Addis Ababa University

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Production of Biodiesel from Castor Seed Oil Via Transesterification with Methanol- Ethanol Blends using Calcium oxide as Catalyst

A Thesis Submitted to the School of Chemical and Bioengineering of Addis Ababa Institute of Technology, in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemical and Bio-Engineering (Process Engineering Stream)

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Abstract

Biodiesel is a renewable and sustainable energy sources with a great potential to replace conventional fuel and causes too much less environmental impact. Vegetable oils which can be edible or nonedible and animal fats can be used as feed stock for biodiesel production. Now a day, nonedible vegetable oils are getting more attraction and castor seed oil is among the nonedible oils having a great potential for biodiesel production. Catalyzed transesterification is most frequently used method for biodiesel production. The catalyst can be homogenous bas or acid heterogenous base or acid and biocatalysts. This research was aimed at producing biodiesel from castor seed oil via transesterification with methanol/ethanol blends. The oil was extracted in soxhlet apparatus using normal hexane as a solvent and its chemical and physical properties were tested and most of the properties were found to be complying with American society for testing for materials (ASTM) quality oil. However, its viscosity was found to be too high. The FAM/E-E (biodiesel) was produced via transesterification of the castor seed oil with methanol and ethanol blends using calcium oxide as solid catalyst. Methanol to ethanol volume ratio, total alcohol to oil molar ratio and catalyst loading were the process variables being studied and Design Expert 7.0.0 software using central composite design was used to investigate the individual and interaction effects of these process variables on the yields of the produced biodiesel. The maximum yield of biodiesel was obtained at 50:50 methanol to ethanol volume ratio, 9:1 total alcohol to oil molar ratio and 2.5% catalyst loading. The properties of the produced biodiesel were tested and most of were found to be complying with that of the ASTM standard biodiesel. However, the density and viscosity were found to be above the ASTM standards. Depending on the results obtained from this study, it can be concluded that the use of mixed methanol and ethanol for transesterification of cator seed oil to biodiesel is viable process. In addition, the use of solid catalyst is a green process since washing of biodiesel with water is not needed and separation of biodiesel from its reaction mixture is easy.

Key words: Castor oil, Methanol/Ethanol blends, Calcium oxide, Transesterification, Biodiesel

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This is to certify that the thesis prepared by Berhane Tsegay entitled: Production of biodiesel from castor seed oil via transesterification with methanol-ethanol blends using calcium oxide as catalyst and submitted in partial fulfillment of the requirements for the degree of Master of Science in chemical and Bio engineering complies with the regulations of the university and meets the accepted standards with respect to originality and quality.

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Declaration

I declare that, this thesis entitled "Production of biodiesel from castor seed oil via transesterification with methanol-ethanol blend using calcium oxide as catalyst" has not been submitted in any form for another degree, diploma or an award at any university or other institution of the tertiary education. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due reference to the literature and discussions. Information taken from published and unpublished work of others has been acknowledged in the text and a list of references is given. The work was under the guidance of Prof.Dr. Ing. Belay Woldeyes, instructor in Addis Ababa University, School of Chemical and Bio Engineering.

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List of Acronyms and abbreviations

ANOVA	Analysis of variance
ASTM	American society for testing materials
AV	Acid value
CN	Cetane number
CP	Cloud point
CSOB	Castor seed oil biodiesel
D.P	Diagnostic plot
E	Ethanol
FAM/E-E	Fatty acid methyl-ethyl ester
FFA	Free fatty acid
FTIR	Furious transform infrared
HV	Heating value
IV	Iodine value
M	Methanol
M.C	Moisture content
M.W	Molecular weight
MR	Molar ratio
PP	Pour point
SV	Saponification value

1. Introduction

1.1. Background

Now a day, fosil fuels are the major sources of energy across the world. However, these energy sources are nonrenewable and highly concentrated in specific part of the world**.** The depletion rate of these fosil fuels is also much fatter than their regeneration rate and are the major sources of greenhouse gases, air pollution and global warming(Ahmad & Khan, 2011). These factors have stimulated scientist and researchers to search a renewable energy source such as biodiesel hydro, biomass, wind, solar, geothermal, hydrogen and nuclear is of vital importance(Demirbas, 2005).

Ethiopia is one of the countries having no petroleum reserves and its annual energy demand is mainly satisfied using imported fosil fuel leading to lack of foreign currency. However, the energy demand is increasing more rapidly because of rapid population growth, industrialization and transportation. Thus, production and utilization of biodiesel can solve the problems related to utilization of fosil fuel such as lack of foreign currency, and environmental impacts.

Biodegradability and non-toxicity nature and less emission of pollutants are some of the important characteristics making the use biodiesel a promising alternative fuel (Fan et al.,2011). The use of biodiesel results in significant reduction in exhaust emissions (Demirbas, 2005). It is also the only alternative fuel that runs in any conventional, unmodified diesel engine and its utilization as fuel enable to reduce carbon dioxide emission by approximately 80% and sulfur dioxide emission by 100% and total unburned hydrocarbons by 90% (Shrirame et al.,2011). Moreover, biodiesel can be easy produced from readily available and renewable sources and safe to handle and use, eco-friendly. Biodiesel is a mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats (Ma & Hanna, 1999). Vegetable oils are the most widely used raw materials for biodiesel production but oils derived from various animal have also been used as a raw material to produce biodiesel (Sruthi Gopal, 2013).

Currently, edible oils are the most widely used oil for biodiesel production. Almost 95 % of biodiesel produced in the world is made from edible vegetable oils which are too much costly. The use of these oils as feed stock for biodiesel production results in food price competition(Leung et al.,2010). Since recent years, nonedible oils have become attractive feed stock for biodiesel

production because of their low cost compared to those edible oils and the plants from which non-edible oils obtained are easy to cultivate in lands where edible plant oils cannot be grown and the cultivation cost for nonedible oil producing plants is much lower than the cost for edible plants oils (Gui, Lee, & Bhatia, 2008). Castor seed oil is belonging to the family of nonedible oils having a promising potential for biodiesel production. It has high oil content (30%–55%).Moreover, castor plant can also well under hot and humid tropical conditions within 4 to 5 months (Atabani et al., 2012).

Transesterification reaction is the most widely used method for biodiesel production in which the triglycerides in the vegetable oils are reacted with a monohydric alcohol(Meher et al. 2006).This reaction is usually carried out in the presence of catalyst and many different chemical and enzymatic catalysts have been used in the process(Shahla et al., 2010). However, alkalis, mainly sodium hydroxide, sodium methoxide and potassium hydroxide are more widely used The choice of acid and alkali catalyst depends on the free fatty acid that the oil contains and bas catalyzed transesterification is more suitable for oils with low free fatty acid (Demirbas, 2003). Since recent years however, the use of solid catalysts in biodiesel production have been increased. This is because solid catalysts are less corrosive and economically attractive. These catalysts can be easily separated from the reaction mixture, and reused so many times(Kumar et al., 2012). Methanol and ethanol are the most widely used alcohols during transesterification. However, alcohols like propanol, butanol can also be used. Ethanol is a preferred compared to methanol because it is derived from agricultural products and is renewable and low environmental impact. However, methanol is the most widely used because of its low cost and high reactivity(Demirbas, 2003).

1.2. Problem statement

Fosil fuel depletion and its price fluctuation has resulted in lack of foreign currency in developing countries with no petroleum reserves(Shrirame et al.,2011). Ethiopia is one of the developing countries having no petroleum reserves and being affected by lack of foreign currency. Thus, searching alternative renewable source of energy such as biodiesel is necessary to overcome these fosil fuel related problems. Ethiopia is highly endowed with wide variety of nonedible oils that can be used as a feed stock for biodiesel production but not well exploited. Castor seed oil is one of the nonedible oils being produced in large quantity and mainly used for animal skin treatment

which is unwise economical use. Thus, production of biodiesel from castor seed oil can be a potential solution to the problems encountered with the use of fosil fuels.

Alkali catalyzed transesterification with its many problems is the most widely used method for the production of biodiesel. This method is sensitive to the free fatty acid content of the oils used and the spent catalyst is not easy to recover. Washing and neutralization are also necessary steps causing huge amount of waste water to be generated. These, problems make the biodiesel production process too costly with high environmental impact(Yan et al., 2010). On the other hand, the use of homogenous acid catalyst is insensitive to the oil used but its yield is low as compared to that of basic catalyst and high catalyst concentration, oil to methanol molar ratio, high reaction temperature and long reaction time are the inherent problems associated with acid catalysts (Thakur & Dange, 2015). In addition, either methanol or ethanol is used as reactant in transesterification reaction. However, biodiesel produced using methanol is not completely renewable. On the other hand, the use of ethanol results in low yield of biodiesel though it is completely renewable because of its low reactivity and its ability to form stable emulsions that make separation process complicated (Gui et al., 2009).

To solve these problems, mixed methanol and ethanol technology has been applied and found to be promising technology in the presence of homogenous catalyst. However, this technology has not been studied for biodiesel production using heterogenous base catalyst. Thus, this study was carried out to investigate the potential of using methanol and ethanol blends as reactant for biodiesel production from castor seed oil in the presence of calcium oxide (CaO) as heterogenous base catalyst. The calcium oxide was chosen because of its low cost and high catalytic activity compared to other solid base catalysts and its use can eliminate water washing and neutralization steps which are much expensive and time-consuming processes. It is also reusable and can process low quality feed stocks (Yan et al., 2010).

1.3. Objectives of the study

1.3.1. General Objective

The general objective of the study was to produce biodiesel via transesterification of castor seed oil with methanol- ethanol blends using calcium oxide (CaO) as heterogenous catalyst.

1.3.2. Specific Objectives

The Specific Objectives of this study were to:

- ✓ Extract and characterize castor seed oil
- ✓ Study the effects of methanol to ethanol volume ratio, total alcohol to oil molar ratio and catalyst loading on the yield of biodiesel.
- ✓ Determine the physico-chemical properties of the biodiesel being produced and compare it with that of standard biodiesel properties.

1.4. Significance of the study

In this study, castor seed oil which can be produced in large quantity on lands which cannot be used for food crop cultivation was used as a feed stock for biodiesel production. Thus, it will be significant in terms of motivating local farmers to produce castor seed in large quantity which can help them improve their income. It can also be significant in terms of shifting the use of castor seed oil from its traditional use like animal skin treatment to biodiesel production which can help minimize the economic losses of castor seed oil and partially substitute fosil fule. Moreover, this study will be significant in terms of partial substitution of methanol which is nonrenewable with ethanol that can be produced from wide range of agricultural product. It can also be used as a reference for those who are interested to modify and improve the catalytic performance of calcium oxide so as to improve the biodiesel production process and maximize its yield.

2. Literature Review

2.1. Rationales to Biodiesel Production

In recent years, worldwide energy crisis associated with fossil fule resources depletion and increased environmental pollutions have initiated the search for sustainable and environment friendly alternative fuels. Biofuels like biomass, biogas, alcohol, vegetable oils, synthetic fuels are becoming important which can be used directly while others need some sort of modification before they are used as substitute of conventional fuels(Sharma, 2009).

Biodiesel has emerged as a promising alternative to petro diesel because of its remarkable characteristics such as biodegradability, less toxicity, and reduced greenhouse gas emission. It can be also used as blending component for diesel fuel in automotive engine (Gupta, 2003). Biodiesel is monoalky esters of long chain fatty acids derived from renewable feed stocks, such as vegetable oil or animal fats. It is mainly composed of fatty acid methyl esters produced from triglycerides in vegetable oils by transesterification with short chain alcohols and is quite similar to conventional diesel fuel in its main characteristics(Meher et al., 2006). Biodiesel is the only alternative fuel which can be used in any conventional, unmodified diesel engine and its use enables to reduce carbon dioxide emission by approximately 80% and sulfur dioxide emission by 100%. It also enables to reduce total unburned hydrocarbons by 90%, and aromatic hydrocarbons by (75-90%) (Shrirame et al., 2011). Technically, biodiesel is described as mono alkyl esters of long chain fatty acids derived from either vegetable oils or animal fats(ONKAR S. et al.,2010)

2.2. Latest Review on biodiesel Production

Many researches have been conducted on transesterification of castor seed oil with short chain alcohols such as methanol to biodiesel in the presence of various catalysts. Some literatures related to biodiesel production from castor oil was discussed and summarized as follow.

Deshpande et al., (2012) produced biodiesel from castor seed oil using two different catalysts (sulfuric acid and sodium hydroxide). The specific gravity, viscosity, acid value and saponification value of the biodiesel were being studied as the response of the process. The result showed that the amount of methanol to oil molar ratio and catalyst concentrations for NaOH were lower than

that of H_2SO_4 used. However, soap formation was observed with NaOH. Similarly, a comparative study on the catalytic performances of sulfuric acid and potassium hydroxide in transesterification of castor seed oil to biodiesel was also made by (Nakarmi & Joshi, 2014). The obtained result also indicated that the best yield (92%) of biodiesel was obtained using KOH catalyst at1:9 oil to methanol ratio, 1% catalyst concentration, 65^{o}c and 3hr reaction temperature and time. While the yield obtained using sulfuric acid was negligible (8.29%) and higher oil to methanol molarity was used. The authors concluded that though KOH was better than sulfuric acid, separation of glycerol was complicated and recombination of the ester produced and the byproduct glycerol was occurred.

Renita.A & Kumar.J, (2015) also studied catalytic performance of homogenous (NaOH and KOH) and heterogenous (CaO and MgO) catalysts on transesterification vegetable oil to biodiesel and it was observed that higher yield of biodiesel was achieved using homogenous catalysts, but additional treatment (neutralization and washing) were necessary resulting in extra cost of production. For every 100ml biodiesel 15 ml water was used to remove remaining trace amount of impurities from the produced biodiesel. In the case of heterogenous catalyst however, washing of biodiesel was not needed and the catalysts could be reused.

Hawash et al., (2016) have also conducted comparative investigation on the catalytic performance of KOH and CaO for transesterification of jatropha oil to biodiesel. The authors report indicated that purification of glycerol produced from heterogenous catalyst was simpler than the one produced from homogenous catalyst and the purity of glycerol was 99.4% for CaO and 50% for KOH catalysts. This, indicated that CaO is technically, economically and environmentally acceptable. It was concluded that heterogenous catalysts are environmentally attractive and best alternative to homogenous catalysts for production of biodiesel.

In addition to catalyst type, the type of alcohol used has also significant effect on the yield and purity of biodiesel. In most cases, methanol is used for transesterification reaction. However, methanol is petroleum derived product. Thus, biodiesel produced using methanol as reactant is not completely renewable. On the other hand, biodiesel produced using ethanol as reactant is completely renewable. However, low reactivity, formation of stable emulsions that make

separation of biodiesel from glycerol complicated are still inherent problems associated with ethanol(Gui et al.,2009).

To solve these problems different studies on utilization of mixed methanol and ethanol has been conducted**.** Lam & Lee, (2011) produced biodiesel from waste cooking oil using mixed alcohol (methano+ethanol) in the presence of acid catalyst and they conclusion that this mixed alcohol technology has great potential for biodiesel production. Another researchers Enontiemonria et al.,(2012) also produced biodiesel from castor seed oil using transesterification with methanol, ethanol and their blends in the presence of sodium hydroxide(NaOH) as catalyst. It has been observed that the highest yield was obtained using the mixed alcohol.

From the literatures provided above, it can be seen that biodiesel production using both homogenous bas and acid catalysts is not economically and environmentally attractive. Basic catalyst is sensitive to the free fatty acid content of the oils used and the spent catalyst is not easy to recover. Washing and neutralization are also necessary steps causing huge amount of waste water to be generated. On the other hand, the use of homogenous acid catalyst is insensitive to the oil used but its yield is low as compare to that of basic catalyst and high catalyst concentration, oil to methanol molar ratio, high reaction temperature and long reaction time are needed.

The literatures also showed that utilization mature of methanol and ethanol blends has a promising potential for biodiesel production in the presence of homogenous base catalyst. However, this technology has not been studied for biodiesel production using heterogenous base catalyst. Thus, this study was carried out to investigate the potentials of using methanol and ethanol blend as reactant for biodiesel production from castor seed oil in the presence of commercial calcium oxide (CaO) as heterogenous base catalyst. The calcium oxide was chosen because of its low cost and high catalytic activity compared to another solid bas catalysts.

2.3. Possible feed stocks for biodiesel production

Vegetable oils are considered to be the primary source of biodiesel and more than 350 oil bearing crops and plants have been identified, as sources of oils for biodiesel production. These oils have become more attractive recently because of their environmental advantages such as renewability and potentially inexhaustible source of energy with an energetic content which is close to diesel

fuel(Demirbas, 2005b). Initially, the vegetable oil fuels were not acceptable because of their high cost. However, increasing petroleum price and uncertainties in its availability have renewed the use of vegetable oil fuels for diesel engines(Demirbas, 2003).

2.3.1. Edible Oils

The use of biodiesel as alternative fule is environmentally feasible but economically less attractive because the cost of virgin vegetable oils is high(Zhang et al.,2003). Currently, more than 95 %of the global biodiesel is being produced from edible vegetable oils since they are readily available on large scale. However, extensive use of edible vegetable oils for biodiesel production has recently been recognized to be the cause for food verse fule price competition and 70%-95 % of the total cost of biodiesel production is payed to raw material cost. This indicates that commercial production of biodiesel from edible oils is economically less attractive (Gui et al., 2008).

2.3.2. Nonedible Oils

To overcome food verses fule price competition, extensive efforts are being conducted to produce biodiesel from non-edible. The use of non-edible oils has become increased because of tremendous demand for edible oils as food. In addition, non-edible oil producing plants can be cultivated in lands where edible oil crops cannot be grown. The cultivation cost of these oils is much lower compared to the cost of edible oil plants(Gui et al., 2008). Various non-edible oils such as Jatropha, cotton seed oil, Neem seed oil etc. have been successfully used to produce biodiesel. It can be also produced from waste used vegetable(Zheng et al. 2006). Some different edible and nonedible producing plants are comparatively presented in table 2.1 as shown below (Shrirame et al., 2011).

