compared to what is obtained in the alkaline process. Unlike the conventional chemical catalytic routes, biocatalysis is applicable with a wide range of triglyceride sources, with FFA ranging from 0.5% to 80% (Gog et al., 2012). Investigation of the kinetics of Rhizopus oryzae lipase indicated that free fatty acids (FFA) contained in waste oils and fats can be completely converted to alkyl esters at temperatures in the range 30 to 40 ^{0}C. On the other hand, alkali catalyzed transesterification reactions, which are often carried out at temperatures in the range 60-70 ^{0}C, are characterized by significant reductions in ester yields in the presence of high FFAs (Gog et al., 2012).

In spite of the attractiveness of biocatalysis, its commercial application is hampered by certain demerits. These include: 1) high production cost of the lipase catalyst; 2) higher reaction times as compared to base-catalyzed reaction systems; and 3) regeneration and re use of biocatalysts limited with a long operating time (Demirbas, 2005).

h. Ultrasound assisted transesterification

The theory of ultrasonication and its application in many reacting systems has been widely reported as this provides the mechanical energy for mixing needed to initiate reaction (Aransiola, Ojumu, Oyekola, & Madzimbamuto, 2013). In transesterification, it causes cavitation of bubbles near the phase boundary between the alcohol and oil phases leading to intensive mixing of the system. The cavitation leads to a localized increase in temperature, and due to the formation of micro jets, neither agitation nor heating are required to produce biodiesel by ultrasound application (Hsiao & Lin, 2013).

As reviewed by Koh and Mohd. Ghazi, ultrasonication increases the chemical reaction speed, the efficient molar ratio of methanol-to-oil, and the transesterification yield of vegetable oils and animal fats into biodiesel. This method clearly works with less energy consumption compared to the conventional mechanical stirring method (Aransiola et al., 2013).

The major problem associated with this method, however, is in the downstream processing. The amount of catalyst used in the process has a significant environmental impact. Large amounts of catalyst tend to produce a larger amount of soap (an undesired product) and part of the catalyst remains in the biodiesel, increasing its pH. After the completion of the transesterification reaction, biodiesel is separated from the alcohol phase and then is washed with water to remove excess catalyst, soap and glycerin, generating large amounts of waste water that should be treated (Hsiao & Lin, 2013). This increases the purification cost, deterring the viability of the process.

2.3. The Chemistry of Transesterification Reaction

Generally, the main contents of vegetable oil and animal fats were triglycerides. The common and industrial method to produce biodiesel is chemically described as the transesterification of oil with short chain alcohol. The overall reaction equation is listed in Fig. 2.1. And this transesterification of triglycerides with alcohol is a three steps reversible reaction as shown in Fig. 2.2. This reaction proceeds essentially by mixing the reactants, however, it may accelerate with the presence of a catalyst (Nishimura et al., 2012).

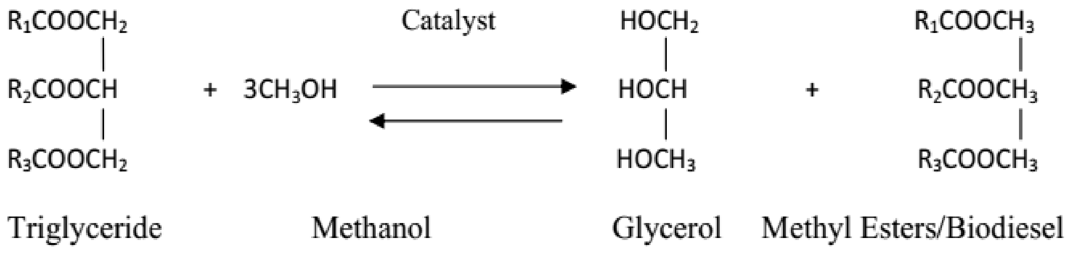
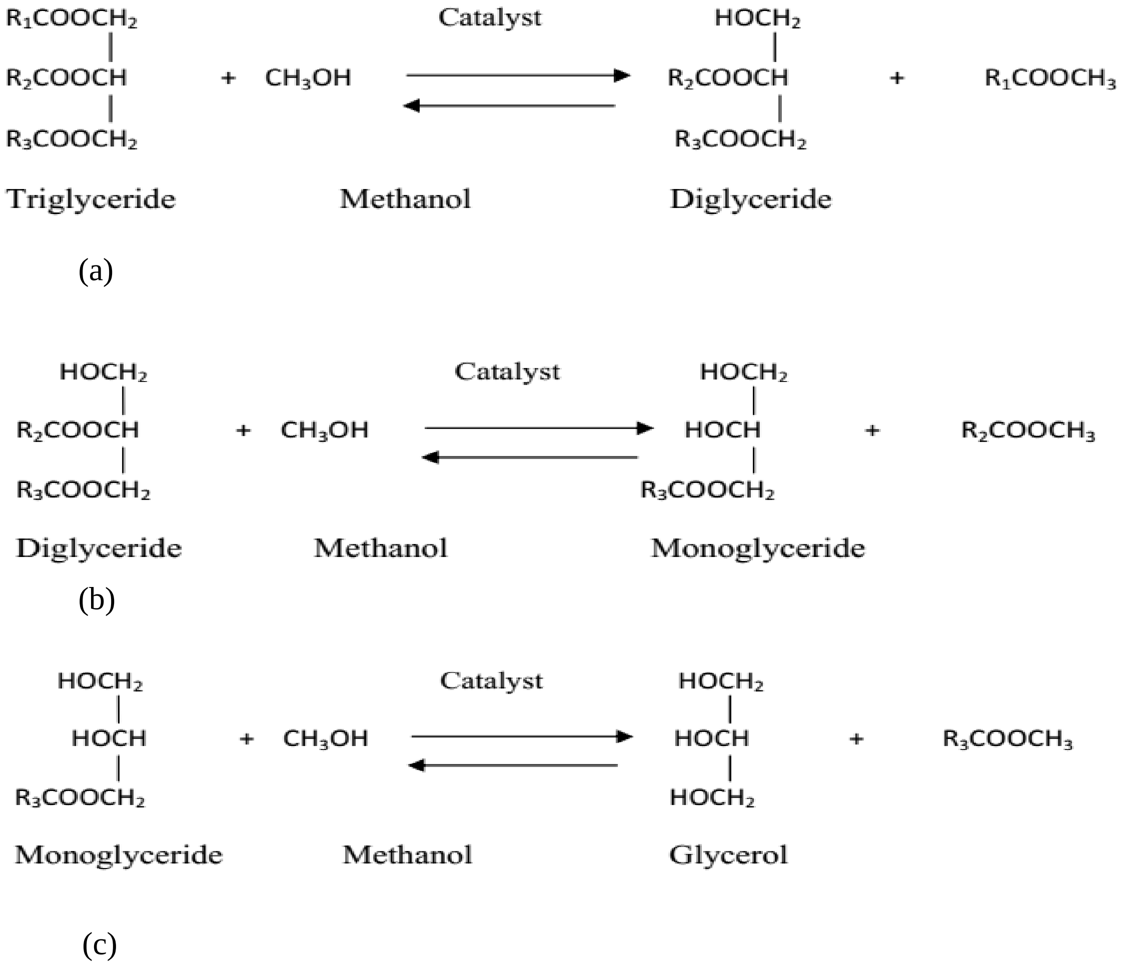


Figure 2.1: The overall transesterification reaction of vegetable oil with alcohol.



(a)

(b)

(c)

Figure 2.2: Stepwise and reversible chemical reactions of vegetable oil (a) triglyceride to diglyceride, (b) diglyceride to monoglyceride, and (c) monoglyceride to methyl ester.

The overall process is normally a sequence of three consecutive steps, which are reversible reactions. In the first step, from triglycerides diglyceride is obtained, from diglyceride monoglyceride is produced and in the last step, from monoglycerides glycerin is obtained. In all these reactions esters are produced. The stoichiometric relation between alcohol and the oil is 3:1. However, an excess of alcohol is usually more appropriate to improve the reaction towards the desired product.

2.4. Factors Affecting Trans-esterification Reaction

The process of transesterification brings about drastic change in viscosity of the vegetable oil. The high viscosity component, glycerol, is removed and hence the product has low viscosity like the fossil fuels. The biodiesel produced is totally miscible with mineral diesel in any proportion. Flash point of the biodiesel is lowered after transesterification and the cetane number is improved. The yield of biodiesel in the process of transesterification is affected by several process parameters which include; presence of moisture and free fatty acids (FFA), reaction time, reaction temperature, catalyst and molar ratio of alcohol and oil (Abdulla et al., 2011).

2.4.1. Reaction Temperature

Reaction temperature is the important factor that will affect the yield of biodiesel. For example, higher reaction temperature increases the reaction rate and shortened the reaction time due to the reduction in viscosity of oils. However, the increase in reaction temperature beyond the optimal level leads to decrease of biodiesel yield, because higher reaction temperature accelerates the saponification of triglycerides (Mathiyazhagan & Ganapathi, 2011) and causes methanol to vaporize resulting in decreased yield (Anitha & Dawn, 2013).

Usually the transesterification reaction temperature should be below the boiling point of alcohol in order to prevent the alcohol evaporation. The range of optimal reaction temperature may vary from 50°c to 60°c depends upon the oils or fats used (Mathiyazhagan & Ganapathi, 2011). Therefore, the reaction temperature near the boiling point of the alcohol is recommended for faster conversion by various literatures. At room temperature, there is up to 78% conversion after 60 minutes, and this indicated that the methyl esterification of the FFAs could be carried out appreciably at room temperature but might require a longer reaction time. In butyl esterification, however, temperature had stronger influence. Temperature increases the energy of the reacting molecules and also improves the miscibility of the alcoholic polar media into a non-polar oily phase, resulting in much faster reactions (Ogbu & Ajiwe, 2013).

2.4.2. Reaction time

The increase in fatty acid esters conversion observed when there is an increase in reaction time. The reaction is slow at the beginning due to mixing and dispersion of alcohol and oil. After that the reaction proceeds very fast. However the maximum ester conversion was achieved within less than 90 min. Further increase in reaction time does not increase the yield product i.e. biodiesel/mono alkyl ester. Besides, longer reaction time leads to the reduction of end product (biodiesel) due to the reversible reaction of transesterification resulting in loss of esters as well as soap formation (Jagadale & Jugulkar, 2012)

2.4.3. Methanol to oil molar ratio

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. In order to shift the reaction to the right, it is necessary to either use excess alcohol or remove one of the products from the reaction mixture. The second option is usually preferred for the reaction to proceed to completion. The reaction rate is found to be highest when 100% excess methanol is used (Abdallah Sayed Ahmed Ali El-Gharbawy, 2016).

Methanol, ethanol, propanol, butanol and amyl alcohol can be used in the transesterification reaction, amongst these alcohols methanol is applied more frequently as its cost is low and it is physically and chemically advantageous (polar and shortest chain alcohol) over the other alcohols. In contrast, ethanol is also preferred alcohol for using in the transesterification process compared to methanol since it is derived from agricultural products and is renewable and biologically less offensive in the environment. The effect of volumetric ratio of methanol and ethanol to oil was studied. Results exhibit that highest biodiesel yield is nearly 99.5% at 1:6 oil/methanol. In comparison, biodiesel yield using methanol continuously increases with the raise of methanol molar ratio (Sharif Hossain & AlEissa, 2015).

2.4.4. Mixing intensity

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. So, Mixing is very important in the transesterification process, adequate mixing between these two types of feedstock is necessary to promote contact between these two feed stocks, therefore enhance the transesterification reactions to occur (Jagadale & Jugulkar, 2012). Most literatures indicate that during the transesterification reaction, the reactants initially form a two-phase liquid system. The mixing effect has been found to play a significant role in the slow rate of the reaction. As phase separation ceases, mixing becomes insignificant. The effect of mixing on the kinetics of the transesterification process forms the basis for process scale-up and design (Shereena & Thangaraj, 2009).

The intensity of the mixing could be varied depending on its necessity in the transesterification process. In general, the mixing intensity must be increased to ensure good and uniform mixing of the feedstock. When vegetable oils with high kinematic viscosity are used as the feedstock, intensive mechanical mixing is required to overcome the negative effect of viscosity to the mass transfer between oil, alcohol and catalyst (Jagadale & Jugulkar, 2012).

2.4.5. Free fatty acid and water content

The FFA and moisture contents have significant effects on the transesterification of glycerides with alcohol using catalyst. The high FFA content (>1% w/w) will happen soap formation and the separation of products will be exceedingly difficult, and as a result, it has low yield of biodiesel product (Berchmans & Hirata, 2008). In addition formation of gels and foams hinders the separation of glycerol from biodiesel. For instance, Water content in waste cooking oil will accelerate the hydrolysis reaction and simultaneously reduce the amount of ester formation (Arun, 2010).

To overcome this problem, supercritical methanol method was proposed. It may be noted that water has less influence in supercritical methanol method (Mathiyazhagan & Ganapathi, 2011). Therefore, water content should not always exceed 0.5% to obtain 90% yield of biodiesel and it is more critical for an acid catalyzed reaction than base catalyzed reaction.

2.4.6. Type and amount of catalyst

Biodiesel formation is also affected by the concentration of catalyst. Most commonly used catalyst for biodiesel production is sodium hydroxide (NaOH) or Potassium hydroxide (KOH) (Mathiyazhagan & Ganapathi, 2011). The type and amount of catalyst required in the transesterification process usually depend on the quality of the feedstock and method applied for the transesterification process. For a purified feedstock, any type of catalyst could be used for the transesterification process. However, for feedstock with high moisture and free fatty acids contents, homogenous transesterification process is unsuitable due to high possibility of saponification process instead of transesterification process to occur.

The yield of fatty acid alkyl esters generally increases with increasing amount of catalyst. This is due to availability of more active sites by additions of larger amount of catalyst in the transesterification process. However, on economic perspective, larger amount of catalyst may not be profitable due to cost of the catalyst itself. Therefore, similar to the ratio of oil to alcohol, optimization process is necessary to determine the optimum amount of catalyst required in the transesterification process (Jagadale & Jugulkar, 2012).

As it was discussed in section 2.2 there are different types of catalyst for transesterification reaction for the production of biodiesel from different types of oil. From the different factors that affect transesterification reaction the type and amount of catalyst utilized is high degree of influences on the yield of biodiesel. Recently heterogeneous catalysts get a high attention for biodiesel production due to its advantageous over homogeneous catalyst. Therefore; it is essential to discuss about solid catalyst and its synthesis in the next section to get a clear understanding about it.

2.5. Solid/Heterogeneous Catalyst

Solid catalysts are highly sophisticated products derived from chemicals by means of several different procedures. The catalytic properties of heterogeneous catalysts are strongly affected by every step of the preparation together with the quality of the raw materials (Vedrineb, 2002). The choice of a laboratory method for preparing a given catalyst depends on the physical and chemical characteristics desired in the final composition. It is easily understood that the preparation methods are also dependent on the choice of the base materials and experience shows that several ways of preparation can be considered, even for a given selection of the base material (Bartholomew, 2006). A solid catalyst mainly consists of catalytic agent, support or carrier and promoters and inhibitors

2.5.1. Catalytic agent

These are the catalytically active component in the catalyst. These components generate the active sites that participate in the chemical reaction. Activity of any catalyst is proportional to the concentration of these active sites. Though concentration of the active sites depends on the amount of catalytically active component, however, it is not always directly proportional.

Availability of active sites depends mainly on the dispersion of catalytic agent. The dispersion is defined as ratio of total number of exposed atoms/molecules of catalytic agent available for reaction to total number of atoms/molecules of catalytic agent present in the catalyst sample (Vedrineb, 2002).

2.5.2. Support or carrier

Support or carrier provides large surface area for dispersion of small amount of catalytically active agent. This is particularly important when expensive metals are used as the active agent. Supports give the catalysts its physical form, texture, mechanical resistance and certain activity particularly for bi-functional catalysts. Area of the support can range from 1-1000m^2/gm. Common supports are alumina, silica, silica-alumina, molecular sieves etc (Vedrineb, 2002).

Support may be inert or interact with the active component. This interaction may result in change in surface structure of active agent and thereby affect the catalyst activity and selectivity. The support may also exhibit ability to adsorb reactant and contribute to the reaction process (Jong, 2009).

2.5.3. Promoters

Promoters are generally defined as substances added during preparation of catalyst that improve the activity or selectivity or stabilize the catalytic agents. The promoter is present in a small amount and by itself has little or no activity (Vedrineb, 2002). Promoters are termed as physical or chemical promoter depending on the manner they improve the catalyst performance.

The additives that maintain physical integrity of the support and/or deposited catalytic agents are termed as physical promoters. For example, addition of small quantities of alumina to an iron catalyst employed in ammonia synthesis prevents sintering of the iron crystallites. Thus, for this catalyst, alumina is a physical promoter. The addition of K_2O to the same catalyst increases the intrinsic activity of the iron crystallites and therefore acts as a chemical promoter. The promoter can be added during catalyst preparation or during reaction (Haber J, Machej T, Serwicka EM, 2014).

2.6. Preparation of Supported Catalysts

In supported catalysts, the catalytically active materials are dispersed over the high surface area support material. Supported catalysts are prepared by deposition of the active metal on the support materials. The main purpose of using a support is to achieve an optimal dispersion of the catalytically active component and to stabilize it against sintering. But in many reactions the support is not inert and the overall process consists of two catalytic functions both for active components and support. Supported catalysts are prepared in two main steps (Regalbuto, 1999).

- Deposition of the precursor of the active component on the support.
- Transformation of this deposited precursor to catalytically active site.

