



JIMMA UNIVERSITY
JIMMA INSTITUTE OF TECHNOLOGY
SCHOOL OF GRADUATE STUDIES
FACULTY OF CIVIL AND ENVIRONMENTAL ENGINEERING
POSTGRADUTE PROGRAM
IN ENVIRONMENTAL ENGINEERING

PRODUCTION, OPTIMIZATION AND CHARACTERIZATION OF BIODISEL
FROM MIXED CASTOR AND JATROPHA SEED OILS

BY: SEYOUM TEFERA HAILMARKOS

**A THESIS SUBMITTED TO JIMMA INSTITUTE OF TECHNOLOGY, FACULTY OF
CIVIL AND ENVIRONMENTAL ENGINEERING, ENVIRONMENTAL ENGINEERING
CHAIR FOR PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTERS OF SCIENCE IN ENVIRONMENTAL ENGINEERING.**

NOVEMBER, 2021

JIMMA, ETHIOPIA

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NOVEMBER, 2021

JIMMA, ETHIOPIA

DECLARATION

I confirm and declare that this thesis entitled **“production, optimization and characterization of biodiesel from mixed castor seed oil and jatropha seed oil”** is my original work and has not been presented for award of degree in any other university.

Seyoum Tefera Signature _____ Date _____

The thesis that prepared with Mr. Seyoum Tefera has been submitted for examination with my approval as a university supervisor.

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ABSTRACT

Biodiesel is a renewable and sustainable alternative energy source with a great potential to substitute conventional fossil fuel with less environmental impact. Vegetable oils which are edible or non-edible, animal fats and waste cooking oils, algal oils either in pure or mixed at different ratios can be used as feed stock for biodiesel production. Selection of feedstock should be systematic and done based up on full life time analysis. Blending of the feedstock should be technical to obtain the best yield and beater economic advantage. Non edible oils are getting more interest for biodiesel production due to their comparative advantage they have, castor seed oil and jatropha seed oil are among the non-edible oils with great potential for the biodiesel production. This study aimed with the production, optimization and characterization of biodiesel from mixed feed stocks of castor seed and jatropha seed oils through transesterification with methanol by using KOH as alkaline catalyst. The oils from the seeds were extracted by Soxhlet using n-hexane as solvent. During extraction oil yield of 34% and 52% was achieved from castor and jatropha seeds respectively. The extracted oils were mixed at different volumetric ratios and their physical and chemical properties were determined in compliance with American society for testing materials (ASTM) and most of the parameters were in agreement with in the ASTM standards. Methanol to oil molar ratio, Castor to jatropha oil volumetric ratio, catalyst concentration were the processes variables selected to investigate their effect on the response which is the biodiesel yield while reaction temperature, mixing intensity, and reaction time were set at optimum values, CCD with three factors and five levels was used to conduct the experiment and design expert software, Response surface methodology (RSM) were used to investigate the individual and the interaction effects of the process variables on biodiesel yield. The optimum yield of biodiesel obtained was at methanol to oil molar ratio of 4, catalyst concentration 0.5%(wt/wt) and at castor to jatropha oil (MCJSO) volume ratio 25:75 which is (which is 1:3) and the optimal biodiesel yield was 91%. The physicochemical properties of the biodiesel were density of 880 kg/m³, Kinematic viscosity 2.2 mm²/s, the acid value 0.561 mg KOH/g oil, the saponification value 230 mg of KOH/g oil, water content 0.027% heating value was 41.42MJ/kg, and most of the obtained values are within the ASTM standards.

Keywords: Biodiesel, Castor seed oil, Jatropha seed oil, Mixed castor and jatropha oil (MCJSO), RSM, Transesterification.

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LIST OF ACRONYMS AND ABBREVIATIONS

ANOVA	Analysis of Variance
ASTM	American Society for Testing Materials
AV	Acid Value
BBD	Box–Behnken design
CCD	Central Composite Design
CN	Cetane number
COME	Castor Oil Methyl Ester
CP	Cloud point
CSO	Castor seed oil
CV	Calorific value
DI	Determinant and Integrated
ELIDI	Ethiopian Lather Development Institute
EN	European Standard
FAM/E-E	Fatty Acid Methyl-Ethyl Ester
FFA	Free Fatty Acid
FP	Flash Pont
FTIR	Furioure Transform Infrared
GHG	Greenhouse gases
HV	Heating Value
IV	Iodine Value
JOME	Jatropha Oil Methyl Ester
JSO	Jatropha Seed Oil
LCA	Life Cycle Analysis
M	Methanol
M.C	Moisture Content
M.W	Molecular Weight
MCJSO	Mixed Castor and Jatropha Seed Oil

MCJSOME	Mixed Castor and Jatropha Methyl Ester
MR	Molar Ratio
OS	Oxidation Stability
PAHS	Polycyclic Aromatic Hydrocarbons
PP	Pour point
RSM	Response surface methodology
SV	Saponification value
SNNPRS	Southern nations nationalities regional state
SWRS	South West Regional State
TAGS	Triacyl glycerol

CHAPTER ONE

INTRODUCTION

1.1 Background

The sky-rocketing of the world energy demand is traceable to the improved economic activities in developing and emerging economies, the escalated growth in world population, industrialization, urbanization and technology. The world energy sector dependent heavily on coal, petroleum and natural gas as sources of energy requirements (Abdulkader,2015). Fossil fuels account for 88% of the primary energy consumption, with oil (35%),coal (29%) and natural gas (24%) as the major fuels, While nuclear energy and hydroelectricity account for 5% and 6% of the total primary energy consumption (Prabhavathi,2015).The continued utilization and consumption of fossil-based (FB) fuels have resulted in the depletion of the finite non-renewable fuel reserve, release life threaten emission of dangerous gases into the environment, are major contributors for terrestrial and aquatic pollution which contribute to the increase in greenhouse gas(GHG)emissions (Awogbemi *et al.*,2021). Fossil fuels remain the dominant source of energy though it is non-renewable and has negative impact on global climate (Abdulkader, 2019;Yadessa & Marchetti, 2017).

Edirne and Nosa (2012) reported that global energy demand is expected to grow by 50% in the year 2025. According to British Petroleum, both oil and gas could be exhausted within the next 50 years while coal reserves can only last for the next 115 years based on the current rate of exploitation (Awogbemi *et al.*,2021). Thus, if population growth and utilization pattern continue at the current rate, the global Petro-diesel reserve will become out of stock within the next few decades Abdulkader, (2019).

Universal Accessibility to clean, safe, and affordable energy has a strong correlation with the quality of life of an individual. This has become one of the greatest challenges in meeting sustainable development goals (Awogbemi *et al.*, 2021). At Rio+20, the 2012 United Nations Conference on Sustainable Development, the creation of a “green economy” was declared to be an important means of achieving sustainable development and eradicating poverty. The concept of a green economy emphasizes the potential for positive interaction between the environment and continuing economic growth (Porthner,2014).

The latest trends in environmental legislation associated with carbon dioxide (CO₂) emission reductions are a great challenge for the industrial sector. It can be assumed that a competitive position for businesses utilizing fossil fuels will be strongly conditioned on the ability to meet strict environmental regulations (Duteka *et al.*,2015). One important goal is to take measures for transportation emissions reduction, with the gradual replacement of fossil fuels by renewable energy sources. Biodiesel fuel is seen as real contributors to reach those goals (Prabhavathi,2015).Therefore,searching and exploring renewable potential resources as alternative energy is a timely and reasonable solution for the depleting resources of crude oil, environmental concern and many uncertainties in assuring its regular supply with a stable price.

Biodiesel is composed of mono-alkyl esters of long-chain fatty acids primarily produced through transesterification by using diverse feed stocks resources like vegetable oils, animal fats or microalgae lipids or agricultural wastes with short chain alcohols by virtue of nucleophilic substitution (Ayola *et al.*, 2020; Lin and Ma ,2020).

Biodiesel has been considered a superior alternative fuel to Petro-diesel due to its dominant advantages including superior biodegradability, energy competitive, and renewable resource with the ability to meet the energy need of the world. It is the feasible solution replacing fossil fuels causing ozone depletion and environmental degradation being free of (SO_x) emissions and acid rain. It is adjudged that biodiesel was a very promising fuel in transportation sector due to the fact that it exhibits similar properties with petroleum diesel. It is a renewable fuel that emits fewer emissions on burning having enhanced combustion due to its higher oxygen content, exhibiting excellent lubricity, containing no carcinogenic PAHs (polycyclic aromatic hydrocarbons), and it can be implemented to existing petroleum diesel engines without retrofitting (Lin and Ma, 2020; Ayoub *et al.*,2021). The application of biodiesel fuel could alleviate the emission of greenhouse gas CO₂ owing to the lower carbon content of biodiesel by about 10 wt% compared to Petro-diesel.

Like Petro-diesel fuel, it can be easily stored anywhere as it has good storage properties. The chemical hazards and risks associated with handling, transportation, and storage of the biodiesel are less than the conventional diesel. Biodiesel can be handled safely because of its biodegradability and greater flash point than petrodiesel.

Owing to their numerous advantages, including their renewability, environmental friendliness, feedstock availability, the flexibility of the production techniques, and their availability in solid, liquid, and gaseous states, bio-fuels have gained sustained popularity as an alternative to FB fuels. Other renewable energy systems like solar and wind do not pollute the environment, but they are incapable of sequestering carbon dioxide (CO₂) emissions and generating (O₂) (Awogbemi *et al.*,2021). Thus, bio-energy and bio-fuels possess the unique ability to sustain the environment and the earth's ecosystem whereas the solar and wind systems have no effects on the natural balance of the earth. For these reasons, among others, the deployment of bio-fuels, especially as a transportation fuel, has continued to increase every year.

Ethiopia is a country with ample water resource as energy sources and diverse ecological climate, the country was traditionally one of energy deficit sub-Saharan African country which imports almost all of the countries petrodiesel demand. The diverse ecological climate offers the country to have huge potential for tapping other renewable sources of energy including of alternative energy resources such as wind, solar, hydropower, geothermal, biomass, biodiesel and bio-ethanol energy because of its location and favorable climate condition (Zenebe *et al.*, 2014). Among various alternative energy source biodiesel fuel has received special attention for this specific study, because in the context of Ethiopia energy security and sustainable green economic development is a critical energy sector development strategic issue.

1.1.1 Jatropha and castor with Ethiopian context

Among the many species, which yield as a source of energy in the form of biodiesel, Jatropha (*Jatropha curcas*) and Castor (*Ricinus communis*) which is an indigenous plant, both seeds belong to the family of Euphorbiaceae (Humphrey *et al.*,2017) has been identified as the most suitable non-edible oil seed bearing plant were growing in different localities in Ethiopia (Pranab, 2011).

According to germwe, (2014) The biofuels suitability distribution varies spatially all over the Ethiopia. And reported that for Jatropha, the western Benishangul and Amhara regional states, north and central Tigray, southern parts of southern nations and nationalities people (SNNPRS), the western and eastern escarpments of the rift valley region and eastward side of

the southwestern highlands of the country are HS. The HS area for castor takes the similar pattern with that of Jatropa, except the HS area is stretched in all directions.

1.1.2 Response Surface Methodology (RSM)

Response Surface Methodology (RSM) is a significant discipline in the statistical design and analysis of experiments (Josph *et al.*,2018). It is a term applied to multivariate techniques that can generate response surfaces and provide optimal solutions for a particular process (Ranade and Padma, 2017). The main goal of response surface methodology is to use a sequence of experimental designs to determine an optimum response. The idea was inspired by the necessity to carry experiments competently using a right choice of a design, and also to obtain the operating conditions with a set of manageable factors that lead to an optimum response (Josph *et al.*,2018).