Table 2-1. Edible and Nonedible vegetable oils

Type of oil	Oil yield (kg/ha)	Oil yield (wt%)
castorseed	1180	30-55
Rubber seed	80-120	40-50
Jatropha	1590	35-40
pongamia	225-2250	30-40
Soybeen	375	20
palm	3000	20
Rape seed	1000	37-50

2.3.3. Biodiesel from castor seed oil

Castor is indigenous to the southeastern Mediterranean Basin, Eastern Africa, and India. Castor plant which is the sours of cator seed is shown in fig 2.1. Castor plant has short growing period (4 to 5 month) compared to other oil producing plants and farmers have greater experience and awareness about its cultivation. Castor seed also contains 30% up to 55% oil by weight (AKPAN et al.,2006).

Figure 2-1. (a) cator plant (b) cator seed

Chemically, castor seed oil is comprised of different acid components such as ricinoleic acid, linoleic acid and oleic acid. The presence of high ricinoleic acid, makes the castor seed oil unique and, highly soluble in alcohol. Castor oil is a colorless to very pale-yellow liquid. The oil also has improved lubricity compared to other oils with similar carbon chain fatty acids(Ramezani et al ., 2010). Biodiesel derived from castor seed oil has several promising advantages. Most of its fuel properties are close to conventional fuel properties(Bello & Makanju 2011). It has high cetane number (high ignition quality), high oxygen content (complete combustion), high flash point (safe for handling and storage). It has also low emission of carbon monoxide (CO), sulphur dioxide (SO_2) and nitrogen dioxide (NO2) compared to conventional diesel(ISMAIl1 et la., 2014). It also needs minimum production cost (Soliman et al. 2014).

2.4. Methods of oil extraction

Oil extraction can be carried out using mechanical extraction(pressing), chemical or solvent extraction, and enzymatic extraction methods. Moreover, accelerated solvent extraction (ASE), supercritical fluid extraction (SFE) as well as microwave-assisted extraction (MAE) methods have also been developed. However, the first three alternatives are most widely used(Atabani et al., 2012).

2.4.1. Mechanical method

This method is the most conventional method which is either manual ram press or an engine driven screw press. It has been noted the use of engine driven screw press, enables to extract 68–80% of the total oil available but the use of the ram presses method, enables to extract only 60–65% of the total oil available in the seed. However, oils extracted using mechanical press method need filtering and degumming(Atabani et al., 2012). The efficiency of mechanical and solvent extraction methods have also been studied by(Bhuiya et al., 2015). It was found that mechanical method of oil extraction was less costly than solvent extraction method. However, in terms of the yield obtained solvent extraction was more efficient. Moreover, solvent extraction method was found to be better, more repeatable, relative ease of preparation and no requirement for extensive training but needs relatively high cost due to the cost of solvent used.

2.4.2. Solvent Extraction Method

This method involves removal of constituents from a solid by means of a liquid solvent. It can be affected by many factors such as particle size, the type of liquid chosen, temperature and agitation of the solvent. Small particle size is preferable as it allows for a greater interfacial area between the solid and liquid. The solvent used should be good selective with low viscosity to circulate effectively. Temperature can also affect the rate of extraction as solute solubility can increase with the increasing temperature(Atabani et al., 2012). In solvent extraction method, hexane is primarily used as a solvent. Nangbes et al. (2013),extracted castor seed oil in soxhlet apparatus using hexane as solvent and about 48% yield was obtained with a total fatty acid composition of 88.41%. Another researcher Asid et al .(2010) \extracted castor seed oil using hexane as a solvent in Soxhlet apparatus and a yield of 43.3% per dry weight with a total fatty acid composition of 97.5% which was rich in ricinoleic acid (>84%) was obtained.

The efficiency of solvent extraction can also be affected by different factors such type of solvent used, solvent to sample(seed) ratio and extraction time etc. Rani & Goud,(2013) studied the effects of type of solvent used (n-hexane, isopropanol, pentane, petroleum ether), Solvent to solid(sample) raio and extraction time .In this study, the effects of hexane to solid ratio and extraction time were optimized and applied for the other solvents. The extraction was carried out near the boiling point of corresponding solvent. It was observed that the maximum yield was obtained using hexane (45.5%). The comparison of mechanical method of extraction and solvent extraction methods is presented in table 2.2 (Jahirul et al., 2013).

Table 2-2. Comparison of Mechanical Vs solvent extraction methods

Chemical method		Mechanical method	
Advantage	Disadvantag	Advantage	Disadvantage
Repeatable result and procee	High solvent contamination	No solvent contamination	Lesss effective
High yille of oil	High safty prolem	Less expensive	Loaor intensive
Reletively simple and quick	High Enviromentl impact	Vergen oilis more sought	Expriance is need

2.5. Methods of Biodiesel production

The most commonly known method used for biodiesel production includes, direct use/blending, microemulsion, pyrolysis and transesterification(Gupta, 2004).

2.5.1. Direct use/Blending

Vegetable oils can directly be used as fule without modifying the engine. The use of vegetable oils as fuel was tested by Rudolf Diesel. Direct use of vegetable oils as fuel has advances such as liuid nature and portability, high heat content, readily viability and renewability. However, fuel atomization difficulty, carbon deposits. thickening and gelling have been reported to be the problems encountered with direct use of vegetable oils. Thus, diluting with conventional fuel or other alcohol can be used for reducing the viscosity of vegetable oil. This method is the simplest method as it does not need any chemical process. A number of studies have been made on the use

of blends of conventional diesel fuel with non-edible vegetable oils, but the use of diluted vegetable oils as fuel is not suitable for long term use in a direct engine(Gupta, 2004).

2.5.2. Pyrolysis method

Pyrolysis is defined as the conversion of one substance into another by means of heat or by heat with the aid of a catalyst. It involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules. The chemistry of pyrolysis process is difficult to characterize due to the presence of different reaction paths and variety of the reaction products that may be obtained from the reactions that occur (Demirbas, 2003). Alkanes, alkenes, carboxylic acids, aromatics and small amounts of gaseous products are some of the products of pyrolysis process. Pyrolysis process can be divided into conventional pyrolysis, fast pyrolysis and flash pyrolysis depending on the operating conditions (Kumar et al., 2003). However, pyrolysis process follows different reaction paths and produces different products making its analysis difficult. In addition, the equipment used for pyrolysis is expensive and the removal of oxygen during the thermal processing also removes any environmental benefits of using an oxygenated fuel. In addition, separate distillation equipment for separation of various fractions is needed. It also requires expensive equipment (Ma & Hanna, 1999).

2.5.3. Microemulsion method

To solve the problem of high viscosity of vegetable oil, micro-emulsions with different solvents have been studied. Methanol and ethanol are the most commonly used solvents used to form microemulsions and is probably better solution to the high viscosity of vegetable oils. Fuel atomization is relatively easy compared to diluting method(Gupta, 2004).

Microemulsions are isotropic, clear, or translucent thermodynamically stable dispersion of oil, water, surfactant and co-surfactant. The droplet diameters in microemulsions ranges from 1-150 nm. A microemulsion can be made of vegetable oils with an ester and dispersant (co-solvent), or of vegetable oils, an alcohol and a surfactant, with or without diesel fuels. Though, microemulsions because of their alcohol content have lower volumetric heating values than diesel fuels, the alcohols have high latent heat of vaporization and tend to cool the combustion chamber, which would reduce nozzle coking (Kumar et al., 2003). However, injector needle sticking, carbon

deposit formation and incomplete combustion have been reported to be the problems encountered when microevolutions are used as fuel(Ma & Hanna, 1999b).

2.5.4. Transesterification method

Though, vegetable oils can be used directly as fuel without any further treatment or processing they are problematic because of their high viscosity and low volatility and they do not burn completely and can form deposits in the fuel injector of diesel engines .This is due to the fact that vegetable oils are made of triglyceride which are much larger molecule, hence they are more viscous and less volatile than conventional diesel fuel(Demirbas, 2003). In addition, poor fuel atomization and incomplete combustion(Sharma, 2009), injector coking, and thickening of the lubricating oil are also other problems caused by direct use of vegetable oils as fuel(Sattanathan, 2015). Thus, to overcome these problems, several methods such as dilution, microemulsions, thermal cracking and transesterification have been proposed which can help reduce the high viscosity of vegetable oils but transesterification is the only effective and widely used method (Demirbas, 2005b).

In transesterification reaction, three consecutive and reversible reactions as shown in figure 2.3 are occurred where the alkoxy groups in the triglycerides are replaced by another alkoxy groups from the alcohol resulting in three mol of fatty acid alkyl ester and one mole of glycerol molecule. Because of its reversibility, the reaction is carried out in the presence of excess alcohol to derive the reaction equilibrium to produce more alkyl esters. The reaction is also very sluggish due to less miscibility of the vegetable oils with the alcohol being used. This can be enhanced through vigorous mixing. In addition, introduction of catalysts also improves the rate of transesterification reaction and biodiesel yield (Ma & Hanna, 1999).

Transesterification of vegetable oils or animal fats with short chain alcohols can be carried out in the presence of homogeneous, heterogeneous and biocatalysts. The most commonly used homogenous catalysts are alkali or acid catalysts such as sodium hydroxide, alkali metal alkoxides (such as sodium methoxide), potassium hydroxide, sulphuric acid, phosphoric acid. Alkali catalyzed transesterification is much faster than acid catalyzed (Freedman et al.,1984). Stoichiometrically 3 mol of alcohol and 1 mol of triglyceride react to yield 3 mol of fatty acid ester and 1 mol of glycerol during transesterification reaction but excess molar ratio is repaired for

greater ester production in a shorter time. The general mechanism of transesterification reaction is given as shown bel. The general equation of transesterification reaction is shown in figure 2.2 and figure 2.3. given below indicates the three-consecutive reaction of the triglycerides below (Meher L.C. et al., 2006)

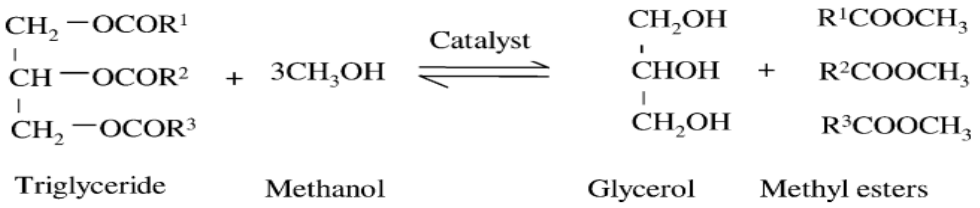

Figure 2-2. General Equation of transesterification reaction

$$\text{Triglyceride} + R^1OH \rightleftharpoons \text{Diglycerides} + RCOOR^1$$

$$\text{Diglycerides} + R^1OH \rightleftharpoons \text{Monoglyceride} + RCOOR^1$$

$$\text{Monoglyceride} + R^1OH \rightleftharpoons RCOOR^1 + \text{Glycerol}$$

Figure 2-3. General Equation for transesterification triglycerides

2.5.4.1. Homogenous bas catalyzed Transesterification

Homogenous base catalyzed transesterification reaction is the most widely used method for biodiesel production(Ma et al .1998). NaOH and KOH are the most commonly used catalysts. These catalyst are less expensive and easy to obtain(Alnuami et al.2014). However, this method is quite sensitive to the free fatty acid content of the oils used. Because the presence of high free fatty acid in the oils results in soap formation when the reaction is carried out in the presence of base catalysts. High energy consumption, lack of catalysts recovery and generation of large amount of wastewater from biodiesel washing have also been reported to be serious problem encountered with homogenous catalyst(Fangrui et al., 1998).

2.5.4.2. Homogenous Acid catalyzed Transesterification

It has been reported that basic catalysts have various advantages such as high reaction rate highest conversion, small amount of catalyst requirement and mild reaction conditions. However, the use of bases as catalysts for transesterification of oils that have high free fatty acid such as waste

cooking oil (2–7% FFA) nonedible oils ,and animal fats (5% to 30% FFA) leads to soap and water formation that is needed to be is either removed with the glycerol or washed out with water but if the FFA content is very high (>5%,) the formation of soap severely inhibits separation of biodiesel and glycerol leading to formation of emulsion(Atray et al 2010). For low quality feed stocks with high FFA and water content such as waste vegetable oil, acid catalysts have been reported to be more suitable. These catalysts are insensitive to free fatty acids content of the oils used. However, the use of acid catalysts has many drawbacks such as highly corrosives, may cause damage to the equipment (Freedman et al.,1984). In addition, the rate of acid catalyzed reaction is very slow and the water content of the oils is required to be low (<0.4%), requires higher alcohol to oil molar ratio (20:1 to 40:1) and catalyst concentration (5%-25%)(Thakur & Dange, 2015).

2.5.4.3. Two step transesterifications

Both the base and the acid-catalyzed transesterification processes have their advantages and disadvantages as previously mentioned. Hence, to avoid the problems associated with the use of these catalysts separately, especially the problems of saponification in base-catalyzed and slow reaction time in acid-catalyzed transesterification, many researchers have adopted the two-stage transesterification. However, the two-stage method has also catalyst removal problems in both stages. The problem of catalyst removal in the first stage can be avoided by neutralizing the acid catalyst, using extra alkaline catalyst in the second stage. However, the use of extra catalyst will increase the cost of biodiesel(Refaat, 2010).

2.5.4.4. Enzyme catalyzed transesterification

Enzymatic catalyzed transesterification is also another method of biodiesel production. both extracellular and intracellular lipases. In this case, either immobilized (extracellular) enzymes or immobilized whole cells (Intracellular enzymes) are used for catalysis and both are reported to be highly efficient. In this process**,** recovery of unreacted methanol and glycerol is much simple and requires less downstream operations. Enzyme catalyzed transesterification of vegetable oils can be carried out at mild reaction condition and is insensitive to the free fatty acid content of the oils and results in low generation of waste compared to chemically catalyzed process. However, enzymatic production of biodiesel on a large scale is still difficult because of high cost of enzyme and the process is too much slow(Ranganathan & Narasimhan, 2008).

2.5.4.5. Super Critical Transesterification

Utilization of supercritical method can improve phase solubility and reduce the effect of mass transfer resistance(Saka & Kusdiana, (2001). This can improve the rate of transesterification reaction thereby improving the yield of biodiesel. The reaction rate is too much faster than that of chemically catalyzed transesterification and separation and purification of product is simple. Super critical method of transesterification is also characterized by high feedstock flexibility, production efficiency and environmentally friendly compared to conventional method(Silva C et al., 2014). Compilate conversion (100%) can be achieved within 10 mini reaction time using super critical methanol condition. However, transesterification of vegetable oil under supercritical methanol could be carried out at high temperature (350^{o}c to 400^{o}c) high pressure (45 to 65 Map) and high methanol to oil molar ratio(Saka & Kusdiana, 2001). Eexpensive equipment such as strong durable reactors, high pressure pumps, efficient control devices etc. are required to resists the high operating conditions. The operation and maintenance costs are also higher than that of conventional processes(Bernal et al., 2012).

2.5.4.6. Heterogenous Catalyzed transesterification

It has been reported that homogeneous (acid and base) catalysts are easily available, have low initial cost, and fast reaction rate with a predictable performance. However, subsequent neutralization, separation and purification steps are needed to obtain desired product. Moreover, the use of these catalysts for large scale production of biodiesel may leads to corrosion of equipment, loss of huge amount of catalyst environmental pollution because of large amount of waste water discharging.

Thus, researchers are now working on heterogeneous catalysts to attain environmentally benign and economically attractive process. Solid catalysts have the potential to process low quality feedstocks. More overs unlike to homogeneous catalyzed process, heterogeneous catalyzed processes can be run in either batch or continuous mode. Heterogeneous catalysts do not get dissolved in the reaction mixture; hence no need of water washing and neutralization steps to separate and recover the spent catalyst there by reducing g cost and time for biodiesel production. In addition, solid catalyzed process generates low amount of waste water. Furthermore,

heterogeneous catalysts have long life time as compared to homogenous catalysts(Yan et al., 2010).

Alkali metal and alkaline earth metal oxides are the most studied solid base catalysts. Other salts, either in pure form, or on a suitable carrier have also been studied. They are relatively inexpensive and give a reasonably fast reaction rate. However, heterogeneous catalysts are less reactive than their homogenous counterparts and more research is still being done to develop more active solid catalyst (Kumar et al., 2012).

2.6. Factors affecting the yield of biodiesel

The most important factors that affect transesterification of vegetable oils are the molar ratio of alcohol: oil, type of alcohol, type and amount of catalyst, reaction temperature, and time, mixing intensity as well as the contents of FFAs and water in oils(Kumar et al.,2003).

2.6.1. Alcohol Type

The type of alcohol used is an important factor affecting the yield of biodiesel. Methanol and ethanol are the most widely used alcohol in transesterification of vegetable oils and fats to biodiesel though other alcohols can also be used. It has been reported that the yield of biodiesel is higher when methanol is used compared to ethanol because of its higher reactivity compared to ethanol (Kumar et al.,2003). Currently, large-scale production of biodiesel uses methanol as main reactant because of its availability, polar nature and low cost. However, methanol is not completely renewable and ethanol considered to be best alternative alcohol for biodiesel production because of its renewability. However, formation of stable emulsions that make separation difficult and costly as well as low reaction rates are the main constraints a raised with the use of ethanol(Lam & Lee, 2011).

Verma & Sharma, (2016) proved that the yield of biodiesel obtained from methanolysis of Karanja oil was 91.05% while that of obtained from ethanolysis77%. This indicated that menthol was better than ethanol for transesterification of vegetable oils. It was also noted that separation of ethyl esters was difficult compared to methyl esters. Moreover, Enontiemonria et al., (2012) also studied the effects of ethanol, methanol and their blends on the yields and properties of castor seed oil biodiesel using NaOH as catalyst and it was conclude from their results that the yield of biodiesel

obtained from methanol was higher than that of obtained using ethanol. Furthermore, they yield obtained using a mixture of the two alcohols was also higher than the yield obtained from the separate methanol and ethanol.

The choice of alcohol to be used depends on its cost, performance and environmental effects. On the basis of feed stock from which the alcohol is obtained, ethanol is found to be more suitable as it can be produced from renewable agricultural resources. On the basis of oil solubility, ethanol is also more preferable over methanol. However, transesterification of oils and fats using ethanol to biodiesel has some limitations such as formation of stable emollitions that make separation and purification of biodiesel complicated (Ramesh et al., 2012).

