Characterization and Optimization of Biodiesel from Cotton Seed Oil using Ethanol with egg shell CaO

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Acronyms and symbols

ANOVA	Analysis of Variance
AV	Acid Value
ASTM	American Society for Testing and Material
CN	Cetane Number
CP	Cloud Point
CSO	Cotton Seed Oil
EN	European Committee for Standardization
FAEE	Fatty Acid Ethyl Ester
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
FP	Flash Point
GC-MS	Gas Chromatography – Mass Spectrometer
HHV	Higher Heating Value
IV	Iodine Value
RSM	Response Surface Methodology
SG	specific Gravity
SV	Saponification Value
XRD	X-Ray Diffraction
μ	Kinematic Viscosity

Abstract

The demand of world energy increases from time to time, this leads to gradual depletion of petroleum reserves, petroleum price rising and increases environmental problems. Beside to the above problems Ethiopia has additional diesel transportation cost. These all problems has motivated the search for sustainable and environment-friendly alternative renewable biofuels such as biodiesel. Since, it is non-toxic and capable of fulfilling an increasing energy demand. In this study biodiesel was produced by transesterification reaction in the presence of CaO with 99.5% ethanol. The biodiesel production process includes CSO extraction and CaO catalyst preparation from chicken egg shell waste. Moreover, this study characterizes the Physico-chemical properties of CSO and ethyl ester according ASTM D6751 standards to use the FAEE as an alternative fuel for diesel engines. All of the measured Physico-chemical properties of the biodiesel was in the range of the international standards.

Design expert 7.0.0 with Box-Behnken was applied to investigate the effect of reaction parameters such as, reaction temperature (70, 75 and 80°C), ethanol to oil molar ratio (6:1, 9:1 and 12:1) and catalyst loading (1, 2 and 3%) on the yield of biodiesel. Significance of the process variables were analyzed by ANOVA. RSM was applied to investigate the interaction effect of process variables on the yield of biodiesel and to find the optimum yield. As the result of RSM optimization, the optimum yield of biodiesel 97.65 % w/w were found at an optimum reaction temperature of 73.71 °C, ethanol to oil ratio of 10.12:1 and a catalyst loading of 1.84 wt% of oil.

Keywords: Cottonseed oil, Trans esterification, CaO, Biodiesel & Optimization

1. Introduction

1.1 Background

The World's economic growth is affected by climatic change, fuel price raise, and the gradual depletion of fossil fuel reserves. The 1970s' energy crisis and people's more attention in environment sparked the study of biodiesel and boomed it rapidly. In the period 2001 - 2009, the production of biodiesel in the world increased by more than 16 times (from 9.57 billion tons to 157.6 billion tons). Except the traditional biodiesel production countries the EU and US, a significant increase of market has been expected in developing countries as China, Brazil, Japan, Indonesia, and Malaysia [1].

In Ethiopia Following the population growth and economic development, the need for more modern fuels has increased significantly over the years. The demand for petroleum has raised by over 70% from 1.1million metric tons in the fiscal year 2000/01, to 1.9 million metric tons in the fiscal year 2007/08. Import values however, grew disproportionately higher by over 500% from USD0.27 billion to USD1.6 billion in the same time period. In (2007/08) the import price of petroleum fuel was exceeded annual export earnings, resulting in a negative balance of trade [2].

Therefore, to increase energy security for economic development, to reduce environmental pollution and dependency on fossil fuel the need to search for an alternative source of energy such as biodiesel is necessary. Since it is renewable, sustainable, biodegradable, and emits low greenhouse gases [3].

Biodiesel fuel is produced through transesterification of refined vegetable oil, waste cooking oil, and oil fats using alkaline catalysts. The transesterification is usually carried out using primary and secondary alcohols. Methanol and ethanol are most frequently used in the production of biodiesel [4]. The most common catalysts used in the production of biodiesel are homogeneous base catalysts such as NaOH and KOH. The advantages of these catalysts are the reaction proceeds at a much higher rate and are less corrosive than the homogeneous acid (H_2SO_4) catalyst. Even though the homogeneous base catalyzed biodiesel production processes are relatively fast, and show high yield, they are still not very cost-competitive with petro diesel ones because of the cost of raw material used and the catalyst cannot be recovered after the reaction. In order to reduce the production cost of biodiesel, some researchers conducted research by using solid catalyst [5].

Calcium oxide is one of the most studied heterogeneous base catalyst for trans esterification reaction. Producing biodiesel using CaO has many advantages, such as higher activity, mild reaction conditions, reusability, and easy availability and low cost [6].

The naturally abundant source of CaO is limestone, in addition the other natural resources are crab shells, egg shells, capiz shells, snail shells, oyster shells, mussel shells. The appropriate utilization of these considerable waste shells for the synthesis of CaO catalyst is expected to decrease the entire dependency on limestone rocks which are non-renewable sources of CaCO3. The CaCO3 content in egg shell is 97.1%. This shells, when thermally treated at 900°C for 120 min, resulted in the formation of CaO catalyst. Using of egg shell catalyst for transesterification of sunflower oil with methanol was resulted 97.75% biodiesel yield [7].

Presently, more than 95% of commercial biodiesel is produced from cotton seed, rapeseed, palm, and sunflower and soybean oil [4]. Out of these cotton seed is cheap in cost so using it as feed stock is 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 [8]. 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 Statement of the Problem

The issue of energy security resulting from the gradual depletion of world petroleum reserves, rising of petroleum price and environmental concerns has energize the search for alternative renewable biofuels. In addition, now a days the country's population growth increases fastly following to this the fuel consumption also increased significantly. For this reason, it needs searching alternative renewable bio fuels that are economically competitive, environmentally acceptable and capable of fulfilling an increasing energy demand.

To produce environmentally friendly and economically acceptable biodiesel using heterogeneous catalyst prepared from chicken egg shell waste is better. Biodiesel production process using homogeneous catalysts such as sodium and potassium hydroxides causes apparatus corrosion, not reusable and requires further process for catalyst separation this leads to extra cost expense, but using a heterogeneous catalysts such as CaO is low cost, easily separated, reusable and provides higher conversion efficiency than a homogeneous catalyst. Thus all simplifies the production and purification processes. Although, most of the researchers has worked with methanol alcohol as a reactant during transesterification reaction it causes significant human health effect and environmental problems when compared to ethanol alcohol. Based on this it is better to use ethanol alcohol instead of methanol since it is locally available, cheap in price and bio based. Therefore, this study seeks to create green environment with reduced cost by overcoming the above limitations.

Moreover, to produce environmentally friendly and economically acceptable biodiesel Cotton seed is preferable. As it is a waste of textile industry its price is less expensive. This makes it a potential alternative feedstock for biodiesel production. So such vegetable based biodiesel can be promote environmental conservation, decrease greenhouse gas emission and solve problems related with energy security.

1.3 Objectives

1.3.1 General Objective

The general objective of this study was to characterize and optimize the biodiesel from cotton seed oil using ethanol with prepared egg shell calcium oxide at laboratory scale and to compare the physico-chemical properties of biodiesel with the standard.

1.3.2 Specific Objectives

The specific objectives of this study were:

- To prepare and characterize calcium oxide catalyst from chicken egg shell.
- To characterize the physico-chemical properties of cotton seed oil and biodiesel.
- To study the effect of reaction temperature, catalyst loading and ethanol to oil molar ratio on the yield of biodiesel.
- To find optimum operating parameters using RSM.

1.4 Significance of the study

Currently in Ethiopia the demand for modern energy sources such as petroleum fuels is increasing with increase in population and economic growth. The country imports its entire petroleum fuel requirement by spending over 46 % of the foreign earning annually. To overcome the above problem the government of Ethiopia gives attention to environmental-friendly renewable energies such as biodiesel since importing of petroleum adds a lot of cost to the country besides to higher environmental pollution through emitting of CO_2 and NO_X gases. So this study is significant on solving problems related to environmental concern, energy security and economy.

Biodiesels developed from vegetable oil reduces environmental pollution, greenhouse emission and has higher combustion efficiency because it is non-toxic, renewable, and biodegradable. The production of biodiesel from locally available resource is reliable, renewable and domestically distributed, this reduces dependency on imported petroleum and energy crisis.

The other significance of this research is to improve the economic development of the country and helps on finding different alternative biofuels so as to increase the farmer's income by creating job opportunity around the rural areas and this motivates agricultural and sustainable development. Besides, using of solid catalyst and cotton seed oil reduces production cost of biodiesel because of reusable nature of catalyst. Generally, the availability of alternative energy sources alleviates the world's petroleum depletion in addition to economic benefits.

2. Literature Review

2.1 Biodiesel

Biodiesel is the general name for fatty acid alkyl esters and the most common alternative fuel for traditional diesel engines. Biodiesel has significantly lower emissions than petroleum based diesel. It does not contribute to a net rise in the level of carbon dioxide in the atmosphere and leads to minimize the intensity of greenhouse effect. In addition, biodiesel is better than diesel fuel in terms of sulphur content, flash point, aromatic content and biodegradability [9].

In Ethiopia the One main issue is that around 65% of the export earnings are to pay for the import of petroleum products. Amongst the identified alternative renewable energy sources, biofuels in particular energy crops received attention as a promising and sustainable energy sources, of which, biodiesel has arisen as a potential candidate for a petro diesel substitute that minimize the escalating budgetary pressure for diesel oil [10].

In the world several seeds such as soybeans, canola, sunflower, Jatropha, coconut, cotton seed, palm, corn and castor oil was used for the production of biodiesel, mainly by the transesterification reaction with short chain alcohols (methanol or ethanol) and employing alkaline catalysts. Out of those Cottonseed oil is the oldest vegetable oil used industrially produced and widely consumed in Brazil. Consumption decreased with the increase in soybean production, but still occupies a place of great economic importance [11].

2.2 Current status of biodiesel production

2.2.1 Europe biodiesel production

Biodiesel markets will likely remain dominated by the European Union and followed by the USA, Argentina, and Brazil. The world biofuels production reached almost 124 billion liters in 2011; 80 % of that global production of liquid biofuels consists of ethanol and 20 % consists of biodiesel. The USA and Brazil are the largest ethanol producers, with 54 and 34 % of global ethanol output in 2009, respectively. EU is the world major player in biodiesel production with a share of 57 % of total world production in 2009. Currently, the production capacity of European biodiesel has reached approximately 22 million tons. In 2011, Germany and France remained by far the leading biodiesel producing nations, while Spain confirmed its position of the third European biodiesel producer, ahead of Italy. Within the EU, the first four largest biodiesel-producing member states that account for two-thirds of total production are Germany (33 % of total European production), followed by France (18 %), Spain (7 %), and Italy (5.6 %) (EBB 2013)[12]. Table 2.1 shows the biodiesel production and consumption of the countries of EU.

Table 2.1 EU biodiesel production and consumption in 2011
Source: Biofuels Barometer (2013) and EBB (2013)

Country	Production (k tonnes)	Country	Consumption (Mtoe)
Germany	4,968	Germany	2,190
Spain	4,391	France	2,299
The Netherlands	2,517	Spain	1,718
France	2,456	Italy	1,263
Italy	2,310	Poland	755
Poland	884	UK	499
Greece	812	Sweden	307
Belgium	770	Austria	449
Others	4,430	Others	2,681
Total	23,538	Total	11,409

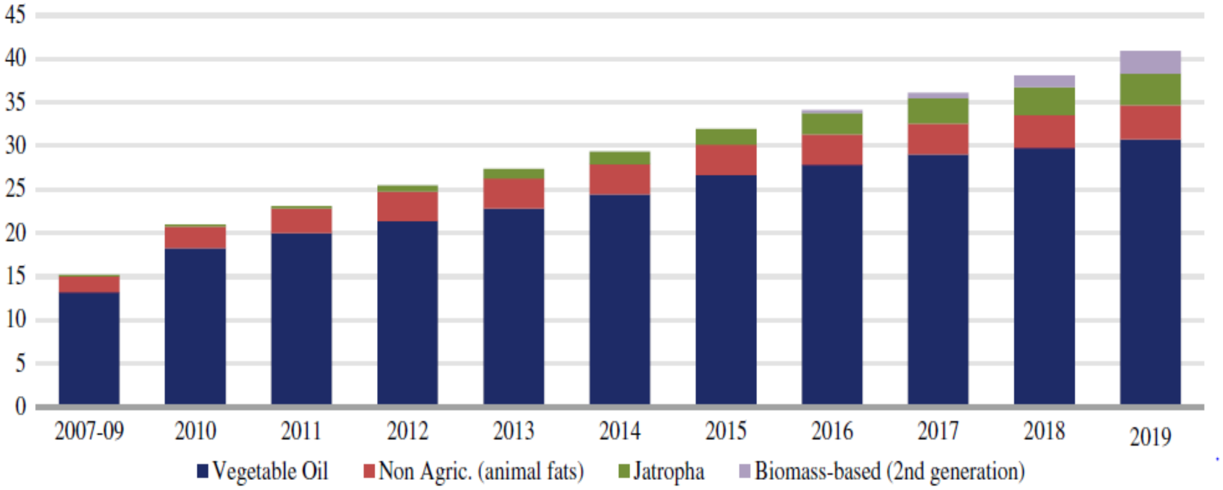


Figure 2.1 Evolution of biodiesel production by feedstock (billion liters). Source OECD-FAO (2010)

2.2.2 Biodiesel Development Status in Ethiopia

The initiative for biofuels development in Ethiopia originally came from the private sector, though it did not take too long to get the government to buy-in. Mitigation of climate change is often presented by governments as a key policy goal for biomass fuel developments, but in the case of Ethiopia, the government is explicit about its reasons for promotion of biofuels. The reasons, among others, are energy security through the use of biofuels and to improve the balance of trade by import substitution and new export market development. Following population growth and economic development, the need for more modern fuels has increased significantly over the years. In general the demand for petroleum in the country indicates that there is a gradual increase from a year of 2000 to 2008.

A Biofuels Development and Utilization Strategy has been formulated by the Ministry of Mines and Energy in August 2007. The objective of the strategy is to facilitate sufficient production of biofuels from indigenous resources so as to substitute imported petroleum and export excess products. The biofuels strategy document identified some energy crops such as sugarcane, Jatropha, castor and palm trees as potential feedstock for biofuels production [2].

2.3 Feed stocks for Biodiesel Production

The primary feed stocks used in the production of biodiesel are vegetable oils, animal fats, and recycled greases. The feed stock used for the production of biodiesel is best if, it is not be competitive with food, land used for the oil plantation and oil production, with forest and other agricultural products [8].

- Animal fats

Animal fats used to produce biodiesel include tallow, choice white grease or lard, fish fat (in Japan) and chicken fat. Compared to plant crops, these fats frequently offer an economic advantage because they are often priced favorably for conversion into biodiesel. Animal fat methyl ester has some advantages such as high Cetane number, non-corrosive, clean and renewable properties. Animal fats tend to be low in FFAs and water, but there is a limited amount of these oils available, meaning these would never be able to meet the fuel needs of the world.

- Used edible oils

Because of the poor quality of soap produced from WCO, a large amounts of WCO are illegally dumped into rivers and landfills, causing environmental pollution. Hence the management of such oils and fats pose a significant challenge because of their disposal problems and possible contamination of the water and land resources.

The production of biodiesel from WCO to partially substitute petroleum diesel is one of the measures for solving the twin problems of environment pollution and energy shortage. In order to reduce the cost of biodiesel production, WCO would be a good choice as raw material since it is cheaper than virgin vegetable oils and other feed stocks. But the problem related with this is its high free fatty acid content and high viscosity.

- Vegetable oils sources

Biodiesel has been predominantly (more than 95 %) produced from edible vegetable oils all over the world, which are easily available on large scale from the agricultural industry. Currently, biodiesel is mainly prepared from rapeseed in Canada, soybean in US, sunflower in Europe and palm in Southeast Asia. The largest biodiesel producers were the European Union, the United States, Brazil, Indonesia, with a combined use of edible oil for biodiesel production of about 8.6 million tons (7.8 million hectares were used) in 2007.

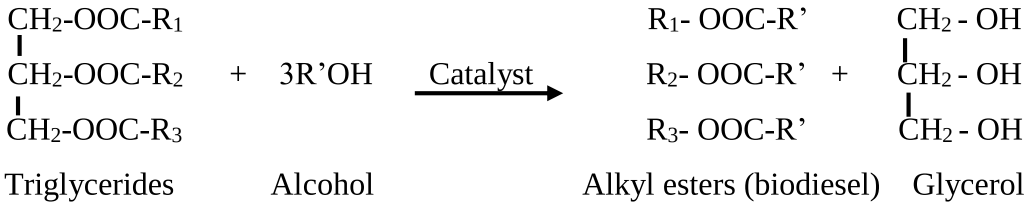
There are a large number of oil plants that produce non-edible oils, such as Jatropha, karanja, tobacco, mahua, neem, rubber, sea mango, castor, and cotton. Of these feed stocks, Jatropha, moringa and castor oils are the most often used in biodiesel production. Cottonseed comes after Soybean, Corn and Canola (rapeseed) in the list of genetically modified crops.