RSM takes interaction effects into consideration. There are three design types of RSM which are widely used. Second-order designs like Central Composite, Box-Behnken as well as Doelhart designs estimate the curvature- interaction of the variables and present it in the form of a quadratic equation (Ranade and Padma ,2017).

a. Central composite design

Box and Wilson (1951), the CCD becomes solution to overcome these problems. This design consists of three parts, namely, a full factorial or fractional factorial design, axial or star points as additional design, and central point with all factors set to 0. These models were commonly used in several optimization purposes such as formulation, product enhancement, and separation both for extraction and chromatographic condition.

b. Box–Behnken design

Box and Behnken (1960) presented a particular class of three-level fractional factorial design with the specification for studying quantitative variables and now this finding was well known as the BBD. This design was more efficient and economical than other three-level designs due to its ability to allow points selection from the three-level factorial arrangement. The characteristics for the BBD are that there are no factorial or extreme points (Riswanto *et al.*,2018).

c. Optimal designs

Optimal designs like the D and I ones are generated based on computer algorithms and called computer-aided designs. They are not orthogonal like classic RSM types. The effects of the variables are correlated in these designs. The main advantage here is that it can be used to fit any type of model (first and second orders, quadratic, cubic) or for any particular research objective like screening or generating a response surface. Besides this, optimal designs afford lesser number of experimental trials than classic types and provide a constrained design space. The D and I in optimal designs stand for determinant and integrated respectively.

1.2 Statement of the problems

Now a days the limited and diminishing resources nature of fossil fuel, the global increasing mismatch between the demand and supply of the fossil fuel which was the main reason for increasing and continuous fluctuations in price of crude oil, and environmental and climate change concern of the global nations and the community at large, become the push factors for the continuous research and development agendas towards for the exploration of an alternative energy source which have comparatively best social, economic and environmental advantages than that of the conventional fossil based fuel.

Fossil based fuel consumptions are the major contributors to the increasing concentration of carbon dioxide (CO₂) in the atmosphere which is a key source of global warming problems which is the major cause for the reduction of agricultural productivity and other biological and social problems. This all have been the reasons for exploring the use of alternative energy source which has a better natural regenerative capacity with less environmental and ecological damage as compared to fossil fuel derivative energy source has become strategic source for alternative energy development.

Exploring renewable energy source which are cheap and have no linkage with food security issues were taken as primary objective for replacement of fossil fuel with renewable energy source as biodiesel.

Ethiopia is one of energy insecure sub-Saharan African country, the country imports the entire petroleum requirement and the demand is increasing from year to year at higher rate and also the country has a suitable ecological condition for the cultivation of castor and jatropha seeds

that can be used as a feed stock for biodiesel production. The diverse ecological climate offers the country to have huge potential of for the cultivation of jatropha and castor non-edible oil seeds which are in turn the promising feedstocks of untapped renewable energy sources of biodiesel.

1.3 Objectives of the study

1.3.1 General objective

The general objective of this study was to investigate biodiesel production potential of mixed jatropha seed oil and castor seed oil (MCJSO), to optimize the selected processes parameters and characterization of the produced biodiesel.

1.3.1 Specific objectives

The specific objectives of the study are:

- To extract crude oil from castor seed and jatropha seed.
- To optimize transesterification processes parameters in biodiesel production from mixtures of castor and jatropha seed oil.
- To characterize biodiesel produced from mixtures of castor seed oil and jatropha seed oil.

1.4 Research questions

Up on the production of biodiesel from mixed jatropha seed oil and castor seed oil, optimization and characterization studies the following research question were answered.

1. How much oil can be extracted from jatropha seed and castor seed?
2. What are the optimal processes parameters for biodiesel production from mixed oils of jatropha and castor seed?
3. What are the physio - chemical quality characteristics of biodiesel produced from mixed castor and jatropha seed oil as compared to the international biodiesel quality standard?

1.5 Justification

This study has great significance in terms of assuring the production of an alternative form of energy that is environmentally friendly from mixed jatropha and castor seed oils (MCJSO) which is a non-edible and abundantly available and grow on non-arable semi-arid and arid land without affecting nearby crops. The agricultural activity they can be practiced as of farm

activity and which has great contribution for additional income generation and energy security issues at the same time. In addition to this the output of the study contribute for energy sector manufacturing industrial development in line with the utilization of castor and jatropha seeds as feedstocks for biodiesel production. Ethiopia is one of the energies in secured nations, as a result the output also contributes to look in to an alternative source of energy which contributes to adjust the trade in balance of the country from importing Petro diesel. This makes jatropha and castor seed crops are eco-friendly plants and promising source of biodiesel than another feedstock.

1.6 Scope of the study

The scope of this study limited to extraction of oil from jatropha seed and castor seed by using Soxhlet extraction method and conversion of the mixed oils into biodiesel through transesterification reaction processes. Trans esterification reaction was carried out by varying reaction parameters alcohol to oil molar ratio, jatropha oil to castor oil volumetric ratio and catalyst concentration to identify the optimal processes parameters on the response parameter which is the biodiesel yield. The theoretical and experimental results were compared and the specific parameters of biodiesel produced were characterized.

CHAPTER TWO

LITRATURE REVIEW

2.1 Introduction

Energy has the most valuable role in the human society, it dictates the technological developments and social progress of a country and in turn improves the quality of life with the rapid economic progress and growing world populations, today the demand for energy is expected to increase higher rate (Babajide,2012).Thus the continuous unmeet in demand and supply in fossil fuel production resulted to an increase in the cost of petroleum fuels that jeopardizes the economic progress of nations. Apart from the global fuel crisis that we are facing, accelerated global warming is the big environmental challenge that the world facing today. In order to solve those problems, for the international community today there is an effort to attain a sustainable economic development as well as environmental security (Bannkovilic *et al.*, 2012).

According to the American society for testing and materials (ASTM), biodiesel is defined as a mono- alkali ester derived from lipid feedstock, such as vegetable oils or animal fats (Avhad & Machat, 2015; Yaddesa & Marchetti, 2017). Biodiesel a promising oxygenated fuel generated from natural and renewable sources, is a fuel comprised of monoalkly esters of long chain fatty acids derived from renewable feed stocks (Ali *et al.*, 2015).

The major components of plant oils and animal fats are triacyl glycerol (TAGS); the esters of fatty acids composition which influence both physical and chemical properties of plant oils and animal fats; correspondingly also deciding the quality of biodiesel (Avhad & Machati, 2015).Vegetable oils derived fuel is one of the alternative fuels which could much the composition futures of diesel oil at relatively low price and which can be adapted for use in existing engine technologies with few or no modifications. It is increasingly being examined as potential substitute for conventional petroleum fuel because of its biodegradability, nontoxic, and relatively environmentally clean burning fuel. In addition to this biodiesel can be blended at any level with mineral diesel to create biodiesel- diesel blend (Atabani, 2012, Atabani *et al.*,2013; Abdulkadir, 2015).

2.2 Feed stocks for biodiesel production

Different types of feed stocks have been assessed and identified for biodiesel production that can be divided into categories based up on the origins of the source obtained as vegetable oils this can be edible oils and non-edible oils, waste oils, animal fats and algal lipids (Avhad & Machati, 2015; Yaddesa & Marchetti, 2017). Globally there are more than 350 oil bearing crops identified as potential source of biodiesel production (Atabani *et al.*, 2013). The wide range of available feed stock for biodiesel production represents one of the most significant factors in producing biodiesel. According to Avhad & Machati (2015) effective replacement of petroleum diesel is feasible only if the feed stocks fulfill two main requirements, the first one is the cost of production of the feedstock should be low or being economical and on the other hand the feed stock should be sufficiently availability at large production scale and environmentally acceptability (Atabani *et al.*, 2013.; Avhad & Machati, 2015.; and Ali *et al.*, 2016). Different sources of literature indicated that, cost of the plant oils used accounts alone for about 60 -80% of the total production cost of biodiesel (Avhad & Machati 2015., Ali *et al.*, 2016). Figure 2.1 shows the general cost break down of feed stocks for biodiesel production (Avhad & Machati, 2015.; Yaddesa & Marchiti, 2017)

As there are wide range of feed stocks so far discovered for the production biodiesel, it is very important to use systematic tool for selection criteria by considering some important factors and take in to account to compare different feedstock for biodiesel production. The most widely used tool used is full life cycle analysis (LCA) (Atbani, 2012., and Atbani *et al.*, 2013).

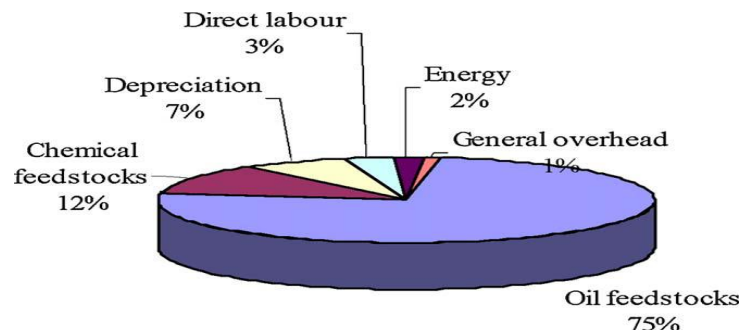


Figure 2.1 : General cost break down of feedstocks for biodiesel production (Avhad & Machati, 2015., Yaddesa & Marchiti, 2017)

2.2.1 Edible oils as feed stock for biodiesel production

Edible oil resources are one of the principal feed stocks for the production of biodiesel and considered as the first generation of biodiesel feedstock because they were the first crops to be used for biodiesel production (Ahmed *et al.*, 2011). edible plant oils which are utilized for the purpose of biodiesel productions are soybeans, palm oil, sunflower, safflower, rapeseed, coconut and peanut (Atabani,2012.;Yaddessa & Marchetti, 2017).However the utilization of edible oils as feed stock for commercialization biodiesel raises many concerns such as food versus fuel crises and major environmental problems such as a serious destruction of vital soil resources, deforestation and usage of much of the available arable land, More ever in the past few decades the price of vegetable oil plants increased dramatically, Which in turn affects the economic viability of edible oils resource based biodiesel industries (Atabani,2012.;Dembries *et al.*,2016.;Yaddessa&Marchiti, 2017).

Despite the above demerits vegetable oils as diesel fuels feedstock have the advantages of their portability, ready availability, renewability, higher heat content, lower aromatic content and bio degradability. And the main disadvantages are higher viscosity, lower volatility and the reactivity of unsaturated hydro carbons (Dembries *et al.*, 2016).

2.2.2. Non-Edible oils as feed stock for biodiesel production

Biodiesel production from non-edible oil seed crops gets considerable attention due to the following reasons , on the first hand non edible oil seed crops can grow on land that is not suitable for agricultural food crop production (i.e. waste lands), eliminate computation for food; i.e. can overcome the problem of controversial food versus fuel issue, also can overcome environmental problems like reduction of deforestation rate, more environmental friendly on the other hand non edible oil seed crops production of non-edible oils are more efficient , produce useful by products and they are very economical in comparison to edible oils (Atabani *et al.*, 2013.; Avhad & Marchetti,2015.;Yaddessa & Marchiti, 2017).

Oils from non-edible feed stock recourses are generally un suitable for humans' consumptions due to the presence of toxic component (Ahmed *et al.*, 2011) and therefore, non-edible oils feed stock resource-based biodiesel production industries are relatively competitive in price as compared to edible oils feed stock resource-based biodiesel production industries (Avhad &

Machati,2015).There are many examples for non-edible oil seed crops such as jatropha tree (*Jatropha curcas*), Karanja (*Pongamia pinnata*), mahua (*Madhuca indica*), castor bean seed (*Ricinus communis*), neem (*Azadirachta indica*), rubber seed tree (*Hevea brasiliensis*), tobacco seed (*Nicotiana glauca*),and rice bran (*Ahmed et al.*, 2011).