The final active component can be in metallic state, oxide form or reduced form depending on the requirements. There are various deposition methods. Most of these involve aqueous solutions and liquid solid interface. In some cases, deposition is also done from the gas phase and involves gas-solid interfaces. The methods most frequently used for supported catalyst preparation are impregnation and ion exchange.

2.6.1. Impregnation method of catalyst preparation

The simplest and probably the most common procedure for dispersing a catalytic species on a carrier involve impregnating the pre-dried support to incipient wetness with an aqueous or non-aqueous solution containing the precursor of the catalytic element or elements. Impregnation can be classified into two categories based on the volume of solution used(Bartholomew, 2006).

- Dry or incipient impregnation

In this method, a previously dried support is contacted with volume of solution equal to its pore volume. The solution contains the required amount of the precursors of the active phase. As soon as the support is placed in contact with the solution, the solution is drawn into the pores by capillary suction. In case of proper wetting, no excess solution remains outside the pore space. Part of the air present in the pores is imprisoned and compressed under the effect of capillary forces (Vedrineb, 2002).

- Wet/diffusional impregnation

In this method the pore space of the support is first filled with the same solvent as used in the impregnating precursor solution. The wetted support is then treated with the impregnating precursor solution. Here the actual impregnation takes place in diffusional condition when solvent filled support is dipped in the precursor solution.

The first phase of saturation of the support by solvent involves the characteristics of dry impregnation. But in the second phase, when solvent saturated support is added to the impregnating solution, high pressure is not developed within the pores. The precursor salt migrates progressively from the solution into the pores of the support (Regalbuto, 1999). The driving force at all times is the concentration gradient between the bulk solution and the solution within the pores. The impregnation time is much longer than for dry impregnation. After impregnation process was finished the next step is drying.

2.6.2. Drying

Impregnation is followed by elimination of the solvent. The impregenated sample is heated in an oven in a flow of gas. The gas may be air, oxygen, nitrogen or any other gas depending on the requirement. The temperature is generally maintained slightly higher than the boiling point of the solvent e.g 110-120^{0}C for water. The elimination of waters from the pores leads to the increase of precursor concentration up to saturation and consequent crystallization, preferably on the seeds resulting from the interaction with the support. Apart from temperature, heating rate affects the drying process (Komiyama, 2006).

2.6.3. Calcination

This high temperature treatment in air is often the last step in producing oxide catalysts or the next to the last step in producing metal or metal sulfide catalysts. Its purpose is to decompose and volatilize the various catalysts precursors formed in preparation, such as hydroxides, nitrates or carbonates, which are not the desired forms for the final catalyst. For decomposition of unsupported hydroxide or carbonate precursors, or precursors supported on inorganic oxide carriers, calcination is typically conducted in air at a temperature of 300-500^{O}C (Boullosa-eiras, 2011). Great care must be taken to carefully pre-dry the solid and to avoid rapid heat-up during calcination since H_20 trapped in the micropores can build up sufficient pressure to crack particulate carriers. Furthermore, exothermic reactions due to decomposing salts can cause localized high temperatures within the catalyst material, which can accelerate sintering of the carrier and catalytic material (Bartholomew, 2006). Multiple changes are occurring during this process including:

- ✓ Active phase generation: the hydroxide form is converted to oxide form.
- ✓ Stabilization of mechanical properties: the catalysts sample is subjected to a more severe heat treatment than that is likely to be encountered in a reactor. This ensures the stability of its textural and structural properties during reaction.
- ✓ Loss of chemically bound water: the chemically bound water is removed at higher temperature.
- ✓ Changes in pore size distribution and surface area due to sintering: treating the sample at high temperature over an extended period of time leads to sintering and consequently decreases the surface area.
- ✓ Changes in phase distribution: higher temperature causes material to crystalize into different structural forms.

The extent of change in the physical characteristics of the final catalyst depends on the calcination temperature, calcination time and gaseous environment of the calcination process.

2.7. Natural Bentonite

Bentonite is an aluminum phyllosilicate generated frequently from the alteration of volcanic ash, consisting predominantly of smectite minerals, mostly montmorillonite (80-90 % by weight). Due to its special properties, bentonite is a versatile material for geotechnical engineering and as well as their demand for different industrial applications *(Abdullahi & Audu, 2017; Noaman et al., 2015)*. For different purposes, different properties are emphasized and appropriate test methods have been developed. Mineralogical and chemical composition affects the properties of bentonite. On the other hand, the measured physical characteristics are frequently used to interpret the mineralogical composition of bentonite.

Two types of bentonite exist: swelling bentonite which is also called sodium bentonite and non-swelling bentonite or calcium bentonite. Majority of bentonites occurring worldwide are of the calcium type *(Abdullahi & Audu, 2017*).

Clay deposits and clay minerals generally vary in nature, no two or more deposits can have exactly same clay minerals and frequently different samples of clay from the same deposits differ. Their physical and chemical properties (swelling ability, plasticity, cation exchange capacity etc) vary typically within and between deposits due to the differences in the degree of chemical substitution within the smectite structure and nature of exchangeable cations present, and also due to the type and amount of impurities present *(Abdullahi & Audu, 2017; Yogendra Prasad Upadhyay, 2013)*. The most common impurities in bentonite clay are quartz, calcite, feldspar, cristobalite, beotite, kaolinite, mica and organic matter while hydrated iron oxide, ferrous carbonate and pyrite are being the minor impurities depending on the nature of their genesis.

Bentonite is widely used in various industrial products and processes such as pharmaceuticals, cosmetics and drilling fluids to modify the rheology and control the stability of systems. It is used as a plasticizer in ceramics, as an emulsifying agent in asphaltic substances, as thickener and extender for paints, as adhesive in concrete mixtures, horticultural sprays and insecticides, adsorbent in removal of dyes and heavy metals, and in bleaching earth in refining oils and fats. (Pushpaletha, Rugmini, & Lalithambika, 2005)

The widespread use of bentonite can be attributed to its physical and chemical properties such as small particle size, high porosity, large surface area and high cation exchange capacity (Onu, Okafor, & Kovo, 2015). The bentonite has excellent adsorption capacity and its adsorption ability is determined by the chemical nature and pore structure (Koyuncu, 2008). In addition to, it is available in abundance in almost all parts of world. Another reason for the wide use of bentonite is the ease of modification by using simple methods (Sanjay & Sugunan, 2008). Recently a large reserve of bentonite has been found in Ethiopian Rift valley and its extension into the Afar depression in northeastern Ethiopia host extensive bentonite deposits. The wide spread silicic volcanism and lake environments produce the most favorable sites for the accumulation of acidic volcanic ash. The alteration of these ashes is the basis for the formation of bentonite.

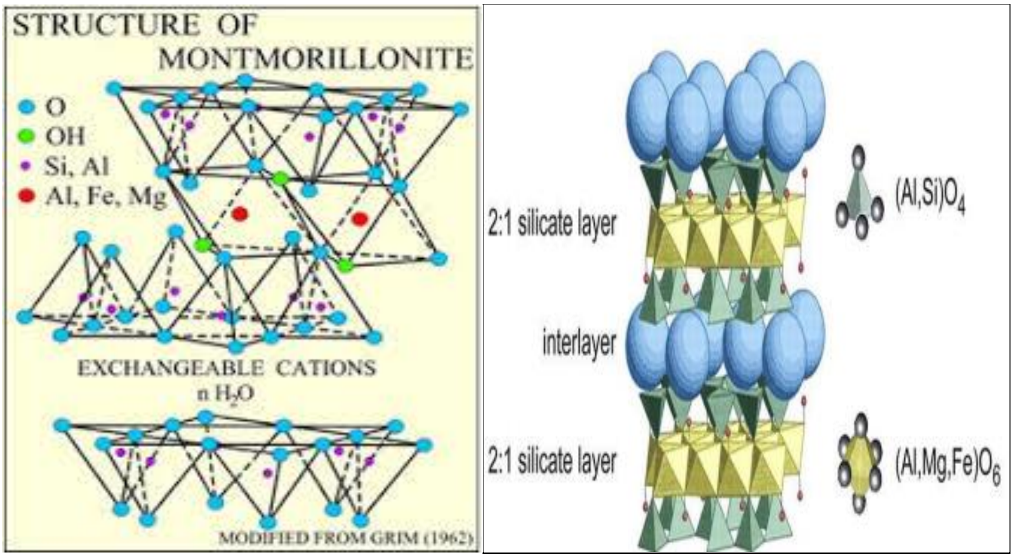


Figure 2.3: Structures of bentonite/ mentmorillonite

2.7.1. Bentonite in Ethiopia

Bentonites here formed by the chemical alteration of volcanic ash in the presence of water such as in a lake. Such a unique volcanic setting has been provided by the spreading of tectonic plates along the East African Rift. Bentonitic clay resources are found in the Afar and oromia regions. They are easily accessible, as they are located near the main road. The main occurrences in afar are located at Ledi, Gewane, Hadar and Warseiso. The Gidicho Island in Lake Abaya in the rift valley is another source of bentonitic clay. This occurrence is of Pleistocene lacustrine origin and occurs in association with diatomite, silt and diatomaceous earth *(Tessema, 2012).*

2.8. Cotton Seed Oil

The cottonseed crop is a fast growing plant with long productive life span of 3-4 months, its ability to survive on drought and poor soils at average and high temperature up to 44°C and a low temperature of up to 4°C cotton was the third biggest of the crops grown worldwide, as measured by acreage: soybean was 47%, occupying 75.4 million hectares; biotech maize (51.00 million hectares at 32%), biotech cotton (24.7 million hectares at 15%) and biotech canola (8.2 million hectares at 5%). The cotton plant (genus Gossypium) is a member of the Malvaceae, or mallow, family. In its native form, cotton grows as a perennial, but it is cultivated as an annual crop in the United States. There are dozens of cotton species native to both the Eastern and Western hemispheres and the use of cotton fibbers can be traced back thousands of years in present-day Peru and Egypt *(Yogendra Prasad Upadhyay, 2013)*.

The fatty acid profile of cottonseed oil is typical of the oleic-linoleic group of vegetable oils since these two-unsaturated fatty acids make up almost 75% of the total fatty acids. Oleic makes up about 22%, linoleic about 52% and linolenic acid is usually less than 1%. Palmitic acid a saturated fatty acid usually associated with β crystals make up around 24% of the total and only minor amounts of other saturated fatty acids, stearic and myristic, are detected in typical cottonseed oils *(O’brien, 2002)*

Cottonseed oil is unique among the commercially important fats and oils in the presence of a relatively complex system of pigments. Most of the pigments are of the gossypol. Gossypol is one of natural toxin in cottonseed oil, according to “Institutional Food Management,” by Mohini Seth (2006) in people; gossypol inhibits sperm production as well as motility.

Gossypol is a toxic phenolic C40 compound present in cotton boll cavities. When the seed is extracted, the gossypol adheres to the protein meal and only a small proportion remains in the crude oil giving it a red-brown colour. This is largely removed during refining – especially through caustic refining and bleaching when it falls to safe levels, not exceeding 1–5 ppm, cids, stearic and myristic, are detected in typical cottonseed oils *(O’brien, 2002).*

The characteristics of a particular cottonseed oil sample are dependent upon the variety of cotton grown and on growing conditions such as temperature, soil conditions, fertilizers, and rainfall, as well as the handling and storage conditions after harvesting. Factors that contribute to variations in the properties of cottonseed oil before it is crushed or extracted from the seed are geographic regions, climate, fertilizers, seed handling, and storage conditions (Pettigrew & Dowd, 2014). Both the chemical and physical properties of fats and oils are largely determined by the fatty acids that they contain and their position within the triacylglycerol molecule. Chemically, all fats and oils are esters of glycerol and fatty acids. Nevertheless, the physical properties of natural fats and oils vary widely. This is because (1) the proportion of the fatty acids varies over wide ranges, and (2) the triacylglycerol structures vary for each individual oil and fat. Fats and oils are commonly referred to as triacylglycerols (triglycerides) because the glycerol molecule has three hydroxyl groups where a fatty acid can be attached (Z. He, Shankle, Zhang, & Way, 2010).

2.8.1. Cottonseed oil in Ethiopia

Cotton is grown in different parts of Ethiopia at elevations above 1000 meters and below 1400 meters. Most of the cotton grown in the country is in and around the Awash Valley, in Gambella, in Omo Valley, Humera and Metema. The majority of the cotton is grown on large farms, some of which are irrigated, and is mostly picked by hand. The cotton from these larger operations is ginned locally. As the seed is a waste of textile industry utilizing it for biodiesel production has an advantage in terms of economic development as well as environmental concern. In addition the prior existence of the seed reduces the land required for cultivation and initial cost of biodiesel, due to this the seed could has a potential to manufacture biodiesel commercially in Ethiopia.*(Gebreyohannes, 2017)*

Figure 2.4: Cotton tree and its seeds

Table 2.2: Targets of Ethiopia's national cotton development strategy (2017-2032)
Source (Francom & Counselor, 2018)

No.	Year			
	2017	2020	2025	2032
Cotton seed production (MT)	79,173	281,120	828,900	1,401,840
Oil content (%)	15%	16%	18%	20%
Cottonseed oil production(MT)	11,876	44,979	149,202	280,368

Chapter 3

3. Materials and Methods

3.1. Preparation of NaOH/Bentonite catalyst

3.1.1. Materials

The materials used for the synthesis of NaOH/bentonite catalyst was natural bentonite, NaOH, distilled water, and hydrogen peroxide.

3.1.2. Methods

The raw bentonite was immersed in hydrogen peroxide solution (30%) at room temperature for 24 h in order to remove organic impurities. The ratio between hydrogen peroxide and bentonite were 2:1 for efficient removal of organic impurities. After the bentonite was soaked for 24 hours excess hydrogen peroxide was removed by heating the mixture gently in a boiling water bath at 100 ^{0}C and subsequently the solution was separated from bentonite. The purified bentonite was washed in distilled water and allowed to settle, the ratio of purified bentonite to distilled water used for washing were 1:4. After settling water and purified bentonite was separated, and the purified bentonite was dried in oven at 110 °C until its moisture content reached 10%. Finally the dried bentonite was crushed using hammer mill to obtain powdered bentonite and sieved using 80/100 meshes and stored in plastic bag.

NaOH/Bentonite catalyst was prepared by using impregnation method at Addis Ababa University, school of chemical and bio engineering laboratory (appendix F). A series of NaOH/bentonite catalysts for biodiesel production was prepared by using the following procedure. By varying the ratios of NaOH to bentonite three samples was prepared. The impregnation process was conducted in a beaker (500 mL) at a temperature of 60 °C for 8 h under continuous stirring. The proportions and mass of the components are shown below in table 3.1.

Table 3.1: Ratio and mass of the components during impregnation

Ratio of NaOH to bentonite	Mass of the components (gram)		Mass of the impregnated catalyst after drying (g)
	NaOH	Bentonite	
2:10	8.00	40.00	45.25
3.5:10	17.50	50.00	62.89
5:10	20.00	40.00	55.74

After the impregnation process, the slurry was subjected for drying in an oven at 110 °C for 24 h to remove water. Then the dried catalyst was subjected to size reduction using mortar and pestle until the desired size obtained. Finally, the catalyst was calcined in a furnace at different temperature 400, 500 and 600 °C by varying the calcination time at 3, 4 and 5 h (appendix C-1). The prepared NaOH/Bentonite catalyst was placed in a desiccators and then packed with polyethylene bag to avoid any adsorption of moisture and other contaminants on the surface *(Soetaredjo, Ayucitra, Ismadji, & Maukar, 2011*).

3.2. Characterization of cottonseed oil

Purified cottonseed oil was obtained from Addis Modjo edible oil Share Company and its physicochemical property data’s were taken from their laboratory results. Fatty acid composition and some analytical values of the purified cottonseed oil were measured by laboratory technicians of the company and its value used as it is for this study.

3.3. Transesterification reaction for the selection of best catalyst

3.3.1. Materials

Cottonseed oil, analytical grade methanol, and NaOH/bentonite catalyst was used for the transesterification reaction to select the best efficient catalyst.

3.3.2. Methods

The performance or efficiency of the synthesized catalysts was primarily tested for the conversion of cottonseed oil to fatty acid methyl ether by using transesterification reaction under constant operating conditions. Transesterification of cottonseed oil was carried out in a three-neck round bottom flask (500 mL) equipped with a reflux condenser, temperature indicator, and mechanical stirrer.

The reactor was placed in a controlled water bath heater at $65^{O}C$ (Ali et al., 2016). A known amount of catalyst loading of 1%w/w of cottonseed oil was added to a known volume of methanol. Then the mixture was heated to the desired temperature (65 °C) in a controlled temperature water bath. Subsequently, 50ml cottonseed oil was added into the mixture under vigorous stirring (500 rpm). The molar ratio of methanol to oil was 9:1 (appendix B-1) and the transesterification reaction was carried out for 3h. At the end of the reaction time, the solution was centrifuged to separate the solid catalyst. The glycerol and biodiesel phases were separated by using a separator funnel. After separation the solution was heated at 105 °C to remove methanol and the pure biodiesel mass and volume was recorded. The efficient catalyst was determined by calculating biodiesel yield using equation 3.1 and design expert Box-Behnken response surface methodology.

$$yield\ (\%) = \frac{wight\ of\ biodiesel}{wight\ of\ cottenseed\ oil} * 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.1$$

3.4. Characterization of the selected catalyst

3.4.1. X-ray diffraction (XRD) characterization

The crystal phase of the raw bentonite and the catalyst were obtained by using powder X-ray diffraction (XRD) patterns recorded on a Rigaku Miniflex Goniometer at 40 kV and 15 mA, using Cu Kα radiation of wavelength 1.54059 at a step size of 0.02° at Addis Ababa university; college of natural and computational science.