- **Cottonseed**

Cottonseed contains averagely 18-25% of oil and 20-25 % high quality protein (Rathore, 2007) but presently cottonseed is not used in food preparations. It is used in animal feed in regulated manner due to the presence of gossypol [13]. Cottonseed oil contains different fatty acids, such as saturated fatty acids (1.2% of myristic acid, 18–25% of palmitic acid, 1–25% of stearic acid, 1–2% of palmitoleic acid), monounsaturated fatty acids (17–38% of oleic acid) and diunsaturated linoleic acid (45–55% of linoleic acid) [11].

2.4 Chemistry of biodiesel production

Biodiesel is produced by means of transesterification. Transesterification is the reaction of a fat or triglyceride with an alcohol in the presence of acid or base catalyst to form esters commonly methyl or ethyl esters and a byproduct, glycerol. It is, in principle, the action of one alcohol displacing another from an ester, referred to as alcoholysis [15].



$$\begin{array}{l} CH_2\text{-}OOC\text{-}R_1 \\ | \\ CH_2\text{-}OOC\text{-}R_2 \\ | \\ CH_2\text{-}OOC\text{-}R_3 \end{array} + 3R'OH \xrightarrow{\text{Catalyst}} \begin{array}{l} R_1\text{-}OOC\text{-}R' \\ R_2\text{-}OOC\text{-}R' \\ R_3\text{-}OOC\text{-}R' \end{array} + \begin{array}{l} CH_2\text{-}OH \\ | \\ CH_2\text{-}OH \\ | \\ CH_2\text{-}OH \end{array}$$

Figure 2.2 General Trans esterification reaction in the presence of a catalyst

2.5 Physico chemical properties and specifications of biodiesel

The fuel specification defines and sets the quality standards for biodiesel. It is based on the standard ASTM D6751. The biodiesel standards in Brazil and the U.S. are applicable for both fatty acid methyl esters (FAME) and fatty acid ethyl esters (FAEE), whereas the current European biodiesel standard is only applicable for fatty acid methyl esters (FAME) [16, 17]. The ASTM and EU biodiesel property specifications with the recommended test methods are given in Table 2.2.

Table 2.2 ASTM Standards for Biodiesel

Property	Test method	Limits	Units
Ca and mg combined	EN14538	5 max.	Ppm
Flash point	D93	93.0 min	ºC
Alcohol control :one of the following must be met: 1.methaol content 2.flash point	EN14110 D93	0.2 max. 130 min.	Vol% ºC
Water and sediment	D2709	0.050 max.	Vol%
Kinematic viscosity @40ºC	D445	1.9-6.0	mm^2/s
Sulfated ash	D874	0.020	% mass
Sulfur	D5453	0.0015max.(S15) 0.05 max.(S500)	% mass
Copper strip corrosion	D130	No.3 max	
Cetane number	D613	47 min.	
Cloud point	D2500	Report to customer	ºC
Carbon residue	D4530	0.050 max	% mass
Acid number	D664	0.50 max	mgKOH/g
Free glycerin	D6584	0.20 max.	%mass
Total glycerin	D6584	0.240 max	%mass
Phosphorus content	D4951	0.001 max	%max.
Na and K combined	EN14538	5max,	Ppm
Oxidation stability	EN14112	3min	H

a. viscosity

Viscosity is a measure of the internal fluid friction or resistance of oil to flow, which tends to oppose any dynamic change in the fluid motion. As the temperature of oil is increased its viscosity decreases. The lower the viscosity of the oil, the easier it is to pump and atomize and achieve finer droplets. In fuels viscosity affects the combustion efficiency by lowering the heating value.

b. Iodine value

This measures the level of unsaturation of the oil and it the amount of iodine in grams absorbed per 100 grams of fuel. The higher the iodine value the higher the unsaturation of the oil.

c. Specific gravity

Specific gravity means relative density with respect to water. The specific gravity of most oils and their methyl esters is higher than that of diesel fossil fuel. This is due to the larger molecular mass and chemical structures of vegetable oils.

d. Total acid number (TAN)

This is the amount of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of oil or biodiesel. In refinery the TAN value indicates to crude oil refinery the potential of Corrosion problem. TAN values can be determined by color indicator titrations. Acid numbers for biodiesels in (mgKOH/g oil) are preferred lower than 3.

e. Flash point

This is the lowest temperature to which a fuel has to be heated for it vaporize and form a combustible mixture with at atmospheric pressure. It is one of the descriptive characteristic of fossil fuel and biofuels. From literature liquids with a flash point less than 60 ^{o}C are flammable and those above this temperature are combustible liquids.

f. Cloud point (CP)

This is the temperature at which wax crystals first appear in diesel or bio wax. In bio diesel sample that is cooled under conditions described by ISO 3015. Solidified waxes and thickening of oils clogs air filters also injection ports in engines.

g. Cetane number (CN)

The cetane number measures the readiness of the fuel to auto-ignite when injected into the engine. Many performance characteristics such as density, heating value are related to Cetane number. Cetane number is the parameter used to determine the quality of biodiesel; it is proportionate to the fuel ignition delay time in CI engines. A fuel’s CN rating can be applied to determine ignition characteristics of biodiesel fuels.

h. Calorific value

Calorific value of a fuel is the thermal energy released per unit quantity of fuel when the fuel is burned completely and the products of combustion are cooled back to the initial temperature of the combustible mixture. It measures the energy content in a fuel. The calorific value of vegetable oils and their methyl esters were measured in a bomb calorimeter according to ASTMD240 standard method.

2.6 Biodiesel production process systems

2.6.1 Batch Process

During batch process the refined vegetable oil is charged to trans esterification reactor in the presence of an excess amount of alcohol, and catalyst. An excess of alcohol is necessary chiefly to ensure full solubility of triglyceride and keep the viscosity of the reaction mixture low and also for shifting the chemical equilibrium. The trans esterification reaction may be considered finished when maximum conversion is achieved. Separation of ester and glycerol is takes place by decantation. Then the ethanol is recovered by rotary evaporator and this is used for next batch. At the end the ester is washed with hot water and dried [18].

2.6.2 Catalytic continuous process

Catalytic continuous process technology of biodiesel production is a conceptual scheme of a continuous process working at low pressure that is capable of processing a feedstock with a larger amount of free fatty acids, such as unrefined non edible vegetable oils, tallow fat and used cooking oil. For this reason in the first reactor the esterification of free fatty acids with ethanol is carried out. Then the transesterification reaction follows in the second reactor. A homogeneous catalyst is currently used, either as alkaline hydroxide or alkaline ethoxide. Ensuring high yield in monoester and minimum amounts of mono or di-triglycerides a minimum of two reactors in series with glycerol intermediate separation ought to be employed. The reaction mixture is then submitted to phase separation in crude ester and glycerol phase and separation can take place by decanting or centrifugation [19].

2.7 Biodiesel production process methods

Vegetable oils and animal fats are comprised of a complex mixture of triglycerides and other minor components, such as free fatty acids, gums, waxes, etc. Triglycerides are esters of glycerol with three chains of aliphatic or olefinic FFAs of variable length (12–24 carbons). Among all the proposed methods to convert oils to biodiesel, transesterification of the triglycerides seems to be the best choice, as the physical characteristics of fatty acid esters (biodiesel) are very close to those of diesel fuel [20].

2.7.1 Hydrolysis and Esterification

The manufacturing procedure is first the hydrolysis of triglycerides and isolating the fatty acids followed by esterification employing the robust technology of a solid heterogeneous catalyst. Significant advantages would be the possibility of extracting high value fatty acids from the lipid material, as well as obtaining high purity glycerol [21].

2.7.2 Trans Esterification Reactions

Trans esterification is the reaction of a fat or oil triglyceride with an alcohol to form esters and glycerol. A catalyst is usually used to improve the reaction rate and yield. There are different types of trans esterification, such as Homogeneous acid-catalyzed trans esterification, Homogeneous alkali (base) catalyzed trans esterification, Heterogeneous acid and base-catalyzed trans esterification, Supercritical and subcritical alcohol trans esterification [22].

2.7.2.1 Types of transesterification reaction

- Supercritical transesterification

This new supercritical methanol process requires a shorter reaction time and a simpler purification procedure because of the absence of dissolved catalyst. Of course this method does necessitate high temperature and pressure (and therefore energy costs) and also requires an expensive workup because of dissolution of the glycerol by-product in methanol under these reaction conditions.

- Homogeneous catalyst transesterification

The transesterification reaction can be catalyzed by Brønsted acids, preferably sulfonic and sulfuric acids, but the reactions rates are low and require relatively high temperatures to get high product yields. The most common homogeneous acid catalysts employed are H_2SO4 and HCl. Currently it is synthesized using homogeneous alkaline catalysts because the transesterification reaction by an acid catalyst is much slower than the base-catalyzed reaction. The most common basic catalysts are KOH, NaOH, NaOCH3 (sodium methoxide), and NaOCH2CH3 (sodium ethoxide). Even though homogeneous catalyzed biodiesel production processes are relatively fast and show high conversions with minimal side reactions, they are still not very cost competitive with petro diesel. The other disadvantages include that:

- ❖ The catalyst cannot be recovered and must be neutralized at the end of the reaction,
- ❖ There is limited use of continuous processing methodologies, and
- ❖ The processes are very sensitive to the presence of water and FFA; consequently they need a high quality feedstock to avoid undesired side reactions (hydrolysis and saponification).

- o Heterogeneous catalysts transesterification

The synthesis of biodiesel using solid base catalysts instead of homogeneous catalysts could have a potential to reduce a production cost by enabling reuse of the catalyst and opportunities to operate in a fixed bed continuous process. Now, the heterogeneous catalytic process has a potential to overcome the disadvantages of homogeneous catalytic process, in particular from the sustainability standpoint of view, some advantages of heterogeneous catalyst are listed below:

- ❖ It can be recovered easily and re-usable.
- ❖ It minimizes purification cost and reduces energy and water consumption.
- ❖ Can be obtained from a variety of waste sources such as bones, ashes, rocks and shells.

Recently, the application of natural calcium sources from waste materials has been considered as a new trend for biodiesel production [14].

Fig2.3 shows that the production process of biodiesel by transesterification. The steps performed during biodiesel productions are alcohol and catalyst mixing, chemical reaction, separation alcohol removal and biodiesel washing and drying [22].

a. Mixing of alcohol and catalyst

At this stage the common alkali catalysts (potassium hydroxide and sodium hydroxide) are mixed with common alcohols (methanol and ethanol) to facilitate the reaction. Alkali hydroxide is dissolved in the alcohol to produce methoxide or ethoxide solution.

b. Chemical reaction

The mixture is then poured into a rector which is contained preheated oil. The reaction system is takes place in a closed reactor to prevent the loss of alcohol. The reaction mixture is kept just near the boiling point of the alcohol to speed up the reaction. Excess alcohol is normally used to ensure total conversion of the oil to its esters.

c. Separation

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

d. Alcohol removal

After the glycerol and biodiesel phases have been separated, the excess alcohol in each phase is removed with a flash evaporation process or by distillation commonly. But currently extractive distillation can instead be used to fasten the process and to be more economical. After the alcohol is being recovered it is used as main raw material.

e. Biodiesel washing

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

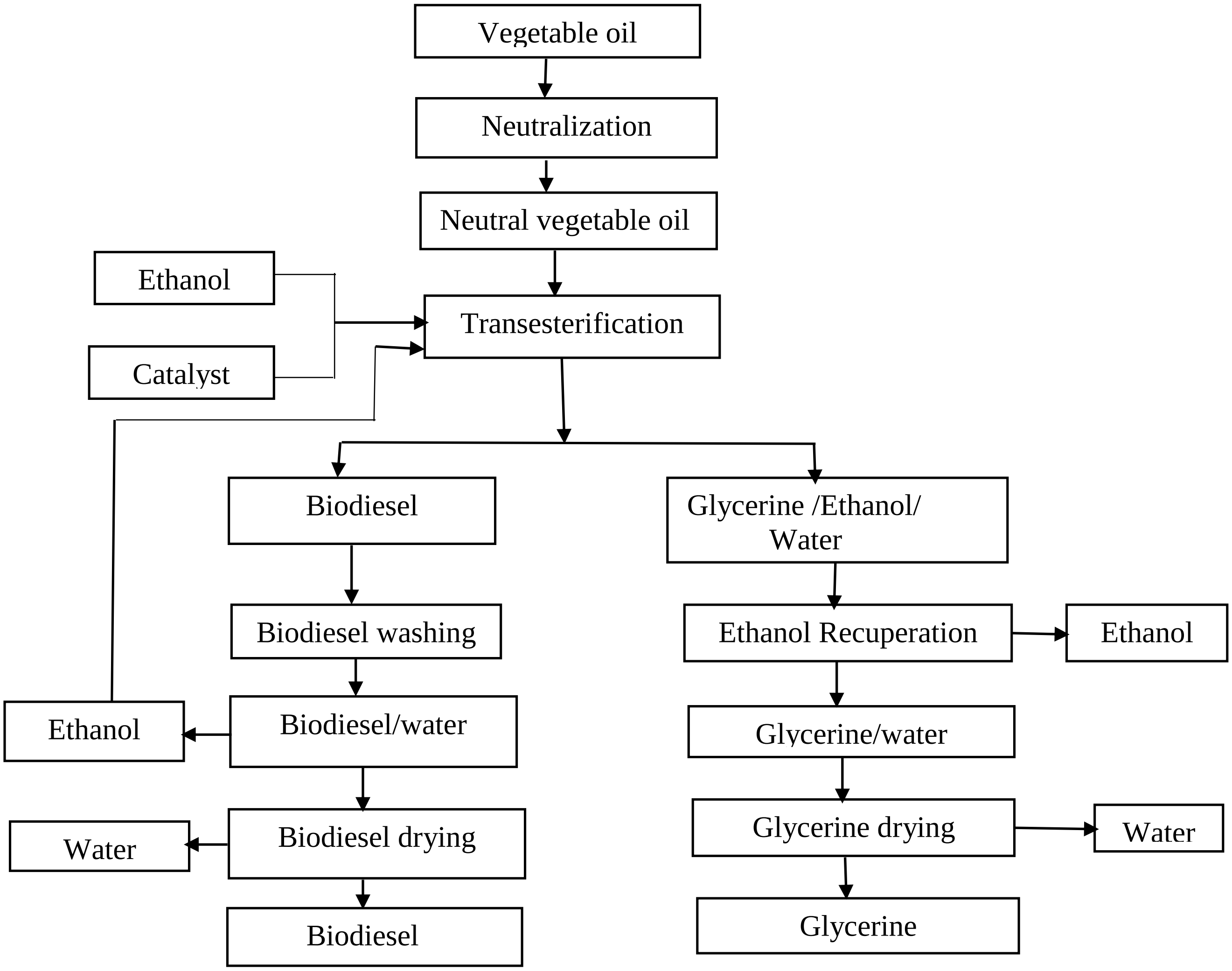


Figure 2.3 Block diagram of Biodiesel production process

2.8 Parameters Affecting Biodiesel Production

Transesterification has been described as a chemical reaction between triglycerides and alcohol in the presence of catalyst to produce mono-esters that are termed as biodiesel. The reaction is either incomplete or the yield is reduced to a significant extent if the parameters are not optimized. The important process parameters, which affect the yield of the transesterification process are the Alcohol to Oil Molar Ratio, Catalyst concentration, Reaction time, Reaction Temperature, Mixing Intensity and Purity of Reactants [14].

2.8.1 Alcohol to oil molar ratio

The stoichiometric transesterification requires 3 mol of the alcohol per mole of the triglyceride to yield 3 mol of the fatty esters and 1 mol of the glycerol. However, the transesterification reaction is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction close to completion in a forward direction. Lower molar ratios require a longer time to complete the reaction. Excess molar ratios increase the conversion rate but separation of glycerol is difficult. A molar ratio of 6:1 is commonly used in industrial processes to obtain methyl ester yields higher than 98% (w/w).

2.8.2 Catalyst

A catalyst is needed to improve the transesterification reaction and yield. The alkaline catalysts such as sodium hydroxide and potassium hydroxide are most widely used. These catalysts increase the reaction rate several times faster than acid catalysts. Alkaline catalyst concentration in the range of 0.5 to 1% by weight yields 94 to 99% conversion efficiency. Further increase in catalyst concentration does not increase the yield, rather it adds to the cost and makes the separation process more complicated.

2.8.3 Reaction Temperature

The rate of the transesterification reaction is strongly influenced by the reaction temperature. Generally, the reaction is carried out close to the boiling point of methanol (60 to 70°C) at atmospheric pressure. With further increase in temperature there is more chance of loss of methanol. Transesterification reaction has been reported to be influenced positively with increase in temperature.

2.8.4 Purity of Reactants

Impurities present in the vegetable oil also affect ester conversion levels significantly. The free fatty acid and moisture content are key parameters for determining the viability of the vegetable oil transesterification process. The starting materials used for base catalyzed alcoholysis should meet certain specification which is that a free fatty acid (FFA) value lower than 3% is needed to carry the base catalyzed reaction to completion (Meher et al., 2006). If the reaction conditions do not meet the above requirements, ester yields are significantly reduced.