Among advantages of non-edible vegetable oils as diesel fuel are their liquid nature, portability, ready availability, renewability, higher combustion efficiency, lower sulfur and aromatic content and higher biodegradability (*Zhang et al.*, 2003).However, the major disadvantages are most non edible oils contain a higher content of free fatty acids (FFAs) which increases the cost of production of biodiesel (*Atabani et al.*, 2013).

2.2.3. Castor seed oil as feed stock for biodiesel production

Castor seed belongs to the Euphorbiaceae family is not only native to Africa but also indigenous to Ethiopia (*Yusuf et al.*, 2015). The plant is drought and pest resistant and can be grown anywhere land is available and also called castor bean (*Atabani et al.*, 2013). Castor seed was considered as one of the most promising non edible oil seed crops due to its high annual seed production and yield and since it can grow on marginal land and semiarid climate (*Patel et al.*, 2016).Castor oil was one of the promising feed stocks for biodiesel production. The oil is produced by means of extraction from castor bean and distinguished by its high content (over 85%) of ricinoleic acid.

On the average, the castor seeds have got an oil contain of 46-55% (*Ogunivi,2006*), its oil having viscous, slightly odor, pale yellow, volatile and non-drying oil characteristics with a bland taste and sometimes used as a purgative (*Atabani et al.,2013, Patel et al.,2016*). The oil is produced distinguished by its high content (over 85%) of ricinoleic acid. No other vegetable oil contains so high a proportion of fatty hydroxy acids. Castor oils have high molecular weight (298), low melting point (5°C) and very low solidification point (-12°C to -18°C) that make it industrially useful, most of all it has the highest and most stable viscosity of any vegetable oil (*Shrirame et al.*, 2011).

The chemical structure of castor oil is of great interest because of the wide range of reactions it affords to the oleo chemical industry and the unique chemicals that can be derived from it. These derivatives are considerably superior to petrochemical products since they are from

renewable sources, bio-degradable and eco-friendly (Nielsen *et al.*, 2011). As castor oil is non-edible, there is no issue of competition with the food market and it can be the promising source of feedstock for biodiesel production. Castor oils and its derivatives are totally soluble in alcohol and display a viscosity of 7- fold higher than other vegetable oils and this elevated level hydro oxalated fatty acids conveys distinctive properties to the oils and biodiesel produced from it (Patel *et al.*, 2016). The use of biodiesel can be either in its pure form or blended from at any level with petro diesel to produce blend (Bouaziz *et al.*, 2017).

2.2.4 Jatropha seed oils as feed stock for biodiesel production

Jatropha curcas L. is a small tree or a large shrub, up to 5-7 m long belonging to the euphrobiaceae family (Atabani *et al.*, 2013). It is drought resistant plant capable of surviving in abandoned and fallowed agricultural lands. It is well adapted in arid and semi-arid regions, in this region it only yields 0.5 tons per hectare, and the plant needs low fertility and moisture content, is important for climate change issues (Demirbas *et al.*, 2016). Depending on the variety of the seed and all other conditions the decorticated seed of jatropha contains an oil content between the range 20-60% in seeds and 40-60 on kernels (Silitogel *et al.*, 2013) , the oil contains approximately 24.60% of crude protein , 47.25% of crude fat and 5.54% of moisture content : the oil fraction of the plant consists of both saturated (14.2% Palmatic acid and 7% steric acid) and unsaturated fatty acids containing (44.7% oleic acid and 32.8 % linoleic acid) (Demirbas *et al.*, 2016).

2.3. Mixed feed stock for biodiesel production

Industrial production of biodiesel still faces a challenge in terms of feed stock availability and various steps involved in fermentation processes (Patel *et al.*, 2012). As the biodiesels can be produced from diverse crops, each country should adopt a strategy to exploit the comparative advantage of different crop in terms of economic, environmental and energy security concerns (Jena *et al.*, 2010). Mixed feed stock for biodiesel production is utilized for the purpose of improvement of the quality of biodiesel in terms of both the physical and chemical characteristics and so as to develop cost effective systems in terms of production cost. Therefore, it is very important to try different mixtures of oils for biodiesel production to full fill the requirement of the biodiesels without depending the availability of specific oil (Jena *et al.*, 2010).

various researches are conducted the production of biodiesel from mixed feed stocks among this blend of jatropha and palm (Sarini *et al.*, 2007), biodiesel blends from edible and non-edible oils (Siltonga *et al.*, 2013), eco-diesel from castor oil in diesel, bio-fuel, alcohol triple blends by (Hurtodo *et al.*,2019).

2.4. Biodiesel production processes

Biodiesel production involves three major steps that begin with processing of raw feedstock (seeds) to the finished products (biodiesel and glycerol by-product). These include, extraction of oil from raw feedstock, refining of the oil (to produce straight vegetable oil) and esterification of the oil to obtain the biodiesel.

2.4.1. Feed stock preparation

The pre-requisite for oil extraction is seed preparation this involves removal of the outer layer of the fruit to expose the kernel or seed and drying to reduce the moisture content (Yaddessa & Marchiti, 2017). Rape seeds have to be dried first from moisture content of about 15% to 9 %, but only if it is to be stored for more than ten days. Subsequently, the rape seeds are cleaned (Takavarasha *et al.*, 2006). Then seeds are decorticated manually so as to remove the outer shell of the seeds, after removing the outer shell it is important to allow the seed to dry further so as to obtain the desirable moisture content.

2.4.2 Oil extraction

Extracting oil from oil seeds is as old as mankind, but the procedures and technologies have evolved. In this second step of the production chain for biodiesel, the oil contained in the seeds has to be expelled or extracted. In extracting oils from oilseeds, the primary goal is to disrupt the cell walls, thereby liberating as much oil as possible (Johnston, 2006). Generally, oil extraction from oilseed crops is similar with minor variations. The main products of the oil extraction operation are crude oil and the important by products such as seeds or kernel cakes. There are three methods that have been identified for the extraction of the oil this are mechanical extraction, solvent extraction and enzymatic extraction (Atabani, 2012; Atabani *et al.*, 2013; Yaddessa & Marchiti 2017). The chemical structure of common vegetable oils was described in figure 2.2.

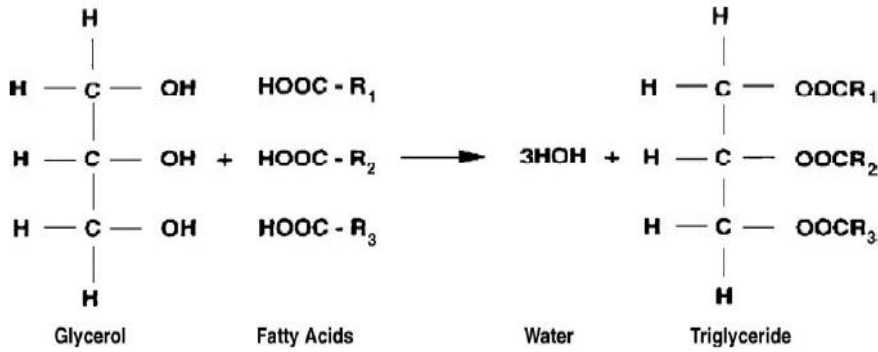


Figure 2.2: The chemical structure of vegetable oil (Singh & Singh, 2010)

2.4.2.1 Mechanical extraction

The technique of oil extraction by mechanical presses is the most conventional among other methods (Yaddessa & Marchiti, 2017). The working principle in mechanical extraction is either a manual ram press or an engine driven screw press (Atabani, 2012). Mechanical expellers or press can be feed with either whole seeds or kernels or a mix of both, but in common practice is to use whole seed (Atabani *et al.*, 2013). It has been found that, engine driven screw press can extract 68- 80%, while the ram presses only achieved 60-65 % of the available oil (Atabani *et al.*, 2013). This border range extraction efficiency is mainly due to the fact that the seeds are subjected to a different number of extractions through the expeller (Leuang *et al.*,2010). Another problem associated with conventional mechanical press is their design is suited for some particular seeds, and therefore the yield is affected if used for other seeds. It has been found that the pretreatment of the seeds can increase the yield of pressing up to 89% after single pass and 91% after dual pass (Atabani, 2012; Atabani *et al.*, 2013).

2.4.2.2 Solvent extraction (chemical extraction)

Solvent extraction (chemical extraction) also called leaching (Yaddessa & Marchiti, 2017) is the technique of removing one constituent from a solid by means of a liquid solvent (Atabani *et al.*, 2013). There are many factors influencing the rate of extraction, these are particle size, the type of liquid chosen, temperature and agitation of the solvent (Atabani, 2012; Atabani *et al.*, 2013).In general, small particle size has a better performance in solvent extraction because it allows for a greater interfacial area between the solid and liquid (Atabani *et al.*, 2013).The liquid chosen should be a good selective solvent and its viscosity should be sufficiently low to

circulate freely (Atabani, 2012). Temperature also affects the rate of extraction as the solubility of the material will increase with increasing temperature (Atabani, 2012;Atabani *et al.*, 2013). Agitation of the solvent also affects as it increases the eddy diffusion and therefore increases the transfer of the material from the surface of the particle. There are three sub classified techniques that are commonly employed in solvent extraction methods which are hot water extraction, Soxhlet extraction and ultrasonic technique (Atabani, 2012; Atabani *et al.*, 2013).

Vegetable oil extraction using solvents is commonly used at the industrial scale. This method offers up to 99% of extraction efficiency and high quality and purity of the oil, compensating the high costs of these extraction processes. Between all solvents used to extract vegetable oils, hexane is the most used. After extraction, the solvent is removed by distillation and can be condensed and reused. However, in the case of castor seeds, the solvent can also extract toxic compounds such as ricin and contaminate the oil (Gonzalze *et al.*, 2020).

Although the chemical extraction method using n-hexane results the higher oil yield which makes it the most preferable, much more reaction time as compared to the others, negative environmental impact as a result of waste water generation, higher specific energy consumption and higher emission of volatile organic compounds and human health impacts (due to working exposures with hazards and inflammable chemicals) were the disadvantages of Solvent extraction (Atabani *et al.*, 2013).

2.4.2.3 Enzymatic oil extraction

In enzymatic oil extraction suitable enzymes are used to extract oil from the crushed seeds (Yadessa & Marchiti, 2017).The processes have main advantages of environmentally clean and do not produce volatile organic compounds. However much longer reaction time is considered as the main disadvantage associated with this technique (Atabani, 2012). In order to solve the problems aqueous enzymatic oil extraction method is introduced and this method use of alkaline protease as a catalyst (Atabani *et al.*, 2013).

2.5. Characterization of the oil and biodiesel produced

Many factors influence the quality of biodiesel produced such as the quality of the fed stock, fatty acid composition, type of production, refining processes and post production parameters (Bhuiya *et al.*, 2016). Therefore, Characterization of the oil is important to know the physical

and chemical properties of the biodiesel produced, quality standards are prerequisite for the commercial use of any fuel product. The standards serve as guide lines for the production processes, guarantee customers with high quality of fuel and provide authorities with approved tools for assessment of safety risks and environmental pollution (Babajide, 2011). The most used standard specifications of biodiesels are American society of testing materials (ASTM6751), European standard (EN) 14214 (Bhuiya *et al.*, 2016).

These standards specify certain physical and chemical characteristics of the biodiesel, which include cetane number, density (kg/m^3), viscosity (mm^2/s), caloric value (MJ/Kg), cloud and pour point ($^{\circ}\text{C}$), Acid value (mg KOH/g oil), ash content (%), flash point ($^{\circ}\text{C}$), copper corrosion, carbon residue, water content and sediment, distillation range, sulfur content (mg/kg) and oxidation stability represents the American society of testing materials (ASTM6751) and European standard (EN)14214 specifications of biodiesel fuels along with the ASTM D975 for petroleum diesel fuel (Atabani, 2012, ;Bhuiya *et al.*, 2016).