3.4.2. Fourier Transformed Infrared radiation (FTIR) characterization

Qualitative and functional groups analysis of the raw bentonite and the catalyst were performed using Fourier Transformed Infrared 65FTIR (PerkinElmer) in the range 4000-400 cm^{-1} wavenumber spectrum using KBr pellet.

3.5. Optimization of transesterification reaction for the selected catalyst

3.5.1. Materials

Cottonseed oil, analytical grade methanol, and NaOH/bentonite catalyst was used for the optimization of selected transesterification reaction parameters.

3.5.2. Methods

The best efficient catalyst was selected from previous experiment and used to find the optimal reaction conditions of the transesterification reaction for the production of FAME. In this experiment, reaction temperature, catalyst to oil weight ratio, and methanol to oil molar ratio were selected as independent input process variables and its level are described in (appendix C-2). The trans-esterification reaction was carried out similarly to the first experiment by varying the above three parameters in three levels. Time of reaction and agitation speed was maintained constant at 3 hours and 500 rpm similar to the above reaction. The optimum values of the selected factors were determined based on the yield of biodiesel using Box-Behnken Design of Response Surface Methodology.

The biodiesel yield produced on each run was determined by using equation 3.1. The weight of biodiesel was measured for each run and the yield was calculated relative to the weight of cottonseed oil as:

3.6. Determination of Physicochemical property of biodiesel

3.6.1. Materials

The main materials used for the determination of the physicochemical property of biodiesel was chloroform, Hanus solution, potassium iodide, sodium thiosulphate, starch solution, potassium hydroxide, hydrochloric acid, ethanol, and diethyl ether solution.

3.6.2. Methods

- Kinematic viscosity, ASTM D.445-10, 2010

Viscosity of the biodiesel was determined using Vibro viscometer. The kinematic viscosity was measured at 40°C according ASTM D.445 procedure. The temperature of a water bath set out at

40°C and then the 50 ml of sample was placed into the viscometer and heated on the water bath for 30 minutes. After equilibrium temperature was maintained, the Vibro viscometer tip was inserted into the sample to measure the dynamic viscosity and then read out the numerical value from the controller. Then the kinematic viscosity was calculated by using the formula:

$$\nu = \frac{\mu}{\rho\ biodiesel} \quad \text{.......} 3.2$$

Where: ν is kinematic viscosity, mm^2/s, µ is dynamic viscosity, mPa.s, and ρ is density, Kg/m^3

- Specific gravity, ASTM D.1298, 2005

Density of the biodiesel was measured by using digital density meter at 25 ^{0}C. The sample to be measured was filled into a U-shaped tube which is induced to vibrate. The frequency of the oscillation of the U-tube is influenced by the mass and therefore by the density of the sample. Then the density of the sample was displayed on the screen and recorded to calculate specific gravity as follows:

$$SG = \frac{\rho\ biodiesel}{\rho\ water} \quad \text{.......} 3.3$$

- Determination of iodine value (IV)

Iodine value was determined by using the method specified by ISO 3961 (1989). 0.25 g of biodiesel was measured and poured into 250 mL conical flask, and then 10 mL of chloroform and 30 mL of Hanus solution was added respectively. The conical flask containing the solution was covered completely and shacked continuously for 30 minutes. 10 mL of 15% potassium iodide solution and 100 mL of distilled water was added and shake it. Finally the solution was titrated against 0.1 N Sodium thiosulfate solution till yellow color formed, then add 2-3 drops of starch solution till the color changed to blue, and then continue with titration up to the blue color was disappeared and the volume of Sodium thiosulfate used was recorded. For blank solution the same procedure was followed without the sample and volume of Sodium thiosulfate consumed was recorded. Then iodine values (IV) was calculated by using the formula:

$$IV = \frac{12.69 * N(V_B - V_S)}{M} \quad \text{.......} 3.4$$

Where N is normality of sodium thiosulphate, M is mass of the sample, Vs is volume of sodium thiosulphate used for sample test, and V_B is volume of sodium thiosulphate used for blank,

- Determination of saponification number (SN)

Biodiesel (2 g) was added to 250 ml conical flask and 25ml of 0.5N ethanolic KOH which was prepared by dissolving KOH pellet in 95% ethanol, was added to the oil. Then the mixture was allowed to boil at 70 ^{0}C for 60 minute with continuous stirring and having a reflux condenser attached on it. After the boiling process was completed 5 drops of phenolphthalein indicator was added to the hot solution and then titrated with 0.5N HCl till the pink color of the indicator was disappeared and the volume consumed was recorded. Similarly blank solution was prepared, titrated and the volume of the titrant recorded. Finally the SN was calculated by using the formula indicated in 3.5;

$$SN = \frac{56.1 * N(V_B - V_S)}{W} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.5$$

Where W is the weight of biodiesel in gram, N is normality of HCl solution, Vs is volume of HCl solution used for sample test in ml, and V_B= is volume of HCl solution used for blank in ml.

- Determination of acid value (AV)

A known amount of biodiesel (2 g) was added to 250 ml round bottom flask and heated to 70 ^{0}C for 3 minute. 25 ml of ethanol and diethyl ether mixture in 1:1 ratio was added to the oil under continuous stirring. Phenolphthalein indicator (5 drop) was added to the prepared solution and titrated against 0.1N KOH solution to the end point i.e. up to the formation of pink color and the volume of KOH used was recorded. The total acidity of oil in mg KOH/gram was calculated using equation 3.6;

$$AV = \frac{56.1 * N * V}{W} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.6$$

Where: V is volume of titrant used for titration (ml), N is normality of aqueous solution of KOH, and W is weight of the sample biodiesel.

- Determination of Flash Point, ASTMD. 93, 2010

The flash point of the biodiesel was determined using open cup method. The cup was filled with the biodiesel and the cup was heated by a Bunsen burner. The temperature of the biodiesel during heating was measured by a thermometer and the temperature at the moment when a flame started over the surface of the biodiesel was recorded and reported as flash point temperature.

- Determination of higher heating value (HHV)

The higher heating value or calorific value of cottonseed biodiesel was determined by using bomb calorimetric method at Geological Survey of Ethiopia, Addis Ababa.

- Determination of FAME content

The composition of the biodiesel produced by transesterification of cottonseed oil and methanol using the synthesized solid catalyst was analyzed using gas chromatography 7890B GC, Inlet condition: Split/Splitless mode, Detector: 5977B MS, Column size of DB-5MS, 30 m x0.25 mm x 0.25µm at JIJE LABOGLASS Pvt. Limited Company, JIJE Analytical Testing Service Laboratory. Peaks of methyl esters were identified and the area of each peak indicates the composition of specific FAME in the biodiesel. The sum of the total areas of the peak in the GCMS result graph shows the amount of FAME in a given biodiesel and it is a measure of purity of the biodiesel. FAME content of the biodiesel was calculated by using the formula described by (Fournier, 2017)

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$$C_{FAME} = \frac{S_A - A_{EI}}{A_{EI}} * \frac{C_{EI} - V_{EI}}{m} * 100\% \text{ ......} 3.7$$

Where: C_{FAME} is FAME content (%), S_A is the sum of all methyl ester peak areas from C_8 to $C_{24:1}$, A_{EI} is peak area for Hexadecanoic acid (internal standard), C_A is concentration (mg/ml) of the Hexadecanoic acid solution (10 mg/ml), V_{EI} is volume (ml) of the Hexadecanoic acid solution used (5 ml), m is precise mass (mg) of the FAME sample (30 mg) or 35µl in volume.

3.7. Catalyst Stability Test

Reusability and stability are the two very important criteria for the application of NaOH/bentonite as a heterogeneous catalyst for biodiesel production. The solid catalyst after the reaction was separated from the liquid mixture (biodiesel, glycerol, methanol, and water) by using a centrifuge at 6000 rpm for 10 minute duration. The recycled catalyst was repeatedly washed (4 times) with methanol with a ratio of 2 to 1 and then the catalyst was dried at 100 ^{0}C for 12 hours. The performance of the recycled catalyst was then examined by carrying out three transesterification reaction cycles at 65^{0}C of reaction temperature, 2wt% of catalyst, methanol to oil molar ratio of 6, 3hr reaction temperature, and mixing intensity of 500rpm and then the yield of biodiesel was measured.

3.8. Design of Experiment

Data analysis for this study was carried out by DESIGN EXPERT 7.0.0 software using Box Behnken with three factors and three levels for each experiment. Box-Behnken design is suitable for the investigation of quadratic response surfaces and generates a second degree polynomial model, which in turn is used in optimizing a process using a small number of experimental runs. This design requires an experimental number of runs according to the formula:

$$N = K^2 \quad + \quad K \quad + C_P \qquad 3.8$$

Where k is the factor number which is three in this case and C_p is the number of replication at the center point which is also three in this case. The design which was developed using Design Expert 7.0.0 resulted in 15 experimental runs for each experiment. The experimental runs were randomized by using design expert to maximize the effects of unexplained variability in the observed responses due to extraneous factors.

3.8.1. Design of experiment for the synthesis of catalyst

For the preparation of catalyst three variable Box-Behnken designs methodology was used to study the combined effects of NaOH to bentonite ratio, calcination temperature, and calcination time on the efficiency of the catalyst by measuring the amount of biodiesel yield for each run. Process variables such as catalyst amount, methanol to oil molar ratio, reaction temperature, reaction time, and mixing intensity were kept constant at 1%, 9:1, 65^{O}C, 3hr, 500rpm respectively in the first round for knowing the effects of catalyst preparation conditions on the yield of biodiesel. The range and levels of the variables was shown in appendix C-1.

Table 3.2: Actual and coded levels of the factors selected for catalyst synthesis

Independent variables	Symbol	Units	Coded and actual levels		
			-1	0	+1
Calcination temperature	A	^{O}C	400	500	600
Calcination time	B	Hr.	3	4	5
NaOH/bentonite ratio	C	-	0.20	0.35	0.50

3.8.2. Design of experiment for optimization of transesterification reaction

For optimizing the yield of biodiesel produced by using the selected catalyst another three factors were selected and their effects were analyzed by using Box-Behnken design. Process variables selected were reaction temperature, molar ratio of methanol to oil and weight percentage of catalyst. Reaction time and mixing intensity were remains constant as the initial value. The upper temperature value ($70^{0}C$) is near to the boiling point of methanol, and catalyst concentration of 3%by weight of oil was based on literature data and effectiveness of the catalyst at 1% from previous laboratory result.

Table 3.3: Actual and coded values of the selected factors for optimization of biodiesel yield

Independent variables	Symbols	Units	Coded and actual levels		
			-1	0	+1
Reaction temperature	A	^{O}C	60	65	70
Methanol to oil molar ratio	B	-	3:1	6:1	9:1
Weight % of catalyst	C	%	1	2	3

Chapter 4

4. Result and Discussion

4.1. Catalyst Characterization

Raw bentonite and the prepared NaOH/bentonite catalyst were characterized by using X-ray diffraction (XRD), and FTIR to understand and ensure the expected changes occurred during catalyst preparation.

4.1.1. XRD Analysis Result

During calcination process sodium hydroxide was undergo a chemical changes to its oxide form (Na_2O) and other impurities such as Na_2O_2. In order to check whether the compounds are formed or not XRD analysis was carried out and compared with standards. The XRD patterns of the catalyst and the raw bentonite are shown in figure 4.1.

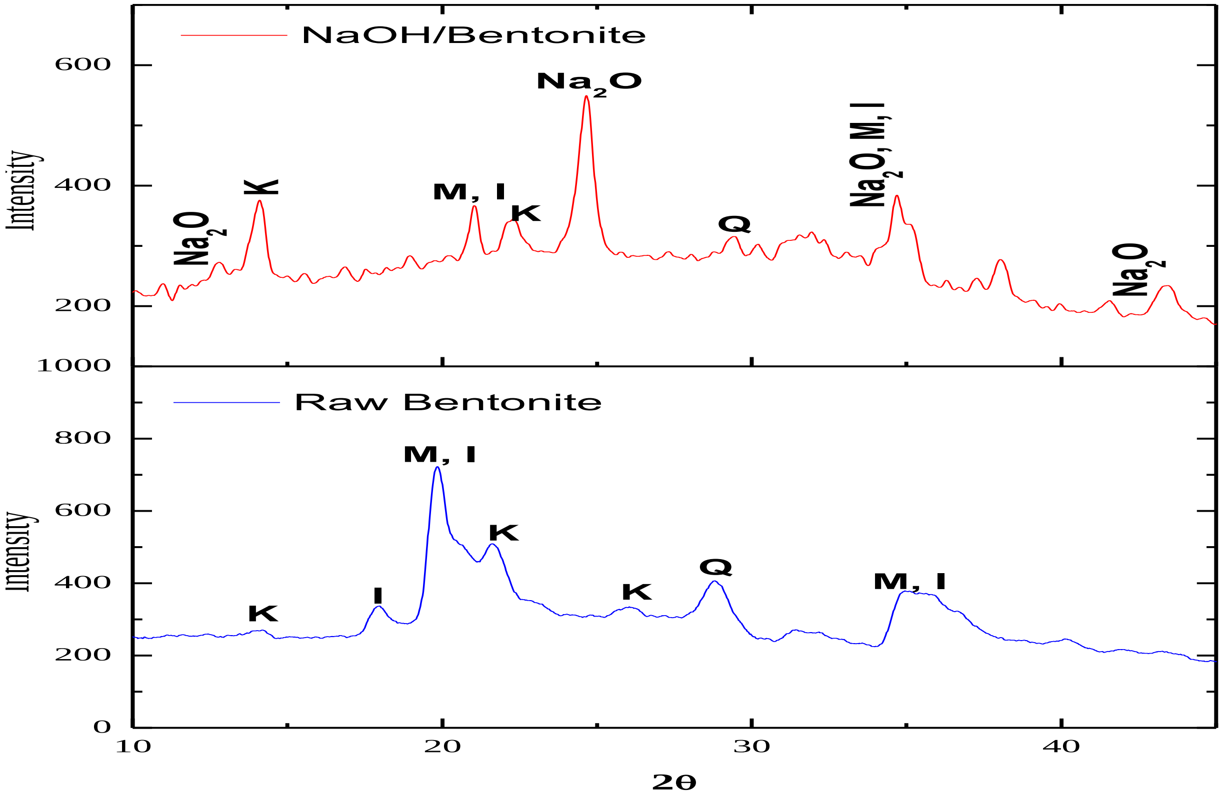


Figure 4.1: XRD patterns of the NaOH/bentonite catalyst and raw bentonite.

As it was shown in figure 4.1 the XRD patterns of raw bentonite has the typical diffraction peaks at $2\theta = 9^0$, 18^0, 20^0, and 35^0 confirmed the presence of montmorillonite (M) as a major phase. Other minor phases are kalonite (K) at a diffraction angle of $2\theta= 14^0$ and 22^0, quartz (Q) at $2\theta=$ 28 and illite (I) at $2\theta= 20^0$ and 35^0 are found. The above listed components are most commonly found in different types of bentonite. It can be observed that no peak associated with sodium hydroxide or other oxides of sodium in the XRD pattern of the raw bentonite which indicates the activity of the raw bentonite for biodiesel production was negligible.

The XRD pattern of the composite catalyst prepared at 20% of NaOH loading shows that the raw bentonite was undergo a change in its crystalinity through the addition of NaOH and calcination. The original phases of the raw bentonite also present with a slight change in its diffraction peak values and crystal structure due to the dispersion of NaOH. The major phase found in the prepared catalyst with high crystalline structure was Na_2O at diffraction angle of $2\theta=$ 12.68, 24.69, 34.68, and 43.48. The presence of Na_2O in the composite catalyst was the cause of high catalytic activity and basicity of the catalyst. Other phases present in the composite catalyst were montmorillonite, kalonite, illite and quartze which were also present in the raw bentonite (ICDD, 2016).

4.1.2. FTIR Analysis Result

The FTIR spectrum of the raw bentonite figure 4.2 reveals the presence of functional groups such as Al(Mg)-O-H stretching (3627.29 cm^{-1}), H-O-H bending (1645.17 cm^{-1}), Si-O-Si stretching (1034.45 cm^{-1}), OH bending bounded Fe^{3+} and Al^{3+} (912 cm^{-1}), and Si-O stretching (792.47cm^{-1}) (R.M.Bassler, and Morrill, 1998).

FTIR analysis showed that the addition of NaOH affected the structure of the bentonite network. The intensity of the Al (Mg)-O-H stretching group decreased with an addition of NaOH and there is a shift in the absorption band of this group from 3627.29 cm^{-1} to 3440.23 cm^{-1} indicted the presence of a new functional group in the catalysts being investigated. A band at about 3440 cm^{-1} indicates the presence of the stretching vibration of Al-O-Na group. The formation of a new functional group reveal that sodium hydroxide was well impregnated on the surface of the bentonite (Soetaredjo et al., 2011).