2.6.2. Alcohol to oil molar ratio

Alcohol to oil molar ratio is very important factor affecting the ester yield. Stoichiometrically transesterification reaction requires 3 moles of alcohol and one mole of oil(triglyceride) to give 3 moles of esters(biodiesel) and one mole of glycerol. However, transesterification reaction is a reversible reaction requiring an excess amount of alcohol to maximize the ester yield and complete conversion of triglyceride to biodiesel can be achieved when 100% excess alcohol is used during transesterification reaction. However, high molar ratio of alcohol to vegetable oil interferes the separation of glycol (Kumar et al.,2003). Over 95% yield of biodiesel can be obtained from transesterification of castor seed oil with short chain alcohol mainly methanol in the range of 6:1 to 9:1 alcohol oil molar ratio. However, glycerol can be dissolved when much excess alcohol is making its separation from the biodiesel difficult. Moreover, conversion of biodiesel and glycerol back to mono-glycerides have been reported with the use of excess methanol to oil molar ratio leading to low yield of biodiesel(Keera et al., 2018).

2.6.3. Type and Amount of catalyst

Generally, there are three kinds of catalyst are known to affect the yield of biodiesel. These catalysts are acid, bas and biocatalysts. The yield of biodiesel can be affected by the amount and type of catalyst used to depend on the nature of the feed stock. Basic catalysts (No matter whether they are liquid or solid) are more preferable than acid catalysts(Kumar et la., 2003). NaOH and KOH are the most effective catalyst used in transesterification reaction compared to the acidic catalyst. Alkali catalyzed transesterification approximately 4000 times faster than acid catalyzed

transesterification. In addition, alkaline catalysts are less corrosive compared to acidic catalysts and they are effective in small amount (0.5%-1%.). due to these factors most commercial biodiesel productions are conducted in the presence of alkaline catalysts(Ramesh V.et al. 2012). However, base catalysts are susceptible to unwanted side reaction resulting in unwanted products such as soap when the oil contains high free fatty acids and water. The formation of soap reduces catalyst activity, biodiesel yields and makes separation of the product difficult(Ogbu & Ajiwe, 2013).

For vegetable oils with higher free fatty acids bio-catalysts (specially enzymes) are more preferable compared to the chemical catalysts. This is because biocatalysts are insensitive to the free fatty acid content of the oil, the reactions carried out in the presences of biocatalysts can be carried out at mild condition and product separation and purification is simple. However, bio catalysts are costly and difficult to scale up. In addition, enzyme catalyzed process is too slow and needs more time to achieve complete convection (Kumar et al., 2003).

The effect of sulfuric acid and potassium hydroxide on the yield of biodiesel derived from castor oil have been studied by of (Nakarmi & Joshi, (2014). The reaction was conducted at various catalyst concentration where amount of catalyst was varied between 2% and 4% for sulfuric acid and 0.5% and 1.5% for KOH. It was observed from this result that the KOH was more powerful than H_2SO_4 and the highest yield (92%) was obtained at 1% for KOH but the yield of biodiesel obtained using H_2SO_4 was negligible (about 6.28%). This study indicate that different catalysts have different catalytic activity and results in different yield of biodiesel. In addition, the amount of catalyst needed is different depending on the type of catalyst used. Thus, selection of appropriate catalyst is important requirement in biodiesel production to attain the desired product and minimize cost and environmental impacts.

2.6.4. Reaction Temperature

The rate of conversion of vegetable oils and fats to biodiesel via transesterification reaction is highly affected by the reaction temperature. However, upon giving enough time, nearly 100% conversion can be achieved even at room temperature. Mostly, transesterification reaction is carried out nearly at the boiling point of the alcohol used. For example, when methanol is used, the reaction temperature would be between 60-70^{o}c at atmospheric pressure to obtain as much higher ester as possible(Kumar et al., 2003). Nakarmi & Joshi, (2014) investigated the effect of

reaction temperature on the yield of castor oil biodiesel. They conducted the transesterification reaction at various reaction temperature (60 ,65 and 70^{o}c) keeping the other variables (catalyst concentration and methanol to oil ratio) constant. It was seen that the optimum yield was obtained at 65^{o}c. Below and above the optimum value the yield of biodiesel was low. At lower temperature, the reaction was not completed and at high temperature, methanol was decomposed (vaporized) resulting low conversion of oil to biodiesel.

2.6.5. Stirrer Speed

Mixing or agitating of reactants is very important to achieve completion of transesterification reaction as it increases the yield of product. Reactants can be well mixed through agitation and the role of agitation is to increase the collision between the particles and diffusion of one reactant into another, thorough mixing of catalyst with reactants and rate of reaction. Increase in stirrer speed will shorten the reaction time and increase the conversion. However, too much higher agitation speed would not result in signifcant increment in the yield of biodiesel(ester)(Gnanaprakasam et al., 2013).

2.6.6. Free fatty acid content (FFA)

In the conventional transesterification of fats and vegetable oils for biodiesel production, FFAs always produce negative effects. The presence of high FFAs in the vegetable oils or animal fats lead to soap formation, consumes the catalyst, reduces its catalytic effectiveness which results a low conversion in biodiesel production. Because the FFAs react with the alkaline catalyst to produce soaps that inhibit the separation of the ester, glycerin, (Canakci & Gerpen, 1999). The resulting soaps leads to increasing in viscosity, formation of gels and foams, and made the separation of glycerol difficult(Demirbas et al.,2016).

2.7. Properties of biodiesel

2.7.1. Density

Density is defined as the mass of unit volume, measured in a vacuum. It is one of the quality parameters in biodiesel standardization. It strongly affects the cetane number, heating value and viscosity of a biodiesel. The density also affects atomization and combustion qualities. Density of biodiesel is dependent on the molar mass, the free fatty acid content, the water content and

temperature. The density of biodiesel is typically higher than that of diesel fuel and is dependent on fatty acid composition (Barabás & Todoru, 2011).

2.7.2. Viscosity

Viscosity which is measure of resistance to flow is one of the most important biodiesel quality indicators. Because it affects engine performance like lubrication and fuel atomization. Biodiesels with high viscosity tend to form larger droplets on injection, which can cause poor combustion, increased exhaust smoke and emissions (Knothe & Steidley, 2005). This leads to an increase in engine deposits and energy requirement for fuel pumping. Similarly, too low viscosity results in very fine spray which leads to insufficient penetration and the formation of black smoke. It also affects the lubricity of the fuel as some elements of the fuel system can only be lubricated by the fuel(Barabás & Todoru, 2011). Biodiesels are 10 time less viscous than the oils from which they are made. Thus, direct use of vegetables oils as fuel in diesel engines results in engine deposits. However, the viscosity of biodiesel is higher than that of the conventional diesel fuel (Knothe & Steidley, 2005).

2.7.3. Acid value

The acid value (AV) of biodiesel is defined the number of milligrams of potassium hydroxide required to neutralize the free acids present in 1 g of sample. It is described as the mass of potassium hydroxide (KOH) in milligrams required to neutralize the acids present in one gram of sample and it can be determined using titration method(Kinast, 2003. Determining the acid number (AN) enables to determine unreacted acids present in the biodiesel. It can be also used as an indication of the condition of the stability of the fuel, because the acid number increases as the fuel ages (Kinast, 2003). Utilization of biodiesel with high acid value leads to various problems such as causes increasing of fueling system deposit and corrosion damaging of fuel pumps and fuel filters (Tyson, 2001).

2.7.4. Iodine value

The iodine value (IV) is another biodiesel quality parameter which has been introduced to evaluate the its stability to oxidation. It is a measure of the total unsaturation of fatty acids measured in g iodine/100 g of biodiesel sample, when formally adding iodine to the double bonds. Biodiesel with

higher iodine number is sensitive to oxidation and is highly dependent on the nature and composition of the feedstocks used in biodiesel production. Biodiesel with high (IV) tends to polymerize and form deposits on injector nozzles and piston rings. This tendency is directly related to the degree of unsaturation of the fatty acids(Barabás & Todoru, 2011).

2.7.5. Heating Value (HV)

The heat of combustion or hot worth of a fuel is a very important measurable parameter that shows the quantity of heat liberated by the fuel at intervals the engine that allows the engines to try and do the work. The heat content (Calorific value) of biodiesel ranges from is 32-42 MJ/kg, that is significantly under the heat content of crude oil diesel (46) MJ/kg (Knothe & Steidley, 2005)

2.7.6. Cetane Number (CN)

The cetane number is also another biodiesel quality indicator or parameter. It is a measure of the fuel's ignition delay. It determines the ignition quality of a biodiesel and influences white smoke and combustion roughness. Higher cetane numbers indicate shorter times between the injection of the fuel and its ignition. Conventional diesel fuels have slightly lower cetane numbers (40-50) than the biodiesels have. Thus, considering the cetane number alone, they would tend to improve operation of the engine with respect to pure diesel(Kinast, 2003). No. 2 diesel fuel usually has a cetane rating between 45 and 50 while vegetable oil is 35 to 45. The cetane number of biodiesels is usually 50 to 60. The ignition quality affects engine performance, cold starting, warm up and engine combustion roughness. Cetane rating is related to the volatility of the fuel where more volatile fuels have higher ratings. A high cetane fuel also may lead to incomplete combustion and smoke if the fuel ignites too soon by not allowing enough time for the fuel to mix with air for complete combustion. Fuels with low Cetane Numbers will result in difficult staring, noise and exhaust smoke. It is important to note that biodiesels can have wide range of cetane number depending on the fatty acid composition of the feedstock (oil) from which they are made and the saturation level of the fatty acids (Saka & Kusdiana, 2001)

2.7.7. Flash point

Flash point of a biodiesel or petro diesel is a temperature at which ignition can occur when it is exposed to flame. It is the lowest temperature at which fuel emits enough vapors to ignite (Sanford et al., 2009). It is one of the most important biodiesel properties which is mainly used as safety criteria in determine the flammability and combustibility of the biodiesel or other fuels. Flashpoint of biodiesel is much higher than petro diesel (Knothe et al., 2005). This means that, biodiesel is safe for storage and transportation than petro diesel. The flash point can be determined by heating a sample of the fuel in a stirred container and passing a flame over the surface of the liquid; If the temperature is at or above the flash point, the vapor will be ignited and an easily detectable flash would be observed (Kaisan et al., 2013).

2.7.8. Cloud and pour points (CP & PP)

The cloud point is defined as the temperature at which crystal growth is large enough (diameter≥0.5 μm) to be visible to the naked eye. In other word, it measures the temperature at which wax crystals or other small crystals of biodiesel(fuel) begin to form in the biodiesel and is one of the biodiesel quality indicators. The pour point (PP) is the minimum temperature a fluid will pour(Dunn & Bagby, 1995).

Table 2-3. ASTM standards of biodiesel and diesel fuel

Property	Methods	biodiesel	diesel fuel
Density at 15^{o}c(kg/m^{3})	ASTMD-1298	0.88	0.84
Viscosity at 40^{o}c(cSt)	ASTMD445	1.9-6	3.06
Flash point(^{o}c)	ASTD93	130min	74
Acid value (mkofKOGH /kg oil)	ASTMD664	0.8max	0.249
Pour point(^{o}c)	ASTD97	-15 to +5	0
Cloud point(^{o}c)	ASTMD2500	-3 to-12	+10
Calorific value (MJ/kg)	ASTMD240	37.5 to 42.8	44.2
Cetane number	ASTTMD976	47min	52

2.8. Advantage and Disadvantages of biodiesel

2.8.1. Advantage

Utilization of biodiesel has many technical economic and environmental advantages. Biodiesel can be stored and used safely than diesel fuel because of its highest flash point. It has also higher cooling capacity. compared to petroleum diesel. Biodiesels have high cetane number compared to diesel fule .The Cetane number is one of the prime indicators of the quality of diesel and higher cetane number means short ignition delay(Demirbas, 2006). The cetane number affects the engine performance parameters such as combustion, stability, drive ability, white smoke, noise and emissions of CO and HC(Meher et al . 2006).

Biodiesel is environmentally attractive fuel because of its biodegradability less toxicity and less greenhouse gases emissions compared to petroleum diesel. Production and use of biodiesel reduce total unburned hydrocarbons by 90% aromatic hydrocarbons by 75%-90%, emission of carbon dioxide 80% and sulfur, by approximately 100%. It has also high (10% by weight) oxygen content and free of sulfur (Shrirame et al.,2011). Biodiesels can also be used as alternative fule without modifying the engine and con avoid dependency on imported petroleum diesel fuel and has a better lubrication capacity leading to long engine life (Venkateswara P & Srinivasa G., 2013).

Mariano et al., (2008) tested and reported biodegradability potential of biodiesel and its blends with diesel fuel. They obtained that pure biodiesel is more biodegradable than both pure conventional diesel fuel and biodiesel and diesel fule blends. Utilization of biodiesel derived from castor oil can be considered as nonhazardous fuel because of its high flash point (190^{o}c) and can be used as additives to enhance the flash point of diesel fule. It can be also used as additive for improving cold flow properties of diesel fuels because of its low cloud point. The cloud point affects fuel flow and the performance of fuel pump

2.8.2. Disadvantage

In addition to the various advantage it offers, there are also disadvantages associated with the use of biodiesel. Commercialization of biodiesel is still costly and less completive with that of diesel fuel because of high feedstock cost , which is about 80% of the total operating cost(Demirbas, 2006). In addition, biodiesel has slightly lower thermal efficiency compared to conventional diesel

fuel because of its higher viscosity, poor spray characteristics and lower calorific value(Sruthi Gopal, 2013). Biodiesels have low energy content than diesel fuel and high viscosity which results in more fuel consumption. Cold start problems, lower energy content, higher copper strip corrosion, and fuel pumping difficulty because of high viscosity are also considered to be another disadvantages of biodiesel usage(Mujeeb et al., 2016).

3. Materials and Methods

3.1. Materials and Equipment used

The materials used in this study were castor seed oil, analytical grade methanol, ethanol, normal hexane and calcium oxide as heterogeneous catalyst. In addition, Potassium hydroxide, diethyl ether, phenolphthalein indicator, hydrochloric acid, aqueous potassium iodide, dam's solution sodium-thiosulphate solutions and starch solution were also used to determine the various physicochemical properties of the biodiesel and its raw material (castor oil).

The major equipments used throughout this experiment were, soxhlet, rotary evaporator, pycnometer, digital vibro viscometer, three necked round bottom flask (reactor) equipped with mechanical stirrer, and condenser, separating Phanuel, Centrifuge, conical flask, balance, oven and mortar and pastel as crusher etc.

3.2. Experimental Methods

3.2.1. Castor Seed Preparation

The purchased castor seed was first handpicked to remove impurities present in it. Then after it was sun dried for four days and manually deshelled to remove its upper cover. The castor seed before and after deshelling is shown in figure 3.1 as shown below. The deshelled seed was oven drying at 80^{o}c for 8 hours to reduce its moisture content. Finally, it was crushed using mortar and pastle for reducing its size and packed in a plastic bag for the next process (extraction).

Figure 3-1. (a) castor seed before deshelled (b) castor seed after deshelled

3.2.2. Castor Seed Oil Extraction

Solvent extraction method as described by (Akpan et al .2006) was adopted for the extraction of the oil and normal hexane was used as a solvent. 200g of ground castor seed was packed in a filter paper and placed in soxhlet apparatus. Then approximately 600 ml normal hexane was poured into 1000 ml round bottom flask. Then after the flask and the soxhlet apparatus were fixed together and placed into a hot water bath. The extraction process was carried for ten hours at a constant temperature of 72^{o}c. After the extraction completed, the oil was obtained by removing the solvent using rotary evaporator. The experimental set up for the extraction processes and rotary evaporator are shown in Fig 3.2 below.

Figure 3-2. (a)Soxhlet apparatus (b) Rotary evaporator (c) crude castor seed oil

The amount of oil extracted was calculated using Eq (3.1) as given below.

$$\%\ \text{Yield of oil} = \frac{\text{Mass of oil obtained}}{\text{Mass of seed used}} \times 100\% \qquad [3.1]$$

3.2.3. Castor Seed Oil Characterization

The extracted oil was subjected to characterization to make sure that the oil can be used as a raw material for the production of biodiesel. The density, viscosity, acid value, saponification value and iodine value were taken as important properties(AKPAN et al., 2006) and being tested to determine the properties of the oil extracted from castor seed.

3.2.3.1. Moisture content determination

The method used by (AKPAN et al., 2006) was adopted to determine the moisture content of the castor seed. 50g ground seed was measured and dried in an oven at 105^{o}c for 6 hr. The dried sample was measured after every 2hrs and the procedure was carried out repeatedly until a constant weight obtained. The dried sample was taken and measured after two hours and placed in a desiccator for 25-30 minutes in order to cool. Then it was reweighted and the percentage of the moisture present in the seed was determined using Eq (3.2). Three replicates were carried out at the same condition on the same mass of sample and the obtained results were averaged and taken as % of the moisture content.

$$Percentage\ of\ Moisture\ content = \frac{W_o - W_1}{W_o} \times 100\% \qquad [3.2]$$

Where W_o and W_1 are weights of sample after and after drying respectively

Where W_o and W_1 are weights of sample after and after drying respectively

3.2.3.2. FT-IR analysis

FTIR analysis was used to determine the functional groups present in the extracted oil. The procedure used by(Yordanov, et al., 2013) was adopted for this analysis and it was carried out in KBr at room temperature. The obtained FTIR spectra were recorded using Shimadzu spectrometer from 4000-400 cm(1/cm) wave number. Finally, the resulting spectra were compared with the spectra of castor oil that have been reported before and the corresponding functional groups were identified. This analysis was conducted in Adigrat pharmaceutical factory.

3.2.3.3. Determination of density (ASTMD1289)

Density is the raio of mass of sample (castor oil) to its volume. The density of the extracted castor oil was determined using pycnometer. The pycnometer which is 50 ml capacity was washed with distilled water and dried in an oven at 110^{o}c. After it was dried well, its weight was measured and then filled with the sample (castor oil) and reweighted. Finally, the density was obtained by subtracting the weight of the empty pycnometer from the weight of the pycnometer plus the sample (oil) and dividing the resulting with the volume of the pycnometer.