2.9 Latest literature review

As studied by [23] the transesterification of CSO using a reaction variables of methanol to oil molar ratio of (4:1- 8:1), reaction temperature of (50-70 °C) and a catalyst concentration of (0.5-2%) . The catalyst using during this study was NaOH as homogeneous catalyst and achieved 93% conversion of the oil to the ester was achieved at a 1 wt% of NaOH to oil mass, 6:1 of methanol to oil molar ratio and a reaction temperature of 60^{o}C. [26] Was performed the same reaction using the same material but using different catalyst KOH and varying the reaction variables. 2^3 factorial design was applied to study the combined effect of temperature (40–60 ^{O}C), catalyst concentration (0.5–1.0 wt %) and methanol to oil molar ratio (6:1–8:1). The optimum yield of 96.23 wt% was obtained at 0.5% w/v KOH, 40 ^{O}C and 6:1 for 90 min. The results of Statistical Analysis of variance (ANOVA) shows that molar ratio has the most pronounced positive effect on the biodiesel yield. The methyl ester was characterized and all the properties were consistent with the ASTM standard. In [24] also performed the same reaction for CSO by using a homogeneous acid catalyst of super acid $SO4^{2-}/ZrO2$ with methanol and 98% of yield was obtained at the optimum conditions of methanol to CSO molar ratio of 9: 1, 3.5 wt% fresh catalyst, 1 h reaction time and reaction temperature of 120 ◦C.

The researcher in [25] was prepared biodiesel from cottonseed oil by transesterification with methanol, using different alkali catalysts (NaOH, KOH, NaOCH3 and KOCH3). The effects of reaction variables such as methanol/oil molar ratio (3:1–15:1), temperature (25–65 °C), catalyst concentration (0.25–1.50%), and stirring intensity (180– 600 rpm) was evaluated experimentally and the maximum yield of 96.9 % was obtained at 6:1 of methanol/oil molar ratio (mol/mol), 0.75% of sodium methoxide concentration (wt.%), 65 °C reaction temperature, 600 rpm of agitation speed and 90 min reaction time. The fuel properties of cottonseed oil methyl esters (COME) were determined and it was compared well with ASTM D6751 and EN 14214. As in [26] was described waste chicken Egg shells were used as a solid catalyst in the transesterification of vegetable oils with methanol to produce biodiesel. They obtained a highly active and reusable solid catalyst simply through the calcination of egg shells. The reusing of waste egg shell to prepare such a catalyst can simultaneously minimize waste of valuable egg shell residues and develop an efficient and less expensive catalyst. As founded in the above paragraph heterogeneous catalyst prepared from egg shell is efficient in terms of cost as well as environmental concern. So that researchers were used it for biodiesel production as followed. Liu et al. [27] studied that the transesterification of oil using CaO as a heterogeneous catalyst and achieved 93% conversion of the oil to the ester at the optimized parameters of methanol to oil molar ratio of 6:1, 5% of CaO to the oil mass, at a reaction temperature of 65 ^oC and a reaction time of 80 min.

As we observed from the above literatures different researchers was studied on biodiesel production from cotton seed oil by transesterification using different catalyst and alcohols. During their study they were used homogeneous acid and alkali catalyst with methanol to obtain optimum yield of biodiesel, but even though they get good yield the use of methanol alcohol has a significant effect on the human health and the environment, simultaneously the use of homogeneous catalyst also causes apparatus corrosion, it requires high quality feedstock, it is not reusable and requires further process for catalyst separation these all leads to extra cost.

So this research aims to overcome the above limitations by using waste chicken egg shell heterogeneous catalyst with ethanol alcohol instead of methanol and homogeneous catalyst since currently ethanol is available easily and it is vegetable based. The low cost and higher efficiency of the chicken egg shell waste catalyst could make the process of biodiesel production more economically feasible and environmentally friendly, by reducing the biodiesel production cost these all makes the biodiesel competitive with petroleum diesel.

3. Materials and Methods

3.1 Materials and Equipments

The materials used for biodiesel production was cottonseed oil, chicken egg shell waste and ethanol. The cotton seed was collected from kality cotton ginning factory and the chicken egg shell waste also collected from restaurants around 5kilo, 6kilo and AAiT Lounges.

Table 3.1 Main Materials/Equipments and Chemical Reagents for biodiesel production

Materials/Equipments	**Purpose**
Oven	to dry the sample
Coffee grinder	to crush the sample
Muffle furnace	to calcined ground egg shell
Decorticator/Jaw crusher	to decorticate the cotton seed
Soxhlet	to extract oil
Filter paper	to put the sample in to the Soxhlet
Rotary Evaporator	to separate hexane from oil
Pycnometer	to measure density
Vibro viscometer	to measure viscosity
Bomb calorimeter	to measure heating value
Bunsen burner	to measure flash point
Digital balances	to weigh the samples
Graduated cylinder	to measure different volumes
Separating funnel	to separate biodiesel from glycerol

Chemicals	**Purpose**
Hexane	to extract oil
H_2SO_4	to delinted cotton fiber
NaOH	to neutralize the crude oil
KOH and Diethyl ether	to determine acid value
HCl and $Na_2S_2O_3$	to determine saponification value
Hanus solution , KI and starch solution	to determine iodine value
Phenolphthalein	as indicator
Ethanol (99.5%)	as reactant
CaO	as catalyst

3.2 Methods

3.2.1 Calcium oxide catalyst preparation and characterization

3.2.1.1 Egg shell catalyst Preparation

The basic steps for catalyst preparation from waste chicken egg shells were Sample Preparation and Calcination.

i. Sample preparation

To prepare chicken egg shell powder first, the collected egg shells were soaked in hot water for 5 to 10 min and it was washed with tap water repeatedly to remove impurities. Then it was dried in an oven at 105°C for about 24 hour. Finally the dried shells were crushed with coffee grinder to a uniform size by sifting the powder using a sieve of 200 mesh.

ii. calcination process

The crushed egg shell powder was put into an alumina crucible and calcined in a muffle furnace at different temperatures such as 900^{o}C and 1000^{o}C for 2 hr to convert the calcium specie presents in the shells into CaO particle**.** After calcination the white powder was stored in desiccator for 24hr**.** Then the calcined CaO was kept in closed vessel to avoid the reaction with CO_2

(a) **(b)** **(c)**

Figure 3.1 catalyst preparation from waste chicken egg shell

(a) Oven dried eggshell, b) Grounded egg shell and c) calcined egg shell)

3.2.1.2 Catalyst characterization

i. Determination of crystalline size using XRD analysis

The structure of the calcium oxide calcined at temperature of 900°C and 1000^{o}C was characterized using X-Ray Diffraction (XRD) (SHIMADZU XRD-7000S) and the crystalinity size of a particle also determined by Scherrer equation. XRD spectra of calcined eggshell samples were obtained with Cu-ka1 (λ=0.154056 nm), a scan speed of 2 °/ minute, and a scan range of 5 to 75°.

Scherrer equation**:**

$$\tau=\frac{\kappa\lambda}{\beta cos\theta} \qquad \text{Equation 3.1}$$

Where:

- τ is the mean size of the crystalline domains
- K is a dimensionless shape factor, with a value close to unity
- λ is the X-ray wavelength;
- β (Δ(2θ)) is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians.
- θ is the Bragg angle in degree.

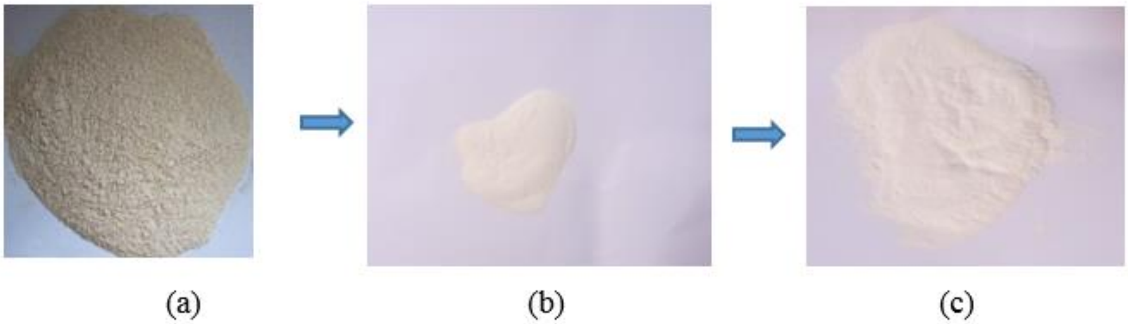


Figure 3.2 chicken egg shell powder before calcined and after calcined at different temperatures. a) Before calcination, b) calcined at 900 °C, c) calcined at 1000 °C

ii. Determination of Surface area using Blain Air Permeability apparatus

The specific surface area of CaO calcined at these temperature was determined using Blain air permeability apparatus by assuming commercial CaO as standard.

Experimental Procedures:

To determine the bulk volume of the compacted powder Place two filter paper disks in the permeability cell and Press down the edges using a rod having a diameter slightly smaller than that of the cell until the filter disks are flat on the perforated metal disk. Next the cell was filled with mercury, ACS reagent grade or better, remove any air bubbles adhering to the wall of the cell. Then level the mercury with the top of the cell by lightly pressing a small glass plate against the mercury surface until the glass is flush to the surface of the mercury and rim of the cell, being sure that no bubble or void exists between the mercury surface and the glass plate. Following to this Remove the mercury from the cell and measure and record the mass of the mercury. Remove one of the filter disks from the cell using a trial quantity of 2.98g of CaO, compress the CaO with one filter disk above and one below the sample. Add mercury into the unfilled space at the top of the cell, remove entrapped air, and level off the top as before. Finally, remove the mercury from the cell and measure and record the mass of the mercury and the bulk volume occupied by the CaO to the nearest 0.005 cm^3 was calculated as follows:

$$v = \frac{w_{A-}w_B}{D} \qquad \text{Equation 3.2}$$

Where:

V = bulk volume of CaO, cm3,

WA = grams of mercury required to fill the cell, no CaO being in the cell,

WB = grams of mercury required to fill the portion of the cell not occupied by the prepared bed of CaO in the cell, and

D = density of mercury at the temperature of test, mg/m^3

- Calibration test shall be that required to produce a bed of CaO having a porosity of 0.500 $\pm$0.005, and shall be calculated as follows:

$$w = \rho v(1 - \boldsymbol{\varepsilon}) \qquad \text{Equation 3.3}$$

Where:

W = grams of sample required,

ρ = density of test sample (for commercial CaO value of $3.34g/cm^3$)

V = bulk volume of bed of CaO, cm3

$\boldsymbol{\varepsilon}$ = desired porosity of bed of CaO (0.500 $\pm$0.005)

$$S = \frac{s_s\sqrt{t_s}}{t_{st}} \qquad \text{Equation 3.4}$$

Where:

S= specific surface area for the sample

s_s=standard specific surface area

t_s= measured time interval of manometer drop for sample test

t_{st}= measured time interval of manometer drop for sample test

3.2.2 Extraction and Characterization of CSO

The chemicals used during experimental analysis was bought from, micron (at Mexico), Ranchem chemical seller (at cherkos), Neway PLC and wise team (at piyasa).

3.2.2.1 Cotton Seed Sample Preparation, Oil Extraction and Refining

i. Seed preparation

The raw cottonseeds used for oil extraction was obtained from the market and kality cotton ginning factory. The collected samples were cleaned properly in order to remove any foreign materials. After that, the cotton seed were dried at 110°C in oven for 12 hr, to a moisture content of 12%. Next to this the dried cotton seed was de-hulled by decorticator with 6mm sieve size. The kernels were separated from the husk by sifting and the cleaned kernels were grounded by coffee grinder to 1mm to 2mm. Then the grounded seeds were stored in a plastic bag until the next process.

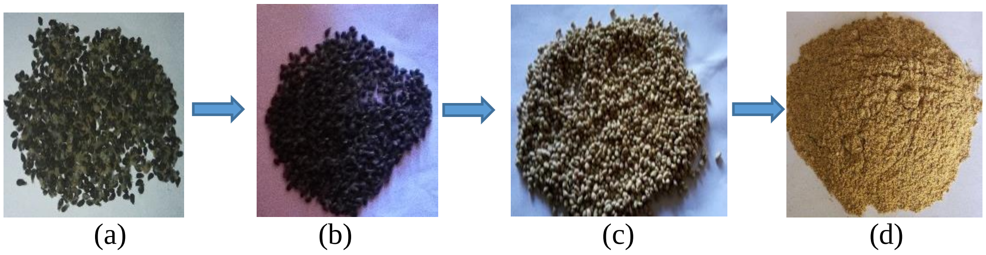

(a) (b) (c) (d)

Figure 3.3 cotton seed sample preparation
(a) Fuzzy Cottonseeds, b) de linted cotton seeds, C) Dehulled cotton seeds and d) Grounded cotton seed)

ii) Oil extraction

The oil was extracted from the grounded kernel by solvent extraction using hexane in the Soxhlet. During the extraction 5ml of hexane was used for 1gm of the grounded seed. The extraction was takes place at 68ºC for 14 hr. After extraction the hexane and oil was separated by rotary evaporator at 70 ºC. Next the solid compounds was separated by centrifugation.

The yield of oil extracted was calculated by:

$$\%\ \text{oil} = \left(\frac{mass\ of\ oil\ obtained}{initial\ mass\ of\ seed}\right) * 100 \qquad \text{Equation 3.5}$$

iii) Crude CSO refining

a) Degumming

The crude CSO contains gums and phospholipids which can increase free fatty acids of the oil. Therefore, these are removed by degumming. During the process initially the crude oil was heated at 70ºC stirring under 1000 rpm in a beaker. Then 3wt% of distilled water (which was first heated to 90 ºC) and 0.2wt% of 85% purity of phosphoric acid was added. After that allow the mixture to stir for 1h. The precipitate was separated by centrifugation at 4000 rpm for 30min and the degummed oil was dried at 100 ºC for 30 min under reduced pressure using rotary evaporator (fractional condenser).

b) Neutralization of oil

During neutralization the degummed oil was poured into a beaker and heated to 80°C, then 2 ml of 0.1M NaOH is added for each 3 g of degummed oil and stir it to a uniform solution. Next 10% of the weight of the oil Sodium chloride, was added to settle out the soap formed. This was poured into a separating funnel and allow to stand for 1h to separate the soap formed. Hot water was added repeatedly to the oil solution until the soap remaining in solution was removed. The neutralized oil was then drawn off into beaker.

(a) (b) (c)

Figure 3.4 Cottonseed Oil Refining

(a) Crude CSO, b) washing of CSO and c) neutralized CSO)

3.2.2.2 Characterization of Cottonseed oil

Fatty acid composition of the cottonseed oil was determined by GC-MS in Addis Ababa University, 4kilo campus. The oil physico-chemical properties were conducted in AAiT Chemical and Bio engineering reaction lab.

i) Characterization of cotton seed oil fatty acids using GC-MS Analysis

GC analysis was performed with Agilent GC system 7820A. Sample analysis was carried out on packed column- Agilent Technologies (30 m × 0.250 mm, 0.25 µm). Samples were injected by a sampler injector at an oven temperature of 325 to 350^{o}C for a total run time of 38 minutes. The data, obtained using MS-Agilent Technologies EMS detector and processed using Chemstation software, were used to obtain fatty acid composition of oils.

ii) Characterization of physico-chemical properties

a. Determination of Moisture content

The empty dish was weighed with and without the amount of kernel and dried in an oven at 105^{o}C for 7hr, weighing it after each 2hr till constant weight is obtained and finally the weight was taken and compared with the initially recorded weight. The formula used to calculate the percentage weight in the seed can be seen from appendix C.

b. Determination of Specific Gravity (SG)

Density bottle (volumetric cylinder) is used to determine the density of the oil. A clean and dry bottle of 50ml capacity was weighed (W_0) then it was filled with the oil, insert stopper and reweighed to give (W_1). The oil was substitute with water after washing and drying the bottle and weighed to give (W_2). Then the specific gravity was determined using the formula in the appendix C.

c. Determination of Kinematic Viscosity (μ), ASTM D 445

The viscosity of oil was determined using Digital Vibro viscometer. The kinematic viscosity was determined at 40°C according ASTM D445 procedure. The temperature of a water bath was set at 40°C and calibrate. 50 ml of sample was placed into the viscometer and allowed the viscometer and sample to equilibrate to the water bath for 30 minutes. The sample was keep in the water thermostat bath until it reaches the equilibrium temperature of 40^{o}C. After maintaining the equilibrium temperature, the Vibro viscometer tip were inserted to the sample to measure the dynamic viscosity and the reading was taken from the controller. Then the kinematic viscosity was calculated by eq. 3.3:

$$\mu = \frac{\nu}{\rho_{cso}} \qquad \text{Equation 3.6}$$

d. Determination of Acid Value (AV), ASTM D 664

Acid value of the oil was determined using the method described by IUPAC (1979) and modified by Egan et al. (1981). 25ml of diethyl ether and ethanol mixture was added to 5gm of oil in a 250ml conical flask and the solution was titrated with 0.1N ethanolic KOH solution in the presence of 5 drops of phenolphthalein as indicator until the endpoint (colorless to pink) was recognize with consistent shaking. The volume of 0.1 N ethanolic KOH (V) for the sample titration was record.