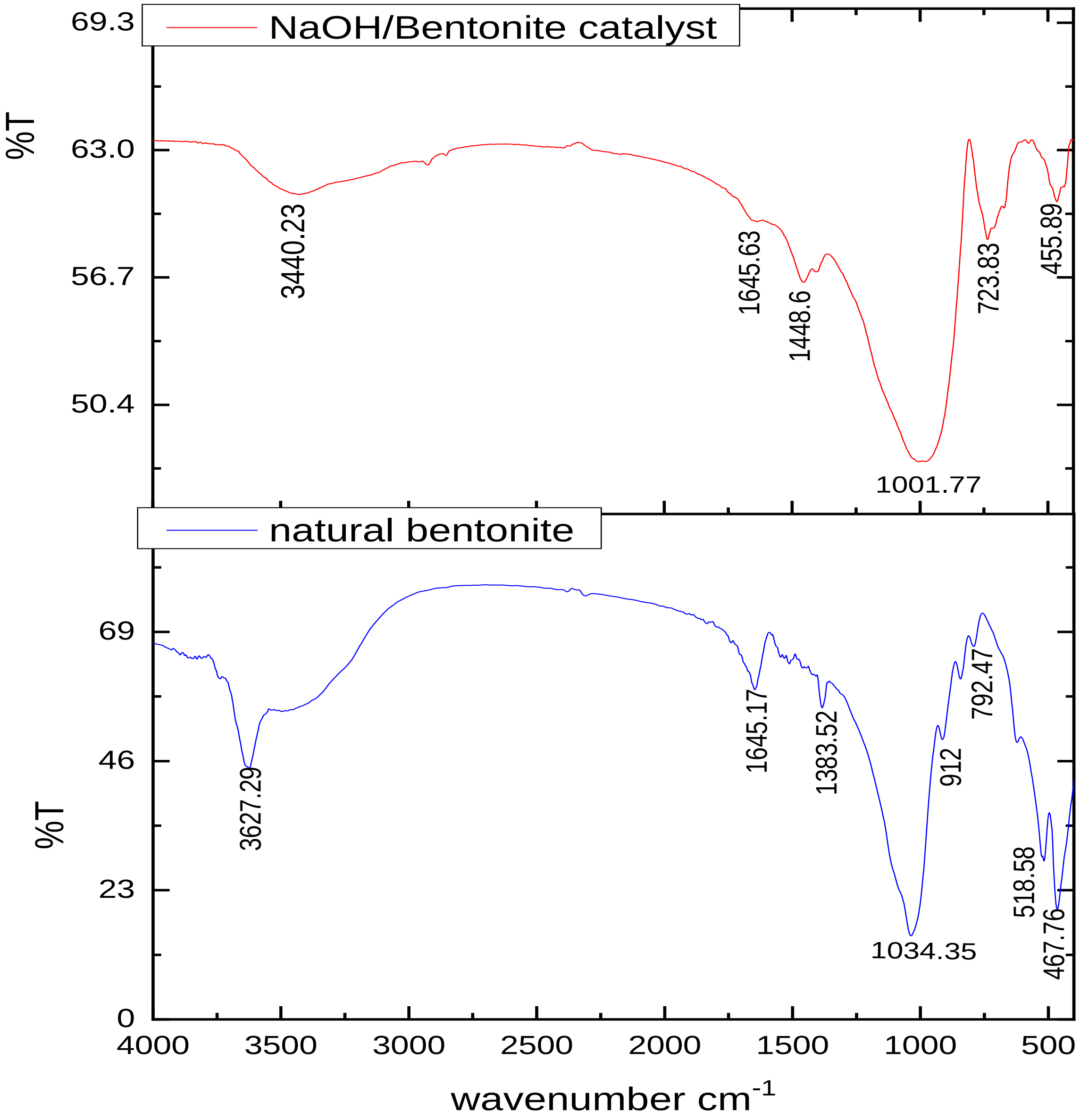


Figure 4.2: FTIR spectrum of natural bentonite and NaOH/Bentonite catalyst

4.2. Physicochemical properties of cottonseed oil

All the physicochemical properties of cottonseed oil were taken from Addis Modjo edible oil share company laboratory result and its value was summarized in table 4.1. All the above values were well agreed with the standards sets for refined oils, due to cottonseed oil was considered suitable for biodiesel production. As the value of FFA was small the probability of ester formation increases since soap formation was reduced. The above physicochemical properties of cottonseed oil also used to compare with the biodiesel produced.

Table 4.1: Physicochemical properties of cottonseed oil.

Properties	Units	Values
Density @ $25^{O}C$	kg/m^3	920
Kinematic viscosity @$40^{O}C$	mm^2/s	30
Acid value	mg KOH/g oil	2.15
Specific gravity	-	0.92
Free fatty acid	-	0.12
Iodine value	g I^2/100g oil	78.2
Saponification value	mg KOH/g oil	187.7
Flash point	^{O}C	230

Source: Addis Modjo edible oil share company laboratory result

4.3. Fatty acid composition of CSO

The data measured by the company indicates that cottonseed oil was found to contain both saturated and unsaturated fatty acids. From the obtained data Linoleic acid was found having the highest composition (55 %) followed by palmitic acid (24.8 %), oleic acid (17.2 %), myristic acid (0.8%) and stearic acid (2.2 %) as shown in Table 4.2. The molecular weight of cottonseed oil was calculated from its fatty acid composition and molecular weights and was found to be 272.3g/mol (appendix A). The types and composition of fatty acids present in the oil can be used to make a comparison with composition of methyl ester of the produced biodiesel.

Table 4.2: Fatty acid composition of cottonseed oil.

Fatty acid type	Structure	Weight %	Molecular weight g/mol
Linoleic acid	C18:2	55	280.5
Palmitic acid	C16:0	24.8	256.4
Oleic acid	C18:1	17.2	282.5
Myristic acid	C14:0	0.8	228.4
Stearic acid	C18:0	2.2	184.5

4.4. Statistical analysis of experimental results for the synthesis of catalyst

4.4.1. Analysis of variance (ANOVA)

The actual results obtained from 15 runs of experiment were recorded and used for analysis of variance using response surface method. From the result of ANOVA the F-value of 395.00 implies the model is significant. Only a 0.01% chance that a "Model F-Value" of 395.00 could occur due to noise. Values of "Prob > F" less than 0.0500 indicate the model terms are significant. In this case A, B, C, AC, BC, B^2, C^2 are significant model terms as it was described in table 4.3. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model

Table 4.3: Analysis of variance (ANOVA) For Response Surface Quadratic Model

Source	**Sum of Squares**	**Df**	**Mean Square**	**F Value**	**p-value Prob > F**	**Remark**
Model	1766.15	9	196.24	395.00	< 0.0001	Significant
A-ratio	122.33	1	122.33	246.22	< 0.0001	
B-temperature	508.77	1	508.77	1024.08	< 0.0001	
C-time	45.09	1	45.09	90.77	0.0002	
AB	0.26	1	0.26	0.53	0.5011	
AC	4.18	1	4.18	8.41	0.0338	
BC	56.95	1	56.95	114.64	0.0001	
A^2	8.542E-003	1	8.542E-003	0.017	0.9008	
B^2	1022.89	1	1022.89	2058.93	< 0.0001	
C^2	6.15	1	6.15	12.39	0.0169	
Residual	2.48	5	0.50			
Lack of Fit	2.34	3	0.78	10.59	0.0875	Not significant
Pure Error	0.15	2	0.074			
Cor total	1768.63	14				

The “ Lack of Fit F-vakue” of 10.59 implies the Lack of Fit is not significant relative to the pure error and there is 8.75% chance that a “Lack of Fit F-value “ this large could occur due to noise. Non –significant lack of fit is good to fit the model.

The "Pred R-Squared" of 0.9787 is in reasonable agreement with the "Adj R-Squared" of 0.9961. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. A ratio of 56.918 in this case indicates an adequate signal.

Table 4.4: Adequacy measures of the developed model

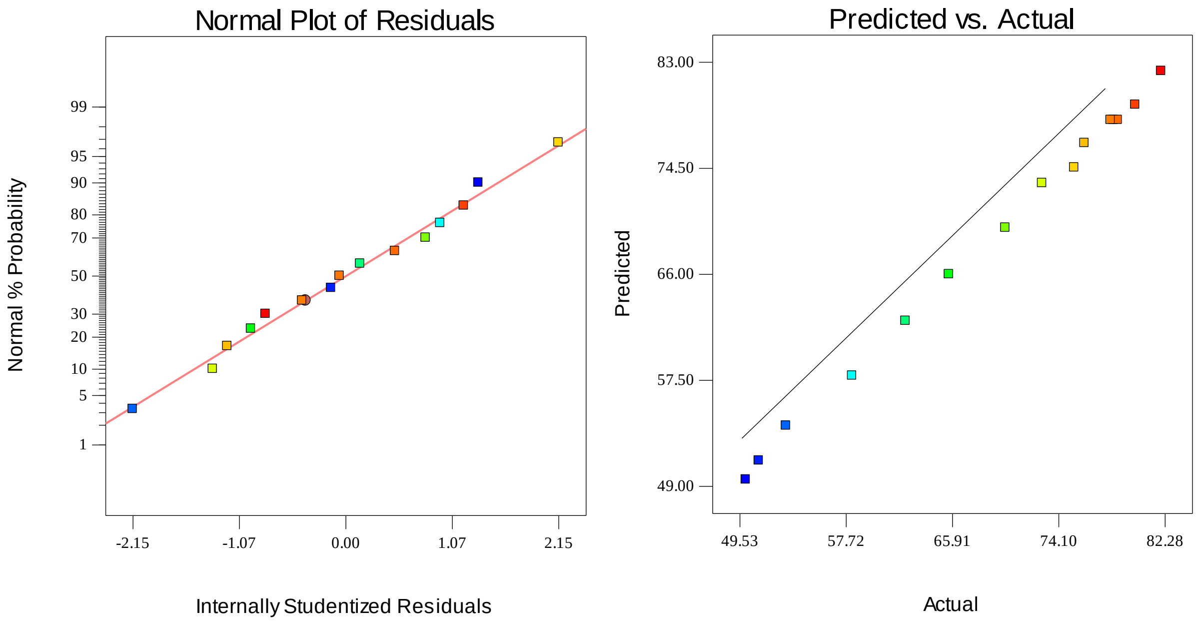
Std. Dev.	0.70	R-Squared	0.9986
Mean	68.77	Adj R-Squared	0.9961
C.V. %	1.02	Pred R-Squared	0.9787
PRESS	37.72	Adeq Precision	56.918

The correlation between the experimental data and the predicted responses was quantitatively evaluated by using the term regression coeffiecient (R^2). The values of R^2 = 0.9986 and Adj-R^2=0.9961 indicated that the predicted values were found to be in a good agreement with experimental values. The R^2 value closer to 1.0 indicates that the regression line is perfectly fits the data. The value of R^2 = 0.9986 confirmes the above statement that means the regression line was perfectly fits the data. Another conclusion made here that only 0.14% of the total variance was not explained by the developed regression model.

The significance of the model also confirmed by using the value of adjusted R- squared (Adj R^2 =0.9961) which is close to 1.0. Predicted R-squared indicates the amount of variation in new data explained by the model. About 97.87% of the variation of the new data was detected by using the developed model in this study. The final equation in terms of significant actual factors is:

$$\begin{aligned}\text{Biodiesel yield}(\%) &= -384.71106 - 53.31522 * ratio + 1.73525 * temperature + 29.15564 \\ &* time + 6.81159 * \text{ ratio} * \text{ time} - 0.037734 * \text{ temperature } * \text{ time} \\ &- 1.66406 * 10^{-3} * temperature^2 - 1.28733 * time^2\end{aligned}$$

The adequacy of the model is further shown by using residual plots. In figure 4.3-a which is the normal probability plot, it can be observed that the residual follow the normal distribution and the assumption of normality for the synthesis of the catalyst was valid.



(a) (b)

Figure 4.3: Graph of (a) normal probability versus studentized residuals, (b) predicted versus actual value of biodiesel yield.

The data were also analyzed to check the correlation between the experimental and predicted yield of biodiesel (%) as shown in figure 4.3-(b). The experimental values were the measured response data for the runs designed by BBD model, while the predicted values were obtained by calculation from the developed quadratic model. It can be seen from figure 4.3-(b) that the data points on the plot were reasonablly distributed near to the straight line (R^2 =0.9986), indicating a good realtionship between the experimental and predicted values of the respnse, and that the underlying assumption of the above analysis were appropriate.

4.4.2. Effects of individual catalyst preparation variables on biodiesel yield

The activity/performance of the catalyst was significantly affected by individual process variables during catalyst preparation. The effect of each process variable during catalyst preparation such as calcination temperature, calcination time and NaOH to bentonite ratio on the yield of biodiesel was discussed here.

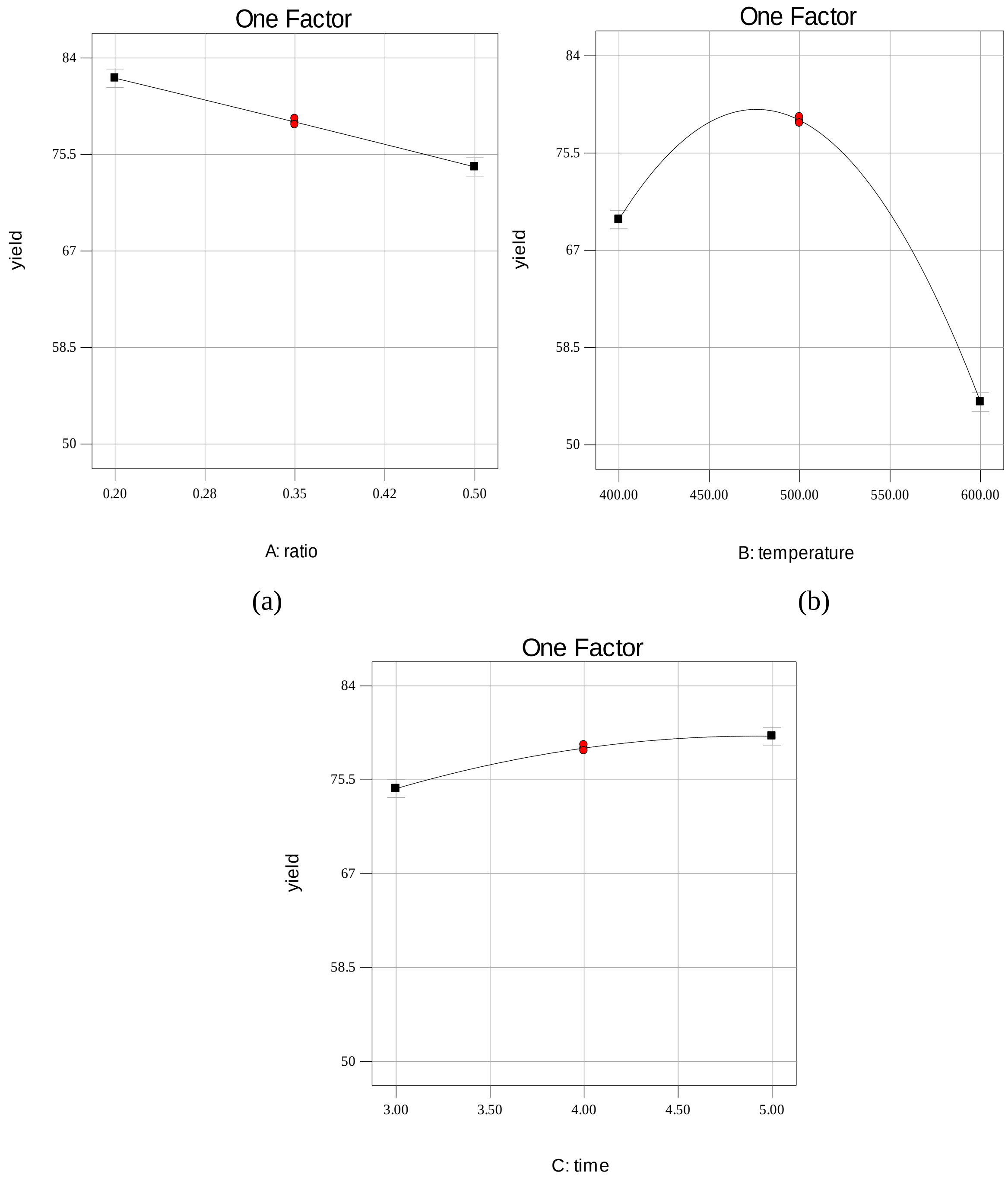
- Effect of NaOH to bentonite ratio

The catalytic effect of NaOH to bentonite ratio on transesterification of cottonseed oil was investigated from the yield of biodiesel. The experimental condition for studing the effect of NaOH to bentonite ratio on the transesterification reaction were; amount of catalyst at 1%w/w of weight of cottonseed oil, methanol to oil molar ratio 9:1, reaction time of 3 h, and the reaction temperature of 65^0C. The results clearly indicate that the ratio of NaOH to bentonite affected the conversion of cottonseed oil into biodiesel.

Increasing the amount of NaOH loading from 20% to 50% linearly decresed the yield of biodiesel as it shown in figure 4.4-(a). The highest yield of biodiesl (82.22) was obtained at 20% NaOH loading . The number of Na_2O active sites in the 20% NaOH loading catalyst was higher than the remaining catalyst having different loading of NaOH resulted in low biodiesel yield. With high levels of NaOH, the interactions between NaOH and the internal layer of bentonite (Al–O–H stretching groups) were excessive and during the calcinations, a new phase of Al–O–Na compound was formed. This new phase compound (Al–O–Na) has lower catalytic activity and basicity than the Na_2O phase. When a high concentration of the Al–O–Na compound was formed, the catalytic activity of the catalyst became lower, leading to a decrease in the biodiesel yield. Another reason for low biodiesel yield was due to surface area reduction of the catalyst as the NaOH loading increases. The contact between the catalyst and reaction mextures decreased as the surface area reduces which inturn reduce biodiesel yield.