3.2.3.4. Determination of Viscosity (ASTMD445)

The viscosity of the obtained castor oil was determined using digital vibro viscometer. The sample (biodiesel) was first heated upto a temperature of 40^{o}c upon inserting in water bath and then inserted into the cup of the viscometer. The tip of the viscometer was then inserted into the viscometer cup containing the sample. After that the dynamic viscosity of the sample was recorded and displayed in the controller. Lastly, the kinematic viscosity was obtained by taking the ratio of dynamic viscosity taken from the digital vibro viscometer to the density of the oil. The experimental set up for viscosity measurement is depicted in figure 3.3 as shown below.

Figure 3-3. Viscosity measurement (VM)

3.2.3.5. Determination of Acid value (AV)

The acid value of the oil extracted from castor seed was determined according to the method described by (Abdulkareem J. et al 2012). In this process, approximately 5ml of sample(oil) was measured using measuring clyinder and placed in a 100ml flask. 50 ml of mixture of ethanol and diethyl ether was prepared by mixing equal volume of ethanol (50%v/v) ethanol and diethyl ether in another beaker and proud into the flask coating the oil. Then 3 drop of phenolphthalein was

added into the mixture. This mixture was titrated using 0.1N of KOH until the color change observed turned to pink. Finally, the acid value was calculated using equation (3.3).

$$AV = \frac{56.1 \times V \times N}{M} \qquad [3.3]$$

Where; V is volume of standard alkali used, N is normality of standard alkali used and W_{oil} is the weight of sample (castor seed oil) used. Then the free fatty acid content was obtained by dividing the acid value obtained in equation (3.3).

3.2.3.6. Determination of Saponification value (SV)

The saponification value of the castor seed oil was determined using indicator method according to the method of (AKPAN et al., 2006). 5ml (4.73g) of castor oil was measured and placed into 250 ml conical flask and 25ml of 0.1N ethanolic potassium hydroxide (KOH) was added. The resulting mixture was then stirred and boiled for 30min in the presence of a reflux condenser. Then after few drops of colour indicator(phenolphthalein) was added to the heated mixture. The heated solution was titrated with 0.5M HCl until the pink color was disappeared. The volume of HCl which causes disappearing of the pink colour was recorded. The saponification value was then calculated using Eq (3.4).

$$SV = \frac{56.1 \times N(V_b - V_a)}{M} \qquad [3.4]$$

Where V_b and V_a are volume of HCl solution used for blank test and sample test and N the actual normality of the HCl and M is mass of the sample used.

3.2.3.7. Determination of iodine value (IV)

The iodine value (IV) of oils or fats is very important parameter since it is used to quantify the amount of double bond present in that oil. It is also used to evaluate its stability to oxidation and higher iodine value indicates more sensitive to oxidation process(Nangbes et al., 2013). In this study, the iodine value of the oil extracted from castor seed was measured using the method described by (Akpan et la.,2006). About 2g of oil was measured and placed in to 250 ml conical flask and dissolved by adding 10 ml chloroform. Then after, about 25ml of Dam's reagent was added to the flask using a safety pipette and stopper was inserted followed by and the content of vigorous shaking and placed in dark place for 2:30 hours.

Afer that 20ml of 10% aqueous potassium iodide was added and titrated with 0.5N sodium-thiosulphate solutions until the yellow colour disappeared. Then few drops of 1% starch were added as an indicator and the titration was continued by adding thiosulphate drop wise until blue disappeared after vigorous shaking. This procedure was also used for the blank test and the iodine value was calculated using the equation given below (3.5).

$$\mathrm{IV} = \frac{12.69(V_b - V_a) \times \mathrm{N}}{\mathrm{M}} \qquad [3.5]$$

Where N represents normality of sodium thiosulphate, M is mass of sample (oil) used, V_a stands for volume of sodium thiosulphate used in sample test and V_b the volume of sodium thiosulphate.

3.3. Production and characterization of biodiesel

3.3.1. Experimental Design

The biodiesel was produced from castor seed oil via transesterification with methanol and ethanol blends and Design Expert software 7.0.0 using central composite design (CCD) was used to design the experiment and investigate the effects of the process variables on the yield of the biodiesel (FAM/E-E). Methanol to ethanol volume ratio (VR), total alcohol to oil molar ratio (MR) and amount of catalyst (Wt% of oil used) were chosen as a process variable while the reaction time, and temperature as well as the speed of the stirrer were taken as constant variables based on literature data. About 20 experiments were conducted and the resulting data was analyzed using design expert software to develop an appropriate model describing the yield of the biodiesel as function of the chosen process variables. The lists and the ranges within which the levels varied are given in table 3.1 as shown below.

Table 3-1. Factors and their Levels

Factor	Code	Level	
		Low	High
Mehnol to ethanol volume ratio	A	30	70
Total alcohol to oil molar ratio	B	6	12
Catalyst loading(wt% of oil used)	C	2	3

The complete random experimental design matrix of the CCD for the specified process variables is presented in table 3.2 shown below.

Table 3-2. Central composite Design matrix for random experiment

Std order	Run Order	M to E VR	Alcohol to oil MR	Catalyst Load	Response(Yield)
1	1	30.00	6.00	2.00	
2	13	70.00	6.00	2.00	
3	10	30.00	12.00	2.00	
4	12	70.00	12.00	2.00	
5	15	30.00	6.00	3.00	
6	8	70.00	6.00	3.00	
7	20	30.00	12.00	3.00	
8	9	70.00	12.00	3.00	
9	4	16.36	9.00	2.50	
10	5	83.64	9.00	2.50	
11	14	50.00	3.95	2.50	
12	3	50.00	14.05	2.50	
13	2	50.00	9.00	1.66	
14	11	50.00	9.00	3.34	
15	19	50.00	9.00	2.50	
16	6	50.00	9.00	2.50	
17	16	50.00	9.00	2.50	
18	18	50.00	9.00	2.50	
19	17	50.00	9.00	2.50	
20	7	50.00	9.00	2.50	

3.3.2. Transesterification Reaction

Three-necked round bottom flask was used as a reactor throughout the experiment. The reactor (flask) was connected with condenser and mechanical stirrer and inserted into hot water bath so as to maintain the reaction at a constant temperature of 65^{o}c.The transesterification resection set up is shown in Fig 3.4. In this experiment, 50 ml castor oil was used for each run and mixture of methanol (99.5%) and absolute ethanol (99.5%) was used for transesterification of the oil. The oil was first transferred to the reactor and heated up to the desired temperature(65^{o}c). Then known (measured) amount of a mixture of methanol and ethanol was added to 250 ml conical flask followed by addition of calculated amount of catalyst (CaO). The obtained mixture of alcohol and catalyst was shaked hot water bath for dissolving the catalyst and transferred to the reactor.

Finally, the mechanical stirrer was set on and the reaction was started. The reaction was carried out at 65^{o}c for 3hrs and the stirrer speed was maintained at 500 rpm. Whereas the volume ratio between methanol and ethanol, molar ration between total alcohol and castor oil and catalyst load

were varied. The reaction temperature and time as well as the agitation speed were fixed based on literature data reported for heterogenous catalyzed reactions. After the reaction time elapsed, the reaction mixture was transferred into separating funnel and allowed to settle oversight until two phase or layers formed. The bottom layer (glycerol + other impurities) was removed and the top layer (obtained biodiesel) was further purified using centrifuge to remove the remaining catalysts then after the product (FAM/E-E) was dried at 115^{o}c for 3 hours to remove the unreacted alcohol and water present in the biodiesel.

Figure 3-4. (a) Transesterification reaction (b) separating funnel

3.3.2.1. Determination of feed materials Required

Amount of Alcohol required

The amount of total alcohol needed was calculated based on the molar ratio of total alcohol to oil as follow. When the total alcohol to oil molar ratio is 6 the amount of methanol and ethanol required is calculated as follow:

$$\frac{\text{Total mole of alcohol}(N_m + N_e)}{\text{Mole of oil } (N_{oil})} = 6 \qquad [3.4a]$$

Mole is expressed as mass of given sample divided by its molecular eight (M_w). The density of methanol ethanol and castor seed oil are 0.79g/ml, 0.789g/ml and 0.946g/ml respectively. The molecular mass of the extracted castor oil was determined using empirical formula developed by(Cheng et al., 2008) from its acid and saponification values.

$$\text{Mw} = \frac{56.1\times3\times1000}{\text{SV}-\text{AV}} = \frac{56.1\times3\times1000}{185.81-4.69} = 929.22\text{g/mol} \qquad [3.4b]$$

Substituting the molecular masses of castor oil (929.22 g/mol), methanol (32g/mol) and ethanol(46g/mol) into Eq (3.4a) the volume of the total alcohol and the volume of methanol and ethanol were determined. The methanol to ethanol volume ration was at 30%/70%(V_m=3/7V_e) then the volume of methanol and ethanol was calculated as follow.

$$\frac{0.791(\frac{\text{g}}{\text{ml}})\times V_m(\text{ml})}{32(\frac{\text{g}}{\text{mol}})} + \frac{0.789(\frac{\text{g}}{\text{ml}})\times V_e}{46(\frac{\text{g}}{\text{mol}})} = 6\left(\frac{0.946\left(\frac{\text{g}}{\text{ml}}\right)\times 50\text{ml}}{929.22(\frac{\text{g}}{\text{mol}})}\right)$$

Substituting all the value, the volume of ethanol was found to be 10.86 ml and volume of methanol 4.65 ml and the total alcohol was the sum of the two (15.33 ml). The same procedure was used to determine the total alcohol required at the specified total alcol to oil molar ratio (4.9,12, and 14) and the specified volume ration between methanol and ethanol.

Amount of catalyst Required

The amount of catalyst needed to speed up the reaction was determined on the basis of percentage mass of the cator oil used as follow. At 2% catalyst to oil mass ratio;

$$\frac{\text{Mass of catalyst}}{\text{Mass of oil used}}\times 100\% = 2\% \qquad [3.4c]$$

$$\text{Mass of catalyst} = \frac{2}{100}\times \text{mass of oil used} \qquad [3.4d]$$

The same procedure was also used when the ratio catalyst to oil mass castor oil is 1.66%,2.5% 3%, and 3.34%. A similar procedure was used to calculate the amount of catalyst required for all runs. Then after purifying and drying, the yield of biodiesel for each experimental run was determined using equation (3.4e) given below.

$$\%\ \text{Yield of biodiesel} = \frac{\text{Mass of biodiesel obtained}}{\text{Mass of castor seed oil used}} \times 100\% \qquad [3.4e]$$

3.3.3. Characterization of Biodiesel

The obtained biodiesel (FAM/E-E) was subjected to characterization to determine if it can full fill the standard biodiesel specifications (requirements). The procedures used to determine the various physico chemical properties such as density, viscosity, acid value, saponification values were also used for that of the biodiesel produced. Other properties like heating value (heat content), cetane number, flash point, cloud point and pour point were also tested. In addition, the biodiesel's functional groups were also identified using FTIR analysis.

3.3.3.1. FTIR Analysis

FTIR analysis was used to determine the functional groups present castor seed oil biodiesel. The procedure used by(Yordanov, et al., 2013) was adopted for this analysis and it was carried out in KBr at room temperature. The FT-IR spectra were recorded using Shimadzu spectrometer from 4000-400 cm(1/cm) wave number. Finally, the functional groups were identified by comparing resulting spectra with the spectra of castor oil biodiesel that have been reported before.

3.3.3.2. Density determination (ASTMD 1298)

The method used to determine the density castor seed oil was also used to determine the density of the biodiesel produced from castor seed oil. The pycnometer was washed with distilled water and dried in an oven. The mass of the empty pycnometer was weighted using digital balance and then filled with sample(biodiesel) and reweighted and the density was calculated.

3.3.3.3. Viscosity determination (ASTMD 445)

The viscosity of the produced castor seed oil biodiesel was determined using digital vibro viscometer which detects dynamics viscosity. The sample (biodiesel) was first heated upto a temperature of 40^{o}c upon inserting in water bath. After maintain the equilibrium temperature, the sample was inserted into the cup of the viscometer and then the tip of the viscometer was inserted into the viscometer cup containg the sample. The measurement of the viscometer was taken and converted to kinematic viscosity by dividing it with the density of the biodiesel.

3.3.3.4. Acid value determination (ASTMD664)

The acid number (AN) is described as the number of milligrams of potassium hydroxide required to neutralize the free acids present in 1 g of sample. It helps determine how much amount of oil remain unreacted in the produced biodiesel. Knowing the acid number is important to determine the stability of a biodiesel, because the acid number increases as the fuel ages(Kinast, 2003). The procedure used determine the acid value of the oil was also used to determine the acid value of the biodiesel produced from it. A 0.1N of ethanolic potassium hydroxide (KOH) solution was prepared by dissolving 0.56 g KOH in 100 ml absolute ethanol (99.5%). Then a neutral solvent was prepared by mixing equal amount of ethanol and diethyl ether (v/v) in another 250 ml conical flask. Then after, 3ml (2.74g) of FAM/E-E obtained from castor oil was measured and poured into 25 ml mixture of ethanol and diethyl ether and shaken to dissolve. Then few drops of phenolphthalein were added to the mixture as a color indicator and the resulting mixture was titrated with 0.1N ethanolic KOH until the color of the solution(colorless) changed to pink and the volume(v) of the titrant (ethanolic KOH) was noted. Finally, the acid voule of the biodiesel was calculated according to Eq (3.6).

$$\mathrm{AV} = \frac{56.1 \times \mathrm{V} \times \mathrm{N}}{\mathrm{M}} \qquad [3.6]$$

3.3.3.5. Determination of Saponification value (SV)

The saponification value of the biodiesel was also determined using a titration method which is similar to the procedure used in saponification value test of the castor oil. About 3ml of biodiesel (2.74 g) was measured and added to 250 ml conical flask containing 25ml of 0.1N of ethanolic potassium hydroxide solution. The mixture was heated in hot plate and stirred using magnetic stirrer for 30 minutes for dissolving the biodiesel. Then after, few drops of color indicator (phenolphthalein) was added and the resulting mixture was titrated with 0.5N hydrochloric acid and a blank test was also conducted under the same condition and the same time on the same amount of the ethanolic KOH solution but with no any sample(biodiesel). The volume of the titrant (0.5N HCl) was then recorded and the saponification value was calculated using Eq (3.7).

$$\mathrm{SV} = \frac{56.1 \times (\mathrm{V_b} - \mathrm{V_a}) \times \mathrm{N}}{\mathrm{M}} \qquad [3.7]$$

3.3.3.6. Determination of Heat value and Iodine value

An empirical formula suggested by (Demirbas, 1998) was used to determine the heating value of the biodiesel from its density value using equation (3.8a).

$$\text{Heat content(HV)} = 79.014 - 43.126 \times \rho \qquad [3.8a]$$

3.3.3.7. Determination of Iodine value

Then the iodine value of the biodiesel was determined empirically from its heat value, and saponification value as follow:

$$\text{HV} = 49.43 - [0.041 \times \text{SV} + 0.015 \times \text{IV}] \qquad [3.8b]$$

Then iodine value was calculated by rearranging equation (3.7b);

$$\text{IV} = \frac{\text{HV} - 49.43 + 0.041 \times \text{SV}}{-0.015} \qquad [3.8c]$$

3.3.3.8. Determination of Cetane Number (CN), ASTM D613

The cetane number which is a measure of ignition quality of the biodiesel was determined using the empirical formula suggested by(Bose P. K, 2009) using the result of Saponification number (SN) and the iodine value (IV) of the biodiesel as follow.

$$\text{CN} = 46.3 + \frac{5458}{\text{SV}} - 0.225\text{IV} \qquad [3.9]$$

Where M represents mass of sample, N normality of HCl solution, V_b volume of HCL used for blank test and V_a volume of HCl acid used in sample test.

3.3.3.9. Falsh point determination, ASTM D 93

An open cup method was used to determine the flash point of the castor oil biodiel. The cup was first filled with the sample(biodiesel) then heated with heating plate. Then after an externally sourced flame was passed over the surface of the open cup containing the sample repeatedly until it burns and the temperature at which the biodiesel starts to burn was recorded and taken to be as the flash point of the biodiesel.

3.3.3.10. Determination of cloud point (CP), ASTM D 2500

Cloud point is very important biodiesel/diesel quality indicator. It is used to determine low temperature operability of the biodiesel. Operating at temperatures below the cloud point of biodiesel leads to filter clogging(Barabás & Todoru, 2011). The method used(Abdulkareem et al 2012) was adopted for this study. The castor seed oil biodiesel was proud into 250 ml capacity beaker and the level to which the biodiesel raised was marked and the placed in a refrigerator (cooler) and the temperature of the beaker was measured using thermometer as soon as the sample starts to form visible crystals and recorded to be the cloud point of the biodiesel.

3.3.3.11. Determination of Pour point (ASTMD 97)

Pour point of a biodiesel is defined as the lowest temperature at which it starts to flow. It also measures the operability of the biodiesel at cold weather condition(Barabás & Todoru, 2011). In this study, the ASTMD-97 standard method was used to determine the pour point of the biodiesel produced from castor oil (Abdulkareem et al., 2012). The sample (castor oil biodiesel) was placed in refrigerator allowed to cooled upto -50^{o}C. Then after, it was taken off and placed in heating plate and the temperature at which the biodiesel starts to melt and flow was noted and recorded to be the pour point of the obtained biodiesel.

4. Result and Discussion

4.1. Castor seed oil extraction and characterization

4.1.1. Castor seed preparation

After deshelling, its upper cover, 3.64 kg castor seed was obtained from 5kg which is 72.80% of the original castor seed used. Similarly, the average percentage moisture content obtained from three runs found to be 4.69% ±0.36 %.

4.1.2. Oil Extraction

The dried castor seed was used for extracting of the oil and about 1097.3g(1160ml) of oil was obtained from 3.64 kg of castor seed which is 30.12% of the mass of the castor seed used. This result fall within the range of the percentage oil content (30 – 55%) of castor seed as reported by (AKPAN et al., 2006). This indicates that the castor seed oil has a great potential for biodiesel production.