2.5.1 Density

Density is physical property and used to evaluate the precise volume of the fuel necessary to supply an adequate composition, specific density is the ratio of density of a given substance or material per density of water at given specific temperature (Yoon, 2008; Siltonga *et al.*, 2013). The density of the diesel oil is important because it affects in engine operation and thus gives an indication of the delay between the injection and combustion of the fuel in diesel engine (ignition quality) and the energy per unit mass, specific energy. Vegetable oils have a density value within the range of 912 to 921 (kg/m^3) (Atabani *et al.*, 2013).

Biodiesel fuels are denser and less compressible than the diesel fuels and this characteristic is one of the most critical obstacles against extensive use of biodiesel. The presence of unsaturated acid with more than two double bonds will increase the density of biodiesel. The density of biodiesel fuel is measured using ASTM D1298 and EN ISO 3675/12185 test methods (Atabani *et al.*, 2013, Bhuiya *et al.*, 2016). As per this standard this standard density should be tested at temperature reference of 15 to 25 $^{\circ}\text{C}$ (Atabani, 2012).

2.5.2. Kinematic viscosity

Kinematic viscosity is coefficient defined as the ratio of dynamic viscosity of a fluid to its density (Yoon, 2008) and Viscosity is defined as the resistance of liquid to flow (Atabani,

2012; Atabani *et al.*, 2013; Silitonga *et al.*, 2013). It refers to the thickness of the oil, and is determined by measuring the amount of time taken for a given measure of oil to pass through the orifice of specified size. Kinematic viscosity is the most important property of bio diesel since it affects the operation of the fuel injection equipment, particularly at low temperature when an increase in viscosity affects the fluidity of the fuel (Atabani, 2012; Atabani *et al.*, 2013).

The kinematic viscosity of biodiesels is determined using ASTM D 445 and according to EN ISO 3104 test methods, according to this test methods the kinematic viscosity of biodiesels is (1.9-6.0 mm²/s) in line with ASTM D 445 and according to EN ISO 3104 (3.5-5.0 mm²/s), (Babajide 2011; Atabani *et al.*, 2013; Bhuiya *et al.*, 2016)

2.5.3. Acid number (AN)

The acid number (AN) is a measure of the carboxylic acid groups free fatty acids (FFAS) contained in fresh fuel sample (Atabani *et al.*, 2013; Bhuiya *et al.*, 2016). Acid value or neutralization number can be expressed as mg of KOH required to neutralize one gram (1gm) of fatty acid methyl esters. 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).

(FAMES) acid number determined using ASTM D 664 and EN 14104 test methods and both standards approved maximum value of 0.5 mg KOH/g. Higher amount of free fatty acids leads to Higher values of Acid number (AN) of the oil have undesirable effect in processes system operations and can cause severe corrosion in fuel supply system and internal composition engine (Atabani, 2012; Atabani *et al.*, 2013; Bhuiya *et al.*, 2016).

2.5.4. Free Fatty Acids (FFA)

This is the amount of free fatty acids contained in the product. Fats and oils are compounds containing three fatty acids each chemically connected to oxygen on glycerin molecule, called triglycerides. Free fatty acids are those structures that are no longer connected to the glycerin. They are a degradation product and a measure of the quality of the fat. A high-quality fat has a low FFA level (Atabani *et al.*, 2013; Bhuiya *et al.*, 2016 ; Yasin *et al.*, 2013).

2.5.5. Saponification value of the oil

Production of biodiesel using an alkali catalyst always produces some amount of soap. After the transesterification reaction is complete, the left-over catalyst and soap tends to concentrate in the glycerol phase; however, some soap and a small amount of catalyst may be left in the biodiesel phase. During the process development, it can be useful to know the amount of soap formed, and how effective the washing process was in removing this soap (Ma and Hanna, 1999).

2.5.6. Iodine value

The iodine value (IV) is an index of the number of double bonds in biodiesel which measures the degree of unsaturation of the biodiesel (Encinar *et al.*, 2010). As the ASTM D6751 does not include specification for IV the determination of iodine value (IV) is conducted according to EN14111 test standards and methods. This standard set a maximum value of 120 mg I₂ /g (Bhuiya *et al.*, 2016).

2.5.7. Moisture content

Moisture content is the percentage amount of water which remains into mono alkali fatty esters. Therefore, it must be removed before biodiesel production or during Easter purification. It is measured according to ASTM E 203 specification and according to this test method a maximum value of 0.05% (m/m) or up to 1500ppm for water is allowed (Atabani, 2012 ; Bhuiya *et al.*, 2016).

2.5.8. Cetane number (CN)

The cetane number is an indication of fuel readiness to auto-ignite when it has been injected in to diesel engine. It was considered as one of the most important parameters in feedstock selection for biodiesel production. The cetane number increases with increasing chain length and saturation fatty acids. Lower CN tends to cause knocking, increase gaseous and particulate matter emissions. Furthermore, excessive engine deposits are formed due to incomplete combustion (Babajide, 2011; Bhuiya *et al.*, 2016).

2.5.9. Flash point (FP)

The flash point of fuel is the temperature at which the vapor or the gaseous component of the fuel turns to ignite or it is the temperature at which a biodiesel ignites when exposed to flame

or spark (Siltonga *et al.*, 2013). Petro-diesels have got a flash point within the range of 50 - 80° c whereas biodiesels have a flash point of over 160°c which signifies that the fire hazard of biodiesels is much less than with other commonly used conventional fuels (Babajide, 2011).Flash point varies inversely with the fuel's volatility. The higher value of FP for biodiesel indicates that the biodiesel is safe for mobility, handling and storage purpose (Bhuiya *et al.*, 2016).

2.5.10 Cloud point (CP) and Pour point (PP)

The Cloud point (CP) of the fuel is the temperature at which a cloud of wax crystals first become visible when the fuel is cooled under controlled conditions during standard test. Pour point (PP) of the fuel is the temperature at which the amount of wax forms a solution is enough to get the fuel (Siltonga *et al.*, 2013). Thus, it is the lowest temperature at which the fuel can flow. The Cloud point (CP) and Pour point (PP) are measured using ASTM D 2500 EN ISO 23015 and D 97 procedures (Atabani *et al.*, 2013).

2.5.11 Caloric value (CV)

Caloric value or heating value is the amount of heat energy released by the combustion of unit value of fuels, clearly higher caloric values are desirable for combustion engine, it has been found that the caloric values of biodiesels are lower than that of diesel fuel due to the higher oxygen content which is about 10-11% in diesel fuel. The requirement for the caloric value is not specified in both D 6751 and EN 14214 biodiesel standards the testing method for the caloric value is done in line with the EN 14213(biodiesel for heating purpose) procedures (Bhuiya *et al.*, 2016).

2.5.12 Oxidation stability

Oxidation stability is an indication of the degree of oxidation, potential reactivity with air and can determine the need for anti-oxidants. Oxidation occurs due to the presence of heat, trace metal, peroxides, light, unsaturated fatty acids chains and the double bonds, which reacts with oxygen being exposed to air. It has been observed that higher unsaturated carbon chain leads to poorer stability which the oxidation rates depend on the number and position of double bonds. The chemical composition of biodiesels fuels makes it more suitable to oxidative degradation than fossil fuel (Atabani *et al.*, 2013)

2.5.13 Carbon residue

Carbon residue for biodiesel fuel is important than that of the diesel fuel owing to its higher correlation with the presence of FFAS, glycerides, soaps, polymers higher unsaturated fatty acids as well as inorganic impurities. However, carbon residue is formed by decomposition of subsequent pyrolysis of the fuel components that can clog the fuel injector (Bhuiya *et al.*, 2016). Carbon residue test is used to indicate the extent of deposits resulting from the composition of the fuel (Atabani *et al.*, 2013). For biodiesel produced from vegetable oil feedstock has carbon residue limit of max 0.05% (m/m) according to ASTM D 4530 and max 0.3(m/m) according to EN ISO10370 respectively.

2.5.14 Sulfur content

Sulfur dioxide is a respiratory irritant, which can affect human health and damage plants. There are a number of natural and anthropogenic sources of sulfur dioxide, but the latter is by far the largest source. Burning fossil fuels in power stations has been the main source of sulfur dioxide. Composition of fuel containing sulfur causes emission of sulfur oxides which was one of the sources of atmospheric air pollution (Scragg, 2009). Most of vegetable oils animal fat-based biodiesel have very low levels of sulfur content therefore contribute low level of emission of sulfur oxides to the atmosphere (Atabani *et al.*, 2013)

2.5.15 Free and total glycerin

Free and total glycerin is measurement of how much triglyceride remains uncontrolled in to methyl esters. Total glycerides are calculated from the amount of free glycerin, mono glycerides, di glycerides and tri glycerides (Atabani *et al.*, 2013)

2.6 Technologies for the production of biodiesel

With the advancement of science and technology, efforts are still continuing to develop and improve vegetable oil properties in order to approximate the properties of diesel fuel. Processes technologies that have been widely used to produce biodiesel from various non-edible feedstock these methods include; pyrolysis, micro emulsification, dilution and transesterification (Sirvastav & Prasad, 2000; Taghizade, 2016).

2.6.1 Pyrolysis

Pyrolysis (thermal cracking) is the thermal decomposition of the organic matters in the absence of oxygen and in the presence of catalyst into another organic compound (Taghizade, 2016). The paralyzed materials can be vegetable oils, animal fats, and natural fatty acids. Thermal decomposition of triglycerides produces alkanes, alkenes, alkaline, aromatic and carboxylic acids (Sirvastav & Prada, 2000). It has been observed that Pyrolysis (thermal cracking) processes are simple, effective, wattle and pollution free.

Pyrolysis of vegetable oils can produce a product that has high cetane number, low viscosity acceptable amount of sulfur, water and sediment content, acceptable copper corrosion values. However, ash content, carbon residue and pour points are unacceptable (Singh & Singh 2010; Atabani, 2012; Atabani *et al.*, 2013).

2.6.2 Micro emulsification technique

Micro emulsification is defined as transparent, equilibrium thermodynamically stable colloidal dispersion of micro structure with diameter ranges from 100 to 1000 Å (Sirvastav & Prada, 2000). Micro emulsion can be made of vegetable oils with an ester and dispersant (co solvent), or of vegetable oils, and alcohols such as ethanol, butanol, hexanol, and a surfactant and cetane improver, with or without diesel fuel. Micro emulsification has been considered as reliable approach to solve the problem of the high viscosity of vegetable oils (Atabani *et al.*, 2013; Aghazadeh, 2016).

2.6.3. Dilution

Dilution method does not require any chemical processes. Non-edible oils can be diluted with diesel so as to reduce viscosity and improve the performance of the engine. It has been reported that the substitution of 100% vegetable oil for diesel fuel is not practical. Therefore 20-25% of vegetable oil to diesel has been considered to give good result. The use of blends of conventional diesel fuel with variety of non-edible oils such as rubber seed, turpentine, linseed, cotton seed, jatropha curcas oils has been described in literature (Singh & Singh 2010; Atabani *et al.*, 2013).

2.6.4 Trans esterification processes

Transesterification processes were the best method among other approaches due to its lowest cost and simplicity. Biodiesel is the main product of this process and glycerol is one of an important bi product (Taghizade,2016).In transesterification (alcoholysis) reaction processes, methanol and ethanol are the two main light alcohols commonly used due to their relative low cost. Tran's esterification consists of a number of consecutive, reversible reactions and the processes have been widely used to reduce the viscosity of triglycerides (Sirvastav & Prasad, 2000). The triglycerides are converted step wise to diglycerides, monoglycerides (Sahide & Jamel, 2011).

Normally most of the oils are converted into biodiesel esters using the base catalyzed transesterification method. But there are certain exceptional cases where in direct transesterification cannot be performed. Such cases appear in raw vegetable oils (non-edible oil) like olive oil, jatropha, castor and cotton seed oil, etc. because these raw vegetable oils possess high free fatty acid (Sattanathan, 2015).