- Effect of calcination temperature

The activity of NaOH/bentonite catalyst for the transesterification reaction was affected by its calcination temperature during catalyst synthesis. As shown in figure 4.4-(b) the yield of biodiesl increased with increasing calcination temperature up to an optimum value due to the formation of active sites of Na_2O. But after the temperature reached to an optimum value the yield start to decrease. This might be due to the formation of additional impurities other than Na_2O during calcination process at high temperature having no activity for the conversion of cottonseed oil to biodiesel. As calcination temperature increases beyond the optimum point sintering process was takes place which increases the particle size and reduces the performance of the catalyst.



(a) (b)

(c)

Figure 4.4: Main effects of a) NaOH to bentonite ratio, b) calcination temperature, and c) calcination time on the yield of biodiesel.

- Effect of calcination time

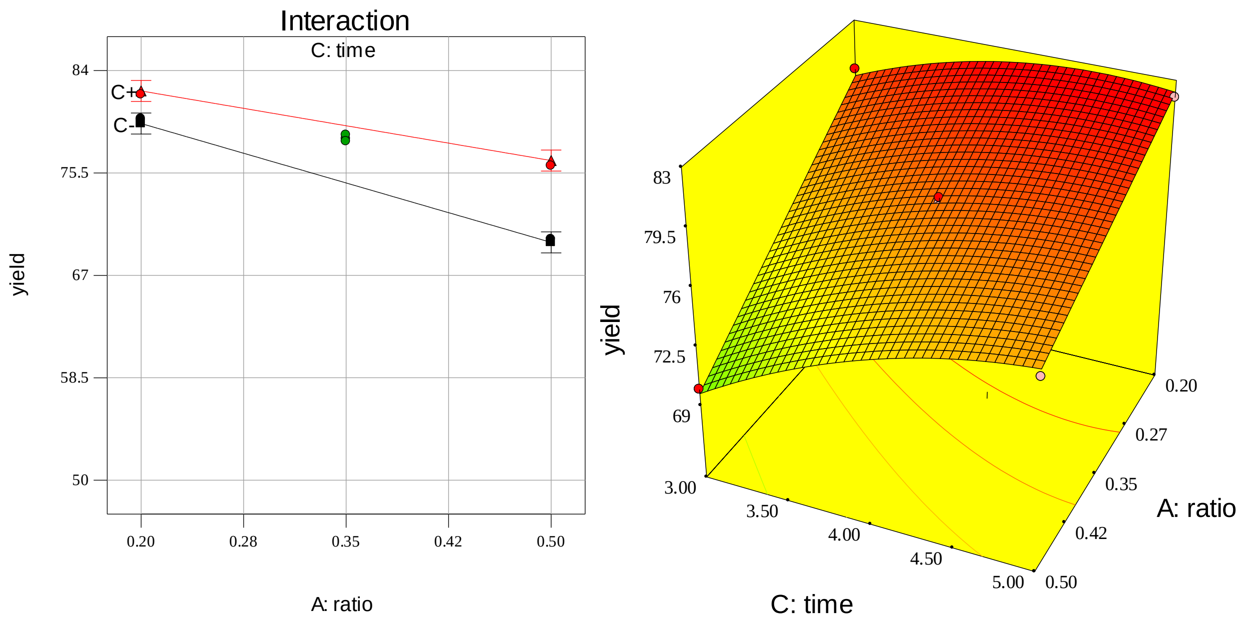
Calcination time during catalyst preparation affects the activity of the catalyst inturn it affects the yield of biodiesel. Figure 4.4-(c) showed that biodiesel yield increased as calcination time increases. The highest yield of biodiesel obtained at the high value of calcination time due to the formation of large number of active sites of Na_2O at optimum value of NaOH to bentonite ratio and calcination temperature. Increasing calcination time beyond 5h does not affect biodiesel yield because NaOH was completely converted to Na_2O and the amount of Na_2O active sites were not increased beyond it.

4.4.3. Effect of interaction between process parameters on biodiesel yield

Contour plots were drawn to show the relationships between dependent and independent variables of the developed model. Each graph presented the effect of two variables on the biodiesel yield, holding the third variable at zero level (mid-point).

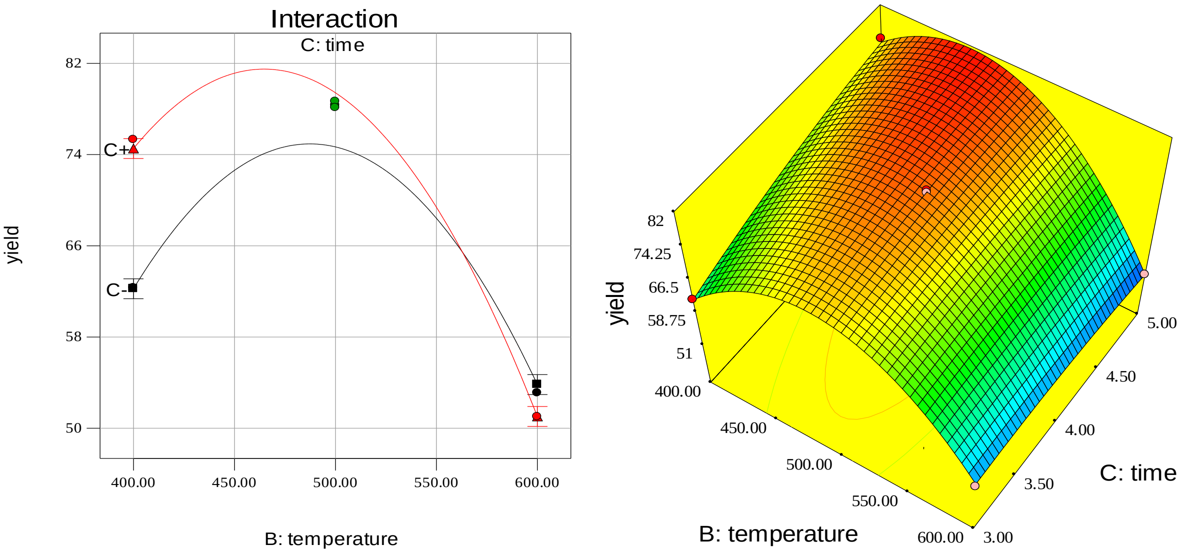
From Figure 4.5 it can be seen that the yield of biodiesel was decreased as the ratio of NaOH to bentonite was increased at all values of calcination time. As th e ratio of NaOH to bentonite was increased the rate of decreasing of biodiesel yield was higher at low calcination temperature than the highest one. Therefore; synthesizing the catalyst at high value of calcination time can give high biodiesel yield relative to the lowest calcination time at any value of NaOH to bentonite ratio. The effect of calcination time has greatly observed at high value of NaOH to bentonite ratio relative to the lowest one.

Figure 4.6 showed that the effect of calcination time and temperature on biodiesel yield when the ratio of NaOH to bentonite was kept constant at 0.35. As the calcination temperature was increased up to the optimum value at all values of calcination time the yield of biodiesel also increased. Increasing calcination temperature beyond the optimum value resulted in the decrease of biodiesel yield at any value of calcination time. However the rate of decreasing biodiesel yield was higher at high value of calcination time relative to the lowest after the optimum value of calcination temperature. Calcination time was highly significant effect at low calcination temperature compared to the highest one. Therefore, highest biodiesel yield has obtained at 5 hr. calcination time and 500 ^{0}C calcination temperature.



(a) (b)

Figure 4.5: Interaction effect of NaOH to bentonite ratio and calcination time on biodiesel yield a) 2-D plot and b) 3-D plot at 500 ^{o}C of calcination temperature.



(a) (b)

Figure 4.6: Interaction effects of calcination time and temperature on biodiesel yield a) 2-D plot and b) 3-D plot at constant NaOH to bentonite ratio of 0.35.

Catalyst preparation parameters was selected based on the yield of biodiesel obtained for each run of experiment. Highest biodiesel yield was obtained NaOH to bentonite ratio of 0.20, calcination temperature of 500^0C, and calcination time of 5 hr. Transesterification reaction was conducted by using the selected catalyst to optimize reaction temperature, methanol to oil molar ratio, and catalyst laoding.

4.5. Statistical analysis of experimental results for the optimization of transesterification reaction

4.5.1. Analysis of variance (ANOVA)

The transesesterification process was carried out using the method described in section 3.2.5 by using the selected catalyst. The actual results obtained from 15 runs of experiment were recorded and used for analysis of variance.

From the result of ANOVA the F-value of the model 566.14 implies the model is significant. There is only 0.01% chance that a “Model F-Value” of 566.14 could occur due to noise. Values of “Prob > F” less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC, BC, A^2, B^2, and C^2 are significant model terms. Values greater than 0.100 indicate the model terms are not significant.

The “lack of Fit F-value” of 0.97 implies the lack of fit is not significant relative to the pure error. There is 54.34% chance that a “lack of Fit F-value” could occur due to noise. Non-significant lack of fit is good to fit the model.

The P-values were used as a tool to check the significance of each of the model coefficients. These values are all given in table 4.5. The smaller P-value the more significant is the corresponding coefficients. In this case all P-values are less than 0.05 all tested variables are significant model terms.

Table 4.5: Analysis of variance (ANOVA) for response surface quadratic model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remark
Model	2695.12	9	299.46	566.14	< 0.0001	Significant
A-methanol to oil ratio	6.84	1	6.84	12.94	0.0156	
B-reaction temperature	168.82	1	168.82	319.16	< 0.0001	
C-catalyst wt%	6.94	1	6.94	13.12	0.0152	
AB	134.56	1	134.56	254.39	< 0.0001	
AC	12.96	1	12.96	24.50	0.0043	
BC	66.02	1	66.02	124.81	0.0001	
A^2	542.94	1	542.94	1026.46	< 0.0001	
B^2	1614.96	1	1614.96	3053.17	< 0.0001	
C^2	439.79	1	439.79	831.45	< 0.0001	
Residual	2.64	5	0.53			
Lack of Fit	1.57	3	0.52	0.97	0.5434	not significant
Pure Error	1.08	2	0.54			
Cor total	2697.76	14				

The model equation in terms of the significant actual factor is as follows:

$$
\begin{aligned}
&Biodiesel\ yield \\
&\quad = -3740.98750 + 42.81 * methanol\ to\ oil\ ratio + 111.77775 \\
&\quad * reaction\ temperature + 99.13625 * catalyst\ wt\% - 0.38667 \\
&\quad * methanol\ to\ oil\ ratio * reaction\ temperature - 0.60 \\
&\quad * methanol\ to\ oil\ ratio * catalyst\ wt\% - 0.8125 * reaction\ temperature \\
&\quad * catalyst\ wt\% - 1.34736 * methanol\ to\ oil\ ratio^2 - 0.83655 \\
&\quad * reaction\ temperature^2 - 10.91375 * catalyst\ wt\%^2
\end{aligned}
$$

The coefficient of regression (R^2), calculated as the ratio of the regression sum of squares to the total sum of squares, was found to be 0.9990 which indicates that 99.9% of the variability in the yield data is explained by the regression model, showing a very good fit of the model. The "Pred R-Squared" of 0.9898 is in a reasonable agreement with the "Adj R-Squared" of 0.9973. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. In this study a ratio of 71.584 indicates an adequate signal.

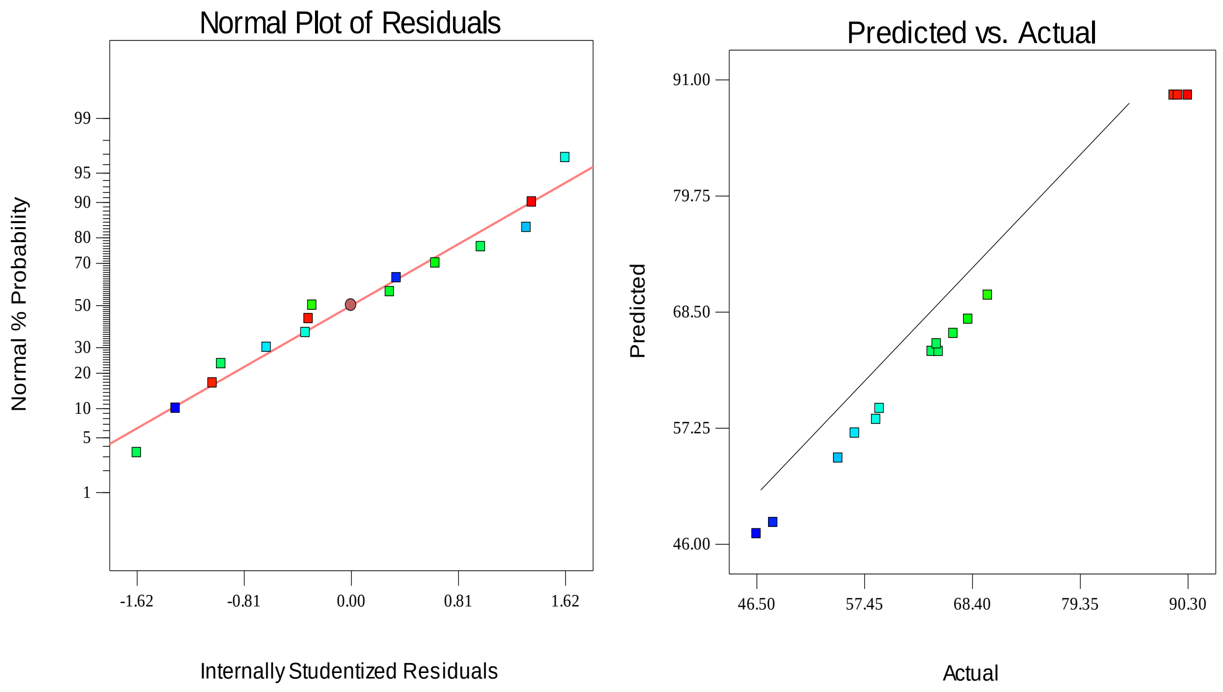
Table 4.6: Values of model adequacy measurement parameters

Std. Dev.	0.73	R-Squared	0.9990
Mean	66.05	Adj R-Squared	0.9973
C.V. %	1.10	Pred R-Squared	0.9898
PRESS	27.51	Adeq Precision	71.584

The above results of the quadratic model indicate that the model provided an excellent explanation for the relationship between the independent variables and the corresponding response.

The adequacy of the model is further shown from the residual plots as shown in figure 4.7. From figure 4.7-(a) which is the normal probability plot, it can be observed that the residuals follow the normal distribution and the assumption of normality is valid. This shows that the quadratic model satisfies the assumption of the analysis of variance (ANOVA).

The data were also analyzed to check the agreement between the experimental and the predicted yield of biodiesel (%) as shown in figure 4.7-(b). The experimental values were the measured response data for the runs designed by BBD model, while the predicted values were obtained from the developed quadratic model equation. From figure 4.7-(b) it can be seen that the data points on the plot were reasonably distributed close to the straight line (R^2= 0.9990), indicating a good agreement between the experimental and predicted values of the response. Therefore the assumptions taken by ANOVA were appropriate.



(a) (b)

Figure 4.7: Adequacy measurement graphs a) Plot of normal probability versus studentized residual and b) plot of predicted versus the actual experimental values of the response.

4.5.2. Main effect of individual process variables on biodiesel yield

The transesterification process was significantly affected by individual transesterification reaction variables. The main effects of all process parameters on biodiesel yield were determined and illustrated from the result of ANOVA.