4.1.3. Oil Characterization

4.1.3.1. FTIR analysis

The result for the FTIR analysis of cator oil is given in table 4.2 as shown below and in figure 4.1. given in appendix A. As it can be seen from table 4.2 shown below, the reign(peak) between 3412 and 3356.14 indicates the presence of OH (alcohol) group with stretching vibration. The absorption band at 1745.58(1/cm) indicates the presence of carbonyl functional groups having stretching vibration. In addition, alkane functional groups(C-H) are also identified at the peaks between 2935-2858.58(1/cm) having stretching vibrational and between 1458-1312 with bending vibration.

Table 4-1. Result of FTIR analysis of castor oil

Reported Value		Experimental value		
Frequency (1/cm)	functional group	Frequency	Functional group	Vibration mode
3450-3200	Alcohol(OH)	3412-3356.14	Alcohol(OH)	Stretching
2930-2850	Alkane(C-H)	2935-2858.55	alkane(C-H)	Stretching
1739.85	Carbonyl(C=O)	1745.58	carbonyl(C=O)	Stretching
1500-1400	Alkene(C=C)	1458-1312	alkene(C=C)	Bending
960-690	Aromatics(C-H)	725.23	aromatics(C-H)	out of plane

4.1.3.2. Physico-chemical property of castor seed oil

The various physico-chemical properties of the oil extracted from castor seed oil tested and the results obtained are summarized in table 4.2 as shown below.

Table 4-2. Summary of Physico-chemical properties of castor oil

Property	Unit	Experimenttal voalue	ASTM standard value
Moisture content	------	4.692±.36	-----
Density(15^{o}c)	g/ml1	0.946	0.957-0.968
Viscosity(40oc)	mm^2/sec	121.56	6.3-8.8
Acivlue	mg KOH/g oil	4.69±0.44	0.4-4
%FFA	-------	2.35	0.2-2
Saponification value	mg KOH/g oil	185.81±6.87	175-187
Iodine value	mgI2/100g oil	94.68	82-88
Molocular weight	g/mol	929.22	

It can be observed from the table 4.2 that the density of the castor oil obtained from this study was found to be 0.946 g/ml which is close to the ASTMD6751 quality oil while the kinematic viscosity was obtained to be 121.56 mm2/sec. This result indicates that cator oil is too viscous and difficult to be used directly as fule. This high viscosity nature of castor oil could be due to the hydrogen bond present in its hydroxyl group(OH) (Ogunniyi d.S, 2006). Similarly, the acid value of the castor oil was obtained to be 4.69 ± 0.44 mg KOH/g sample(oil) which is also higher the ASTM standard value. This variation may be occurred due to variation in storage condition, maturity of the seed used (SALiMOn et al., 2010).It can be also due to the quality of the oil obtained. The saponification value which was obtained to be 185.81 mg KOH/g sample which is well within the range that a standard oil has. The iodine value of the oil extracted from castor seed as was also obtained to be 94.68gI2/100g oil. This result is an indication for the presence of high amount of unsaturated fatty acids (double bonds) in the oil. It also indicates that the oil is nondrying (has iodine value of less than 100gI2/100g oil).

4.2. Biodiesel (BD) Production Analysis

4.2.1. Analysis of variance (ANOVA).

Equation (3.4d) was used to calculate the actual yield of biodiesel and the corresponding result is presented in appendix C and analyzed using design expert software 7.0.0. The statistical analysis of variance (ANOVA) for the yield of biodiesel obtained using central composite design (CCD) is presented in table 4.3 as shown below.

Table 4-3. Statistical analysis of variance (ANOVA

Sources	Sum of squares	DF	Mean squres	F-value	P-value (pro>F value	Significant
Model	7089.74	9	787.75	524.15	< 0.0001	
M to E VR (A)	474.66	1	474.66	315.83	< 0.0001	
Total alcohol to oil MR(B)	1008.50	1	1008.50	671.03	< 0.0001	
Catalyst load(C)	345.86	1	345.86	230.13	< 0.0001	
AB	20.80	1	20.80	13.84	0.0040	
AC	58.86	1	58.86	39.16	< 0.0001	Significant
BC	104.40	1	104.40	69.47	< 0.0001	
$A^{\wedge 2}$	478.74	1	478.74	3138.54	<0.0001	
$B^{\wedge 2}$	2810.95	1	2810.95	1870.33	< 0.0001	
$C^{\wedge 2}$	294.64	1	2594.68	1726.43	< 0.0001	
Residual	15.03	10	1.50			
Lack of fit	4.50	5	0.90	0.43	0.8142	not significant
Pure error	10.53	5	2.11			
Cor Total	7104.77	19				

From table 4,3 given above, it can be observed that the Model F-value of 524.15 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, AB, AC, 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 your model. The "Lack of Fit

F-value" of 0.43 implies the Lack of Fit is not significant relative to the pure error. There is a 81.42% chance that a "Lack of Fit F-value" this large could occur due to noise. The lack of fit must be nonsignificant for the model to model satisfactory.

The table 4.3 also shows that the p- value of the model cofficient for methanol to ethanol valuem ratio, total alcohol to oil molar ratio and ctalsys loading in both linear and quadirtic form are mch less than 0.0001. This indicates all the factors being studied sginificantly affected the yield of biodiesel. Inaddition, the the p- value for the interaction between methano to ethanol volume ration and catalyst loading as well as the interaction between total alcohol to oil molar ratio were less than 0.0001. This also indicates that thethe yield of biodiesel was significantly affected by the interaction between process variables.

4.2.2. Model Adequacy Checking

Checking the adequacy of the model developed to describe the variation of the yield of biodiesel as faction of the chosen process variable is important. This can be made using the R-squared Adj R- squared, Pred R-Squared and Adeq precision values that are given in table 4.4 as shown below.

Table 4-4. Model validity measures

Std. Dev	1.23	R-Squared	0.9979
Mean	57.21	Adj R-Squared	0.9960
Cv	2.14	Pred R-Squared	0.9931
Press	49.31	Adeq Precision	66.194

From table 4.4 given above, it can observe that "Pred R-Squared" vaue of 0.9931 is in reasonable agreement with the "Adj R-Squared" value of 0.9960 and their difference is 0.0029 which is less than 0.2 . This suggestes that the developed model fits the acatual reponse data. The R-squared value was obtained to be 0.9979 which is close to unity. This indicates that 99.79% of the total variation of the yield of biodiesel was captured by the developed model. That means, only about 0.0021% of the total variation in the yield of biodiesel was not detected. The "Adeq precision" measures the signal to noise ratio. A ratio greater than 4 is desirable for the model to be satisfactory.

In this study, a ratio of 66.194 indicates an adequate signal and the model can be used to navigate the design space.

The regression coefficient and corresponding 95% high and low confidence interval (CI) shown in table 4.5 can also be used to investigate the effects of the different process variable on the yield of biodiesel. The higher value of regression coefficient indicates strong effect on the process. Table 4.5 shows that the regression coefficients for methanol to ethanol volume ratio, total alcohol to oil molar ratio and catalyst loading as well as the interaction between methanol to ethanol volume ratio and catalyst load (AC) and interaction between total alcohol to oil molar ratio and catalyst loading (BC) were found to be high indicating that the yield of the biodiesel was strongly affected by the process variables being studied as well as by the interaction that occurred between them.

Table 4-5. Regression coefficients and corresponding 95% CI (Low and high)

Factor	Estimated Coffient	DF	Standard error	95% CI		VIF
				low	High	
Intercept	79.84	1	0.50	78.73	80.95	
M to E VR (A)	5.90	1	0.33	5.16	6.63	1.00
Total alcohol to oil MR(B)	8.59	1	0.33	7.85	9.33	1.00
Catalyst load(C)	5.03	1	0.33	4.29	5.77	1.00
AB	1.61	1	0.43	0.65	2.58	1.00
AC	-2.71	1	0.43	-3.68	-1,75	1.00
BC	-3.61	1	0.43	-4.58	-2,65	1.00
$A^{\wedge 2}$	-5.76	1	0.32	-648	-5.04	1.02
$B^{\wedge 2}$	-13.97	1	0.32	-14.69	-13.25	1.02
$C^{\wedge 2}$	-13.42	1	0.32	-14.14	-13,70	1.02

4.2.3. The Regression Model equation

The model equation, which relates the response (yield of FAM/E-E) to the independent variables (factors) in terms of the coded factors is given below. The model equation in terms of the coded variables is depicted in equation(A) as shown blow.

The final equation in terms of coded factors is:

Yield =+79.84+5.90*A+8.59*B+5.03*C+1.61*A*B-2.71*A*C----------[A]

-3.61*B*C -5.76*A^2- 13.97*B^2-13.42*C^2

Where

A = Methanol to ethanol volume ratio

B = total alcohol to castor oil molar ratio

C =represents amount of catalyst used (wt% of the oil).

From the model equation given in (A), it can be obserebed that the yield of biodiesel was linarly increased with increasing in methanol to ethanol volume ratio, total alcohol to oil molartio and catalyst concentration. However,at higher volume ratio, molar ratio and catalyst concentration it was decreased in a quadratic manner.

4.2.4. Graphical analysis (DP)

The adequecy of the develo[ped model can also be checked using graphical analysis of residuals.The folloewing graphical plots were used for checking the model adequacy;

1) Normal probability plot of the studentized residuals to check for normality of residuals.
2) Studentized residuals versus predicted values to check for constant error.
3) Externally Studentized Residuals to look for outliers, i.e., influential values.

4.2.4.1. Normal Probability of Residuals

The normal probability plot is a graphical method used to check whether the error occurred during the experimental analysis is normally distributed throughout the experiment. The normality assumption of analysis of variance (ANOVA) is valid if all the data points lie along the straight line of the normality plot of residuals. The normal probability plot of residuals versus internally studentized residuals is depicted in figure 4.2 as shown below. The figure shows that that the data points are approximately located along the straight line. This indicates that the quadratic polynomial model developed fits or satisfies the normality assumption of analysis of variance (ANOVA). That means error distribution is throughput the experiment is approximately normal.

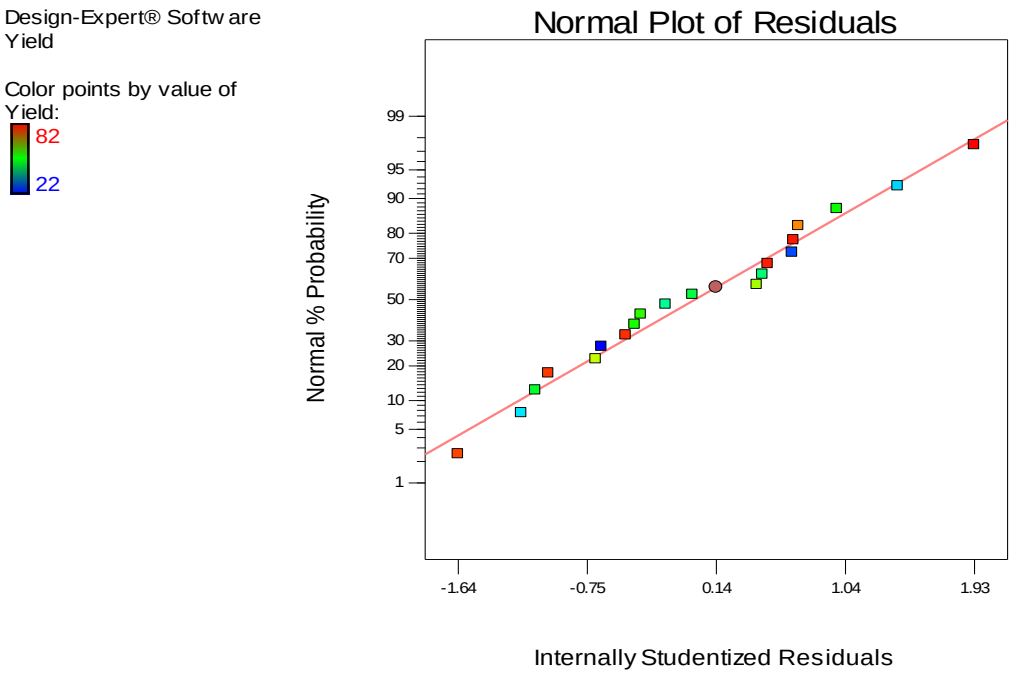

Figure 4-1.Normal Probability plot of residuals

4.2.4.2. Actual versus predicted plot

The plot of actual value versus predicted value is another graphical method that can be used to determine the adequacy of the model. A model is considered to be perfect if the slope of the line is unit (all data points are perfectly along the line) which corresponds zero error. The graph of the predicted value verses actual value of this study is shown in figure 4.3. It can be observed from the graph that all the data points are approximately close to the line of perfect fit. This indicates that the real(experimental) data is closely related to the data predicted from the model. This means that the model can adequately describe the biodiesel production process under the specified conditions.

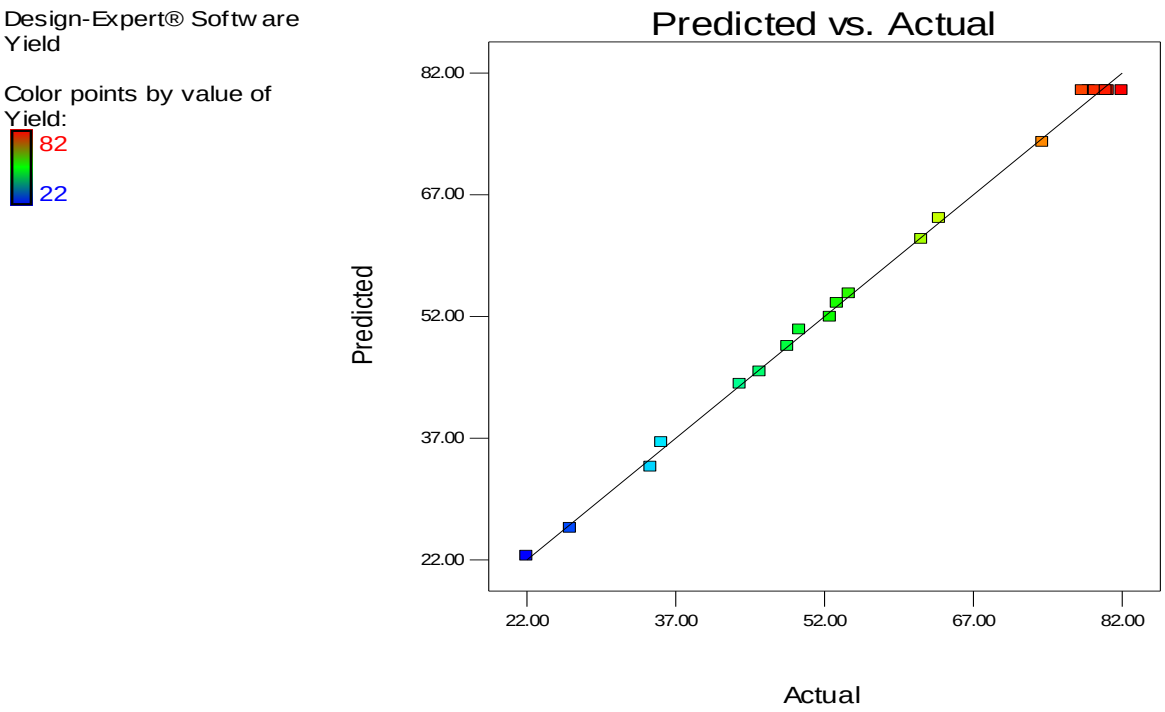

Figure 4-2. Predicted versus Actual plot

4.2.4.3. Residual vesrsus predicted plot

The plot of the residual versus predicted value is also another graphical technique used to assess the validity of the model. The model developed to describe the process is considered to be perfect if the residuals are structureless. This graph is used to assess non-linearity, unequal error variances, and outliers. The residual value verse predicted value for this study is given in figure 4.3. From this graph it can be observed that the residual values are not uniquely structured. That means no need of an improvement for minimizing personal error.

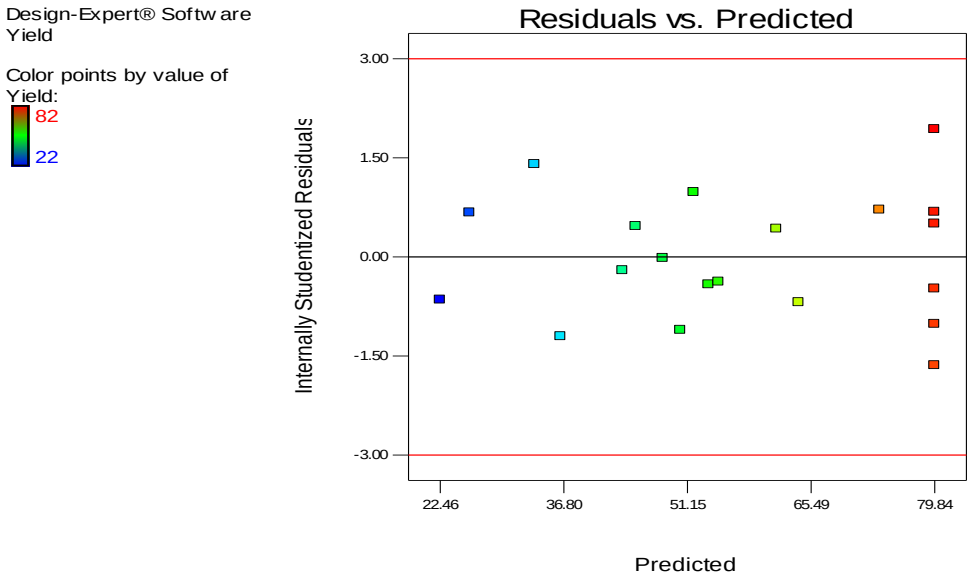

Figure 4-3. Residual Versus Predicted plot

4.2.5. Effect of individual factors on the yield of biodiesel

The result shown in the analysis of variance (ANOVA) indicated that the yield of biodiesel was highly influenced by the process variables (methanol to ethanol volume ratio, total alcohol to oil molar ratio and catalyst load) being studied under the specified operating conditions. The interaction effect between process variables was also highly significant. The interaction between methanol to ethanol volume ratio and total alcohol oil molar ratio, methanol to ethanol volume ration and catalyst loading, as well as total alcohol to oil molar ratio and catalyst loading were also significant.