Table 2.1: Chemical properties of castor and jatropha seed oil (Vashist *et al.*, 2011)

Parameter	JSO	CSO	JOME 100%	COME 100%	High speed Diesel
Density at 25 ⁰ c (Kg/m ³)	960	950	875	905	810
Kinematic viscosity (mm ² /s)	240	230	13	12.5	3.05
Flashpoint (⁰ c)	340	305	140	115	53
Firepoint (⁰ c)	350	320	150	121	56

2.7. Biodiesel production processes by transesterification reaction

Common vegetable oils or animal fats are esters of saturated and unsaturated monocarboxylic acids with the trihydric alcohol glyceride. The esters are called triglycerides which can react with alcohol in the presences of catalyst a process is known as transesterification. The simplified form of its chemical reaction is presented in equation as shown on figure 2.3.

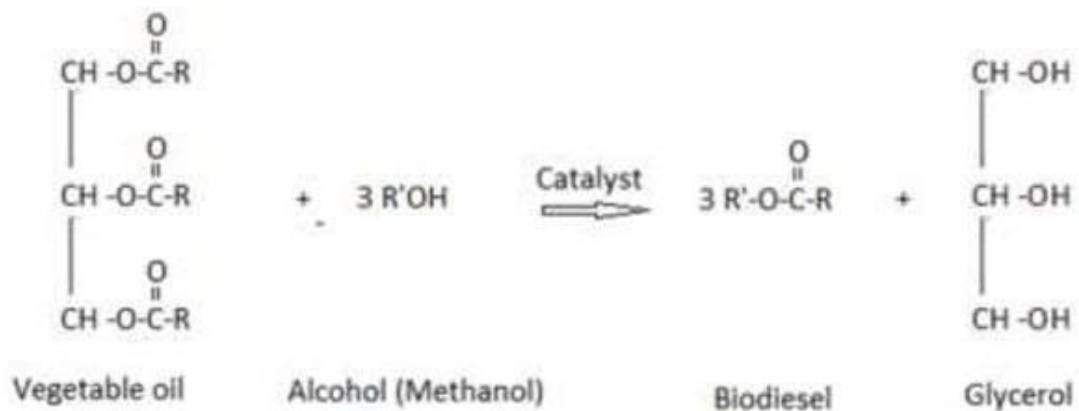


Figure 2.3: Transesterification's reaction of triglycerides (Stamenkovic *et al.*, 2011; Zhang *et al.*, 2003)

The most common way to produce biodiesel is by transesterification, which refers to a catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl esters (i.e., biodiesel) and glycerol (Figure 2.3). Triacylglycerols (triglycerides), as the main component of vegetable oil, consist of three long chain fatty acids esterified to a glycerol backbone. When triacylglycerols react with an alcohol (e.g., methanol), the three fatty acid chains are released from the glycerol skeleton and combine with the alcohol to yield fatty acid alkyl esters (e.g., fatty acid methyl esters or FAME). Glycerol is produced as a by-product. Methanol is the most commonly used alcohol because of its low cost. The general processes flow diagram of biodiesel production from non-edible oil seeds was shown on figure 2.4.

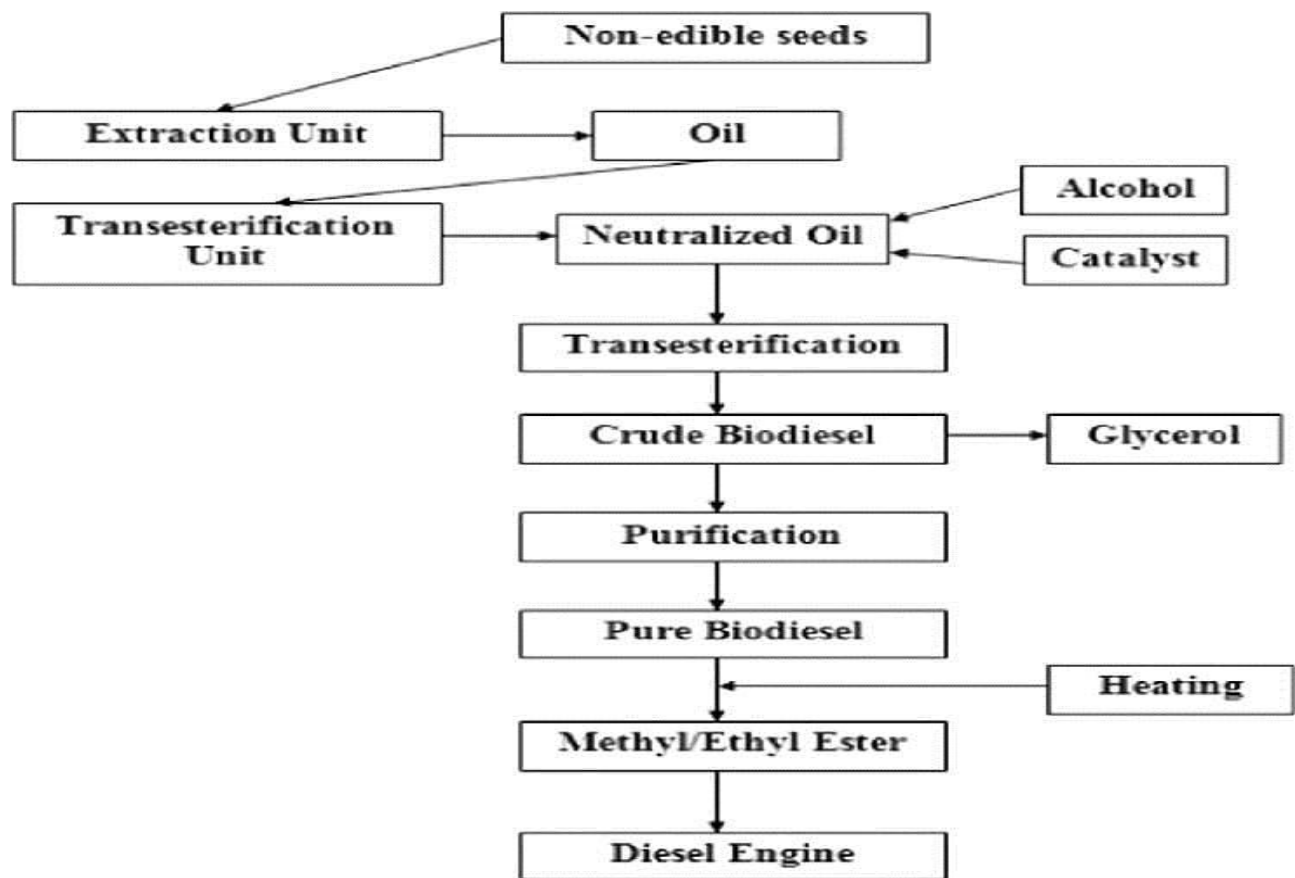


Figure 2. 4: Flow diagram of the transesterification of triglycerides (vegetable oil) with methanol to produce fatty acid methyl esters.

2.7.1 Homogenous acid catalyzed transesterification processes

An acid catalyst is used for the processing of triglycerides for biodiesel production. Sulphuric acid, sulphonic acid and hydrochloric acid are used as acid catalysts. The process starts by mixing the oil directly with the acidified alcohol, and then the separation and transesterification occur in one step, with the alcohol acting both as a solvent and as an esterification reagent (Stamenkovic *et al.*, 2011; Zhang *et al.*, 2003)

Despite its insensitivity to free fatty acids in the feedstock, acid-catalyzed transesterification has been largely ignored mainly because of its relatively slower reaction rate. Freedman *et al.* (1984) investigated the transesterification of soybean oil with methanol using 1 wt.% concentrated sulfuric acid (based on oil). They found that at 65°C and a molar ratio of 30:1 methanol to oil, it took 69 h to obtain more than 90% oil conversion to methyl esters. Canakci and Gerpen (1999) studied the effects of the molar ratio of alcohol to soybean oil, the reaction

temperature, the amount of catalyst, and the reaction time on the ester conversion by acid-catalyzed transesterification. (Zhang *et al.*, 2003)

2.7.2 Enzyme catalyzed processes

Enzyme such as lipase catalyzed reactions have advantages over the previously mentioned methods which include: the generation of no by-products, easy product recovery, mild reaction conditions, catalyst recycling, insensitivity to free fatty acid and water content in waste cooking oil (Du *et al.*, 2004; Ha *et al.*, 2007). Enzyme-based transesterification is carried out at moderate temperatures with high yields, but this method cannot be used in industry today due to high enzyme costs, and the problems related to its deactivation caused by feed impurities.

2.7.3 Homogenous alkaline catalyzed transesterification

Conventional biodiesel production is done via base catalyzed transesterification using homogeneous alkaline catalysts. This is the most commonly used technique as it is considered to be the most economical process (Singh *et al.*, 2006; Stamenkovic *et al.*, 2011). According to Zhang *et al.*, (2003) alkali-catalyzed transesterification on the laboratory scale have been carried out at reaction temperature near the boiling point of the alcohol (e.g., 60°C for methanol) and a 6:1 molar ratio of alcohol to soybean oil were recommended (Freedman *et al.*, 1984; Nouredini and Zhu, 1997).

Homogenous alkaline catalyzed transesterification is the most employed in commercial sectors. The processes use homogenous catalysts such as an alkaline metal alkoxides and hydroxides, and sodium or potassium carbonates. In the method of basic metanalysis, almost in all the cases sodium hydroxide or potassium hydroxide have been used, both in concentration from 0.4% to 2% w/w of oil (Zakir, 2016). The reasons these catalysts preferred are best operative conditions, high conversion rate in minimum time, good catalytic activity and economical.

2.8. Factors that influence the transesterification reaction.

The yield of biodiesel in the process of transesterification is affected mainly by process parameters which include; the presence of moisture and free fatty acids, reaction time,

reaction temperature, catalyst and molar ratio of alcohol and oil (Sirvastav and Prasda, 2000). The effect of each parameter discussed in detail as follows.

2.8.1 Effect of temperature and reaction time

2.8.1.1 Effect of temperature

Reaction temperature is the important factor that will affect the yield of biodiesel. For example, higher reaction temperature increases the reaction rate and shortened the reaction time due to the reduction in viscosity of oils. Usually, the transesterification reaction temperature should be below the boiling point of alcohol in order to prevent the alcohol evaporation (Sirvastav and Prasda, 2000). The range of optimal reaction temperature may vary from 50°C to 60°C depends upon the oils or fats used. Therefore, the reaction temperature near the boiling point of the alcohol is recommended for faster conversion by various literatures.

2.8.1.2 Effect of reaction time

Reaction time is another factor which affects the transesterification process of biodiesel production. The increase in fatty acid esters conversion observed when there is an increase in reaction time (Sirvastav & Prasda, 2000).

2.8.2 Effect of molar ratio of alcohol to oil

One of the most important parameters affecting the yield of biodiesel is the molar ratio of alcohol to triglyceride. Theoretically the ratio for transesterification reaction requires three moles of alcohol for one mole of triglyceride which means to produce three mole of fatty acid ester and one mole of glycerol required (Sirvastav & Prasda, 2000). On the other hand, an excessive amount of alcohol makes the recovery of the glycerol difficult, so that the ideal alcohol/oil ratio has to be established empirically, considering each individual process (Sirvastav & Prasda, 2000).

2.8.3 Effect of catalyst on transesterification processes

The type and amount of catalyst require in the transesterification process usually depend on the quality of the feedstock and the production process of biodiesel. For a purified feedstock any type of catalyst could be used for the transesterification process. However, for feedstock with high moisture and free fatty acids content, homogenous transesterification process is

unsuitable due to high possibility of saponification process instead of transesterification process to occur.