- Effect of methanol to oil molar ratio

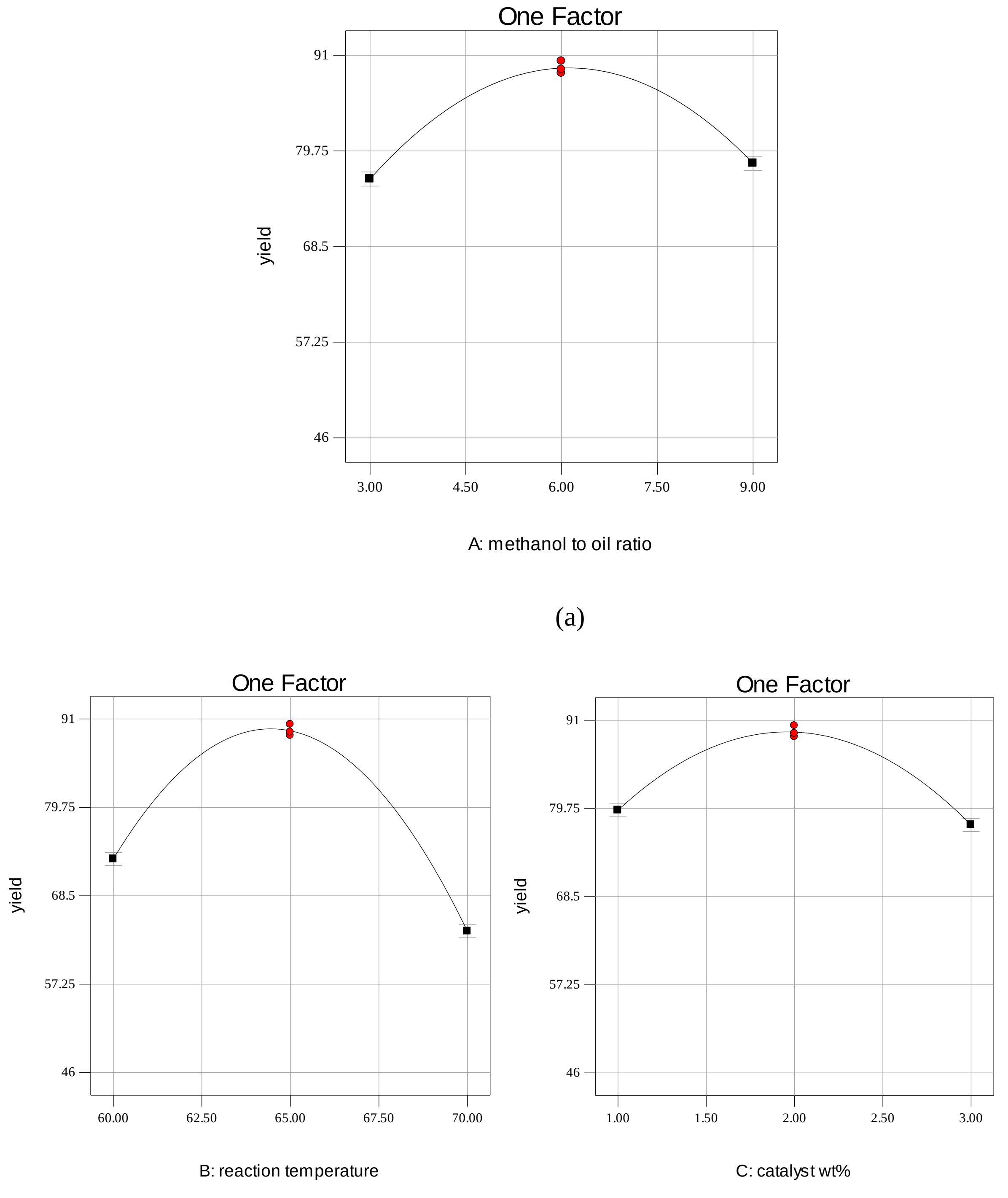
The stoichiometric ratio for transesterification reaction requires 3 mole of methanol for 1 mole of triglyceride to produce 3 mole of fatty acid methyl ether and 1 mole of glycerol, but usually, a higher molar ratio of methanol to triglyceride was required to drive the reaction towards completion and produce high yield of FAME as a product. Figure 4.8-(a) showed that the yield of biodiesel increased with increasing methanol to oil molar ratio up to an optimum value of 6 because excess methanol drives the reaction to the right for more products, but the yield started to decrease as the ratio increased beyond its optimum value. The decreasing of yield after the optimum value of methanol to oil molar ratio was due to the separation problem resulted from an increase in glycerol solubility with excess methanol. The result obtained in this study is in a good agreement with previous studies conducted (Fan, Wang, & Chen, 2011).

- Effect of reaction temperature

The yield of biodiesel increased with an increase in reaction temperature up to an optimum value (fig 4.8-b). This was due to the decrease of viscosity of oil, which results in an increase of the solubility of oil in methanol, which in turn improve the contact between methanol and oil and increases the yield of biodiesel. But after the optimum reaction temperature the yield of the transesterification reaction was started to decreased due to the fact that the amount of methanol in the reactor was reduced at high temperature. At a temperature near or above the boiling point of methanol the methanol was started to evaporate and not fully recovered by using the reflux condenser. Additionally at high temperature the saponification is higher and makes the separation of glycerol difficult, which leads to the yield of biodiesel decreased.

- Effect of catalyst amount

The yield of biodiesel increased from 79.5075 at 1% NaOH/bentonite catalyst to 89.3% at 2% catalyst as it has shown in figure 4.8-(c). The increase of biodiesel yield with increasing catalyst loading from 1% to 2% was due to an increase in the number of active basic sites of Na_2O in the reaction system. However, increasing the catalyst beyond the optimum concentration of 2% led to a decrease in biodiesel yield. The decrease of biodiesel yield as the catalyst concentration increased beyond 2% was due to the formation of soap and emulsion at higher catalyst concentration which hinders the separation of glycerol from biodiesel.



(a)

(b)

(c)

Figure 4.8: The main effects of a) methanol to oil molar ratio, b) reaction temperature, and c) catalyst loading on biodiesel yield.

4.5.3. Interaction effects of transesterification reaction parameters on yield

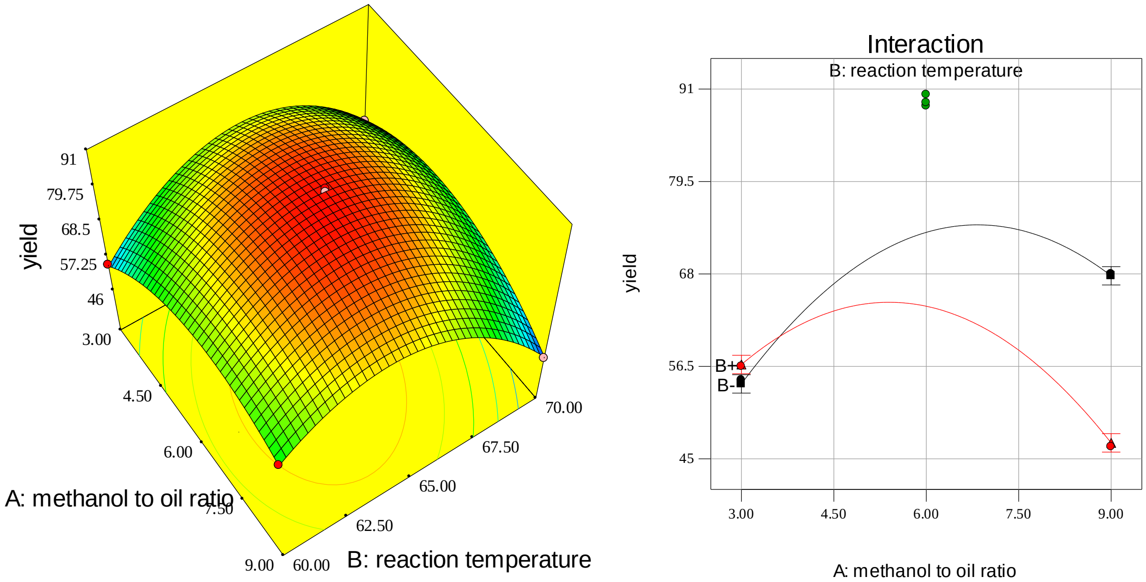
The three dimensional response surface plots was obtained by plotting the response variable as a function of two independent variables by maintaining the remaining variable at the mid values. The plots are helpful in understanding both the main effects and the interaction effects between factors.

- Interaction effect of temperature and methanol to oil molar ratio on yield

Figure 4.9 shows that the effect of temperature and methanol to oil molar ratio on biodiesel yield when the catalyst was kept at 2%. At low value of methanol to oil molar ratio, increasing the temperature from 60 ^{0}C to 70^{0}C also increased the yield of biodiesel. The increasing of biodiesel yield continues up to methanol to oil ratio reached a value of 4 and then started to decrease. However increasing methanol to oil molar ratio up to a value of 6 for each low and high value of reaction temperature also increases the yield of biodiesel. The increasing rate of biodiesel yield was high at low temperature compared with the highest one. Increasing the methanol to oil molar ratio after the optimum value for each temperature value can decrease the yield. But the decreasing rate of biodiesel yield as the molar ratio of methanol to oil increased beyond the optimum value was higher at high reaction temperature. The effect of molar ratio of methanol to oil on biodiesel yield was depending on the value of reaction temperature. Therefore it is better to run the experiment at optimum value of methanol to oil molar ratio and at low reaction temperature to get high yield of biodiesel.

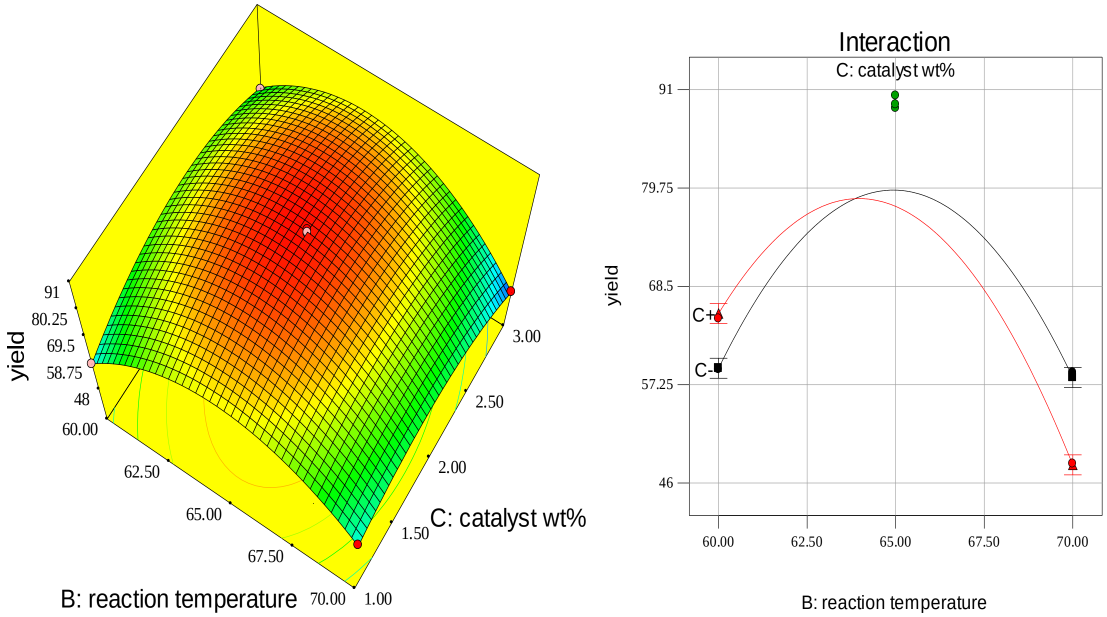
- Interaction effect of catalyst loading and temperature on yield

From figure 4.10 it can be seen that up to the intersection point of the two lines represented by 1% and 3% catalyst loading the yield of biodiesel increased with increasing catalyst amount from 1% to 3%. But beyond the intersection point when the catalyst loading increased from 1% to 3%, the yield of biodiesel was decreased at any value of temperature. Therefore to get high yield of biodiesel running the experiment with 3% catalyst loading up to the reaction temperature of 64^{0}C and beyond it running the experiment with 1% of catalyst loading were advised in this study.



(a) (b)

Figure 4.9: Interaction effects of reaction temperature and molar ratio of methanol to oil on biodiesel yield (a) three dimensional view (b) two dimensional view.



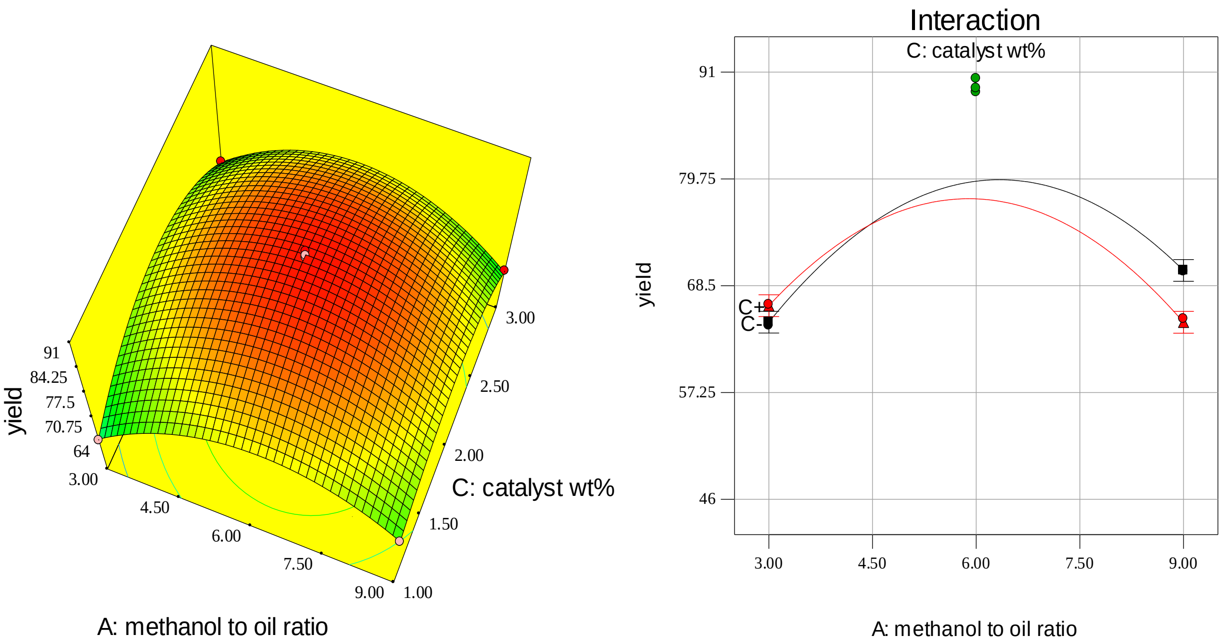
(a) (b)

Figure 4.10: Interaction effect of reaction temperature and amount loading on biodiesel yield a) 3- Dimentional view b) 2-Dimentional view.

- Interaction effect of methanol to oil molar ratio and catalyst loading on yield

It can be seen that from figure 4.10, up to methanol to oil molar ratio of 4.5 the yield of biodiesel increased with increasing catalyst amount from 1% to 3%. But beyond this the yield of biodiesel decreased with increasing the reaction temperature. Therefore, to get high biodiesel yield running the experiment at high value of catalyst amount up to the value of methanol to oil molar ratio reached 4.5 and beyond it running the experiment with 1% of catalyst amount were advised.

Increasing the molar ratio of methanol to oil up to the optimum value with all values of catalyst loading was increased biodiesel yield. But the increasing rate was higher at low value of catalyst loading. Increasing the molar ratio of methanol to oil beyond the optimum value has decrease biodiesel yield for all values of catalyst loading, however the decreasing rate was higher at high value of catalyst loading.



(a) (b)

Figure 4.11: Interaction effect of methanol to oil molar ratio and catalyst amount on biodiesel yield (a) three dimensional view (b) two dimensional view.

4.6. Optimization of process variables

The optimum percentage yield of biodiesel was predicted to be 89.8% and this was obtained at the optimum condition of process variables: methanol to oil molar ratio of 6, reaction temperature of 64.45 ^{0}C, and catalyst loading of 2%. Three experiments were conducted at these process parameters values to validate the adequacy of the proposed model and the experimental values of 90.3% yield of biodiesel was obtained and this is in a good agreement with the predicted value.

Table 4.7: Optimum values of the dependent and independent variables

Constraints Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Methanol to oil molar ratio	is target =6.00	3	9	1	1	3
Reaction temperature	is in range	60	70	1	1	3
Catalyst loading (%)	is target=2	1	3	1	1	3
Biodiesel yield	maximize	46.5	90.3	1	1	3
Solution						
Solution Number	Methanol to oil molar ratio	Reaction temperature	Catalyst loading (%)	Biodiesel yield	Desirability	Remark
1	6	64.45	2	89.7423	0.996	Selected

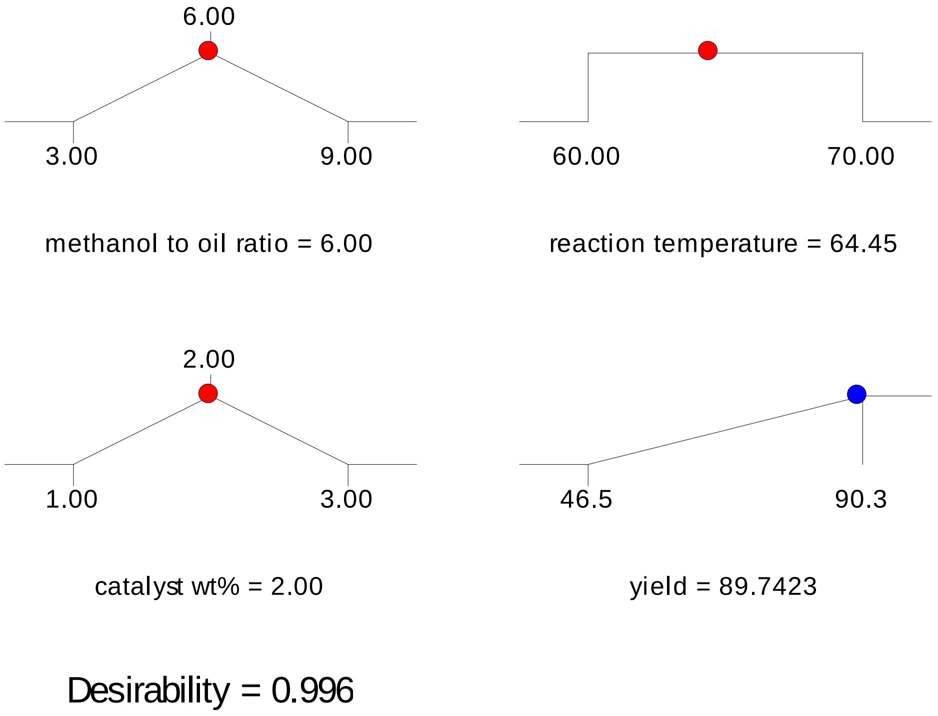


Figure 4.12: Ranges and optimum values of dependent and independent variables for the optimization of transesterification parameters.

4.7. Catalyst stability test result

The optimum transesterification reaction variables obtained was reaction temperature of 65^{0}C, catalyst loading of 2wt%, and methanol to oil molar ratio of 6. At the first transesterification reaction using fresh catalyst a maximum of 90.3% biodiesel yield was obtained. For the first, second and third generation catalyst transesterification reaction was conducted similarly to the fresh catalyst and biodiesel yield of 85.6%, 81%, and 76.2% were obtained (fig 4.13). The decreasing of biodiesel yield was due to the deactivation, poisoned and leaching of possible basic sites during the transesterification reaction.