4.2.5.1. Methanol to ethanol volume ratio

The regression model equation given in equation(A) indicated that the regression coefficients for methanol to ethanol volume ratio were very large in both linear and quadratic forms but positive in the case of linear model and negative in the case of quadratic model. This implies that the yield of biodiesel was increased at lowere methanol to ethanol volume ratio but it was decreased with further increasing in methanol to ethanol volume ratio. The effect of methanol to ethanol volume ratio on the yield of castor oil biodiesel at a fixed total alcohol to oil molar ration and catalyst loading is represented in figure 4.4 shown below.

It can be observed from the figure that the yield of biodiesel was increased with increasing methanol to ethanol volume ratio and the maximum. yield was obtained at 50%:50%. The reason could be, the reaction mixture was dominated by ethanol which is less reactive than methanol at the specified temperature. This can cause the yield to become low (Lam & Lee, 2011). Moreover, the yield was also slightly decreased as the volume ratio increased beyond 50%. The reason could be as the reaction mixture is dominated by methanol; the oil solubility could be decreased making the effect of mass transfer resistance significant. This makes the reaction rate and yield of biodiesel low (Lam & Lee, 2011).

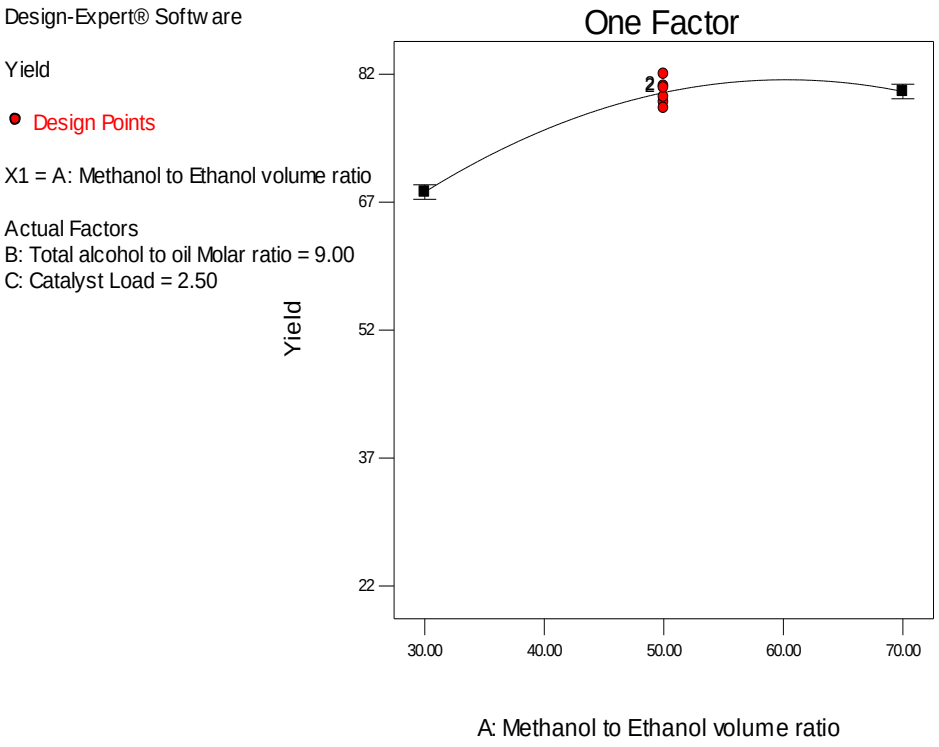

Figure 4-4. Effect of methanol to ethanol VR

4.2.5.2. Total alcohol to oil molar ratio

The alcohol to oil molar ratio is also important factor affecting transesterification reaction and then the yield of biodiesel. Theoretically, transesterification reaction, requires 3 mol of alcohol to produce 3 mol of biodiesel and 1 mol of glycerol. However, transesterification reaction is a

reversible reaction, thus, an excess alcohol is more frequently used to derive the reaction to wards the product side(Demirbas, 2003).

As it can be observed from equation(A) (regression model equation), the variation of the yield of biodiesel was linear at low total alcohol (methano+ethanol) to oil molar ratio and its with positive coefficient. This indicates that the yield of biodiesel was increased linearly when the total alcohol to oil molar ratio increased. However, the yield was decreased with further increasing in molar ratio between total alcohol and feed stock(oil). The effect of alcohol to oil molar ratio on the yield of biodiesel is shown in figure 4.5. The graph shows that total alcohol to oil molar ratio has a significant effect on the yield of biodiesel. The yield of was increased with increasing total alcohol to oil molar ratio from 6:1 to 9:1 and the maximum yield (82%) was obtained at 9:1. An excess amount of alcohol is important to increase the rate of transesterification reaction thereby increasing the yield of biodiesel. However, increasing the total alcohol to oil molar ratio beyond 9:1 led to decrease the yield of biodiesel. When too much alcohol is used in transesterification reaction a glycolysis reaction would occur (reaction between biodiesel and glycerol) leading to low yield of biodiesel. In addition, monoglycerides and diglycerides may act as co-solvents to homogenize the phases of excess alcohol, glycerol and biodiesel. As a result of these, separation of glycerol and biodiesel may become difficult leading to lowered yield of the product(Shu et al., 2009).

In heterogeneous catalysis system, reaction normally takes place on the surface and within the pores of the catalyst. Thus, when there is too much excess alcohol, it will compete with the other reactant (oil) for the limited surface area and therefore low biodiesel yield could be attained. Apart from that, over excess of alcohol can also cause extremely fast reaction rate. Because of these reasons, biodiesel and glycerol could still remain adsorbed on the surface of the catalyst and thus limiting the availability of catalyst active sites(Lam & Lee, 2011).

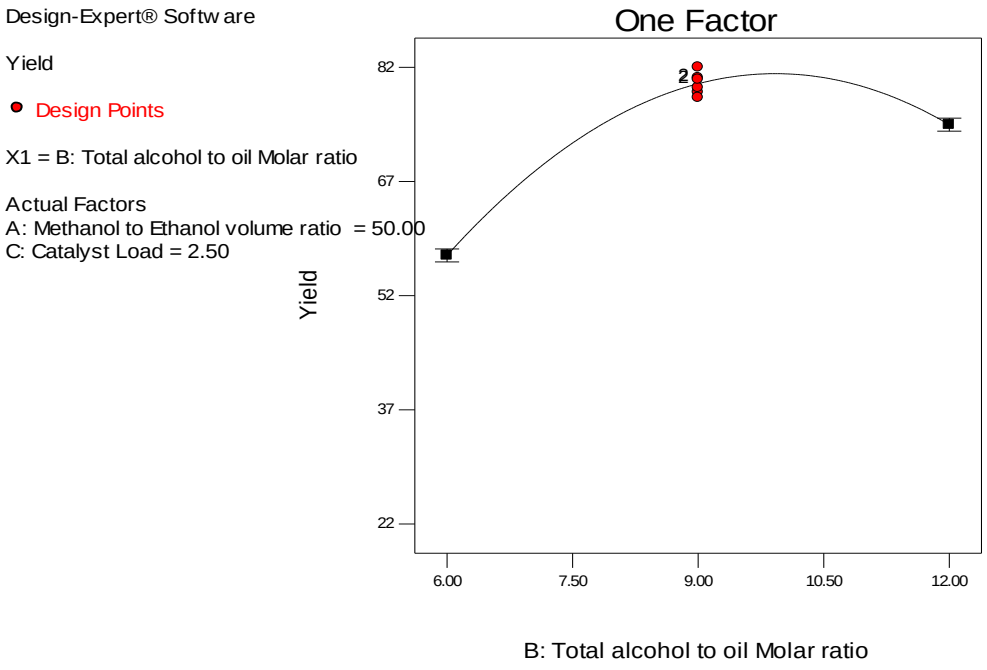

Figure 4-5. Effect of Total alcohol to oil MR

4.2.5.3. Effect of Catalyst loading

Catalyst is also another important factor affecting the transesterification reaction and yield of biodiesel being produced. The role of catalyst is to provide sufficient active sites for the reaction to occur. The analysis of variance (ANOVA), shows that the coefficients of the regression model with respect to the catalyst (C) concentration in both linear and quadratic form were large. This indicates the yield was highly affected by the amount of catalyst used. The yield was linearly increased with increasing amount of catalyst but decreased with further increasing catalyst concentration.

The effect of amount of catalyst on the yield of biodiesel is shown in figure 4.6. The figure shows that, the yield of biodiesel was increased with increasing the amount of catalyst used from 2% to 2.5% and the maximum ester yield which is 82.0% was obtained at 2.5 wt% catalyst loading 9:1 total alcohol (methanol +ethanol) to oil molar ratio and 50% methanol to ethanol volume ratio.

This is because, as more catalysts are added, the active sites available increased thereby facilitating the reaction(Yang,et al. 2009). The maximum yield was obtained at 2.5%. At this catalyst load,

82% yield of biodiesel was obtained which is the maximum yield. However, as the catalyst load was increased further beyond 2.5% the yield was decreased. Because an excess catalyst results in sop formation. It also causes the viscosity of the product to increase making the its separation from the glycerol difficult (Yang,et al. 2009). The castor seed oil was also converted to biodiel via transesterification reaction in the presence of recycled calcium oxide (CaO) as catalyst. The reaction was carried out the at 9:1 total alcohol to oil molar ratio,50% methanol to ethanol volume ratio and 2.5% catalyst load and about 42.4% yield was obtained. This indicates that the cast of biodiesel production can be reduced when solid catalysts are used.

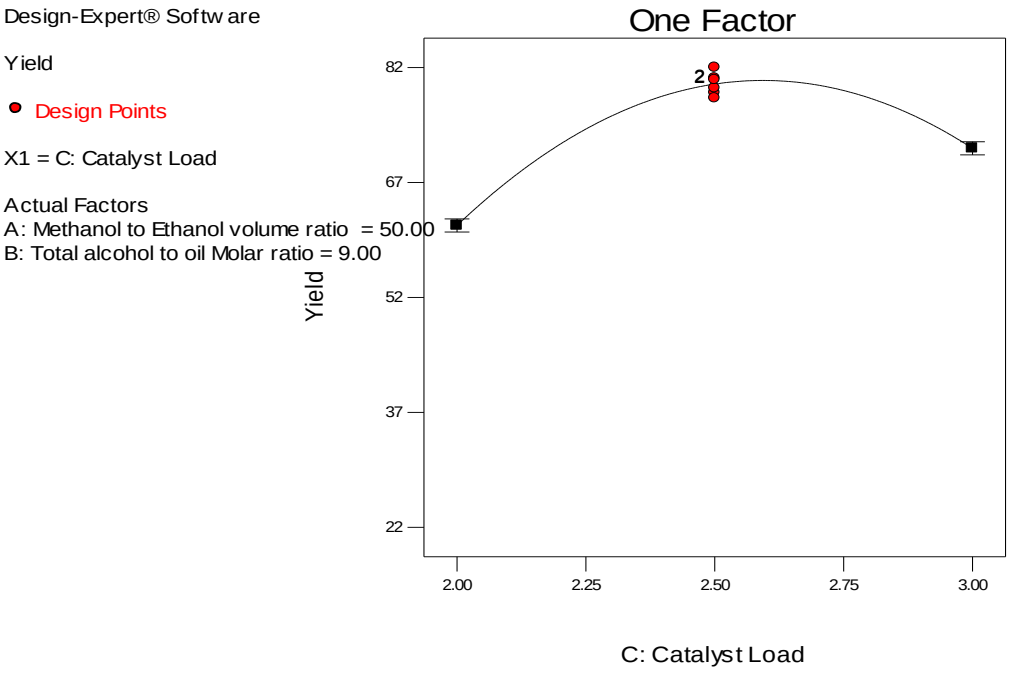

Figure 4-6. Effect of catalyst loading

4.2.6. Effect of Interaction between process variables

The analysis of variance (ANOVA) as given in table 4.3 shows that the yield of biodiesel was highly affected by the interaction between methanol to ethanol volume ratio and catalyst loading as well as between total alcohol to oil molar ratio and catalyst loading. The effect of interaction between process variable on the yield of biodiesel was also investigated using response surface (3D) and contour plots which were drawn keeping the third variable constant at its center point.

4.2.6.1. Effects of Interaction between M to E VR and Total alcohol to oil MR(AB)

From the analysis of variance (ANOVA), it can be observed that effect of interaction between methanol to ethanol volume ratio and total alcohol to oil molar ratio on the yield of biodiesel was highly significant. Figure 4.7 and figure 4.8 shows the response surface(3D) and contour plots obtained by drawing the yield of biodiesel as function of total alcohol to oil molar ratio and methanol to ethanol volume ratio. The catalyst load was held constant at 2.5%. These figures indicate that the yield of biodiesel was increased from 47.23% to 55.8% with increasing M/E volume ration from 30/70 to 50% at 6:1 total alcohol to oil molar ratio. In addition, the yield was also increased from 47.23% to 61.19% as the total alcohol to oil molar ratio increased from 6:1 to 12:1 when M/E volume ratio was fixed at 30% methanol. Moreover, the yield at higher total alcohol to oil molar ratio (12:1) and low M/E volume ratio (30%) was lower that the yield obtained at higher total alcohol to oil molar ratio (12:1) and higher M/E volume ratio (70%). This implies that the effect of interaction between total alcohol to oil molar ratio on the yield of biodiesel was positive. This result is also conveyed in the analysis of variance (ANOVA).

Figure 4.7 and 4.8 also shows that the yield of biodiesel was more sensitive to the variation of total alcohol to oil molar ratio as compared to the variation in volume ratio between methanol and ethanol. This is because transesterification reaction is a reversible reaction requiring higher molar ratio of alcohol to oil(Demirbas, 2003). In addition, the yield of biodiesel at higher methanol to ethanol volume ratio was higher than the yield at low methanol to ethanol volume ratio. At higher ethanol compared to methanol low yield was obtained. Because, ethanol is less reactive than methanol. Moreover, formation of methyl ester is easier than ethyl ester because of formation of stable emulsions with ethanol making separation of the biodiesel difficult(Musa, 2016).

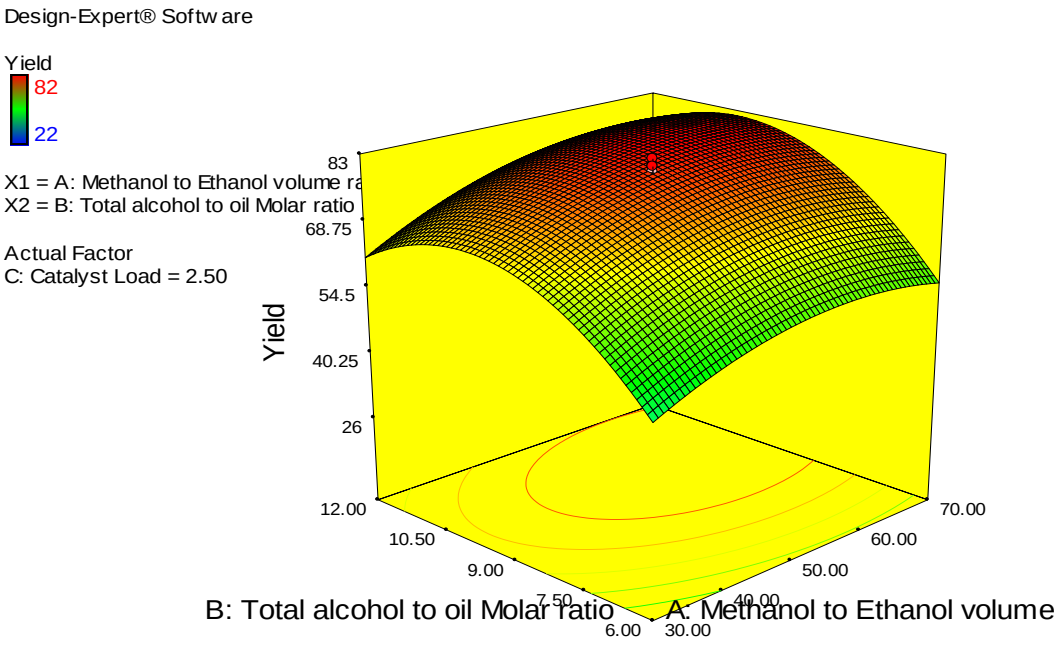

Figure 4-7. 3D plot: Interaction between M/E VR and total alcohol to oil molar ratio MR

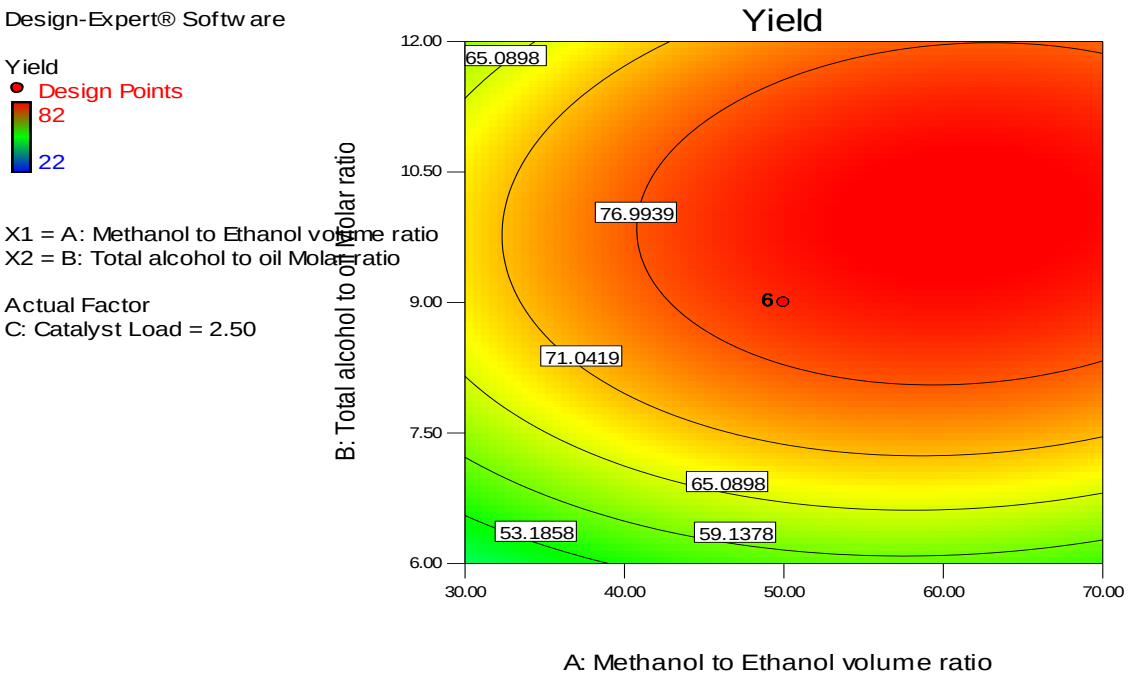

Figure 4-8. Contour plot: Interaction between M/E VR and total alcohol to oil MR

4.2.6.2. Effect of interaction between M/E VR and Catalyst loading (AC)

The response surface(3D) and contour plots showing the interaction between methanol to ethanol volume ratio and catalyst concentration on the biodiesel yield are depicted in figure 4.9 and 4.10 respectively. These figures were dawn as function of M/E volume ratio and catalyst loading while keeping the total alcohol to oil molar ratio constant at 9:1. It can be observed from these figures that the yield of biodiesel was shown to increase with increasing both M/E volume ratio and catalyst loading. The yield was increased as the volume ratio of M/E increased from 30/70 to 70/30. It was also increased with increasing the amount of catalyst used from 2% to 2.5%. This is because higher catalyst loading makes the reaction rate fast and then the yield of biodiesel higher. The reason is that catalysts provide active sites for the reaction to occur. The maximum yield was obtained at 9:1 total alcohol to oil molar ratio, 50/50 volume ratio of M/E and 2.5% catalyst loading. Upon increasing further in both M/E volume ratio and catalyst loading, the yield of biodiesel decreased. This decreasing may be due to the fact that of cator seed oil is more soluble in ethanol than methanol leading to low reaction rate(Musa, 2016). In addition, the decreasing the yield of biodiesel with increasing catalyst loading may due to formation of soap and increasing viscosity of the produced biodiesel making the separation of biodiesel form the glycerol byproduct difficult(Yang,et al. 2009).