Alkaline metal hydroxides (KOH and NaOH) are highly efficient catalysts for the transesterification reaction of glyceride with methanol, which completes at a short reaction time (Wang *et al.*, 2012.; Sirvastav & Prada, 2000). The yield of fatty acid alkyl esters generally increases with increasing amount of catalyst. Most commonly used catalyst for transesterification is sodium hydroxide (NaOH) or potassium hydroxide (KOH) are easily soluble in methanol to form sodium and potassium methoxide (Silitonga *et al.*, 2013).

2.8.4 Mixing Intensity

Most literatures indicate that during the transesterification reaction, the reactants initially form a two-phase liquid system. The mixing effect has been found to play a significant role in the slow rate of the reaction. As phase separation ceases, mixing becomes insignificant. Understanding the effect of mixing on the kinetics of the transesterification process forms the basis for process scale-up and design (Silitonga *et al.*, 2013).

2.8.5 Free fatty acid and water content

The water and FFA content are key parameters for determining the viability of the vegetable oil transesterification process. In the transesterification process the vegetable oil should have an acid value less than 2.5% and all materials should be substantially anhydrous. If acid value is greater than 2.5%, pretreatment is required before transesterification takes place. Water content is an important factor in the conventional catalytic transesterification of vegetable oil. Water can cause soap formation and frothing. In general, literature among listed factors affect the yield of biodiesel in the transesterification process, the most crucial parameters were the molar ratio of alcohol to oil, temperature and catalyst concentration. The chemistry of saponification processes was shown on figure 2.5.

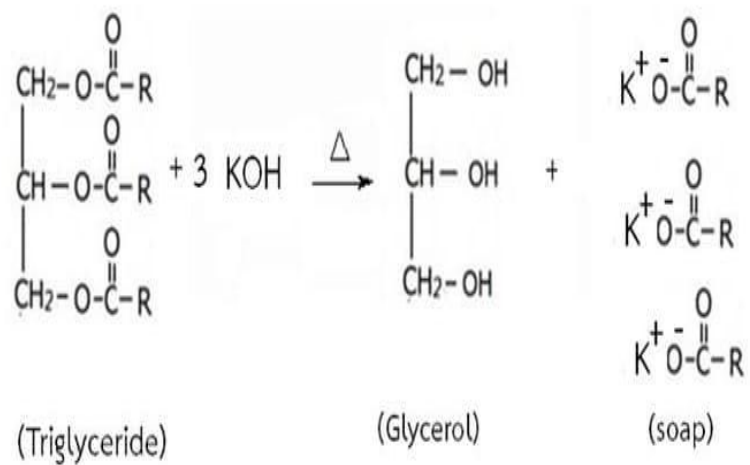


Figure 2.5: saponification of triglyceride

CHAPTER THREE

MATERIALS AND METHODS

3.1 Description of the study area

The samples of castor and jatropha seeds were collected from Gojeb district, Gimbo woreda in Kaffa zone, of SWRS and located at a distance of 430 Km from Addis Ababa the capital of Ethiopia and 35 Km from Bonga the capital of kaffa zone. Figure 3.1 below shows the map of the study area.

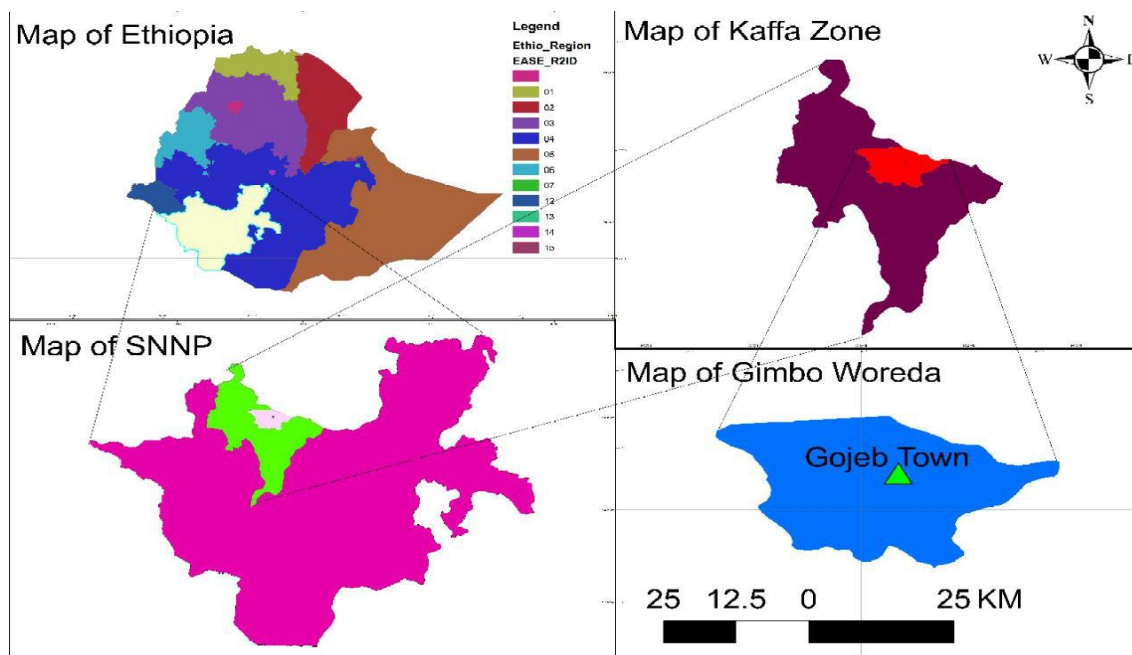


Figure 3.1: Map of the study area

3.2. Materials and equipment used

The main raw materials used in this study were castor seed oil, jatropha seed oil, analytical grade methanol, ethanol, normal hexane and potassium hydroxide oxide as alkaline base catalyst. Sodium hydroxide, diethyl ether, phenolphthalein indicator, hydrochloric acid, aqueous potassium iodide, were also used to determine the various physicochemical properties of the biodiesel and its raw material (castor oil and jatropha oil). The major equipment's and apparatus used in this study were Soxhlet apparatus, rotary evaporator,

pycnometer, digital vibro-viscometer, three necked round bottom flasks (Glass reactor) equipped with mechanical stirrer and condenser, separating funnel, Centrifuge, conical flask, digital balance, oven, high temperature furnaces and mortar and pestle. Summaries of the chemicals used during the study with their grade and purity are presented in table 3.1 below.

Table 3. 1. Chemicals and reagent used

S. N	Chemicals and reagents	Grade/purity
1	n-hexane	99% w/w
2	Methanol	99% w/w
3	Ethanol	98% w/w
4	Phosphoric acid	98% w/w
5	Hydrochloric acid	98% w/w
6	Sulfuric acid	98% w/w
7	Sodium hydroxide	Analytical grade
8	Potassium hydroxide	Analytical grade
9	Diethyl ether	Analytical grade
10	Phenolphthalein indicator	Analytical grade
11	Sodium thiosulphate	Analytical grade
12	Aqueous potassium iodide	Analytical grade
13	Distilled water	100%
14	Chloroform	Analytical grade

3.3. Experimental methods

All experimental works were conducted at Jimma University department of Chemistry, Organic and Inorganic Chemistry research laboratory. Castor and jatropha seeds were collected from Gojeb district at Gimbo woreda in Kaffa zone. While collecting the feed stock careful on-site screening operations including selection of the beans according to their condition were implemented. Seeds with poor quality are rejected and seeds in good condition were cleaned further, dried open to the sun, the outer shell (the cotyledon) of the seed removed, the seeds are crushed and oven dried. The moisture content of the seeds was determined prior the extraction of the oils.

Oil extraction was done from crushed pastes of castor and jatropha seed independently by means of chemical solvent using n-hexane. The yield of the oils from each feedstock was determined. The castor and jatropha oils were mixed at different mix ratios and was subjected further to treatment processes to improve the quality of oil which in turn improves the quality

of biodiesel .the mixed oils were analyzed for the most important physicochemical properties which have significant effect on the desired product quality were determined prior to the biodiesel production processes. The mixed castor and jatropha oils were subjected to a transesterification reaction with methoxide (a mixed solution of methanol and potassium hydroxide) for biodiesel production.

The crude biodiesel was subjected to separation processes of glycerol and methanol. Glycerol was separated using a separator funnel whereas methanol was distilled off. As the separation processes completed, the biodiesel was subjected to the washing process with hot distilled water to remove the soluble impurities. And dried in an oven so as remove undesirable moisture contained in it. Finally, the obtained biodiesel was characterized and checked for its characteristic's properties with the international standard. The general experimental setup is shown in figure 3.2.

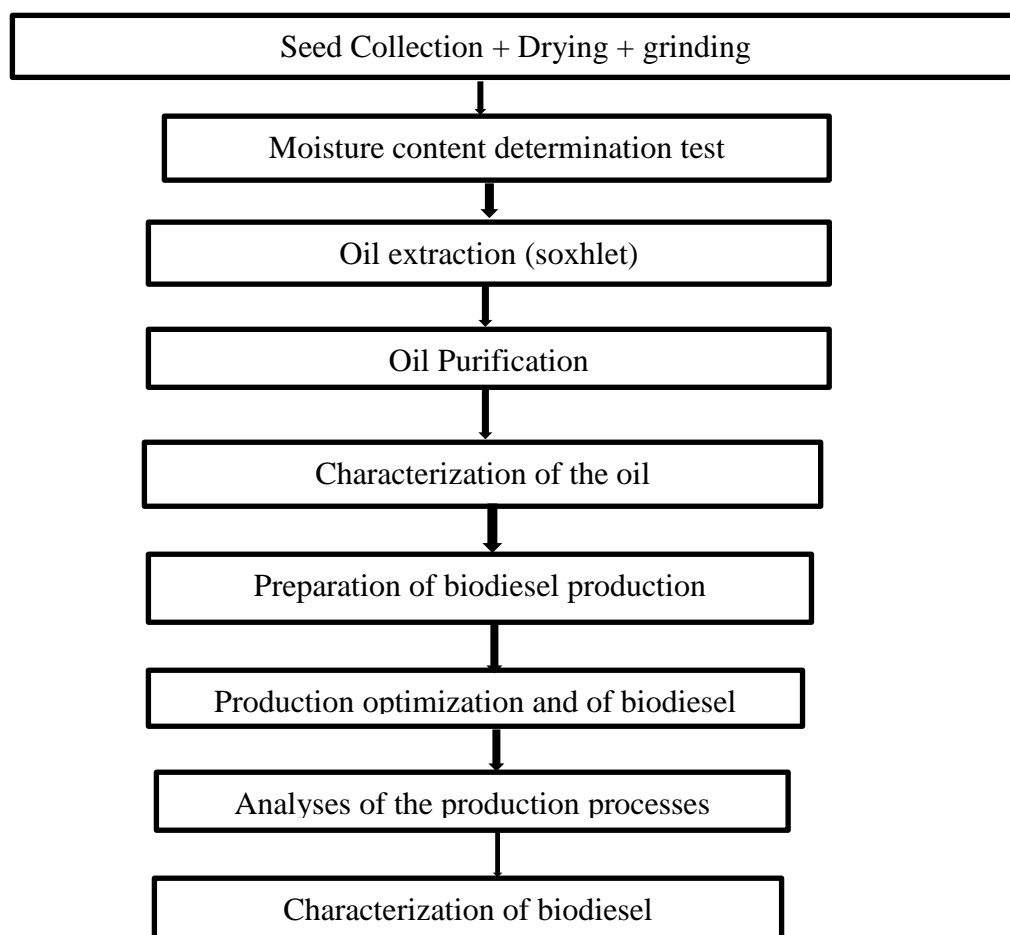


Figure 3.2: The general experimental setup

3.4 Seed collection and preparation

Castor and jatropha seed were collected from Gojeb site and transported to Jimma University department of Chemistry, Organic and Inorganic Chemistry research laboratory. For both seeds hand cleaning was implemented to remove the impurities and foreign materials contained the cleaned seeds were dried open to the sun for 5 days until the cover of the bean starts to crack. The outer shell of the seed was deshaled from nibs (cotyledon) manually by hand.