The total acidity of oil in mg KOH/ gram was calculated using the following equation:

$$\text{AV}= \frac{56*N*V}{W} \qquad \text{Equation 3.7}$$

Where, V = the volume expressed in milliliter of 0.1N solution of ethanolic KOH.
W = the weight of oil sample (the mass in gram of the test portion)
N = concentration of ethanolic KOH
56 = molar mass of KOH

Then, the % FFA value was calculated from the acid value as followed:

$$\%\mathrm{FFA} = \frac{AV}{2}$$

e. Determination of Saponification Number (SN)

Saponification value was determined using indicator method according ISO 3657 (1988). 2g of the sample was weighed and added to a conical flask then 25ml of 0.1N ethanolic KOH solution also added. Next the sample was constantly stirred, and allow to boil at 70 ºC for 60min and a reflux condenser was connected to the flask containing the mixture. After that,3 to 5 drops of phenolphthalein indicator was add to the warm solution and then titrate with 0.5M HCl (volume Va was record) to the endpoint until the pink color of the indicator was disappeared. Then a blank was prepared following the same procedure and (volume Vb was record). Then the SN was calculated using the equation below:

$$\mathrm{SN}= \frac{56.1 * N(V_{B-V_S})}{W} \qquad \text{Equation 3.8}$$

Where, W= weight of oil taken in gram, N= normality of HCl solution,

VS= volume of HCl solution used in test in ml,

VB= volume of HCl solution used in blank in ml.

f. Determination of Iodine Value (IV)

The method specified by ISO 3961 (1989) was used. Weigh approximately 0.25 g of the oil into a 250 mL conical flask and Add 10 ml of chloroform and 30 ml of Hanus solution, then close the flask completely by Para film and leave the solution for 30 minutes with shaking continuously. Next to this add 10 ml of 15% potassium iodide solution and 100 ml of distilled water then 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 where blue solution formed and then continue with titration till the blue color is disappeared (Volume (ml) of $Na_2S_2O_3$ at end point represents S). For blank the same procedure was conducted as above but without sample (Volume (ml) of $Na_2S_2O_3$ at end point represents B). Then the iodine value (IV) was calculated by:

$$\mathrm{IV} = \frac{12.69 * N(V_B - V_S)}{M} \qquad \text{Equation 3.9}$$

Where, N = normality of sodium thiosuphate,
M = Mass of the sample
V_S = Volume of sodium thiosuphate used for sample test
V_B = Volume of sodium thiosuphate used for blank,

3.2.3 Production and Characterization of biodiesel

3.2.3.1 Biodiesel production process

The experiment was conducted in a 250 mL two-necked flat-bottom flask equipped with a reflux condenser and a mechanical stirrer. During the reaction, initially the neutral oil was measured and poured in to a conical flask and it was pre-heated for 30 min at 50 ^oC. Then a specified amount of calcium oxide was weighed and dissolved in the required amount of anhydrous ethanol (99.5%). Next the calcium ethoxide solution was added to the pre-heated oil and placed on a hot water bath with a constant agitation speed of 400 rpm. After the reaction taking place for 2hr it was completed and stopped. Followed to this the product was poured in to separating funnel and it was kept for 24 hr until phase separation is formed. Finally the catalyst was removed by filtration and the biodiesel also purified by washing with hot distilled water.

Figure 3.5 Experimental set-up for batch transesterification reaction

- The amount of Feed required for biodiesel production was calculated below:

The amount of CSO used for each run was 30 ml. Now the amount of ethanol required for transesterification reaction when the alcohol to oil ratio was 6:1 can be calculated as follows:

$$\frac{n_{ethanol}}{n_{oil}} = \frac{\frac{m_{ethanol}}{M_{ethanol}}}{\frac{m_{oil}}{M_{oil}}} = 6 \qquad \frac{\frac{\rho_{ethanol} * V_{ethanol}}{M_{ethanol}}}{\frac{\rho_{oil} * V_{oil}}{M_{oil}}} = 6 \qquad \text{Equation 3.10}$$

Where, molar mass of ethanol = 46g/mol

Avg.molecular weight of CSO = Moil

ρ_{oil}= 0.92g/ml, $\rho_{ethanol}$=0.789g/ml

The amount of catalyst required when the catalyst loading was 1% also calculated below.

$$\frac{\text{mass of catalyst}}{\text{mass of oil}} = 1\% \qquad \text{Equation 3.11}$$

The yield of biodiesel for each run of transesterification reaction was determined by eq.3.9 below:

$$\text{Yield (\%) of FAEE} = \frac{\text{mass of biodiesel produced}}{\text{mass of oil feed}} * 100 \qquad \text{Equation 3.12}$$

The feed required for all experiment was calculated the same as above using eq3.8 and eq3.9.

3.2.3.2 Characterization of Physico-chemical property of biodiesel

The physico-chemical properties of FAEE, such as specific gravity, density, kinematic viscosity, acid value, saponification value ,iodine value and flash point was determined following the same procedure as used for CSO. These testes was conducted in 5 kilo AAiT Chemical and Bio Engineering Reaction laboratory according to ASTM D6751 procedure.

a. Determination of Heating value (calorific value)

The higher heating value of biodiesel was determined using oxygen bomb calorimeter, this was done in geological survey of laboratory at mechanisa. This was determined via the equivalent methods of (ASTM E 711, or ASTM D 5468). First 1g biodiesel sample was prepared and then the oxygen bomb was charged. A distilled water of 2000 gram was filled in the calorimeter bucket and the bucket was set in the calorimeter. The calorimeter was left to run for five minutes while the controller brings the jacket temperature up to equilibrium with the bucket. Then the bomb was fired and the bucket temperature was raised within 20 seconds after firing. Temperature reading was started at about 6 minutes after firing. Within one minute interval, the thermometer was read until the temperature reached a stable maximum and remained constant for at least two minutes.

Then the final temperature was recorded. After recording, the thermometer was raised and the bomb was removed from the bucket. Then the biodiesel heat of combustion was computed by using the following equation:

$$HHV=\frac{[m_w * c_{w+(m_c)app}]\,(t_m + c - t_o) - \sum b}{M} \qquad \text{Equation 3.13}$$

Where: HHV= higher heating value [cal/g]
M =Mass of the fuel [g]
MwCw = the mass and specific heat of the calorimeter water Cw = 1cal/goC
t_o = first temperature reading of main test [^{o}C]
t_m =last temperature reading of main test [^{o}C]
c = Correction for heat exchange between calorimeter and the surrounding
$\sum b$ =correction for heat exchange between calorimeter and the surrounding, cal

The correction is calculated from the formula

$$C = m'\Delta n - (\Delta n + \Delta \nu)\, F \qquad \text{Equation 3.14}$$

Where m'= duration of main test [min]
Δn= Average temperature fall for every minute of the pre-test
$\Delta\nu$ =Average temperature rise for every minute of the pre-test

The factor F can be approximated to
F = 1.0, if the temperature rise in 1st minute of the main test is higher than in the 2nd.
F = 1.25, if temperature rise in the 1st minute and 2nd minutes of the main test are about the same.
F = 1.5, if temperature rise in the 1st minute of the main test is less than in the 2nd minute

The correction $\sum b$ consists of heat value added by glowing of the ignition wire 1cm = 1.5cal.

b. Determination of Cetane Number (CN**)**, ASTMD 613

Cetane number of the FAEE was determined using the empirical formula suggested by using the result of SN and IV of the biodiesel.

$$CN = 46.3 + \left(\frac{54.58}{SN}\right) - 0.225(IV) \qquad \text{Equation 3.15}$$

c. Determination of Flash Point, ASTMD 93

The flash point of the biodiesel was determined using open cup method. The cup was filled with the biodiesel up to the mark (about 75 ml) and the cup was heated by a Bunsen burner. Small open flame was maintained from an external supply of natural gas.

Periodically, the flame was passed over the surface of the oil. When the flash temperature was reached the surface of the oil catch flame, the temperature at the moment was noted and reported as flash point temperature.

3.3 Design of Experiments

Data analysis for this study was carried out by DESIGN EXPERT 7.0.0 software using Box-Behnken with three factors and three levels to determine the experimental conditions that maximize the synthesis of biodiesel resulting from the reaction and to evaluate the effects of the process variables such as, reaction temperature (70, 75 and 80 ^oC), ethanol to oil molar ratio (6:1, 9:1 and 12:1) and catalyst loading (1, 2 and 3% wt.). To obtain maximum conversion the reaction speed and reaction time was kept constant at 400 rpm and 2 hr respectively. The Process Parameters were optimized Using Response Surface Methodology (RSM) and Significance of the result was set from analysis of variance (ANOVA).

4. Results and Discussion

4.1 Catalyst Characterization

The amount of chicken egg shell used for calcination was 100g. This powder was calcined at different temperatures such as 900 ºC and 1000 ºC with constant time of 2hr. During calcination weight loss was observed.

4.1.1 Determination of Surface area using Blain Air Permeability apparatus

The surface area of CaO calcined at 900 ºC and 1000ºC was calculated based on the data obtained from Blain Air Permeability apparatus as described in the appendixA1. The result obtained was 88.85 m^2/g and 79.0 m^2/g respectively. The catalyst with higher surface area has higher catalytic activity.

4.1.2 XRD Analysis of CaO

As observed from (fig4.1) Based on the XRD analysis the powder calcined at 900 ºC and 1000 ºC shows that a well crystallized structure. Diffraction pattern of eggshell samples at various calcination temperatures showed a slight characteristic variation in CaO at 900 ºC and 1000 ºC. XRD spectra of calcined eggshell samples were obtained with Cu-ka1 (λ=0.154056 nm) at 37.5º, a scan speed of 2 ˚/ minute, and a scan range of 5 to 75˚. Fig 4.1 shows 100% decomposition of $CaCO_3$ to CaO.

The sharp peaks resulted at 2θ was 32.5 º, 34 º, 37.5 º, 54.75 º, and 64.75 º. The crystalline size of CaO was calculated from the XRD data using eq3.1 and the result shows that the particle size of CaO calcined at 900ºC and 1000ºC were 36 nm and 41nm respectively. So the catalyst used for transesterification was selected by testing of their conversion efficiency. Therefore, the CaO calcined at 900ºC was used to produce biodiesel, since the catalyst that has small particle size gives higher yield. As [28] studied the yield obtained by using CaO calcined at 900˚C was decreased by 5% when CaO calcined at 1000˚C was used .This may be due to exposition of the catalyst with air because when the CaO contacts to air it adsorbs CO_2 and this leds to $CaCO_3$ formation there by decreases the biodiesel yield.

Table 4.1 physical property of cao at different calcination temperature

Physical property	CaO calcined at 900 ^{o}C	CaO calcined at 1000 ^{o}C
Surface area(m^2/g)	88.85	79.0
Crystal(nm)	36	41

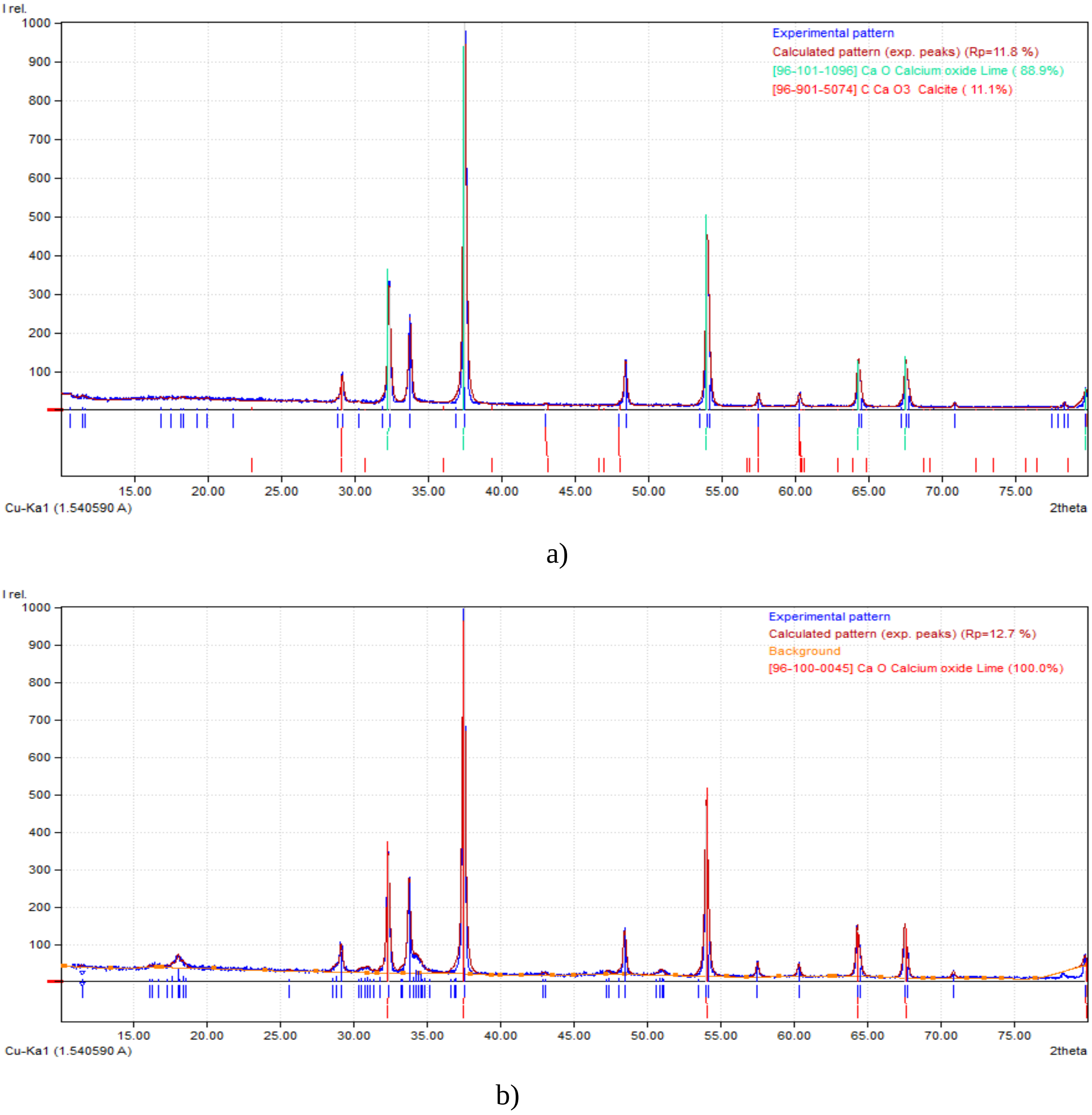


Figure 4.1 XRD pattern of calcium oxide powder calcined at different temperature

a) @ 1000 ^{o}C, b) @ 900 ^{o}C.

4.2 Cottonseed oil characterization

4.2.1 Cotton Seed preparation, Oil extraction and refining

4kg of seed was brought from kality cotton ginning factory. During seed preparation first it was cleaned, oven dried at 110 ^oC for 12 hr to moisture content of 12 %. During the moisture determination three samples (40g, 50g and 60 g) were prepared and the aveg. Moisture content was obtained in table 4.1 using appendix C.

Table 4.2 moisture content determination of cotton seed

Samples	Drying time in hrs			
	0	12 hr	14 hr	16hr
Weight of sample1(g)	40 g	37.34 g	35.21 g	35.10 g
Weight of sample2(g)	50 g	48.92 g	46.95 g	44.88 g
Weight of sample3(g)	60 g	57.26 g	54.89 g	52.84 g

The moisture content of CSO for the three samples were 12.25%, 10.24% and 11.93% respectively and the average moisture content was obtained 11.47 %w/w.

From 4kg of raw cotton seed 3.7 kg of cleaned kernel was obtained and was grind to 1mm to 2mm using coffee grinder to increase extraction efficiency. Then oil was extracted by Soxhlet extraction using hexane. Based on eq. 3.2 the yield of extracted oil from 100g of grounded seed was resulted as 24.5g (24.5 %). The crude oil was contained some amount of impurities such as free fatty acids. So to neutralize these free fatty acids it needs to know the amount of FFA that existed in the oil. Therefore, The FFA resulted from the titration was 2.21mg KOH/g oil. So to neutralize 1.2lit of crude CSO 736ml of 0.1N NaOH solution was used.

4.2.2 Fatty acid composition of CSO from GC-MS Analysis

The fatty acid composition of crude oil influences the cetane number and cold flow properties of biodiesel. The fatty acid composition of the oil was determined using GC-MS. The peaks obtained were identified using the standards of fatty acids. Based on GC-MS analyses from fig4.2 the highest peaks that contains above 90% qualities was selected as dominant composition of CSO. The calculated Percentage composition for the selected fatty acids were listed in table 4.2. The cottonseed oil was found to contain both saturated and unsaturated fatty acids. Linoleic acid was found which was contained the highest composition (59 %) followed by oleic acid (35%), palmitic acid (0.637%), myristic acid(0.72%) and stearic acid (4.03%) as shown in Table 4.2. Except palmitic acid all values well comparable to the compositions founded by [11]. The low percent of palmitic acid may be due to the cotton growing soil nature and fertilizer used, temperature, and seed variety. The average molecular mass found was 280.2 g/mol as described in appendix B2.