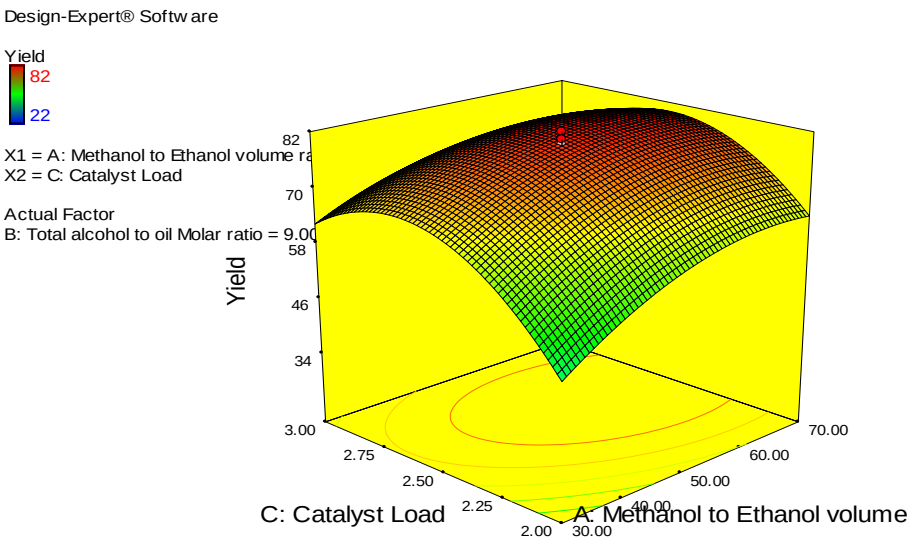

Figure 4-9. 3D plot: Interaction between M/E VR and Catalyst loading

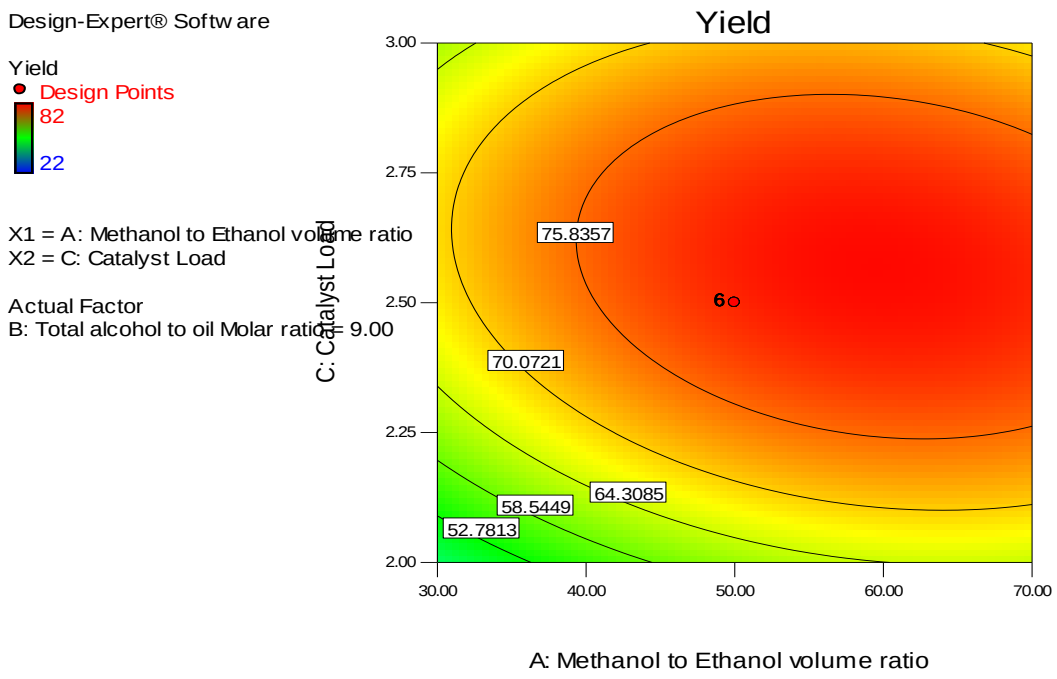

Figure 4-10. Contour Plot: Interaction between M/E volume ratio and catalyst loading

4.2.6.3. Effect of interaction between Total alcohol to oil MR and Catalyst loading (BC)

The effect of interaction between total alcohol to oil molar ratio and catalyst load on the yield of cator seed oil biodiesel was also analyzed using response surface(3D) and contour plots. The 3D and contour plots representing the effect of interaction between methanol and ethanol volume ratio and catalyst loading are depicted in figure 4.11 and 4.12 respectively. These plots were drawn keeping the third variable (methanol to ethanol volume ratio) constant at its center value (50%).

The 3D plot shown in figure 4.11 indicates that the yield of biodiesel was increased with increasing total alcohol to oil molar ratio and reached its maximum at 9:1 total alcohol to oil molar ratio. Similarly, it was also increased with increasing catalyst load from 2 to 2.5%. However, it was decreased with further increasing catalyst load. This may be due to increasing viscosity making separation of biodiesel from glycerol difficult. It was also due to soap formation as a result of increasing the amount of catalyst. Similar trends can be observed from figure 4.12 which is the contour plot showing interaction between the two factors. It was drawn at constant methanol to ethanol volume ratio of 50%:50%. The figure also shows that, the yield of biodiesel was increased

as the amount of catalyst (CaO) increased from 2 to 2.5(%wt of oil used). Similarly, the yield was also increased with increasing molar ratio of alcohol (methano+ethanol) to oil. The maximum yield was obtained at 9:1 total alcohol to oil molar ratio and 2.5% catalyst loading.

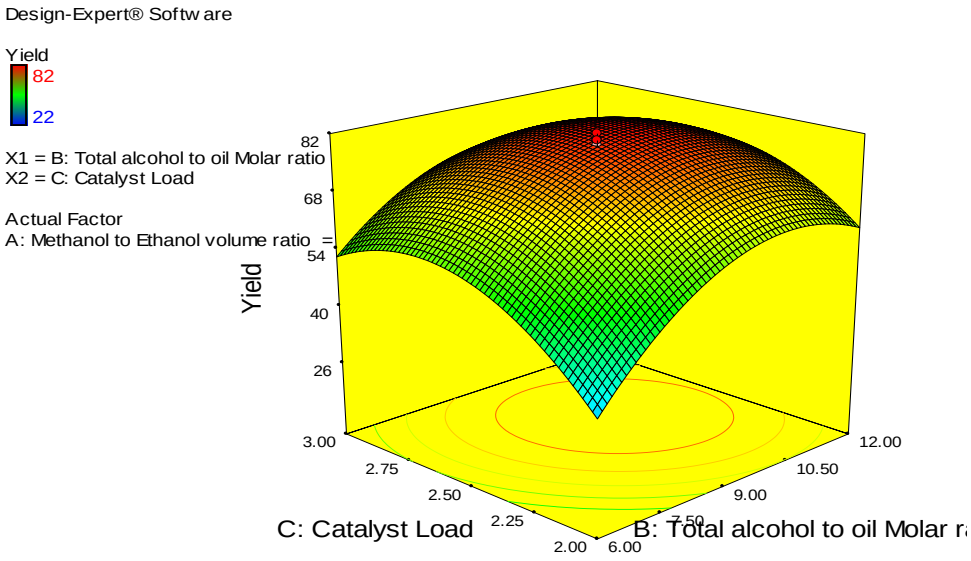

Figure 4-11. 3D plot: Interaction between total alcohol to oil MR and Catalyst loading

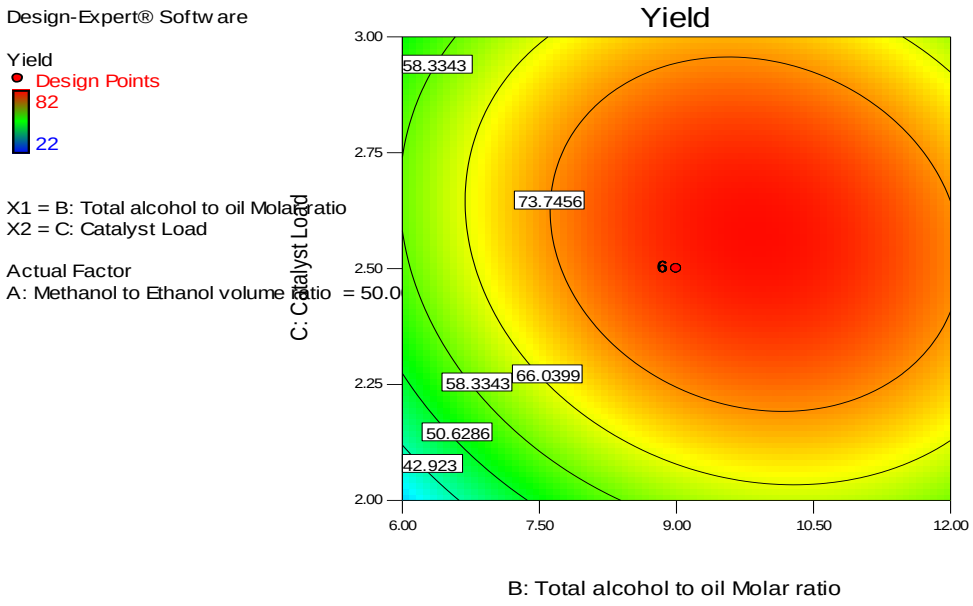

Figure 4-12. Contour plot: Interaction between total alcohol oil MR and catalyst load

4.3. Characterization of biodiesel

4.3.1. FTIR Analysis

The result obtained from Fourier transform infrared spectrometry (FTIR) analysis are presented in table 4.7 as shown below and in appendix E(b). The result of FT-IR analysis of biodiesel, shows that the spectra of both castor sed oil and cator oil biodiesel were similar. However, the carbonyl group (C=O) group represented by the reign at 1745.58 was shifted to 1732.02 in the biodiesel. In addition, the ester functional group(C-O) in the castor seed oil was depicted by the peak at1162 (1/cm) but it was shifted to 1193.93 in the case of the biodiesel. This indicates that the castor oil was converted to biodiesel. In addition, the presence of new spectra in the biodiesel (Tariq et al., 2011).

The alkane groups(C-H) were indicated in the reign between 2947.23- 2846.93 with stretching vibrations while alkene groups(=C-H) by the peak at 3007.02(1/cm) with stretching vibration. Moreover, the peaks between at 3439.08 -334625(1/cm) indicates for the presence of carboxylic (OH) functional groups in biodiesel. These functional groups are similar to the functional groups reported by (Ngusale et al., 2015). The reign between 1246.-1174 confirmed the presence of C-O-C functional group and the peak at 725.23. indicates repeated alkene functional group $(CH_2)_n$. the reign between 1435-1417 indicates the presence of O-CH3 functional groups in the biodiesel (Donnell et al., 2013).

Table 4-6. Result of FTIR analysis of castor oil Biodiesel

Functional group No	Wave Namber		Mode of vibration
	Repored	Experimental	
CH2	2950-2850	2973.31	Stretching
CH3	2980-2950	2947.23	Stretching
(Ch2)n	920-720	725.23	Out of plane bending
Ester(C-O)	1300-1000	1246-1035.77	Bending
carbonyl(C=O)	1750-1730	1732.08	Bending
OH(alchol)	3400-3200	3439.04-3346.5	Stretching
Aromatic hydrocarbon	1475-1350	1435.04-1417.39	Bending

4.3.2. Physico-chemical property of Biodiesel

4.3.2.1. Density of Biodiesel

The density of the castor oil biodiesel was determined according to the method used to determine the castor oil density and the result was obtained to be 913.8 kg/m^3. This result shows that the density of the castor oil biodiesel was slightly higher than that of the standard density which is 860-900 kg/m^3 (Barabás & Todoru, 2011)**.** This higher density may be due to higher viscosity of the castor oil used to produce the biodiesel. It has been described that density is an important property of biodiesel and it must be maintained with in the standard limits to allow complete combustion in diesel engine (Ibeto et al. 2012).Thus the obtained biodiesel should be blended with petro diesel in order to lower the density and solve the problems that might be encountered due to higher density.

4.3.2.2. Viscosity

The dynamic viscosity of the biodiesel determined using digital vibro viscometer was obtained to be 17.0 mPa.s at 40^{o}c. This result was converted to kinematic viscosity by dividing it with density of the biodiesel and it was obtained to be 18.58mm^2/sec. This result indicates that the kinematic viscosity of the extracted oil was reduced significantly during the transesterification reaction but still higher than the ASTM standard limits. Thus, the obtained biodiesel is highly viscous and difficult to be used as fuel in its pure form and needs to be blended with conventional fuel.

4.3.2.3. Acid value test (ASTMD664)

In determining acid value acid value of the biodiesel, three replicates were carried out and the obtained results are presented appendix C(a).The maximum allowed acid value for biodiesel is 0.8mg KOH/g sample(Barabás & Todoru, 2011). In this study the acid value of the biodiesel was reduced from 4.69 KOH/g oil to 2.66 mg KOH/g oil during the transesterification process and the corresponding %FFA content from 2.35% to 1.33% which is higher than the standard limit that a standard biodiesel has.

4.3.2.4. Saponification value test

The saponification value the castor seed oil was reduced from 186.81 to 180.52 mg of KOH per gram during the transesterification reaction. This result falls within the ASTM standard result (175-187).

4.3.2.5. Heat and Iodine value

Heat content and iodine value of the castor oil biodiesel were determined using empirical formula suggested by (Demirbas, 1998). The heating value(content) of the produced biodiesel was obtained to be 39.61 MJ/kg while the. This result indicate that the obtained biodiesel has great protentional to be used as fule. Similarly, the iodine value was obtained to be 80.12 g I_2/100 g. This result indicates the obtained biodiesel is less prone to oxidation which can occur during storage, distribution or within the vehicle fuel system itself. Because biodiesel with low iodine value has low risk of satblity. This implies that the obtained biodiesel can be stored for long time without being deteriorated(Barabás & Todoru, 2011).

4.3.2.6. Cetane number

The cetane number which is a measure of ignition quality of the biodiesel was also determined using the empirical formula suggested by(Bose P. K, 2009) using the result of Saponification number (SN) and the iodine value (IV) of the biodiesel. The cetane number was obtained to be 54.1. This result is above the minimum requirement as specified by ASTM standards.

4.3.2.7. Flash point

For biodiesel derived from castor seed oil, the minimum flash point requirement is 130^{o}c(Tunio et al., 2016). In this study the flash point was measured and obtained to be 218.5^{o}c which is much higher than the minimum requirement. This result indicates that the biodiesel produced from cator seed oil can be used and handled safely.

4.3.2.8. Cloud and pour points

The cloud point of the produced biodiesel was obtained to be 3.6^{o}c. This result indicates that biodiesel derived from castor seed oil is suitable to be used at low temperature. In addition, the pour point was also found to be -2.3^{o}c. Bothe cloud and pour points of the produced biodiesel are

low compared to biodiesels derived from other vegetable oils. The cloud point is an indication of cold flow ability of the biodiesel. When a biodiesel having a cloud point below the standard limit is used, its lubricating properties could be reduced and may plug filters(Kinast, 2003).

4.4. Comparison of the obtained biodiesel with ASTM Standard Biodiesel

The physico-chemical properties of the biodiesel being produced from castor seed oil are summarized in table 4.7 as shown below.

Table 4-7. Comparison of the obtained biodiesel with ASTMD standard

Property	Experimenttal value	ASTMD standard value
Density at 15^{o}c(g/ml)	0.9138	0.86-0.90
Viscosityat 40^{o}c(mm^2/sec)	18.58	1.9-6
Acivlue(mg KOH/g oil))	2.66±0.21	0.8max
%FFA	1.33	0.4max
Saponification value(mg KOH/g oil15)	180.52±5.26	------
Iodine value (mgI2/100g oil)	80.12	82-88
Heating value(MJ/kg)	39.61	37.5-42.8
Flash point(^{o}c)	218.46	130 min
Cloud point (^{o}c)	3.6	-3 to 12
pour point(^{o}c)	-2.3	-15 to 5
cetane number	54.1	47 min

Table 4.7 given above shows that most of the properties of the biodiesel produced from castor seed oil were found to be reasonably close to that of the ASTM standard biodiesel. The heat content was obtained to be 39.61 MJ/kg which is within the ranges of ASTM standards. The obtained cetane number is also acceptable since it is higher than minimum requirements. The iodine number was obtained to be 80.45 mgKOH per100 gram of sample (biodiel) which is also slightly lower than the standard value but the deviation is very small. Moreover, the flash point cloud and pour points were also acceptable. However, density and kinematic viscosity values of the obtained biodiesel were deviated from their ASTM standard value. Higher density of castor oil biodiesel is contributed by higher castor oil viscosity (Okullo et al., 2012).