The deshaled seeds were extra dried to the sun for five days and crushed to paste by using mortar and pestle. The pastes were further dried in to the oven at 105°C for 2hr to reduce the moisture content to create a favorable condition for easy oil extraction. The dried pastes were weighted packed in to plastic bags per 60 grams each and ready for the oil extraction processes. The pictorial representations of the activates under taken as castor and jatropha seed preparation processes was presented in figure 3.3.



Figure 3.3: The castor and jatropha seed preparation processes

3.5 The proximate analysis of the seeds

3.5.1 Determination of the seed moisture content (MC)

The proximate analysis of the seed's moisture content was analyzed according to ASTM D1762 procedures and test standards. 50 grams of the cleaned sample of castor and jatropha seeds beans were prepared the cleaned and dried crucible weight was measured. The crucible with crashed Castor and jatropha Seeds were dried in to an oven at 105°C for 7h. The sample weight was recorded every 2 hours continuously until 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. 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. The moisture content of the feed stock was calculated by using the equation 3.1.

$$MC\% = \left[\frac{W_1 - W_2}{W_2} \right] \times 100 \quad [3.1]$$

Where: W_1 is initial weight of each seed powder sample before drying,

W_2 is final weight of each powder sample after drying and (MC) % is moisture content.

3.6. Seed oil extraction from castor and jatropha seed paste

Solvent extraction method as described by (Akpan *et al.*, 2006) was adopted for the extraction of the oil using normal hexane as a solvent. 60g of each castor and jatropha seed pastes were packed in a thimble independently and placed at the center of Soxhlet apparatus. 180 ml normal hexane was poured into 250 ml three necked round bottom flask. Then after the flask and the Soxhlet apparatus were fixed together and connected to a condenser. The extraction process was carried for three hours at a constant temperature of 65°C (near the boiling point of the solvent). The experimental set up oil extraction processes using of Soxhlet extraction was attached on annex A-1.

After the extraction completed, the oil obtained was subjected to the removal of the solvent using rotary evaporator immersed in a boiled water bath at 70°C for 30 minutes. The amount of oil extracted was calculated using equation (3.2).

$$oil\ yield\ \% = \left[\frac{mass\ of\ oil\ obtained}{mass\ of\ seed\ used} \right] \times 100 \quad [3.2]$$

3.6.1 Purification of the oil

The extracted oils were refined by degumming and neutralization processes.

3.6.1.1 Degumming

A two-step degumming processes were implemented to remove free fatty acid phosphatides of crude oil by the method of water degumming and acid with water degumming. In the first step the oil was heated to 70⁰C and then 3% (v/v of oil) distilled water was added to the heated oil. In the second step the bleached oil was mixed with water and then heated again to 70⁰c, following this 2% (v/v of oil) phosphoric acid solution was added and the mixtures were stirred at speed of 200 rpm for 1 hour at a temperature of 70⁰C. Then after separation processes of the impurities were conducted by using a centrifuge with a rotational speed of 800 rpm for 20 minutes.

3.6.1.2 Neutralization of the extracted oil

The free fatty acid content of oil was determined and found to be 2.77 for castor oil and 8.05 for jatropha oil, for castor seed the free fatty acid was neutralized by 0.5 N solution of NaOH. This was done by diluting (0.86 gram of NaOH pleat per 100 ml of oil) to neutralize and coagulate the FFA (Antony *et al.*, 2011). Whereas for jatropha seed oil which has high free fatty acid contents a two-step neutralization process was carried out. The neutralization process was conducted by heating the oil at 70⁰C and adding NaOH. The mixture of oil and NaOH was stirred at 200 rpm at a temperature of 70⁰C for 1 hour. The coagulated free fatty acid (soap) was separated by using centrifuge with rotational seeped of 800rpm for 20 minutes. Then after the mixed solution was washed with a distilled water to remove a trace NaOH. Finally, removal of trace water was done through oven drying at a temperature of 105⁰C for 1 hour. This process brings the free fatty acid content of the oil to below 2% which is favorable condition for biodiesel production

3.7. Castor and jatropha seed oil characterization

The extracted oils were subjected to characterization processes to realize the suitability of the oil to be used as a potential feed stock for the production of biodiesel. The moisture content,

density, viscosity, acid value, saponification value and iodine value were determined for oil extracted from castor and jatropha seeds as well as for the mixed oils.

3.7.1 Determination of oil moisture content

10 grams of the sample oils were weighted and thoroughly mixed by string on the dish and heated, in an oven at $105 \pm 10^\circ\text{C}$ for 1 hour. Then the dish was removed from the oven and close the lid. Cool in a desiccator containing phosphorus pentoxide or equivalent desiccant and weigh. Heat in the oven for a further period of 1 hour, cool and weigh. Repeat this process until change in weight between two successive observations does not exceed 1 mg.

$$\text{Moisture and volatile matter Percent by weight} = (W1/W) \times 100 \quad [3.3]$$

Where, $W1$ = Loss in gm of the material on drying

W = Weight in gm of the material taken for test

3.7.2. Determination of density

Density is the ratio of mass of sample (extracted oils and biodiesel) to its volume. The density of the extracted oils and the biodiesel were determined by preliminary mass and equivalent volume measurement relations using a digital balance and a graduated beaker. The graduated beaker which is 100 ml capacity was washed with distilled water and dried in an oven at 110°C . After it was dried well, its weight was measured and then filled with the samples (castor oil, jatropha oil, mixed oils and the biodiesel) and reweighted again. Finally, the density was obtained by subtracting the weight of the empty beaker from the weight of the beaker plus the sample (oil) and dividing the resulting mass with the volume of the sample (oil) measured.

$$\text{density}(\rho) = \left[\frac{w_2 - w_1}{V_0} \right] \quad [3.4]$$

Where: W_1 the weight of the graduated beaker,

W_2 is the weight of the beaker plus the sample (oil)

$(W_2 - W_1)$ is the resulting mass of the sample oil

V_0 is the sample (oil) measured. And (ρ) is density of the sample oil

Specific gravity of each sample oil (S_g) was calculated by evaluating the ratio of equivalent masses of the oil and masses water at room temperature.

$$S_g \text{ of the oil} = \left[\frac{\text{density of the oil}}{\text{density of water}} \right] \quad [3.5]$$

$$Sg \text{ of the oil} = \left[\frac{M_o}{M_w} \right] \quad [3.6]$$

Where: sg is specific gravity of the sample oils taken

M_o is mass of 50 ml of the sample oils at room temperature

M_w is mass of 50 ml of water at room temperature

From relations of equation 3.4 a above density of each sample oils was determined by *density of the oil* (ρ) = [*specific gravity of the oil* \times *density of the water*][3.7]

3.7.3. Determination of viscosity (ASTMD445)

The viscosity of the extracted (castor, jatropha) and mixed oils at different proportions were determined using digital Sine-Wave vibrio viscometer(SV-10, 2011, Australia). The samples (the extracted oils and the mixed oils) were heated at a temperature of 40°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. The displayed reading in the controller was recorded as a dynamic viscosity of the sample. At the end, the kinematic viscosity was obtained from the relation of equation by taking the ratio of dynamic viscosity taken from the digital vibro viscometer to the density of the oil using the following equation.

$$\mu = \left(\frac{v}{\rho} \right) \quad [3.8]$$

Where μ is kinematic viscosity, mm² /s

v is dynamic viscosity of oil, mg/mm. s (measured by using vibro-viscometer) and ρ is density of each sample oils, g/cm³

3.7.4. Determination of acid value (AV)

The acid value of the extracted (castor, jatropha) and mixed oils at different proportions were determined according to the method described by (Abdulkareem *et al.*, 2012). The mass of the test sample was taken based on the color and expected acid value as shown on the table. 3.2 based up on the standard 2.5 grams of the samples were taken for castor and jatropha oil respectively the volumes of each oil were calculated based up on the density relations. The samples are mixed thoroughly before weighing. 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 poured into the flask containing the oil. Weigh accurately appropriate amount of the cooled oil sample in a 250 ml conical flask. 100 ml of freshly neutralized hot ethyl alcohol and one ml of phenolphthalein indicator solution was added in to conical flask. The mixtures were boiled for about five minutes and titrate while hot against standard alkali solution shaking vigorously during the titration. Then 3 drop of phenolphthalein indicator was added into the mixture. This mixture was titrated using 0.1N of KOH until the color change observed to pink. Finally, the acid value was calculated using equation (3.9).

$$AV = \left[\frac{56.1 \times V \times N}{M} \right] \quad [3.9]$$

Where: V is volume of standard alkali used, N is normality of standard alkali used and M is the Mass of sample (oil) used. AV is the acid value of each oil samples

Table 3. 2. Sample size of the mass of the test samples for the acid value test

Expected acid value	Mass of the test portion	Accuracy of weighing of the test portion
<1	20 g	0.05 g
1to4	10 g	0.02 g
4to15	2.5 g	0.01 g
15 to 75	0.5 g	0.001 g
>75	0.1 g	0.0002 g

3.7.4.1 Determination free fatty acid

The free fatty acid (FFA) content of the extracted (castor, jatropha) and mixed oils was obtained by using the result of the acid value of each oil obtained in equation (3.9) above empirically determined using the equation (3.10)

$$\% \text{ of FFA} = \left[\left(\frac{AV}{2} \right) \right] \quad [3.10]$$

Where: % FFA is percentage of free fatty acid each of the oils and AV is acid value of the oil.

3.7.5. Determination of saponification value (SV)

The saponification value of the castor oil, jatropha oil and mixed oils of the two feed stocks were determined using indicator method. The sample mixed thoroughly and weigh about 2.0

g of dry sample each feedstock and poured into a 250 ml Erlenmeyer flask. 25 ml of 0.1N ethanolic potassium hydroxide (KOH) solution was added into the flask. And the resulting mixture was then stirred and boiled for 30min in the presence of a reflux condenser. Conduct a blank determination without (the oil) along with the sample. Then after few drops of color indicator (phenolphthalein) was added to the heated mixture. The heated solution was then titrated with 0.5M HCl until the pink color disappeared. The volume of HCl which causes disappearance of the pink color was recorded. The saponification value was then calculated using equation (3.11).

$$SV = \left[56.1 \times N \times \frac{V_b - V_a}{M} \right] \quad [3.11]$$

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

3.7.6. 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} wave number. Finally, the resulting spectra were compared with the spectra of biodiesel, castor and jatropha oil and diesel fuel that have been reported before and the corresponding functional groups were identified. This analysis was conducted in Ethiopian leather industry development institute (ELIDI) research laboratory, at Addis Abeba City, Akaki Kality sub city.

3.8. Production optimization and characterization of biodiesel

3.8.1 Production processes of biodiesel

Biodiesel was produced by using three main input components: mixed (castor seed and jatropha seed) oils, alcohol (methanol), and alkaline catalyst by transesterification processes. In this production processes the reactor was immersed in to water bath on the magnetic stirrer with heating mantle that provide the mixing requirement in a temperature controlled hot plate. In addition, the condenser fixed to the middle neck of the bottle to provide cooling system for the experiment to control the leakage of methanol by supplying cooled water through the inlet and the hot water was rejected through the outlet part. The base catalyst (KOH) and alcohol

(methanol) were mixed in a catalysts preparation reactor to prepare potassium methoxide and then added to the pre heated oil in the reactor. Prior to the startup of biodiesel production process, the following production reaction conditions, the reaction temperature, mixing intensity stirring rate and reaction time were kept constant at 60°C, 400 rpm and 1 hours respectively, three different sets of categories for biodiesel production conditions were varied.