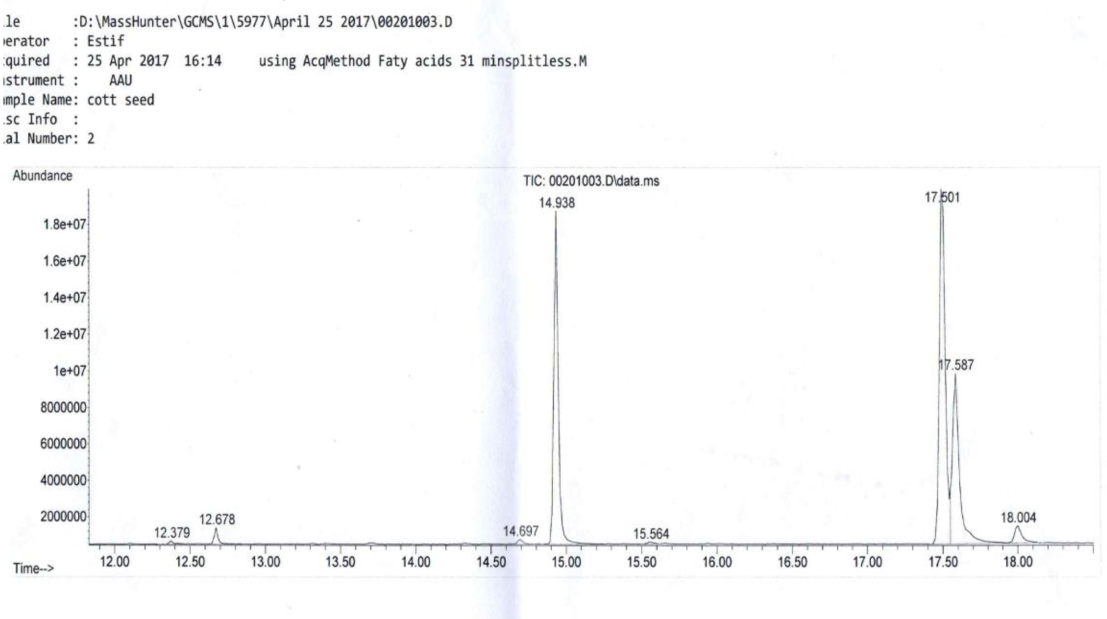


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Figure 4.2 Fatty acid composition of CSO from GC-MS

Table 4.3 fatty acid composition of cotton seed oil obtained from GC-MS

Fatty Acid compositions	Systemic Name	Structure	Wt%	M.weight in g/mol
Linoleic	Cis-9,cis-12-octadecadienoic	C18:2	59.2	165.75
Oleic	Cis-9-Octadecenoic	C18:1	35.38	99.7716
Palmitic	Hexadecanoic	C16:0	0.637	1.6307
Myristic	methylTetradecanoic	C14:0	0.72	1.6416
Stearic	Octadecanoic (methyl stearate)	C18:0	4.03	11.4452
Total wt.			100	280.2

4.2.3 Characterization of Physico-chemical property

The density, specific gravity, kinematic viscosity, moisture content acid vale, saponification vale iodine value and flash point of the cotton seed oil were determined and the result obtained are given in table 4.3. The properties were determined based on ASTM D6751 procedures using eq.3.3- eq.3.6 as given in appendix C.

Table 4.4 Physico-chemical properties of cotton seed oil

Properties	units	values
Density @15 °C	g/cm^3	0.920
Kinematicviscosiy@40 °C	mm^2/s	30
Specific gravity	-	0.921
Moisture content	Vol %	0.032
Acid value	mg KOH/g oil	2.15
Free fatty acid	-	1.07
Iodine value	$gI_2/100g$	102.28
Saponification value	mg KOH/g oil	177.3
Flash point	°C	184

All the above values were well agreed with the standards sets for refined oils, due to cottonseed oil was considered suitable for biodiesel production. In addition the obtained kinematic viscosity and specific gravity of cotton seed oil was in agreement the values reported by Dominic Okechukwu Onukwuli et al[4] .

As the obtained FFA value was small the probability of ester formation increases since soap formation may decreased. The obtained moisture content also with in the recommended value because the presence of water inhibits the transesterification of glycerides.

4.3 Characterization of Biodiesel

The amount of ethanol and catalyst required for 30 ml of CSO to conduct transesterification reaction was determined using eq.3.7 and eq.3.8. Based on this the amount alcohol to oil ratio for 6:1 and catalyst concentration of 1% were 34.46 ml and 0.276g respectively. The same procedure was followed for all runs as calculated in appendix D.

4.3.1 Characterization of physico- chemical properties

Density, specific gravity, kinematic viscosity, moisture content, acid value, iodine value and saponification values of the biodiesel (FAEE) were determined following the same procedure as used for the oil, whereas heating value, flash point and cetane number were determined using bomb calorimeter, Bunsen burner and eq.3.10, respectively. The determined values are given in in table 4.4.

The values of biodiesel physico-chemical properties obtained in this study was achieved the international specifications ASTM D6751. Moisture content, acid value, heating value, and cetane number of the biodiesel obtained in the present study was well comparable with results obtained by Dominic Okechukwu Onukwuli et al [4], but the result of saponification was less than the literature value, this may be due to the catalyst differenc. The previous work was used homogeneous catalyst, this also has more probability of soap formation as reported in[20]. where as in this study biodiesel was produced using heterogeneous catalyst which have the ability to reduce soap formation. The kinematic viscosity, density and flash point of biodiesel were well agreed with the results obtained by David M. Fernandes et al,[11].

Table 4.5 Physico-chemical properties of biodiesel (FAEE)

Property	units	values
Density @15 °C	g/cm^3	0.872
Kinematicviscosiy@40 °C	mm^2/s	4.20
Moisture content	Vol %	0.025
Acid value	mg KOH/g oil	0.21
Free fatty acid	mg KOH/g oil	0.105
Iodine value	gI$_2$/100g	80.6
Saponification value	mg KOH/g	136.1
Flash point	°C	169
Heating value	MJ/g	39.32
Cetane number	-	54.23

4.4 Statistical Analysis of the Experimental Results

4.4.1 Analysis of variance (ANOVA)

The Model F-value of 845.27 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, BC, A^2, B^2, C^2 are significant model terms. 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 4.6 Analysis of variance (ANOVA) for Response Surface Quadratic Model

Source	Sum of Squares	Df	Mean Squares	F -value	p-value Prob > F	
Model	1802.69	9	200.30	845.27	< 0.0001	significant
A-temperaure	18.12	1	18.12	76.47	< 0.0001	
B-ethanol to oil ratio	1001.95	1	1001.95	4228.27	< 0.0001	
C-catalyst loading	14.77	1	14.77	62.33	< 0.0001	
AB	5.625E-003	1	5.625E-003	0.024	0. 8819	
AC	0.56	1	0.56	2.34	0.1698	
BC	8.29	1	8.29	35.00	0.0006	
A^2	180.42	1	180.42	761.38	< 0.0001	
B^2	457.030.4	1	457.03	1928.69	< 0.0001	
C^2	56.20	1	56.20	237.18	< 0.0001	
Residual	1.66	7	0.24			
Lack of Fit	1.20	3	0.4	3.51	0.1285	not significant
Pure Error	0..46	4	0.11			
Cor Total	1804.35	16				

The "Lack of Fit F-value" of 3.51 implies the Lack of Fit is not significant relative to the pure error. There is a 12.85% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

- Model adequecy checking

The "Pred R-Squared" of 0.9889 is in reasonable agreement with the "Adj R-Squared" of 0.9979."Adeq Precision" Measures the signal to noise ratio. Aratio greater than 4 is desirable. For this case the ratio of 79.344 indicates an adequate signal. This model can be used to navigate the design space.

Table 4.7 Model adequacy measures

Std. Dev.	0.49	R-Squared	0.9991
Mean	86.26	Adj R-Squared	0.9979
C.V. %	0.56	Pred R-Squared	0.9889
PRESS	19.94	Adeq Precision	79.344

The regression coefficient (R^2) quantitatively evaluates the correlation between the experimental data and the predicted responses. Results of R^2= 0.9991 and Adj-R^2= 0.9979 obtained explicates that the predicted values were found to be in good agreement with experimental values. Since the R^2 value is closer to 1.0 it indicates that the regression line perfectly fits the data. Similar to that in this investigation, R^2 obtained was 0.9991, which was close to 1. Results imply that the predicted values were found to be in good agreement with experimental values (R^2= 0.9991 and Adj-R^2= 0.9980), indicating the achievement of the RSM. The model's goodness of fit was checked by regression coefficient (R^2). In this case, the value of the coefficient (R^2 = 0.9991) from Table 4.7 indicated that only 0.09 % of the total variance was not explained by the developed regression model. The obtained R^2 values suggest good adjustments to the experimental results. The adjusted determination coefficient (Adj-R^2= 0.9979) was also satisfactory for confirming the significance of the model. Pred R-Squared indicating that the model will probably explain a high percentage (about 98.89 %) of the variability in new data. "Adeq precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. In this study 79.344 indicates an adequate signal.

Table 4.8 Regression coefficients and the corresponding 95% CI High and Low

Factor	Coefficient Estimate	Df	Standard Error	95% CI low	95% CI high	VIF
Intercept	95.96	1	0.22	95.45	96.48	
A-temperature	-1.50	1	0.17	-1.91	-1.10	1.00
B- ethanol to oil ratio	11.19	1	0.17	10.78	11.60	1.00
C-catalyt con.	1.36	1	0.17	0.95	1.77	1.00
AB	-0.038	1	0.24	-0.61	0.54	1.00
AC	-0.37	1	0.24	-0.95	0.20	1.00
BC	-1.44	1	0.24	-2.02	-0.86	1.00
A^2	-6.55	1	0.24	-7.11	-5.99	1.01
B^2	-10.42	1	0.24	-10.98	-9.86	1.01
C^2	-3.65	1	0.24	-4.21	-3.09	1.01

Final Equation in Terms of Coded Factors:

$$\text{yield} = +95.96 - 1.50 * A + 11.19 * B + 1.36 * C - 0.038 * A * B - 0.37 * A * C - 1.44 * B * C - 6.55 * A^2 - 10.42 * B^2 - 3.65 * C^2$$

Final Equation in Terms of Actual Factors:

$$\text{yield} = -1520.48725 + 39.14650 * \text{temperature} + 25.71492 * \text{ethanol to oil ratio} + 25.88025 * \text{catalyst con} - 2.50000E{-}003 * \text{temperature} * \text{ethanol to oil ratio} - 0.074500 * \text{temperature} * \text{catalyst con} - 0.48000 * \text{ethanol to oil ratio} * \text{catalyst con} - 0.26184 * \text{temperature}^2 - 1.15761 * \text{ethanol to oil ratio}^2 - 3.65350 * \text{catalyst con}^2$$

As shown in fig.4.3 below, the normal probability plot indicates the residuals following by the normal % probability distribution, in the case of this experimental data the points in the plots shows fitted to the straight line in the figure, this shows that the quadratic polynomial model satisfies the assumptions analysis of variance (ANOVA) i.e. the error distribution is approximately normal.

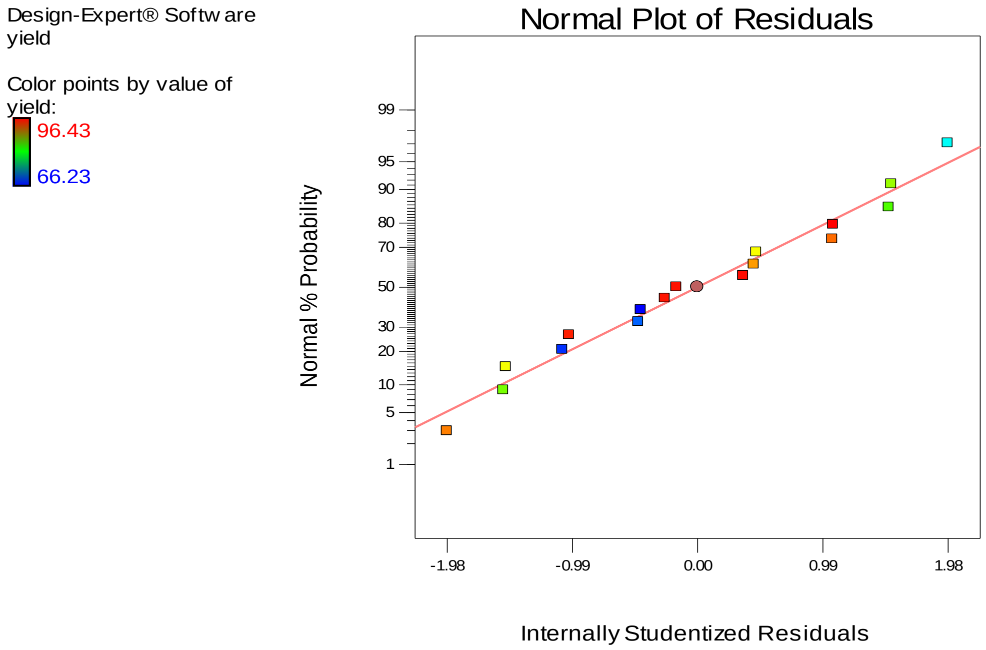

Figure 4.3 Normal probability plot of residuals

If the model is correct and the assumptions are satisfied, the residuals should be structure less; in particular, they should be unrelated to any other variable including the predicted response. A simple check is to plot the residuals versus the fitted (predicted) values. A plot of the residuals versus the rising predicted response values tests the assumption of constant variance. Fig 4.4 shows that random scatter which justifying no need for an alteration to minimize personal error.

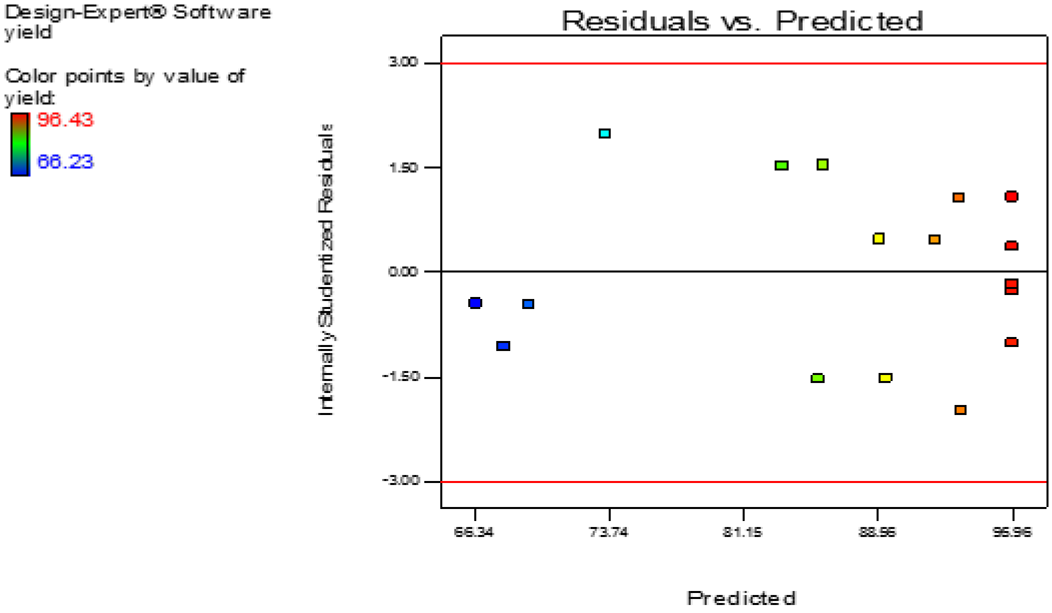

Figure 4.4 Residual versus predicted values plot

4.4.2 Response Surface plot for the Experimental Variables

In order to analyze the regression equation of the model, three-dimensional surface and 2D contour plots were obtained by plotting the response (yield of biodiesel) on the Z axis against any three variables while keeping the other variable at zero level. These plots are created to analyze the change in the response surface. Conical shape response surface plot indicates optimum operating conditions. The response optimized value for the production of biodiesel was based on the three process variables described on the response surface plot. The response surface plots of the quadratic model are shown in Figure (4.5, 4.7 and 4.9). It was reported that Response surface plots provide a method to predict the yield of biodiesel for different parameter values of the tested variables and the interaction plots help in identification of the type of interactions between these variables. The axes of the contour plot are the experimental variables and the area within the axes is termed the response surface.

Figure (4.5) shows the response surface plots developed as a function of temperature and ethanol to oil ratio, while the catalyst load. Was kept constant at 2%. It was observed that the yield of biodiesel was more sensitive to temperature change, when the temperature change from 70 to 75 ^{o}C the yield of biodiesel reaches at the peak and beyond 75 ^{o}C the yield slightly decreased. The reason for this observation is due to the fact that when the temperature approaches to the boiling point of ethanol, loss of alcohol would be occurred and this reduces the yield of biodiesel as founded in [29].