5. Conclusion and Recommendation

5.1. Conclusion

Castor seed oil is one of the nonedible oils with great potential for biodiel production because of its various promising advantages. Cultivation of castor plant needs no intensive resources and is one of the drought resistant plant. In addition, the plant can be easily grown in lands which are not suitable for agricultural practice and large quantity of seeds can be produced from the plant. Thus, the use of castor seed oil as feed stock for biodiesel production can be a means for improving local farmers income as well as for reducing dependency on petroleum fuels.

In this study, castor seed oil was converted to biodiesel via transesterification with a mixture of methanol and ethanol. Firstly, the oil was extracted using Soxhlet apparatus and about 30.12% yield of castor seed oil was obtained. The resulting obtained oil was subjected to characterization to determine its quality requirements for biodiesel production and most of its properties were within the ASTM standard limits.

Secondly, calcium oxide catalyzed transesterification was used to produce the biodiesel using mixture of methanol and ethanol as a reactant. The reaction parameters being studied were methanol to ethanol volume ratio, total alcohol to oil molar ratio and catalyst loading and their effects on the yield of biodiesel was studied using Deign express 7.0.0 software.

The obtained result indicates that utilization of mixed methanol and ethanol for production of biodiesel has a considerable potential. Because the technical benefits of methanol were incorporated with the economic and environmental benefits of ethanol. In addition, the catalyst (CaO) was easily separated without the need to wash the biodiesel. This can effectively reduce separation cost and waste water discharging. Moreover, the recycled catalyst was also reused once a times at the optimum conditions and about 40.5% yield was obtained. Thus, the conclusion is that calcium oxide can be considered as a potentially promising catalyst. From the statistical analysis of variance (ANOVA), the yield of the ester was found to be strong function of both the individual and interaction effects. The yield of biodiesel was increased with increasing in all the studied variables and the maximum yield was 82% which was obtained at 50% methanol to ethanol volume ratio, 9:1 total alcohol toloil molarity and 2,5% catalyst concentration.

The quality of obtained biodiesel was also tested by deterring its physico-chemical properties and comparing it with that of the standard biodiesel. Most of the physico-chemical properties of the

produced biodiesel within the ASTM specification. However, density and viscosity were higher than the ASTM standard limits. Thus, the obtained biodiesel needs blending with diesel fuel before it is used.

5.2. Recommendation

In this study, the castor oil used as a feed stock for biodiesel production was extracted through Soxhlet apparatus using normal hexane and bout 30.12% percentage yield on a dry mass basis was obtained. However, higher percentage yield of the oil was expected because castor seed oil has been reported to have 30-55% by weight. Moreover, the process was time consuming and much expensive due to the cost of solvent used. The yield of biodiesel obtained was also lowere than the expected yield. Thus, to make the production of biodiesel from castor seed oil technically, economically and environmentally feasible, the following improvements are recommended to be under taken;

- Comparative study on mechanical and solvent extraction should be under taken
- The calcination of calcium oxide (CaO) should carried out and its catalytic performance should be investigated in comparison to its uncalcined calcium oxide.
- The effect mixing intensity, reaction time and temperature on the yield of biodiesel should be investigated.

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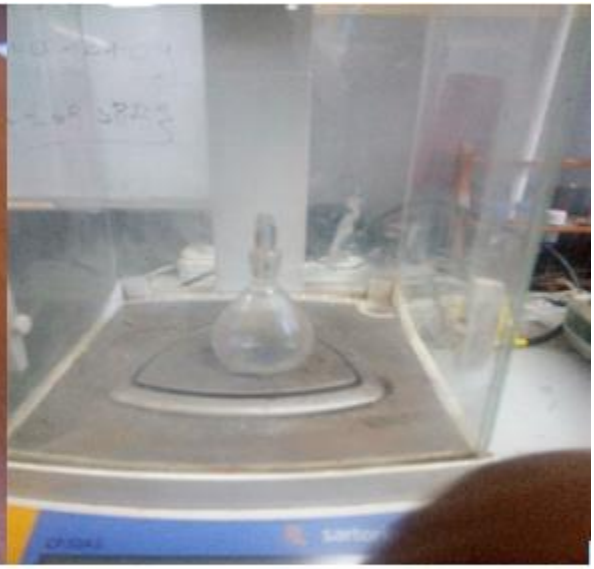
7. Appendices

7.1. Appendix A: Figures for samples and laboratory equipments

Figure(a) Castor seed before deshelling Figure(b) deshelled cator seed

Figure (c) Soxlhet aparatue (d) rotary Evaporator

(e) Castor seed oil



(f) Pycnometer and digital balance

(g) Reactor

(h) separating funnel

(i)Viscosity of oil

(j) Viscosity of Biodiesel

(k) Purified Biodiesel

(m) Castor seed oil and biodiesel

7.2. Appendix B: Calculation of Castor seed oil properties

(a) Moisture content

Time(hrs)	Mass(g)		
	Run 1	Run 2	Run 3
0	50	50	50
2	48.893	48.921	48.387
4	47.547	47.638	47.614
6	47.536	47.439	47.582
Difference	2.464	2.561	2.418
% M.C	4.928	5.122	4.836
Average %M.C	4.692		

The standard deviation is calculated as follow:

$Variance(V^2) = \frac{\sum(X_i - X)^2}{N-1}$ =0.1307

The standard deviation is the square root of the variance which is 0.36

(b) Viscosity

$$Viscosity = \frac{Dynamic\ viscosity}{density} = \frac{115\ mpa.s}{0.946\frac{g}{ml}} = 121.56\frac{mm^2}{sec}$$

(C) Acid value test

The acid value was determined using equation (3.3)

$$AV = \frac{56.1 \times 0.1 \times N \times V_{KOH}}{M}$$

Run No	Mass(g)	Normality	V(ml) of KOH	AV	%FFA
1	4.73	0.1	4.2	4.48	2.24
2	4.73	0.1	3.6	4.27	2.14
3	4.73	0.1	4.5	5.33	2.78
average	4.73	0.1	4.10	4.693	2.35

$\text{Variance}(V^2) = \frac{\sum(X_i - X)^2}{N-1} = \frac{\sum(X_i - 4.692)^2}{3-1}$ =0.1945

$\text{Standard deviation} = \sqrt{0.1945}$ =0.44

(d) **Saponification value calculation**

$$SV = \frac{56.1 \times 0.5 \times (V_b - V_a)}{M}$$

Run No	Oil (g)	Normality of HCl	V_b (ml) of CHl	V_a(ml) of HCL	SV mgKOH/g oil
1	4.73	0.5	75.6	45.3	179.68
2	4.73	0.5	76.2	44.8	186.21
3	4.73	0.5	76.8	44.5	193.33
average	4.73	0.5	76.2	44.86	185.81

$\text{Variance}(V^2) = \frac{\sum(X_i - X)^2}{N-1} = \frac{\sum(X_i - 185.81)^2}{3-1}$ =94.14

$\text{Standard deviation} = \sqrt{0.1945}$ =6.87

(e) **Iodine value calculation**

The volume of the sodium thiosulphate solution recorded for blank and sample test were 48.76ml and 33.84 reactively.

$IV = \frac{12.69(V_b - V_a)}{M} = \frac{12.69 \times (48.76 - 33.84)}{2}$ =94.68g I_2/100g oil

7.3. Appendix C: Actual (Experimental) and predicted Yield of biodiesel

No	Run Order	M to E VR	Alcohol to oil MR	Catalyst Load	Actual Yield	Predicted Yield	Residual Value
1	1	30.00	6.00	2.00	22	22.46	-0.46
2	13	70.00	6.00	2.00	35.6	36.45	-0.85
3	10	30.00	12.00	2.00	43.5	43.64	-0.14
4	12	70.00	12.00	2.00	63.6	64.09	-0.49
5	15	30.00	6.00	3.00	45.5	45.17	0.33
6	8	70.00	6.00	3.00	48.3	48.31	-0.014
7	20	30.00	12.00	3.00	52.6	51.91	0.69
8	9	70.00	12.00	3.00	61.8	61.50	0.30
9	4	16.36	9.00	2.50	53.3	53.62	-0.32
10	5	83.64	9.00	2.50	74	73.45	0.55
11	14	50.00	3.95	2.50	26.4	25.89	0.51
12	3	50.00	14.05	2.50	54.5	54.79	-0.29
13	2	50.00	9.00	1.66	34.5	33.42	1.08
14	11	50.00	9.00	3.34	49.5	50.35	-0.85
15	19	50.00	9.00	2.50	78.7	79.84	-1.14
16	6	50.00	9.00	2.50	80.6	79.84	0.76
17	16	50.00	9.00	2.50	79.3	79.84	-0.54
18	18	50.00	9.00	2.50	82	79.84	2.16
19	17	50.00	9.00	2.50	78	79.84	-1.84
20	7	50.00	9.00	2.50	80.4	79.84	0.56

7.4. Appendix D: Calculation of biodiesel properties

(a) Acid value

$$AV = \frac{56.1 \times 0.1 \times N \times V_{KOH}}{M}$$

Run No	Mass(g)	Normality	V(ml) of KOH	AV	%FFA
1	2.74	0.1	1.3	2.66	1.33
2	2.74	0.1	1.2	2.46	1.23
3	2.74	0.1	1.4	2.87	1.44
average	2.74	0.1	1.3	2.66	1.33

$$\text{Variance}(V^2) = \frac{\sum(X_i - X)^2}{N-1} = \frac{\sum(X_i - 2.66)^2}{3-1} = 0.042$$

$$\text{Standard deviation} = \sqrt{0.042} = 0.21$$

(b) **Saponification value**

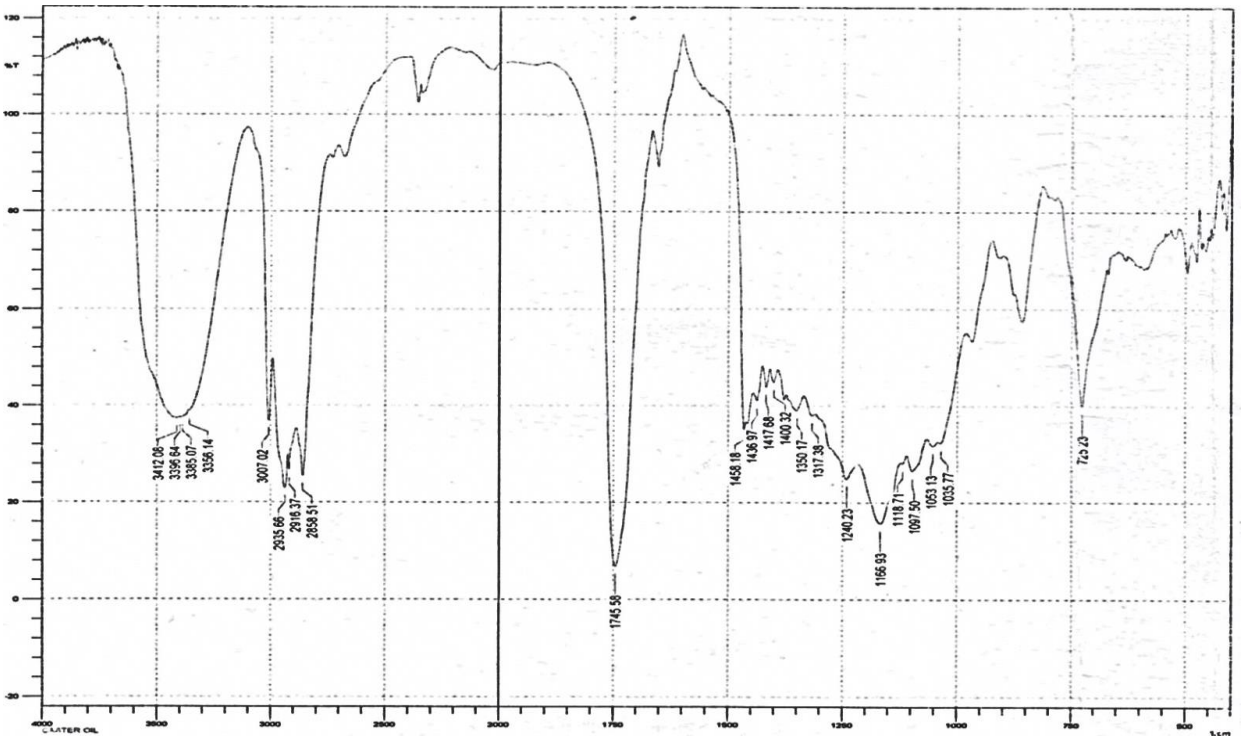
$$SV = \frac{56.1 \times 0.5 \times (V_b - V_a)}{M}$$

Run No	Oil (g)	Normality of HCl	Vb (ml) of CHl	Va(ml) of HCL	SV mgKOH/g oil
1	2.74	0.5	63.2	45.7	179.15
2	2.74	0.5	63.8	46.6	176.08
3	2.74	0.5	64.5	44.3	186.32
average	2.74	0.5	63.83	46.2	180.52

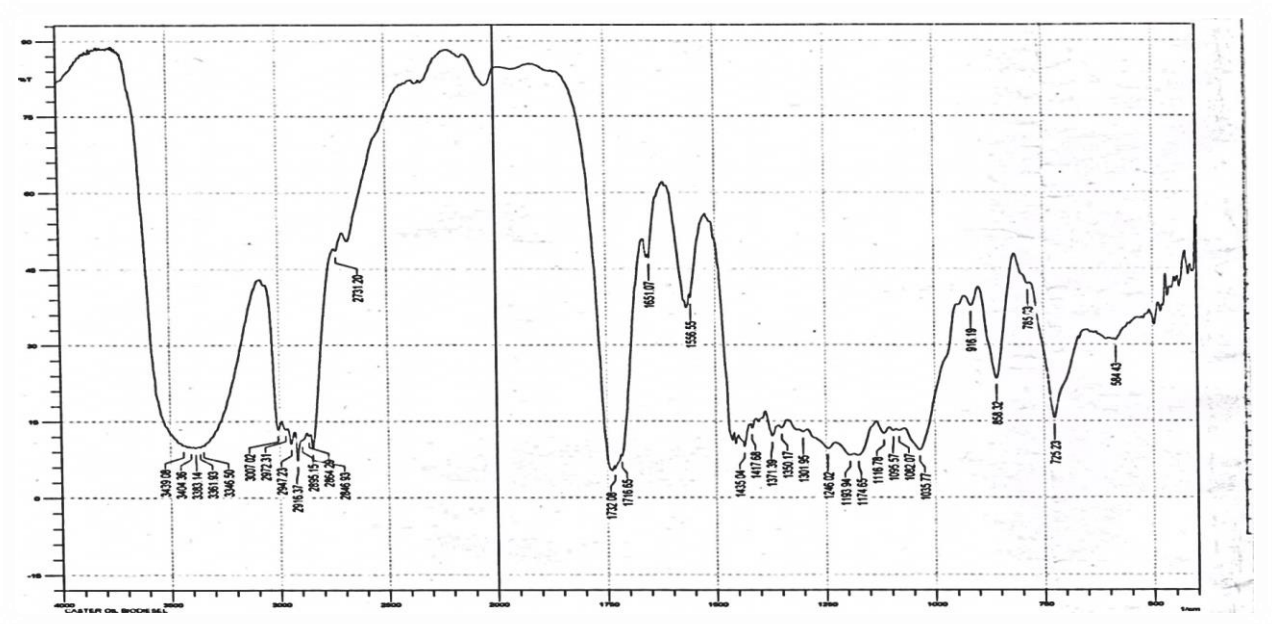
$$\text{Variance}(V^2) = \frac{\sum(X_i - X)^2}{N-1} = \frac{\sum(X_i - 180.52)^2}{3-1} = 27.62$$

$$\text{Standard deviation} = \sqrt{27.62} = 5.26$$

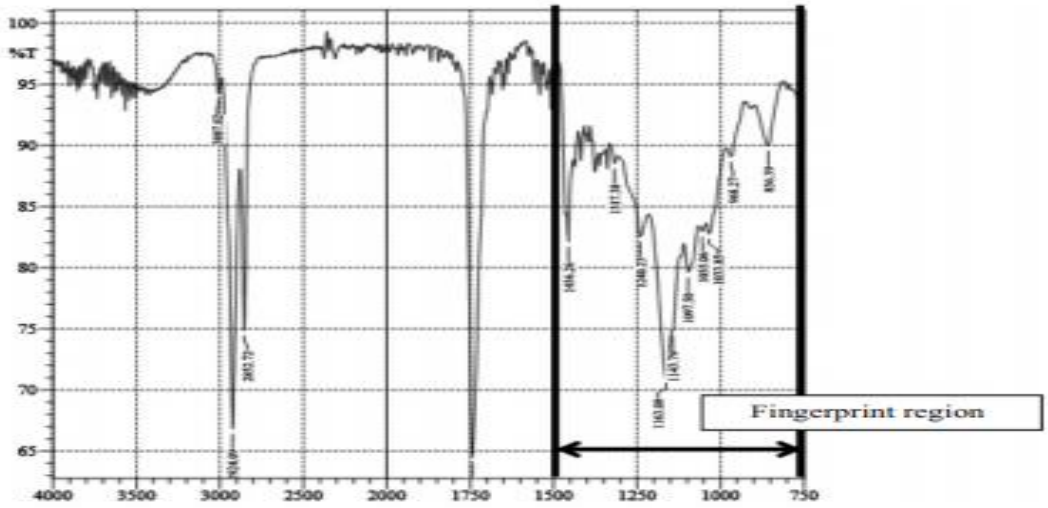
7.5. Appendix E: FTIR spectra of castor oil, castor oil Biodiesel and diesel fule



(a) FTIR spectra of castor seed oil



(b)FTIR spectra of Castor seed oil Biodiesel



(c) FTIR Spectra of Conventional diesel fuel((ISMAIl1 et a. 2014)