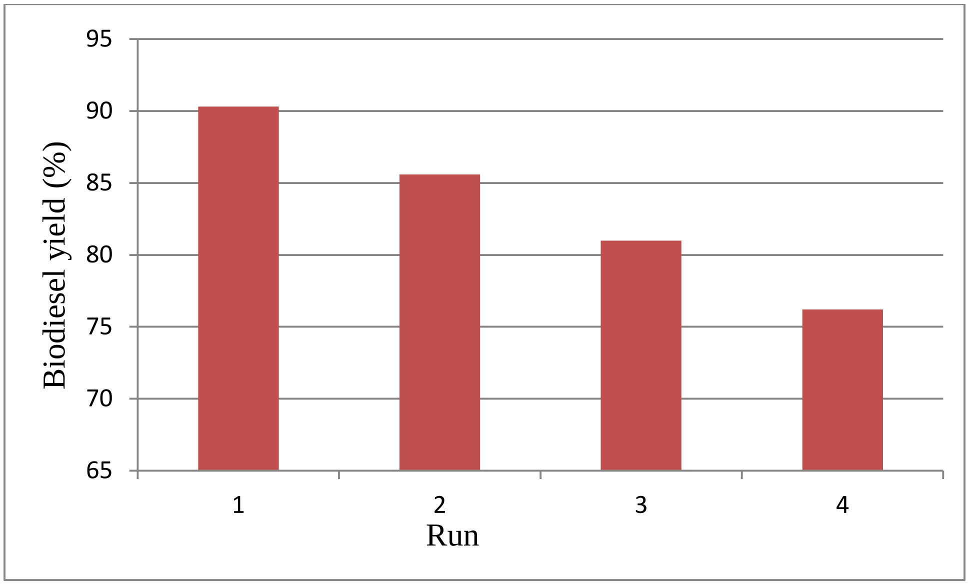


Figure 4.13: Biodiesel yields using recycled catalyst

4.8. Physicochemical properties of biodiesel

- Specific gravity

The density of the produced biodiesel was measured using a digital density meter as described in section 3.2.6 and obtained a value of 0.872g/ml. then by using density of water the specific gravity was determined using a simple formula and the value is 0.872, which is less than the cottonseed oil specific gravity.

- Kinematic viscosity

The dynamic viscosity of the biodiesel measured at 40^0c using vibro viscometer was 3.64mPa.s. The kinematic viscosity can be calculated using the equation 3.2 and the result obtained was $4.18mm^2/s$ which is in acceptable value according to ASTM.445.

- Iodine value of biodiesel

The iodine value of biodiesel was determined based on ISO 3961 (1989) stated under section 3.2.6. Based on the volume of sodium thiosulphate consumed for the blank and sample containing solutions iodine value of 102.03 g I_2/100 g CSB was obtained by using equation 3.4.

- Acid value

Based on the volume of potassium hydroxide consumed during the titration and by using equation 3.6 the acid value of the biodiesel obtained was 0.21mg of KOH/g CSB; which is in range of ASTM standards.

- Higher heating value

The result obtained from Geological Survey of Ethiopia indicated that the analyzed cottonseed biodiesel have a calorific value of 8940.93 cal/gm or 37.416 MJ/kg, which is above the minimum heating value of biodiesel. Compared to diesel fuels cottonseed biodiesel was low heating value.

- Saponification number

The procedure used to determine the saponification value of biodiesel was described in section 3.2.6. The saponification value was then calculated by using equation 3.5 and gives a value of 136.1 mg KOH/g CSB.

- Flash point

As it was measured according to the procedure described in section 3.2.6 the flash point of the produced biodiesel was 192 ^{O}C.

Table 4.8: Properties of cottonseed biodiesel with comparison with biodiesel standards

Property	Units	ASTM D6751	Cottonseed biodiesel
Density	Kg/m^3	-	870
Kinematic viscosity	Mm^2/s	1.9-6.0	4.18
Flash point	^{O}C	min. 93	192
Acid value	mg KOH/g CSB	max.0.50	0.21
Iodine value	g I_2/100 g CSB	-	102.28
Saponification number	mg KOH/g CSB	-	136.1
Calorific value	MJ/kg	min 35	37.416

The physicochemical properties of the produced biodiesel were within a range of international standards as described in table 4.8. The calculations for each property are described in (appendix D).

4.9. GC-MS analysis result

GCMS analysis indicated that there are 27 fatty acid methyl ester types were found in cottonseed biodiesel from which Hexadecanoic acid ($C_{17}H_{34}O_2$) is an internal standard used for analysis. The analysis showed that FAME product consisted of predominantly 9-Octadecenoic acid methyl ester, (E) (32.94%), 9, 12-Octadecadienoic acid (Z, Z) - methyl ester (31.81%), Hexadecanoic acid, methyl ester (internal standard) (14.82%), 13-Docosenoic acid, methyl ester, (Z) (4.52%), Methyl stearate (3.95%), Docosanoic acid, methyl ester (2.94%), cis-11-Eicosenoic acid, methyl ester (2.05%), Eicosanoic acid, methyl ester (1.51%), and Ethyl Oleate (1.01%) which accounts 95% of the total FAME components (appendix F).

The FAME content of the CSB obtained by using equation 3.7 was 95.8%, which agreed with international standards. The methyl ester composition of the biodiesel confirms that the fatty acids contained in the oil were converted into methyl ester during transesterification reaction.

Chapter 5

5. Conclusion and Recommendation

5.1. Conclusion

The options to reduce the cost of biodiesel are the use of non-edible oils and by using heterogeneous catalyst instead of homogeneous catalyst to make the production process simple. In this study, NaOH/bentonite heterogeneous catalyst was synthesized at different parameters and its performance for biodiesel production from cottonseed oil was investigated.

Parameters for the synthesis of NaOH/bentonite catalyst for transesterification of cottonseed oil were investigated and optimized using Box Behnken Design of Response Surface Methodology. From the result of ANOVA catalysts prepared at 500^0C calcination temperature, calcination time of 5hr and NaOH to bentonite ratio of 0.20 gives the highest yield of biodiesel. All the characterization techniques used for the selected catalyst confirmed that the preparation of NaOH/bentonite was successful in creating the active and basic Na_2O component.

The effects of different operational parameters of the transesterification reaction on biodiesel yield were also studied. The result indicated that, the yield of biodiesel was found dependent on reaction temperature, catalyst loading, and methanol to oil molar ratio. The stability of the catalyst was also studied to check the performance of the recycled catalyst. The result showed that it can be used the recycled catalyst without incorporating calcination step during regeneration of the catalyst up to third generation with 15.6% reduction of biodiesel yield. The produced biodiesel by using the selected best catalyst and under the optimal reaction conditions was characterized and it's physio-chemical and fuel properties found to be in a good agreement with international standards.

From the result of the study, the synthesized NaOH/bentonite catalyst using impregnation method shows high catalytic activity for transesterification reaction. Therefore, it can be utilized as potential catalyst for producing biodiesel from cottonseed oil.

5.2. Recommendation

Recently biodiesel production using heterogeneous catalyst gets a great attention due to its environmental benefit and simple production process. Besides the studies conducted in this thesis the following recommendations are suggested for future work:

- Synthesize the catalyst using different methods to investigate the effects on the performance of the catalyst requires further study.
- As the characteristic of the catalyst affects its efficiency, selecting the best catalyst by taking its different characteristics as a response instead of biodiesel requires additional study.
- The one main advantage of using heterogeneous catalyst was its recyclability, but the efficiency was low compared to the fresh catalyst which requires further study to investigate the reason of low efficiency.
- The economic feasibility of biodiesel production using heterogeneous catalyst requires further investigation to confirm its advantages compared to homogeneous catalyst.
- The efficiency of the synthesized catalyst for the conversion of cottonseed oil into FAME can be further described by measuring FAME using GC-MS analysis for each run which requires additional study.

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Appendix

A: Determination of molecular mass of cottonseed oil

By referring table 4.2 the molecular weight of CSO was calculated as follows:

$$Mwt_{cso} = 0.55 * Mwt\ of\ \text{Linoleic acid} + 0.248 * Mwt\ of\ \text{Palmitic acid} + 0.172 * Mwt\ of\ \text{Oleic acid} + 0.008 * Mwt\ of\ \text{Myristic acid} + 0.022 * Mwt\ of\ \text{Stearic acid}$$

$$Mwt_{cso} = 0.55 * 280.5 + 0.248 * 256.4 + 0.172 * 282.5 + 0.008 * 228.4 + 0.022 * 184.5$$

$$Mwt_{cso} = 272.3 g/mol$$

B: Amount of feed materials required for the reaction

B1: Amount of feed materials required for the transesterification reaction to select best catalyst

The amount of oil used was determined based on the size three neck reactor; which is 250 ml. Therefore 50 ml of oil was used for each reaction.

- Methanol required

For 50 ml of cottonseed oil was calculated based on the molar ratio of methanol to oil which is 9.

$$\frac{n_{methanol}}{n_{oil}} = 9$$

$$Vmethnol = \frac{9 * mass\ of\ CSO * molecualr\ wight\ of\ methanol}{\rho methnol * molecular\ weight\ of\ CSO}$$

Methanol to oil molar ratio	9
Density of methanol (g/ml)	0.791
Molecular weight of CSO (g/mol)	272.3
Molecular weight of methanol (g/mol)	32
Mass of CSO (g)	46

$$Vmethnol = \frac{9*46*32}{0.791*272.3} = 61.5\ ml$$

Fixed amount of methanol was added for each reaction for the first experiment because the molar ratio of methanol to oil was constant.

- Amount of catalyst required

The amount of catalyst used was calculated based on the weight of the oil used. In the first experiment the mass of catalyst used was 1wt %of CSO.

$$Mass\ of\ catalyst\ (g) = 0.01 * Mass\ of\ CSO$$

$$Mass\ of\ catalyst\ (g) = 0.01 * 46\ (g)$$

$$Mass\ of\ catalyst\ (g) = 0.46\ g$$

B2: Amount of feed materials required for the transesterification reaction for the selection of optimum reaction parameters.

By using similar equation used in appendix C1 the amount of feed materials required were summarized below:

Table B-1: Amount of feed materials required for the transesterification reaction.

Mass of CSO (g)	Molar ratio of methanol to oil	Mass of catalyst (wt % of CSO)	Volume of methanol used (ml)	Mass of catalyst used (g)
46	3	1	20.5	0.46
	6	2	41.0	0.92
	9	3	61.5	1.38

C: Biodiesel yield calculation

The yield of biodiesel for each reaction was calculated by using the following formula:

$$yield\ (\%) = \frac{wight\ of\ biodiesel}{wight\ of\ cottenseed\ oil} * 100$$

The weight of cottonseed oil was constant for each experiment which has a value of 46 gram. By Measuring the weight and volume of biodiesel produced the yield of reaction was calculated and summarized below in table.

Table C-1: Yield of biodiesel produced by NaOH/Bentonite catalysts prepared at different parameters

Run	Factor			Amount of biodiesel		Yield (%)
	A:NaOH/Bentonite ratio	B:calcination temperature	C:calcination time	Volume (ml)	Mass (g)	
1	0.20	400.00	4.00	38.7	33.58	72.8261
2	0.50	400.00	4.00	34.6	30.08	65.6522
3	0.20	600.00	4.00	30.7	26.77	58.1957
4	0.50	600.00	4.00	26.5	23	50
5	0.20	500.00	3.00	42.2	36.8	80
6	0.50	500.00	3.00	37.0	32.2	70
7	0.20	500.00	5.00	43.4	37.72	82
8	0.50	500.00	5.00	40.4	35.09	76.087
9	0.35	400.00	3.00	32.9	28.66	62.3043
10	0.35	600.00	3.00	28.2	24.43	53.0935
11	0.35	400.00	5.00	39.8	34.64	75.3043
12	0.35	600.00	5.00	26.9	23.46	51
13	0.35	500.00	4.00	41.6	36.03	78.3261
14	0.35	500.00	4.00	41.4	36.18	78.6478
15	0.35	500.00	4.00	41.3	35.93	78.1087

Table C-2: Yield of biodiesel produced at different transesterification reaction parameters

Run	Factor			Biodiesel produced		Yield (%)
	A:methanol to oil molar ratio	B:reaction temperature	C:catalyst amount (wt % of mass of oil)	Volume (ml)	Mass (g)	
1	6.00	70.00	3.00	26.3	22.172	48.20
2	9.00	70.00	2.00	25.0	21.39	46.50
3	9.00	65.00	1.00	37.5	32.2	70.00
4	6.00	60.00	1.00	31.8	27.14	59.00
5	3.00	65.00	3.00	35.7	30.59	66.50
6	6.00	60.00	3.00	35.0	29.808	64.80
7	9.00	65.00	3.00	35.2	29.9	65.00
8	9.00	60.00	2.00	36.6	31.28	68.00
9	6.00	65.00	2.00	48.0	41.078	89.30
10	6.00	65.00	2.00	47.9	40.8802	88.87
11	3.00	65.00	1.00	34.6	29.578	64.30
12	6.00	65.00	2.00	48.3	41.538	90.30
13	6.00	70.00	1.00	31.8	26.979	58.65
14	3.00	60.00	2.00	29.5	25.208	54.80
15	3.00	70.00	2.00	30.5	25.99	56.50

D. Physicochemical properties of biodiesel

- Specific gravity

Density of biodiesel measured using digital density meter:

$\rho_{\text{biodiesel}}$ = 0.872g/ml

$$S.G = \frac{\rho \text{ biodiesel}}{\rho \text{ water}} = \frac{0.872\text{g/ml}}{1.00\text{g/ml}} = 0.872$$

- Kinematic viscosity

$$\mu = 3.64 mPa.s \text{ @ } 40\ ^{0}\text{C}$$

$$\nu = \frac{\mu}{\rho\ biodiesel} = \frac{3.64\ mPa.s}{872 kg/m^3} = 4.18 mm^2/s$$

- Iodine value

Table D-1: Amount of sodium thiosuophate used during the titration

No.	Amount of Na_2SO_3 consumed in (ml)	V_B-V_S(ml)
Sample 1	21.5	20
Blank solution 1	41	
Sample 2	22.6	20.2
Blank solution 2	42.8	
Average		20.1

$$IV = \frac{12.69 * N(V_B - V_S)}{m}$$

$$IV = \frac{12.69 * 0.1(20.1)}{0.25}$$

$$IV = 102.03\ g\ I_2/100g\ CSB$$

- Acid value

Table D-1: Amount of KOH used during titration

No.	Initial volume of KOH (ml)	KOH used during titration (ml)
Sample 1	0	0.12
Sample 2	0	0.13
Average	0	0.11

$$AV = \frac{56.1 * N * V}{W}$$

$$AV = \frac{56.1 * 0.1 * 0.11}{3}$$

$$AV = 0.21 mg\ KOH/g\ CSB$$

- Saponification number

Table D-3: Volume of hydrochloric acid used during the titration

No.	Amount of HCl consumed in (ml)	V_B-V_S(ml)
Sample 1	8.2	9.8
Blank solution 1	18	
Sample 2	8.5	10
Blank solution 2	18.5	
Average		9.9

$$SN = \frac{56.1 * N(V_B - V_S)}{W}$$

$$SN = \frac{56.1 * 0.5 * 9.9}{2}$$

$$SN = 138.85 mg\ KOH/g\ CSB$$

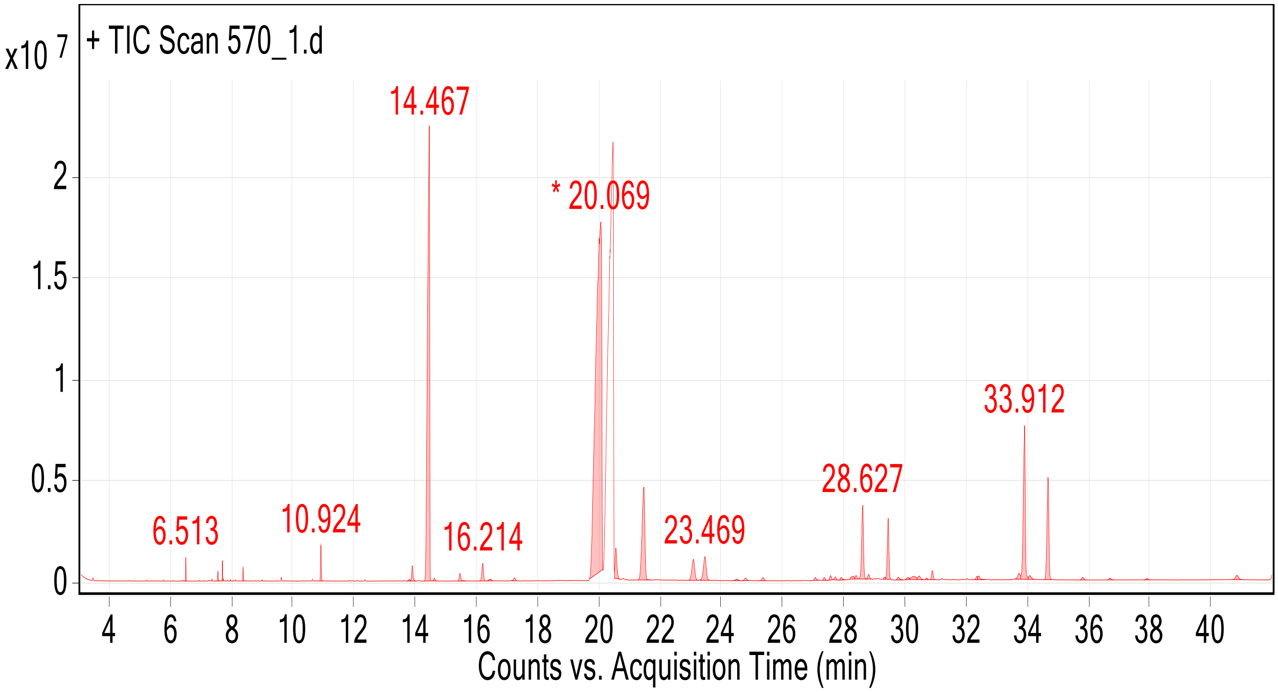
E: GCMS analysis result and FAME content of CSB

$$C_{FAME} = \frac{S_A - A_{EI}}{A_{EI}} * \frac{C_{EI} - V_{EI}}{m} * 100\%$$

$$C_{FAME} = \frac{738350859 - 109406681}{109406681} * \frac{10 - 5}{30} * 100\%$$

$$C_{FAME} = 95.8\ \%$$

GCMS analysis result graph



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JIJE Analytical *Testing* Service Laboratory