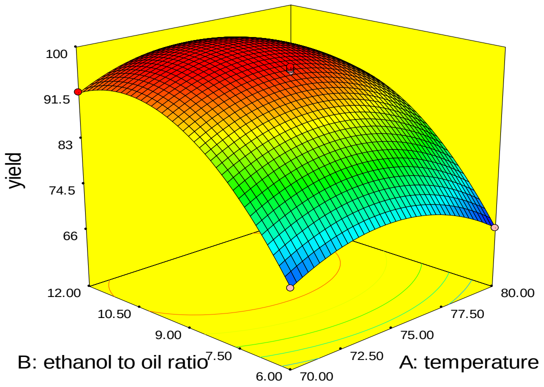

Figure 4.5 Response surface plots of the effect of ethanol to oil ratio and temperature on the yield of biodiesel at fixed catalyst load.

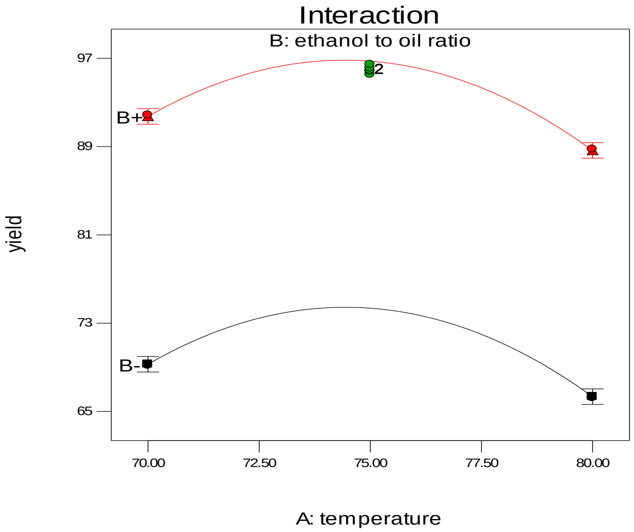

Figure 4.6 Effect and interaction of temperature and ethanol to oil ratio (fixed) on the yield of biodiesel at center of catalyst loading

As we observed from figure (4.6) there is no an interaction effect between ethanol to oil ratio and temperature at the given interval, but Positive yield was observed at 12:1 ethanol to oil ratio and around 75 °C reaction temperature. The yield of biodiesel at 6:1 ethanol to oil ratio is less than at 12:1 ethanol to oil ratio in the same temperature.

As we can see below Figure (4.7) represents the response surface plots developed as a function of catalyst concentration and temperature, while ethanol to oil ratio was kept constant at 9:1. At a definite catalyst concentration, the yield of biodiesel increased slightly with reaction temperature from 70 to 75°C and nearly reached at a peak. However, upon increasing the reaction temperature beyond 75 °C, there was a gradual decline in the yield, because as the reaction temperature closes to the boiling point of ethanol that could lead to loss of ethanol as reported by Musa Umaru and Aboje Audu Alechenu ,2015[33]. As shown from the figure (4.8) the maximum yield of biodiesel was occur in the region of 75 °C temperature and 2% catalyst loading.

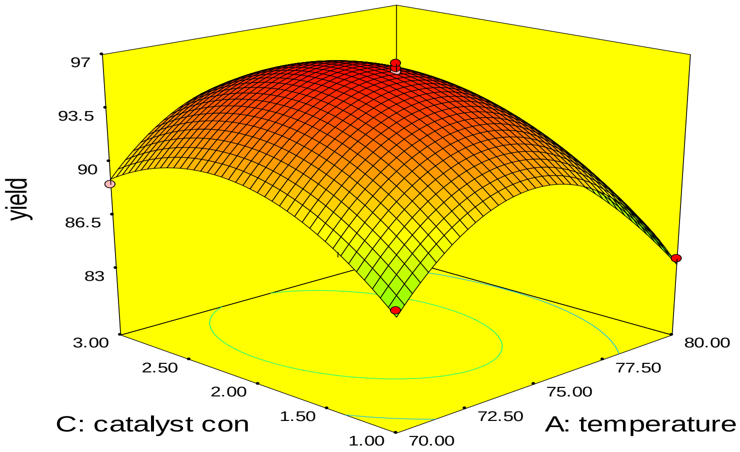

Figure 4.7 Response surface plots of the effect of catalyst load and temperature on the yield of biodiesel at fixed ethanol to oil ratio.

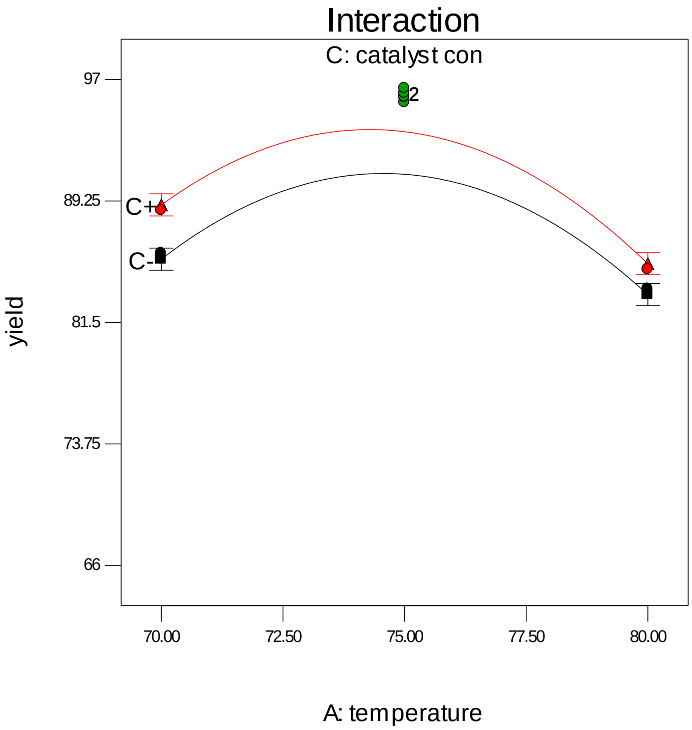

Figure 4.8 Effect and interaction of temperature and catalyst load (fixed) on the yield of biodiesel at center of ethanol to oil ratio.

As we observed from figure (4.8) there was no an interaction between catalyst loading and temperature, but Positive yield was observed at low temperature and high catalyst loading and also at high temperature and low catalyst loading. Because at low catalyst loading high temperature is required in order to obtain positive result the same is true at low temperature and high catalyst loading. Low temperature and catalyst loading might not be enhanced the transesterification reaction to convert the oil into FAEE. Too much catalyst used might initiate a saponification reaction and higher temperature also may causes ethanol vaporization and solubility of reactants this causes difficulties in glycerol separation. The highest yield of biodiesel was observed at 75 ^{o}C reaction temperature and 2% catalyst loading.

As we can see below Figure (4.9) shows the response surface plots developed as a function of ethanol to oil ratio and catalyst loading, while the temperature was kept constant at 75^oC. Upon increasing the catalyst loading from 1 to 2% with an increase of ethanol to oil ratio from 6:1 to 9:1, the yield of biodiesel increased highly. Beyond this ratio the yield of biodiesel was gradually decreased. The highest yield was obtained at 9:1 ethanol to oil ratio and 2% catalyst loading. The decrement of biodiesel yield with increasing of catalyst loading from 2% - 3% may due to the formation of complexity during glycerol separation. The addition of an excess amount of catalyst beyond the optimum point increases the formation of an emulsion and the viscosity. This also retards the glycerin separation [33].

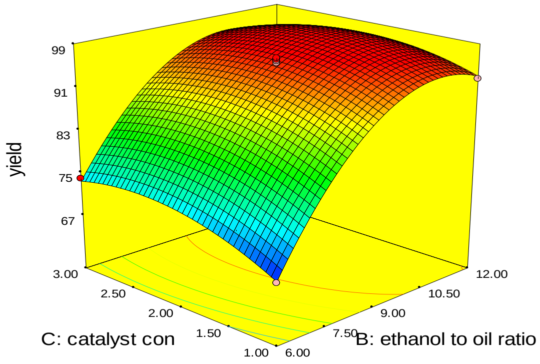

Figure 4.9 Response surface plots of the effect of catalyst load and ethanol to oil ratio on the yield of biodiesel at fixed temperature

As it observed from figure (4.10) the ethanol to oil ratio and catalyst load has small interaction prior to 12:1 and it has positive effect on the yield of biodiesel at high catalyst loading until the ethanol to oil ratio reach 9:1. But, Beyond 9:1 ethanol to oil ratio at fixed catalyst loading the yield of biodiesel slightly decreases due to the fact that emulsion is formed (difficulty during product separation).

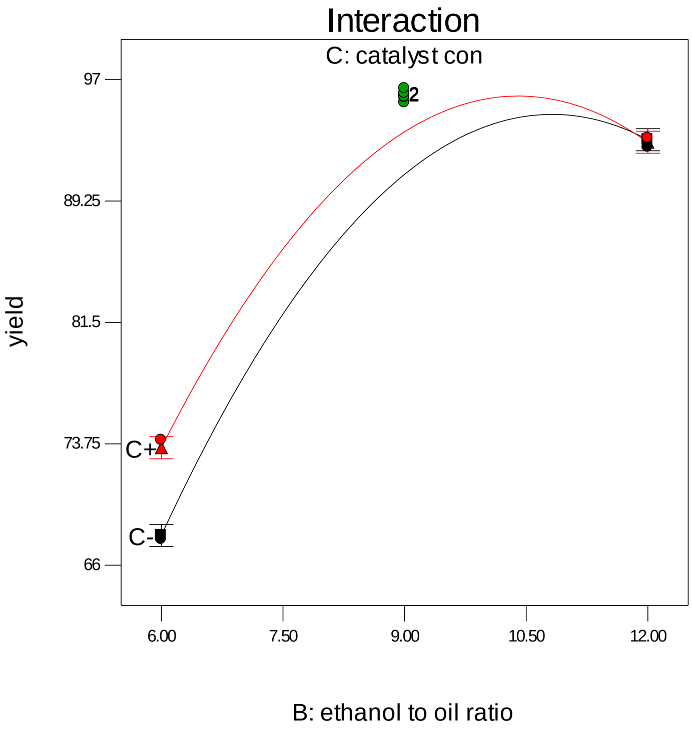

Figure 4.10 Effect and interaction of ethanol to oil ratio and catalyst loading (fixed) on the yield of biodiesel at center of temperature.

4.4.3 Individual effect of experimental variables on the yield of biodiesel

4.4.3.1 Effect of temperature

Figure 4.14 represents the effect of reaction temperature on the yield of biodiesel at constant ethanol to oil ratio and catalyst concentration at the center point. As shown on the figure 4.14 the yield of biodiesel was very sensible to the reaction temperature. The yield was highly increased as temperature increased from 70 ^oC to 75 ^oC. Optimum yield of biodiesel was obtained around 74.5 ^oC. When the reaction temperature was increased from 75 ^oC to 80 ^oC the biodiesel yield was decreased gradually due to vaporization of ethanol because as ethanol loses its amount in contact with reactant in transesterification reaction decreased, as studied in [29,32].

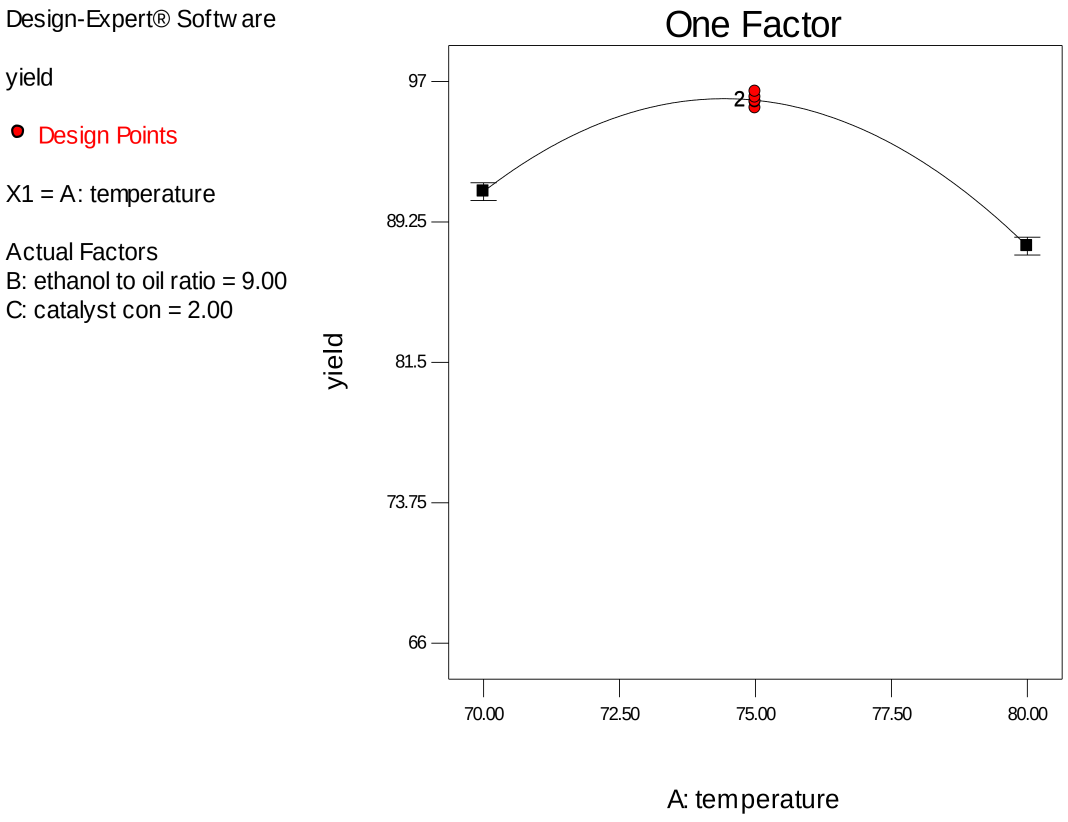

Figure 4.11 Effect of reaction temperature on biodiesel yield

4.4.3.2 Effect of ethanol to oil molar ratio

Figure 4.15 shows the effect of ethanol to oil molar ratio on the yield of biodiesel at constant temperature and catalyst concentration in the center point. In addition the figure shows that, the yield of biodiesel is highly affected by ethanol to oil ratio, as the ethanol to oil ratio increases from 6:1 to 9:1 the yield sharply increases. Whereas, beyond 9:1 the yield of biodiesel slightly decreased. The decrease in biodiesel yield at a high molar ratio beyond 9:1 could be due to the dissolving of glycerol in the ethanol and this hinders the interaction of ethanol with catalyst [31].

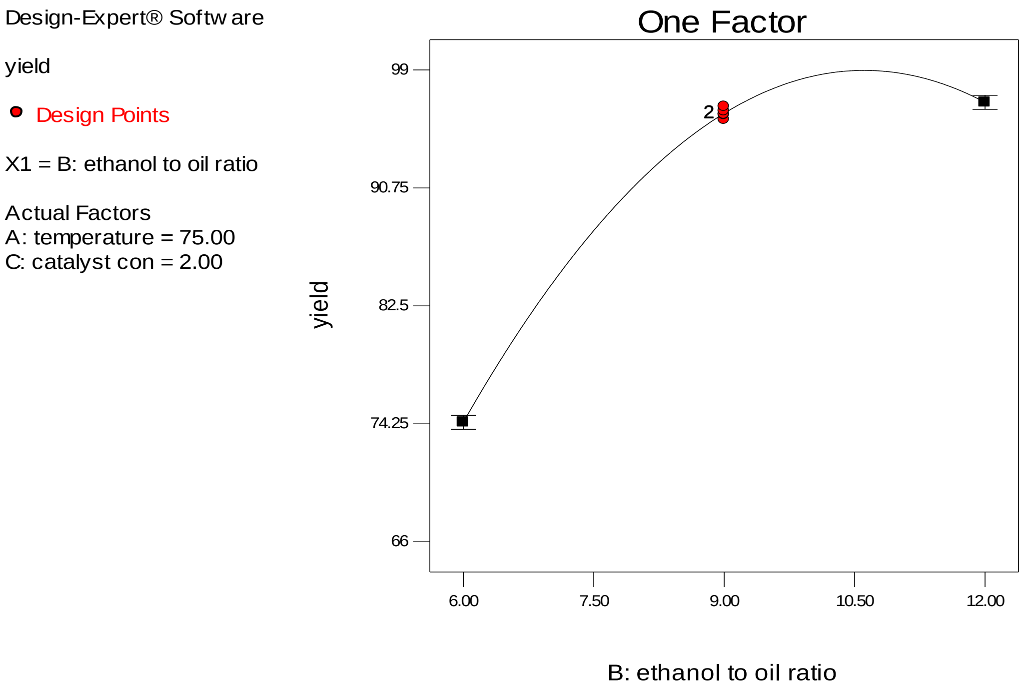

Figure 4.12 effect of ethanol to oil ratio on the yield of biodiesel

4.4.3.3 Effect of Catalyst loading

Figure 4.16 shows the effect of catalyst loading on the yield of biodiesel at constant temperature and ethanol to oil ratio in the center point. As shown in the figure the yield of biodiesel was affected by catalyst loading, as the amount of catalyst increase from 1% to 2% an increase in biodiesel yield was observed, beyond 2 % the biodiesel yield was slightly decreased, because increase in loading might cause viscous nature of catalyst and reactants, this increases the difficulties in mixing and separation process [30]. Insufficient amount of catalyst results incomplete reaction so this reduces the yield.

In this study, the biodiesel yield 96.43% was obtain at a reaction time of 2 hr, 2 wt. % of CaO derived from chicken-eggshell catalyst, temperature of 75 ^oC, and ethanol/oil molar ratio of 9:1, while the previous work reported by Yie Hua Tan et al [31], the highest yield of biodiesel production was 94% and 96%, obtained using CaO derived from ostrich- eggshell and chicken-eggshell, respectively. The optimum operating conditions employed in the previous study was at 2hr reaction time, catalyst to oil ratio of 1.5 wt. %, temperature of 65 ^oC, and ethanol/oil molar ratio of 12:1. The difference may be due to better catalyst preparation.

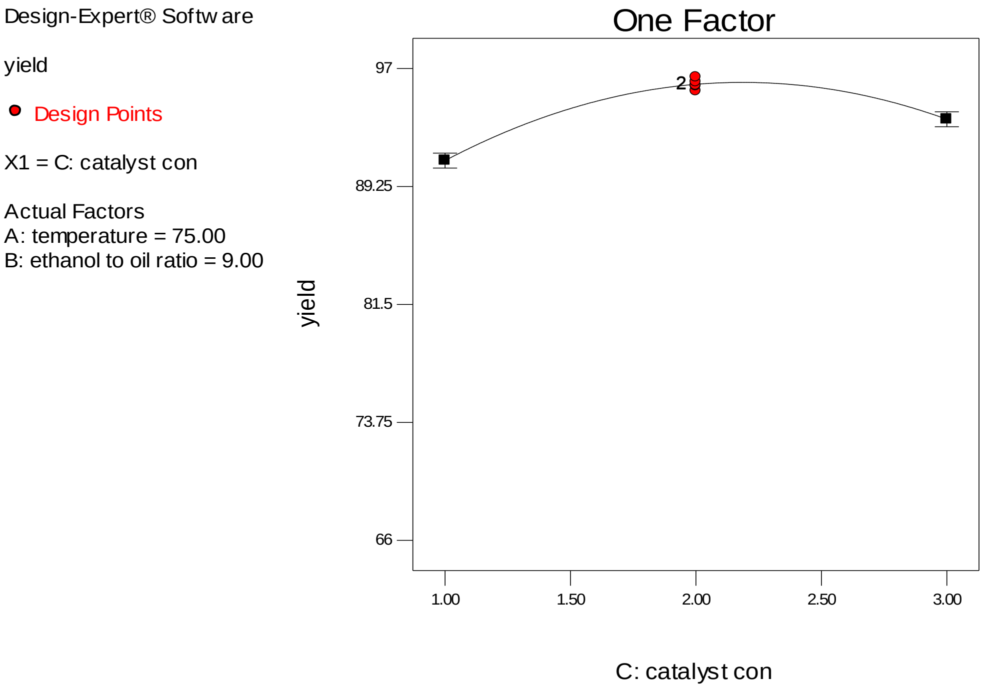

Figure 4.13 Effect of catalyst loading on the yield of biodiesel

4.5 Optimization of operating process variables in transesterification reaction using RSM

Response surface methodology (RSM) is a collection of statistical and mathematical techniques useful for developing, improving, and optimizing processes. It also has important applications in the design, development, and formulation of new products, as well as in the improvement of existing product designs. The optimization of reaction parameters for biodiesel production from CSO using transesterification reaction were summarized below:

Table 4.9 Goal of optimization and limits of process parameters

Name	Goal	Lower limit	Upper limit
Temperature(ºC)	In range	70	80
Ethanol to oil ratio	In range	6	12
Catalyst loading.(%)	In range	1	3
Yield(%)	maximize	66.23	96.43

The optimum possible solutions in transesterification reaction to produce biodiesel was presented in table 4.9 and in Figure (4.14-4.16) below in the form of response surface plot. The predicted optimum yield of biodiesel 98.3938 % was observed at 73.71 ºC, 1.84 % and 10.12 of ethanol to oil ratio. The yield was selected by considering the economic benefit and environmental effect.

Table 4.10 Optimum posssible solutions

Number	Temperature	Ethanol to oil ratio	Catalyst loading	Yield	Desirability	
1	73.89	9.66	2.69	96.9602	1.000	
2	75.30	9.93	2.30	98.2545	1.000	
3	76.69	11.35	2.04	97.0787	1.000	
4	73.94	10.02	2.74	97.2761	1.000	
5	75.72	9.68	2.14	97.684	1.000	
6	75.49	11.01	1.83	98.4051	1.000	
7	75.35	10.49	1.32	96.6776	1.000	
8	75.09	10.23	2.48	98.3066	1.000	
9	74.03	11.31	1.52	97.445	1.000	
10	75.96	11.51	2.15	97.4247	1.000	
11	75.38	11.41	2.31	97.7906	1.000	
12	71.45	10.86	2.16	96.7127	1.000	
13	75.33	11.24	1.79	98.163	1.000	
14	73.71	10.12	1.84	98.3938	1.000	Selected
15	72.86	10.26	2.35	98.1501	1.000	
16	74.30	10.87	1.45	97.6112	1.000	
17	75.95	10.06	2.18	98.119	1.000	

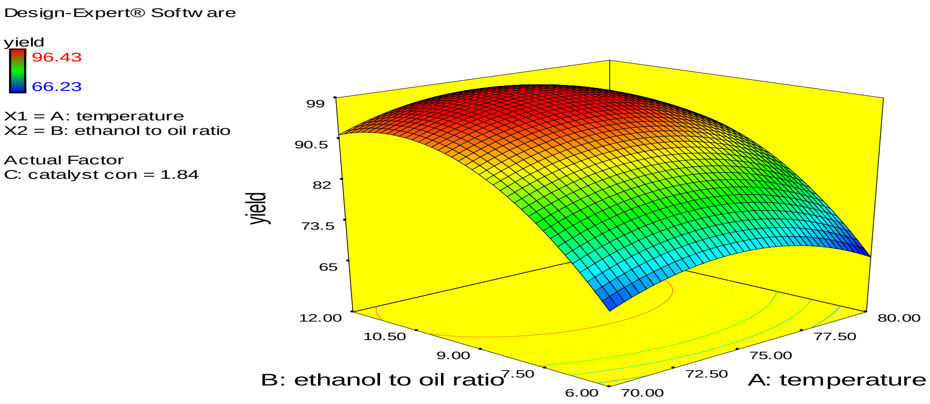

Figure 4.14 Response surfaces of predicted biodiesel yield at fixed catalyst loading

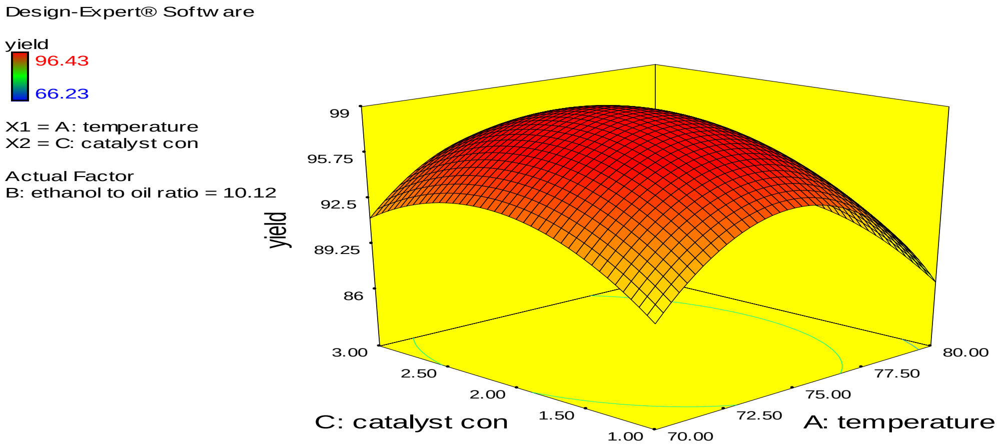

Figure 4.15 Response surfaces of predicted biodiesel yield at fixed ethanol to oil ratio

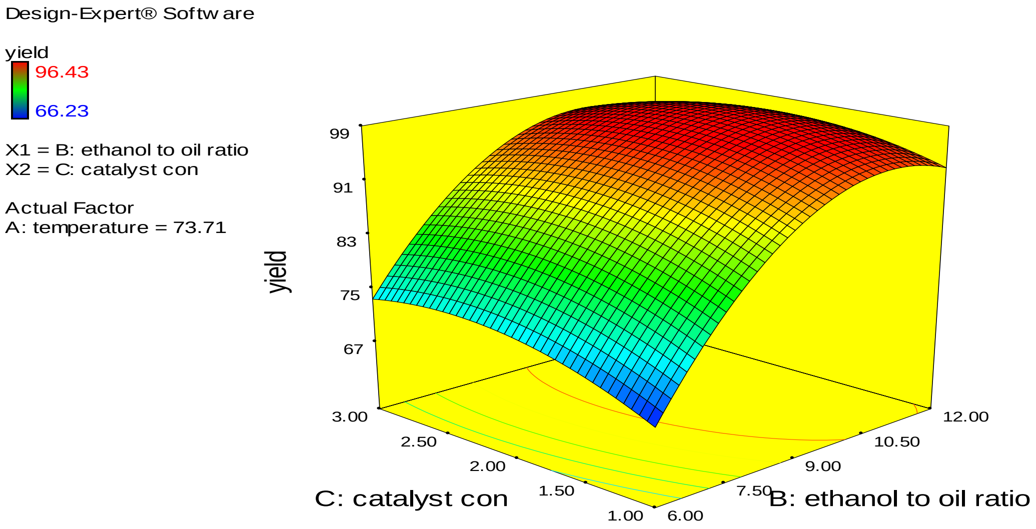

Figure 4.16 Response surfaces of predicted biodiesel yield at fixed reaction temperature

4.6 Model validation

Based on the results of RSM the optimum process conditions in the transesterification reactions were 73.71 ^{o}C, 1.84 % and 10.12:1 ethanol to oil ratio. In order to confirm the validity of the RSM model results a confirmation experiment with triplicate set was conducted at the above-specified optimum process conditions predicted by the model. Under these conditions the yield of biodiesel was found 97.65 %, which were close to the RSM result of 98.3938%. This shows the experimental values were found to be close to the predicted values and hence the model was validated. Thus the model was useful to predict the yield of biodiesel and also to obtain optimum process parameters for transesterification reaction of CSO.

5. Conclusion and Recommendation

5.1 Conclusion

In this research biodiesel was produced using ethanol alcohol with chicken egg shell calcium oxide catalyst at constant reaction time of 2 hr and agitation speed of 400 rpm. The result shows that biodiesel production using egg shell calcium oxide was a considerable potential specially in terms of simplification of separation process, waste reduction and producing environment-friendly product. Thus all decreases the production cost of biodiesel.

At catalyst loading of 1.84% optimum ethyl ester yield of 97.65 % was obtained. Therefore, it can be concluded that egg shell CaO is an effective catalyst for the production of biodiesel from cotton seed oil through transesterification.

As obtained from the experiment all the physico-chemical properties of biodiesel was meet the ASTM D6571 standards.

During the experimental work the effect of reaction temperature, catalyst loading and ethanol to alcohol oil ratio on the yield of biodiesel has been investigated. The analysis obtained from design expert 7.0 (Box-Behnken) for the three factor with three level was show that the increase in catalyst loading, reaction temperature and ethanol to oil ratio up to the optimal point was increase the yield of biodiesel. In contrast, insufficient amount of factor leds to incomplete conversion and further increase of these factors were reduced the yield of biodiesel this could be due to catalyst leaching, alcohol loss and formation of emulsion which made difficulty in the separation of biodiesel from glycerol.

Furthermore, from these three parameters and their interaction effect, all the three parameters have been affect the yield of biodiesel even though, the effect of ethanol to oil ratio and reaction temperature was higher than catalyst loading.

5.2 Recommendation

The Oil used for transesterification was extracted using hexane but, beside to cost it was taken long extraction. For this reason extraction using mechanical pressing is recommended.

In the present work biodiesel production was conducted in batch process system, but it should be scaled up to continuous process system. Even though, this study was used low cost egg shell catalyst once at a time, further research should be done on catalyst recycle that may be more cost effective biodiesel production.

The low-cost egg shell catalyst should be used in a large-scale industrial process of biodiesel production in order to make the process cheap and environmentally kind.

Comparative study of biodiesel production using commercial CaO and chicken egg shell CaO should be done in order to compare the yield. In addition to this, those catalyst should be analyzed both using XRD and BET to determine the exact structure and surface area of the catalyst.

Moreover, further work should be done on glycerol purification and utilization of it for ethanol production purpose. Designing of ethanol pilot plant Integrating with the biodiesel to utilize the byproduct glycerol may reduce the production cost of biodiesel (by reduce the expenses for ethanol).

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Appendices

Appendix A: calculation of surface area and crystal size of cao

A1: surface area of cao calculation

The surface area of cao calcined at 900 ºC was calculated based on the data obtained from Blain Air Permeability apparatus.

s_s=155.2g/cm^3

t_s= 8.25 sec

t_{st}= 25.17 sec

$$S = \frac{s_s\sqrt{t_s}}{\sqrt{t_{st}}} = 155.2\frac{\sqrt{8.25}}{\sqrt{25.17}} = 88.85 \text{ m}^2/\text{g}$$

The surface area of cao calcined at 900 ºC was calculated based on the data obtained from Blain Air Permeability apparatus

s_s=155.2m^2 /g

t_s= 6.52sec

t_{st}= 25.17 sec

$$S = \frac{s_s\sqrt{t_s}}{\sqrt{t_{st}}} = 155.2 \text{ m}^2/\text{g}*\frac{\sqrt{6.52}}{\sqrt{25.17}} = 79.0 \text{ m}^2/\text{g}$$

A2: calculation of CaO crystalline sizes

- The mean crystalline size of calcium oxide calcined @900 ºC was calculated using eq3.1

  Data's from XRD

  FWHM=0.24 **λ**=0.1540590

  K=0.94 B=0.24*π/180 = 0.00419

  θ = 37.5/2=18.75

  cos18.75 = 0.9469

$$\tau = \frac{\kappa\lambda}{\beta cos\theta} = \frac{0.94 * 0.1540590}{0.00419 * 0.9469} = 36.5\text{nm}$$

- The mean crystalline size of calcium oxide calcined @1000 ºC also calculated using eq3.1