Doc. No:	JATSL/F5.10-3.1
Page 1 of 2	
Ver. No:	04
Effective Date:	July 08, 2017

Analytical Test Report

Customer Name:	AAiT	Test Report No:	141
Contact Person:	Lamesgin Desta	Report Date:	03/06/2019
Sample Type:	Biodiesel	Test Request No:	Not Specified
Sample Source:	Cotton Seed Oil	Tel (Mob):	+251 922 82 59 06
Sample Collected By:	Customer	Fax:	Not Specified
Sample Collection Date:	21/04/2019	E-mail:	lamesgindb@gmail.com
Sample Receiving Date:	21/05/2019	Tested By:	LE-02
Sample Condition:	Normal	Dates Tested:	01/06/2019

Lab No: J-0570/2105/19, Customer Code: Biodiesel – Cotton Seed Oil, Test Method: GC-MS

S/N	Name	RT	Formula	Area	Area %
1	Octanoic acid, methyl ester	6.51	$C_9H_{18}O_2$	1018192.00	0.14
2	2,4-Decadienal	7.56	$C_{10}H_{16}O$	488863.00	0.07
3	2,4-Decadienal, (E,E)-	7.71	$C_{10}H_{16}O$	907943.00	0.12
4	Nonanoic acid, 9-oxo-, methyl ester	8.38	$C_{10}H_{18}O_3$	702090.00	0.10
5	Methyl tetradecanoate	10.92	$C_{15}H_{30}O_2$	2928244.00	0.40
6	9-Hexadecenoic acid, methyl ester, (Z)-	13.91	$C_{17}H_{32}O_2$	2268179.00	0.31
7	Hexadecanoic acid, methyl ester	14.47	$C_{17}H_{34}O_2$	109406681.00	14.82
8	17-Octadecynoic acid, methyl ester	14.63	$C_{19}H_{34}O_2$	397327.00	0.05
9	9,12-Octadecadienoyl chloride, (Z,Z)-	15.47	$C_{18}H_{31}ClO$	1379581.00	0.19
10	Hexadecanoic acid, ethyl ester	16.21	$C_{18}H_{36}O_2$	3255249.00	0.44
11	Heptadecanoic acid, methyl ester	17.26	$C_{18}H_{36}O_2$	622769.00	0.08
12	9-Octadecenoic acid, methyl ester, (E)-	20.47	$C_{19}H_{36}O_2$	243193177.00	32.94
13	9-Octadecadienoic acid (Z)-, methyl ester	20.56	$C_{19}H_{36}O_2$	6164946.00	0.83
14	Methyl stearate	21.48	$C_{19}H_{38}O_2$	29175041.00	3.95
15	Linoleic acid ethyl ester	23.09	$C_{20}H_{36}O_2$	6686616.00	0.91
16	Ethyl Oleate	23.47	$C_{20}H_{38}O_2$	7438742.00	1.01
17	Octadecanoic acid, ethyl ester	24.80	$C_{20}H_{40}O_2$	687137.00	0.09
18	Cyclopropaneoctanoic acid, 2-octyl-, methyl ester	25.37	$C_{20}H_{38}O_2$	759168.00	0.10
19	cis-11-Eicosenoic acid, methyl ester	28.63	$C_{21}H_{40}O_2$	15134253.00	2.05
20	cis-13-Eicosenoic acid, methyl ester	28.82	$C_{21}H_{40}O_2$	928957.00	0.13
21	Eicosanoic acid, methyl ester	29.46	$C_{21}H_{42}O_2$	11145742.00	1.51
22	6,9,12-Octadecatrienoic acid, methyl ester	30.90	$C_{19}H_{32}O_2$	1621585.00	0.22
23	13-Docosenoic acid, methyl ester, (Z)-	33.91	$C_{23}H_{44}O_2$	33381528.00	4.52
24	Docosanoic acid, methyl ester	34.68	$C_{23}H_{46}O_2$	21730471.00	2.94
25	Erucic acid ethyl ester	35.81	$C_{24}H_{46}O_2$	572614.00	0.08

Remark:

1. This test report is only for specific sample (s) which has been tested by JIJE Analytical *Testing* Service Laboratory.

Verified by			***Authorized by***		
Name	**Signature**	**Date**	**Name**	**Signature**	**Date**
Gemechu Sorsa	…………	03/06/2019	**Mulugeta Terefe**	…………	03/06/11
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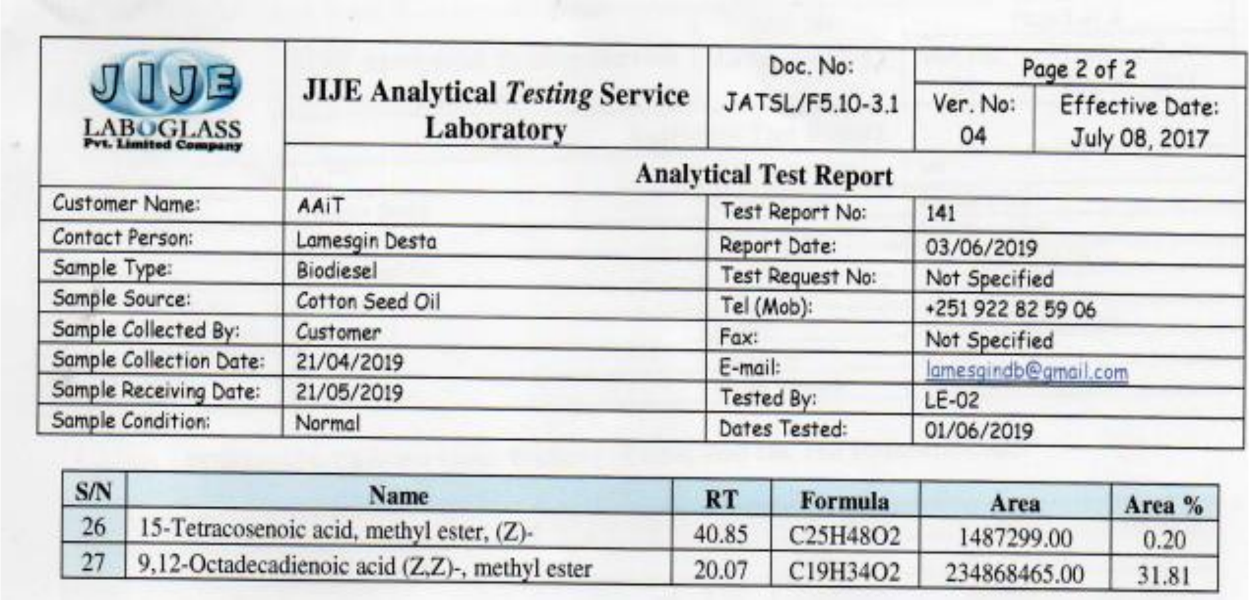
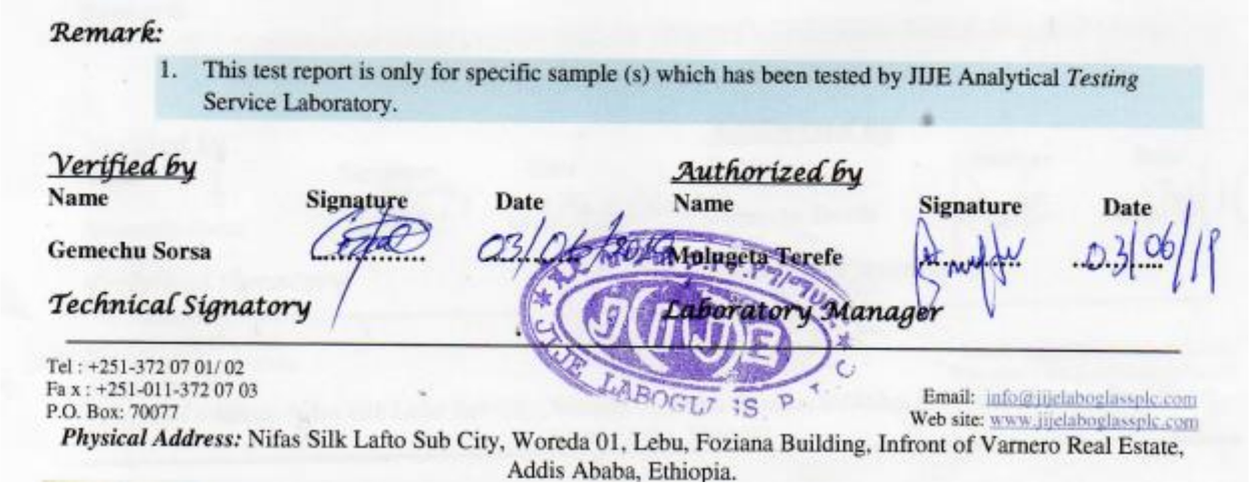
Physical Address: Nifas Silk Lafto Sub City, Woreda 01, Lebu, Foziana Building, Infront of Varnero Real Estate, Addis Ababa, Ethiopia.



JIJE LABOGLASS Pvt. Limited Company	**JIJE Analytical *Testing* Service Laboratory**	Doc. No: JATSL/F5.10-3.1	Page 2 of 2 Ver. No: 04	Effective Date: July 08, 2017
	Analytical Test Report			

Customer Name:	AAiT	Test Report No:	141
Contact Person:	Lamesgin Desta	Report Date:	03/06/2019
Sample Type:	Biodiesel	Test Request No:	Not Specified
Sample Source:	Cotton Seed Oil	Tel (Mob):	+251 922 82 59 06
Sample Collected By:	Customer	Fax:	Not Specified
Sample Collection Date:	21/04/2019	E-mail:	lamesgindb@gmail.com
Sample Receiving Date:	21/05/2019	Tested By:	LE-02
Sample Condition:	Normal	Dates Tested:	01/06/2019

S/N	Name	RT	Formula	Area	Area %
26	15-Tetracosenoic acid, methyl ester, (Z)-	40.85	$C_{25}H_{48}O_2$	1487299.00	0.20
27	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	20.07	$C_{19}H_{34}O_2$	234868465.00	31.81



Remark:

1. This test report is only for specific sample (s) which has been tested by JIJE Analytical *Testing* Service Laboratory.

Verified by			***Authorized by***		
Name	**Signature**	**Date**	**Name**	**Signature**	**Date**
Gemechu Sorsa	....	03/06/2019	**Mulugeta Terefe**		03/06/19
Technical Signatory			***Laboratory Manager***		

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	GEOLOGICAL SURVEY OF ETHIOPIA	**Doc.Number:** **GSE/F 5.10-2**	**Version N**
	GEOCHEMICAL LABORATORY DIRECTORATE		**Page 1 of**
ocument Title:	**Hydrocarbon Laboratory Analysis Report**	**Effective date:**	**May, 2017**

Issue Date: - 03/06/2019
Customer Name: - Lamesgin Desta.
Request No: - GLD/357/19
Report No: GLD/TR/297/19
Sample type: - Liquid
Sample Preparation: - None
Date Submitted: - 27/05/2019
Number of Sample: -One (1)
Elements to be determined:- Calorie.
Method of analysis:- Adiabatic Calorie Metter.

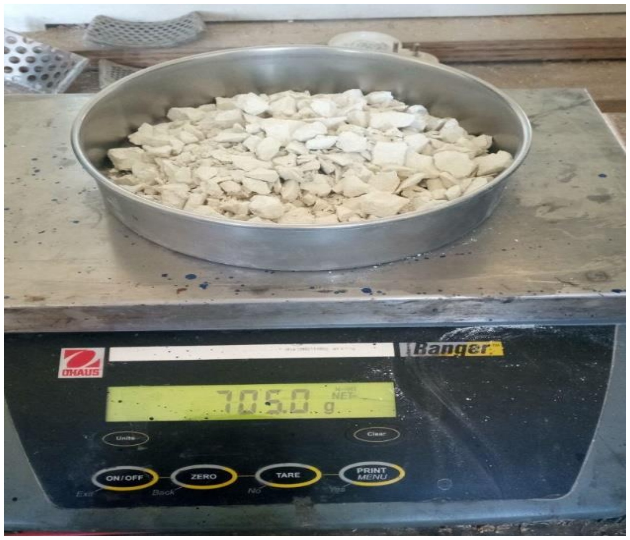
Collector's Code	Calorific Value cal/gm
CSB(Biodiesel)	8,940.93

Note: - This result represent only for the sample submitted to the laboratory.

Analysts	Approved By	Quality Control
Hayimanot Bayeh	Alemnesh Abate	Negash Worku
Shashie Hailie		

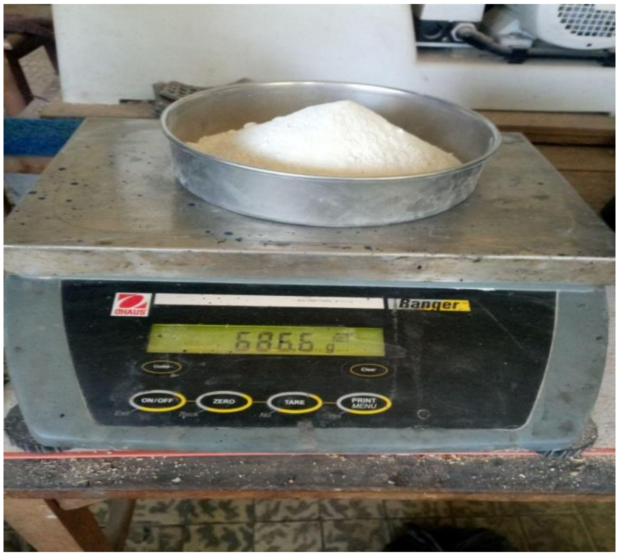
F: Experimental setup and equipment's used

a) Raw bentonite



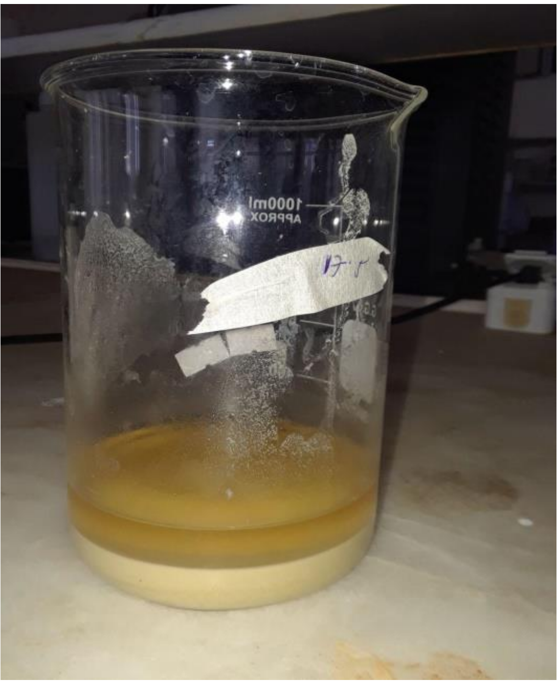
b) Crushed bentonite

c) Hammer mill



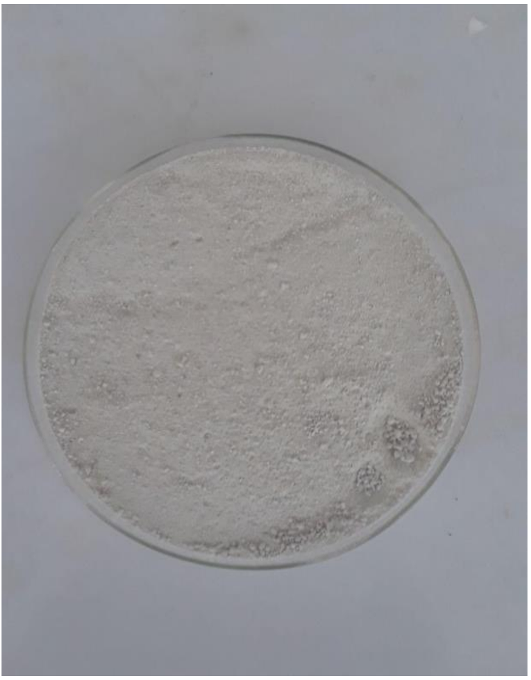
d) Powdered bentonite

e) Rotary mixer



f) Impregnated sample

g) Oven for drying



h) Dried sample

i) Muffle furnace for calcination

j) NaOH/bentonite catalyst

k) Three neck reactor for reaction

l) Separator funnel

m) Biodiesel sample

n) Recycled catalyst

o) XRD analysis equipment

p) FTIR analysis equipment