  Data's from XRD

  FWHM=0.21 **λ**=0.1540590

  K=0.94 B=0.22*π/180 = 0.003837

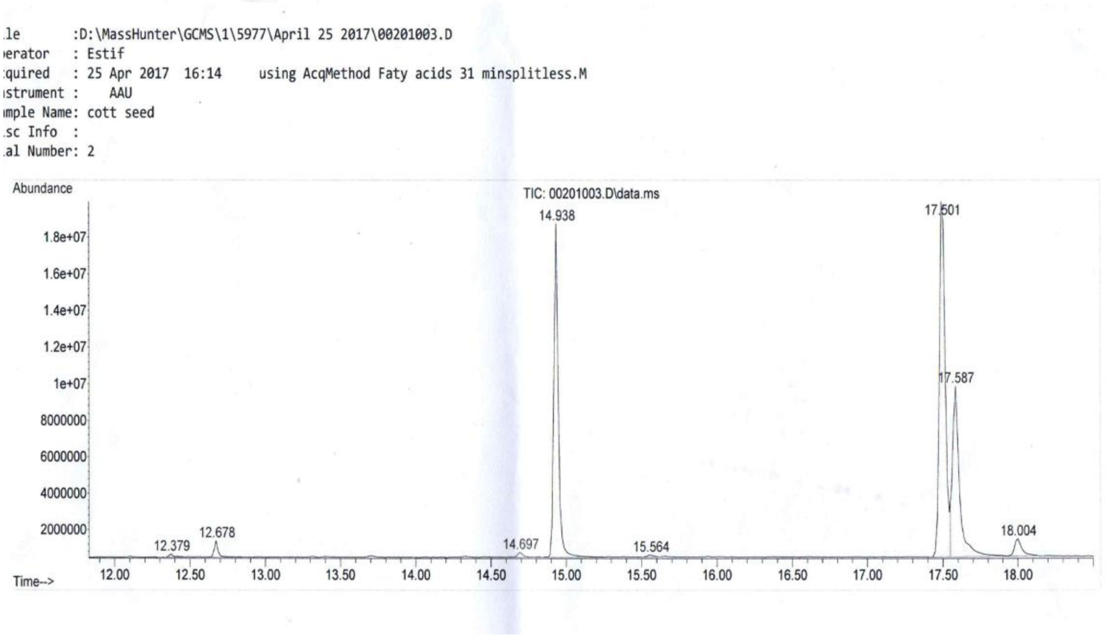
  θ = 37.5/2=18.75

$$\cos 18.75 = 0.9469$$

$$\tau = \frac{0.94 * 0.1540590}{0.003837 * 0.9469} = 41\text{nm}$$

Appendix B: Fatty acid composition of CSO from GC-MS analysis

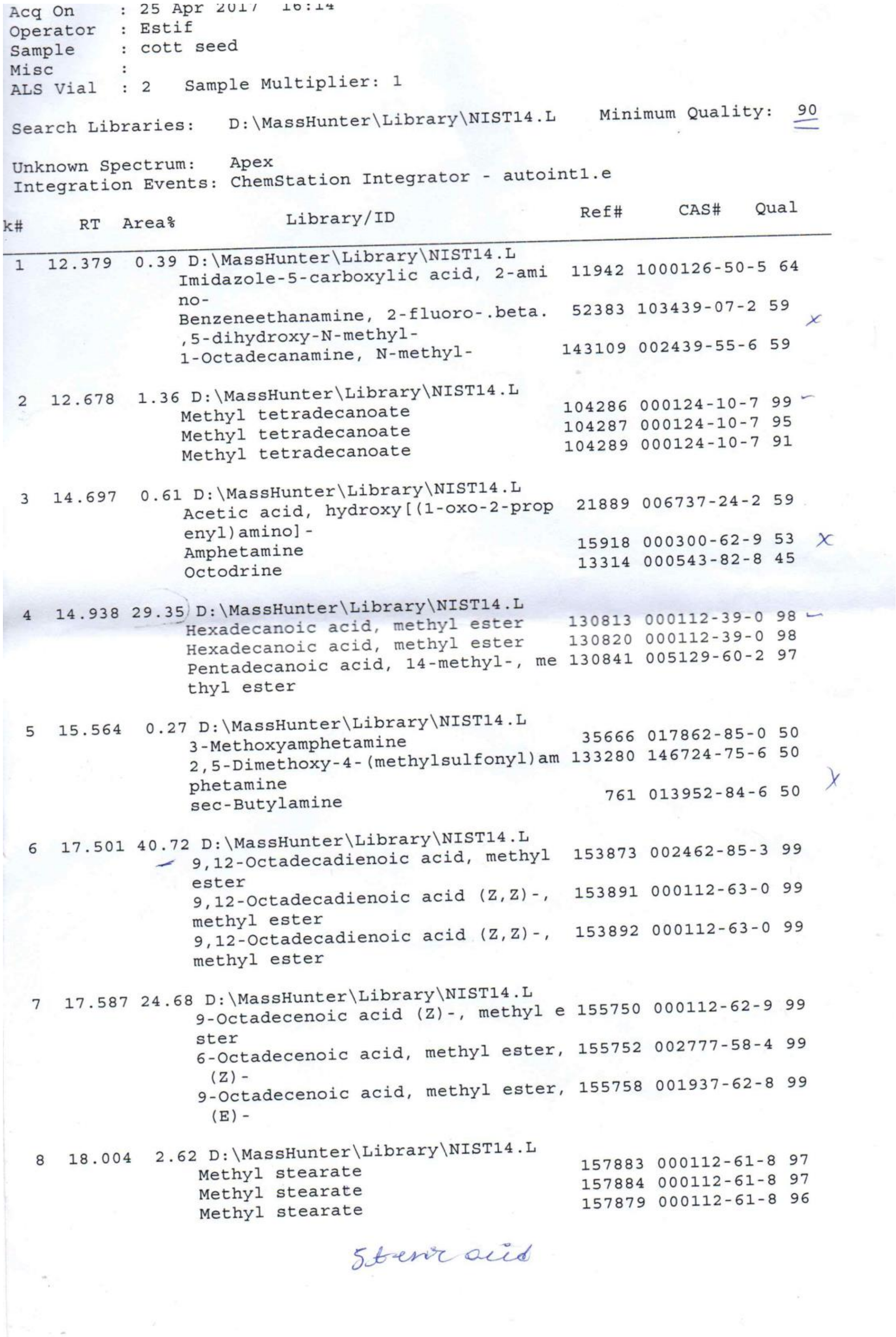
B1: Qualitative analysis report



```
.le        :D:\MassHunter\GCMS\1\5977\April 25 2017\00201003.D
erator     : Estif
:quired    : 25 Apr 2017  16:14     using AcqMethod Faty acids 31 minsplitless.M
istrument :    AAU
imple Name: cott seed
.sc Info  :
.al Number: 2
```

Integration peak list

Peak	Start	RT	End	Height	Area	Area %
1	4.396	4.423	4.733	90322.57	846896	1.63
2	5.563	5.634	5.807	95907.57	634940.41	1.23
3	12.627	12.672	12.766	897182.85	1494916.99	2.88
4	14.65	14.69	14.754	254471.14	557967.97	1.08
5	14.88	14.933	15.094	18248836.13	36787946.61	70.99
6	17.427	17.489	17.543	19500888.65	51818954.73	100
7	17.543	17.584	17.758	9363092.99	30969785.92	59.77
8	17.92	18.001	18.149	964358.6	3532402.13	6.82



```
Acq On      : 25 Apr 2017   16:14
Operator    : Estif
Sample      : cott seed
Misc        :
ALS Vial    : 2   Sample Multiplier: 1

Search Libraries:    D:\MassHunter\Library\NIST14.L    Minimum Quality:  90

Unknown Spectrum:    Apex
Integration Events: ChemStation Integrator - autoint1.e

k#      RT   Area%              Library/ID                  Ref#      CAS#    Qual
------------------------------------------------------------------------------------
 1  12.379   0.39 D:\MassHunter\Library\NIST14.L
                 Imidazole-5-carboxylic acid, 2-ami  11942 1000126-50-5 64
                 no-
                 Benzeneethanamine, 2-fluoro-.beta.  52383 103439-07-2 59
                 ,5-dihydroxy-N-methyl-
                 1-Octadecanamine, N-methyl-        143109 002439-55-6 59

 2  12.678   1.36 D:\MassHunter\Library\NIST14.L
                 Methyl tetradecanoate              104286 000124-10-7 99
                 Methyl tetradecanoate              104287 000124-10-7 95
                 Methyl tetradecanoate              104289 000124-10-7 91

 3  14.697   0.61 D:\MassHunter\Library\NIST14.L
                 Acetic acid, hydroxy[(1-oxo-2-prop  21889 006737-24-2 59
                 enyl)amino]-
                 Amphetamine                         15918 000300-62-9 53
                 Octodrine                           13314 000543-82-8 45

 4  14.938  29.35 D:\MassHunter\Library\NIST14.L
                 Hexadecanoic acid, methyl ester    130813 000112-39-0 98
                 Hexadecanoic acid, methyl ester    130820 000112-39-0 98
                 Pentadecanoic acid, 14-methyl-, me 130841 005129-60-2 97
                 thyl ester

 5  15.564   0.27 D:\MassHunter\Library\NIST14.L
                 3-Methoxyamphetamine                35666 017862-85-0 50
                 2,5-Dimethoxy-4-(methylsulfonyl)am 133280 146724-75-6 50
                 phetamine
                 sec-Butylamine                        761 013952-84-6 50

 6  17.501  40.72 D:\MassHunter\Library\NIST14.L
                 9,12-Octadecadienoic acid, methyl  153873 002462-85-3 99
                 ester
                 9,12-Octadecadienoic acid (Z,Z)-,  153891 000112-63-0 99
                 methyl ester
                 9,12-Octadecadienoic acid (Z,Z)-,  153892 000112-63-0 99
                 methyl ester

 7  17.587  24.68 D:\MassHunter\Library\NIST14.L
                 9-Octadecenoic acid (Z)-, methyl e 155750 000112-62-9 99
                 ster
                 6-Octadecenoic acid, methyl ester, 155752 002777-58-4 99
                  (Z)-
                 9-Octadecenoic acid, methyl ester, 155758 001937-62-8 99
                  (E)-

 8  18.004   2.62 D:\MassHunter\Library\NIST14.L
                 Methyl stearate                    157883 000112-61-8 97
                 Methyl stearate                    157884 000112-61-8 97
                 Methyl stearate                    157879 000112-61-8 96
```

Stearic acid

B2: The main fatty acid compositions of CSO

Fatty Acid compositions	Systemic Name	Formula	Structure	Retention Time(RT)	Results from GC-MS	Wt%	M.weight in g/mol
Linoleic	Cis-9,cis-12-octadecadienoic	$C_{18}H_{32}O_2$	18:2	17.501	51818954.73	59.2	165.75
Oleic	Cis-9-Octadecenoic	$C_{18}H_{34}O_2$	18:1	17.587	30969785.92	35.38	99.7716
Palmitic	Hexadecanoic	$C_{16}H_{32}O_2$	16:0	14.938	557967.97	0.637	1.6307
myristic	methylTetradecanoic	$C_{14}H_{28}O_2$	14:0	12.678	634940.41	0.72	1.6416
stearic	Octadecanoic (methyl stearate)	$C_{18}H_{36}O_2$	18:0	18.004	3532403.13	4.03	11.4452
Total wt.					87514051.16	100	280.2

B3: molar mass calculation for CSO

Molecular mass of CSO = molecular mass of (linoleic acid + oleic acid + Stearic acid + Palmitic acid + myristic acid)

= 280g/mol*0.592 + 282g/mol*0.3538 + 284g/mol*0.0403 + 256g/mol*0.00637 + 228g/mol*0.0072

= 280.2 g/mol

Appendix C: physico chemical properties of cotton seed oil

- Moisture content% (w/w) = $\frac{W1-W2}{w1}*100\%$
- Density: The density of cotton seed oil was measured using Pycnometer at 15 ^{O}C.

ρ_{cso} = 0.92 g/ml

- Specific gravity: The specific gravity was measured at 30^{O}C.

$$SG = \frac{\rho_{cso}}{\rho_{water}} = \frac{920\ kg/m_l}{1000kg/_{ml}} = 0.92$$

- Dynamic viscosity: Dynamic viscosity was measured at 40 ^{o}C

Temperature (^{o}C)	Dynamic viscosity (mpa.s)
46	20
44	23.8
42	25.7
40	27.7

Now the kinematic viscosity of the oil @ 40 ^{o}C was determined by:

$$\mu = \frac{\nu}{\rho_{cso}} = \frac{27.7 mpa.s}{0.92\frac{g}{ml}} = 30\ \mathrm{mm}^2/\mathrm{s}$$

- Acid value

During titration the solution was kept until its color changed to pink.

samples	Initial volume (mgKOH)	Titration volume (mgKOH)	PH
Sample 1	0	1.2	9
Sample 2	0	1.1	9
average		1.15	

$$\mathrm{AV} = \frac{56.1*0.1*1.15}{3}$$

=2.15 mg of KOH/goil.

Therefore, %FFA $= \frac{AV}{2} = \frac{2.15}{2} = 1.07$

- Iodine value

0.25g of oil was used to test iodine value. During the titration pink color changes to colorless was the end point.

No.	Initial value (Na_2SO_3in ml)	Final value (Na_2SO_3 in ml)	VB-VS (In ml)
Sample1	0	23	20.6
Blank1	0	43.6	
Sample2	0	25.2	19.7
Blank2	0	44.9	
Avg.			20.15

The average iodine value obtained using eq3.6 was 102.28.

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

$$= \frac{12.69*0.5*20.15}{0.25}$$

$$= 102.28$$

- Saponification value

sample	Initial HCl consumed in(ml)	Final HCl consumed in (ml)	Vb-Vs	Avg.
Sample 1	0	20.7	5.99	5.99
Blank1	0	26.69		
Sample2	0	20.3	6.35	6.35
Blank2	0	26.65		

$$SN = \frac{56.1*0.5*(-19.3)}{10} = 177.42$$

C1: Properties of different Vegetable Oils

Vegetable oil	Kinematic viscosity at 40 ^oC(mm^2/s)	Density (kg/L)	Cetane no.(^oC)	Flash point (^oC)	Pour point (^oC)	Cloud point (^oC)	Heating value (MJ/kg)
corn	34.9	0.9195	37.6	277	-40	-1.1	39.5
cottonseed	33.5	0.9148	41.8	234	-15	1.7	39.5
crambe	53.6	0.9048	44.6	274	-12.2	10.0	46.5
linseed	27.2	0.9236	34.6	241	-15	1.7	39.3
peanut	39.6	0.9026	41.8	271	-6.7	12.8	39.8
rapeseed	37	0.9115	37.6	246	-31.7	-3.9	39.7
safflower	31.3	0.9144	41.3	260	-6.7	18.3	39.5
sesame	35.5	0.9133	40.2	260	-9.4	-3.9	39.3
soyabean	32.6	0.9138	37.9	254	-12.2	-3.9	39.6
Sunflower	33.9	0.9161	37.1	274	-15	7.2	39.6
palm	39.6	0.918	42.0	267	-	31.0	-
babassu	30.3	0.946	38.0	150	-	20	-
Pongamia	36.4	0.9135	42.2	150	-16	1.9	39.7
diesel	3.06	0.855	50	70	-16	-	43.8

Appendix D: calculation of feed required for transesterification reaction

The amount of feed required for each run of transesterification reaction was calculated below based on:

$$\frac{n_{ethanol}}{n_{oil}} = \frac{\frac{m_{ethanol}}{M_{ethanol}}}{\frac{m_{oil}}{M_{oil}}} = 6 \qquad \frac{\frac{\rho_{ethanol} * V_{ethanol}}{M_{ethanol}}}{\frac{\rho_{oil} * V_{oil}}{M_{oil}}} = 6 \qquad \text{Equation 0.1}$$

Where, molar mass of ethanol = 46g/mol

Avg.molecular weight of CSO (Moil) = 280.2 g/mol

ρ_{oil}= 0.92g/cm^3, $\rho_{ethanol}$=0.789g/cm^3

1cm^3=1ml

$$\text{Vethanol}=\frac{6*46\text{g/mol}*0.92\text{g/cm3}*30\text{ml}}{0.789g/cm3*280.2g/mol}=43.46\text{ml}$$

The same procedure is applied for 9:1 and 12:1.

The amount of catalyst required when the catalyst loading was 1% also calculated below.

$$\frac{\text{mass of catalyst}}{\text{mass of oil}}=1\%$$ Equation 0.2

Mass of catalyst = 0.01 * 0.92 g/cm3 * 30ml =0.276 g

The Mass of 2% and 3% was obtain the same to this

D1: Physico chemical properties of biodiesel (FAEE)

- kinematic viscosity

Temperature (^oC)	Dynamic viscosity (mpa.s)
44	1.80
42	2.85
40	3.864

Now the kinematic viscosity of the biodiesel @ 40 ^oC was determined by:

$$\mu=\frac{\nu}{\rho_{cso}}=\frac{3.864mpa.s}{0.92\frac{g}{ml}}=4.2\ \text{mm}^2/\text{s}$$

- Acid value

samples	Initial volume (mgKOH)	Titration volume (mgKOH)
Sample 1	0	0.12
Sample 2	0	0.13
average		0.11

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

=0.21 mg of KOH/goil.

Therefore, %FFA $= \frac{AV}{2} = \frac{0.21}{2} = 0.105$

- Saponification value

sample	Initial HCl consumed in(ml)	Final HCl consumed in (ml)	Vb-Vs	Avg.
Sample 1	0	8.2	9.8	9.8
Blank1	0	18		
Sample2	0	8.3	9.81	
Blank2	0	18.12		

$$SN = \frac{56.1*0.5*(9.8)}{2} = 136.1$$

- Iodine value

No.	Initial value (Na_2SO_3in ml)	Final value (Na_2SO_3 in ml)	VB-VS (In ml)
Sample1	0	23	20.6
Blank1	0	43.6	
Sample2	0	25.2	19.7
Blank2	0	44.9	
Avg.			20.15

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

$$= \frac{12.69*0.5*20.15}{0.25}$$

$= 102.28$

Appendix E: pictures of samples and some laboratory Equipments

E1

E2

E3

E4

E5

E6

E7

E1 (Soxhlet extraction), E2 (crude CSO), E3 (Neutralized CSO)

E4 (Biodiesel and Glycerol Separation), E5and D6 (Biodiesels), E7 (Bunsen burner)

Appendix F: Experimental results obtained based on the experimental design

Std	Run	Factor 1 A:temperature oC	Factor 2 B:ethanol to oil ratio	Factor 3 C:catalyst con %	Response 1 yield %
1	13	70.00	6.00	2.00	69.16
2	2	80.00	6.00	2.00	66.23
3	12	70.00	12.00	2.00	91.84
4	17	80.00	12.00	2.00	88.76
5	6	70.00	9.00	1.00	85.91
6	14	80.00	9.00	1.00	83.64
7	4	70.00	9.00	3.00	88.63
8	1	80.00	9.00	3.00	84.87
9	8	75.00	6.00	1.00	67.64
10	16	75.00	12.00	1.00	92.68
11	3	75.00	6.00	3.00	73.98
12	9	75.00	12.00	3.00	93.26
13	10	75.00	9.00	2.00	95.52
14	15	75.00	9.00	2.00	95.85
15	7	75.00	9.00	2.00	95.89
16	11	75.00	9.00	2.00	96.12
17	5	75.00	9.00	2.00	96.43