The first sets of production conditions were done by keeping the molar ratio of methanol to oil molar ratio, the volumetric ratio of castor oil to jatropha oil fixed and by varying the other factor catalyst concentration for each fixed factors considered. The second sets of production conditions were methanol to oil molar ratio, the catalyst load fixed and varying the other factor volumetric ratio of castor to jatropha oil for each fixed factors considered, another set of biodiesels were produced. Thirdly, the methanol to oil molar ratio were varied by keeping the other two factors the volume ratio of castor seed oil to jatropha oil and the catalyst concentration constant another set of biodiesels also produced. For each of productions the feed materials requirements the amount of alcohol and catalyst determined the production and synthesis of biodiesel were conducted. After the transesterification reaction was completed, the crude biodiesel was separated from the glycerol using a separator funnel and the methanol was distilled off. The purification of the crude biodiesel was conducted by washing process with hot water was used to remove the impurities from the biodiesel and dried in an oven to get a pure biodiesel. Finally, the obtained biodiesel was checked for its physico chemical properties and compared with the international.

At the end of each experimental run output, vigorously shake the solution and then transfer it in to separator funnel and allow it to keep for 24 hours to settle then the biodiesel and sediment layers clearly observed, the biodiesel was separated from sediment by draining the bottom layer (sediment) carefully. After separation the biodiesel was treated by washing with hot distilled water until the washing distilled water become clear, then the biodiesel was dried in an oven to get a pure biodiesel, and the biodiesel yield was determined by using equation (3.12)

$$\% \text{ Yield of biodiesel} = \left[\frac{\text{mass of biodiesel obtained}}{\text{mass of mixed oil used}} \right] * 100 \quad [3.12]$$

3.8.2 Feed material requirement for the transesterification process

For each experimental run, 30 ml mixed oil were used. The amount of methanol and catalyst required was calculated by using relations as follows:

3.8.2.1. Amount of methanol required

The amount of methanol required when the molar ratio of methanol to oil is(A:O) was calculated by using equations (3.13 and 3.14)

$$(A:O) = \frac{\text{mole of methanol}}{\text{mole of oil}} \quad [3.13]$$

$$(A:O) = \left(\frac{\text{mass of methanol}}{\text{molecular mass of methanol}} \right) / \left(\frac{\text{mass of the oil}}{\text{molecular mass of the oil}} \right)$$

$$(A:O) = \left[\frac{\text{density} * \text{volume of methanol}}{\text{molecular mass of methanol}} \right] / \left[\frac{\text{density} * \text{volume of the oil}}{\text{molecular mass of the oil}} \right]$$

From the above relations the methanol requirement (volume of methanol was determined as

$$V_{\text{of methanole}} = \frac{[(A:O) \times \text{molecular mass of methanol} \times (\text{density} \times \text{volume of the oil})]}{[\text{molecular mass of the oil} \times \text{density of the oil}]} \quad [3.14]$$

3.8.2.2. Amount of catalyst required

The amount of catalyst required given catalyst weight to oil Wight ratio (C)% was determined by equation (3.15 and equation 3.16)

$$(C \%) = \frac{[\text{mass of catalyst}]}{[\text{mass of the oil used}]} \quad [3.15]$$

$$= \frac{[\text{mass of catalyst}]}{[\text{density} \times \text{volume of the oil}]}$$

$$\text{catalyst (KOH)require} = [(C\%) \times (\text{density volume of the oil used})]. \quad [3.16]$$

By knowing the best yield, the optimum parameter was known then the last experiment was conducted with the optimum parameters obtained from the conducted experiments to obtain the optimum biodiesel yield. Finally, the biodiesel was characterized for its physicochemical properties and compared with the international standards. Values of the feed material requirement was attached on annex-D.

3.9 Optimization of biodiesel production processes

The optimization conditions of production of biodiesel from mixed oils of castor and jatropha was established by using response surface methodology (RSM). The three selected production factors chosen to study the optimization processes were, methanol: oil molar ratio (A:O), CSO: JSO mixed oil volumetric ratio and catalyst loading weight (C%).

The assigned values minimum and maximum for each factor were methanol to mixed oil molar ratio [A: 4–9], the minimum value methanol to mixed oil molar ratio was selected near the minimum value of the stoichiometry whereas the maximum was assigned based on previous studies (Abdulkader,2015; Ayola *et al.*, 2020; Sirvastav & parasd,2000). Mixed oil volumetric ratio [B: 25–75] which are assigned based up on the previous studies (Barbase *et al.*, 2010; Dharma *et al.*, 2016) and the property of the feed stocks and catalyst concentrations [C: 0.5–1.5% m/m] which was assigned based up on the literature and previous studies (Dasilva *et al.*, 2006; Dasilva *et al.*, 2009).

The other factor's reaction temperature (T), reaction time (t), and mixing intensity were set fixed and assigned based up on the best reaction conditions for biodiesel productions, and data from literature 60⁰c ,1 hour and 400 rpm respectively (Ayobe *et al.*, 2020; Ayola *et al.*, 2020; Dasilva *et al.*, 2009). On the determination of each studied factors optimal value of each parameter, other parameters were kept constant while adopting each optimal value attained for the optimization of the next parameter. Finally, the overall production was completed using the optimal parameters obtained, the overall methyl esters were taken for further characterization of the mixed castor and jatropha biodiesel.

3.10 Design of experiments for biodiesel production processes

A design expert software Version 11.0.0, was used in this study. The experimental plan was carried out based on three factors; five level designs referred as rotatable central composite design (CCD). The selection of CCD as the experimental design was because CCD was more precise for estimating factor effects (Rande & padama,2017;Josphe et al 2018). The interaction effect between factors was evaluated and optimized in the full factor space. The five levels of values for the independent variables were explicit of their coded and uncoded forms in Table

4. The value of independent variables is expressed in their coded values, -1, 0, +1 interval shows the low, center, and high level of each variable, respectively.

The minimum value methanol to mixed oil molar ratio was selected near the minimum value of the stoichiometry whereas the maximum was assigned based on previous studies. The minimum and the maximum values for mixed oil volumetric ratio and catalyst concentrations are assigned based on previous study and literature data, the values $(-\alpha, \alpha)$ for three factors was $\alpha= 1.68$ and this was evaluated by using equation [3.17]. And each value is shown on table 3.3.

$$\pm\alpha = (2^k)^{1/4} \quad [3.17]$$

Where k is the number of independent variables which is three, for three factors $\alpha= 1.68$.

Table 3.3. Factors and values for the experiment

S.N	Independent variables	code	unit	-1.68	-1	0	1	+1.68
1	Alcohol to oil molar ratio (A:O)	A		2.3	4	6.5	9	10.7
2	Mixed oil volumetric ratio (CSO: JSO)	B	-	8	25	50	75	92
3	Catalyst concentrations (C)	C	Wt %	0.4	0.5	1	1.5	1.6

The design requires experimental number of runs (N) according to the following equation

$$N = 2^k + 2k + cp \quad [3.18]$$

$$N = 2^3 + 2*3 + 6 = 20$$

Where: K is the factor number which is three in this case and Cp is the number of replications at the center point which is six there for; The design consisted of twenty experimental runs, including six replicates at the center points. The center points were utilized to define the experimental error and the reproducibility of the data.

3.11 Characterization of the 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 physio 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.

3.11.1 Determination of Heat value

An empirical formula suggested by (Demirbas, 1998) was used to determine the heating value of the biodiesel from its density value using equation (3.19).

$$(HV) = [79.014 - 43.126 * \rho] \quad [3.19]$$

3.11.2 Determination of Iodine value

The iodine value of the biodiesel was determined empirically from its heat and saponification values by using equations (3.20 and 3.21) as follow:

$$(HV) = 49.43 - [0.041 \times SV + .015 \times IV] \quad [3.20]$$

Then iodine value was calculated by rearranging equation (3.20);

$$IV = \frac{[HV - 49.43 + 0.041 * SV]}{0.015} \quad [3.21]$$

3.11.3. 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, 2009) using the result of saponification number (SN) and the iodine value (IV) of the biodiesel as equation (3.22).

$$CN = \left[46.3 + \frac{5458}{SV} - 0.225IV \right] \quad [3.22]$$

3.11.4 FTIR Analysis

FTIR analysis was used to determine the functional groups present mixed castor and jatropha seed oil biodiesel. The procedure used by (Yordanov, *et al.*, 2013) was adopted for this analysis and it was carried out 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 the diesel fuel. This analysis was conducted at Ethiopian leather development institute.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1. Castor seed oil extraction and characterization

4.1.1. Castor and jatropha seed preparation

After deshelling, the upper cover, 2.125 kg castor seed was obtained from 3 kg which is 70.83% and 1.98 Kg of jatropha seed was obtained from 2.5kg which is 79.20% of the original castor seed and jatropha seed used respectively. Similarly, the average percentage moisture content obtained from three runs found to be 4.86% \pm 0.028% for castor seeds and 3.3% \pm 0.082% for jatropha seed. The result obtained for the moisture content of the feed stocks falls within the range of the ASTM D 1762-84 ranges (3%-10%) as reported by Jenk *et al.*, (1989) and this indicates the suitability of the feed stocks for the processes of extraction. The analyzed result was attached on the annex A.

4.1.2. Oil extraction

The dried castor seed and jatropha seeds were used for extraction of the oil. From 2.125 kg of dried castor seed, 776 ml of oil which is equivalently (737.6g) extraction was achieved (yield of the oil is 34.71%) and from 1.98 Kg of jatropha seed, 1072 ml of oil which is equivalently (1029.6g) extraction was achieved (yield of the oil is 52%). The obtained result for castor seed oil fall within the range of the percentage oil content (30 – 55%) of castor seed as reported by (Akpan *et al.*, 2006) and within the range of the percentage oil content of 54.90% jatropha seed as reported by (Su *et al.*, 2014) with n-hexane. The obtained result in agreement with the suitability of both castor and jatropha seed oils has a great potential for biodiesel production.

4.1.3. Characterization of the oil

The physio-chemical properties of the oil extracted from castor, jatropha seed oil and mixed oils of the two were experimentally investigated results obtained were summarized in table 4.1.

Table 4. 1. Physicochemical properties of castor, Jatropha and mixed oil experimental

parameter	unit	CSO	JSO	25	50	75
density	Kg/m ³	950.00	960.00	952.50	955.00	952.50
WC	%	0.005	0.003	-	-	-
AV	mg KOH/g	5.04	16.1	13.34	10.57	7.805
SV	mg KOH/g	300	305	178.60	178.60	163.00
FFA	mg KOH/g	2.77	8.05	6.67	5.285	3.9
Iv	mg KOH/g	66	45	-	-	-
CN	mg KOH/g	49.64	54	-	-	-
HHV	(MJ/kg)	38.04	37.61	37.94	37.83	37.94
MW	gm/mol	965.05	1175.40	988.88	1005.44	1129.62

It can be observed from the table 4.1 that the density of both castors, jatropha and mixed oils obtained was found to be within the range of 952.50-955.00kg/m³ which is very close to the ASTM D6751 standard for the quality of non-edible plant-based oil. Similarly, the acid value of the mixed oil found to be within the range of (7.805 - 13.34) mg KOH/g. the lowest value was for pure castor oil and the highest value was for pure jatropha oil, the values of the mixed oils fall within the range of these two pure oils. as result of this two-step transesterification processes was selected for the production of biodiesel. The saponification value of the pure oils was found to be 163.00 and 178.60mg KOH/g sample for castor and jatropha oil respectively. The respective result of the mixed oils falls within the range of this values and it was well within the range of ASTM standard. The iodine value of the oil extracted from castor, jatropha and mixed oils seed as was also found within the ranges of (45-66) gI₂/100g oil.

4.2. Biodiesel (BD) Production Analysis

4.2.1. Analysis of variance (ANOVA)

Equation (3.12) was used to calculate the actual yield of biodiesel and the corresponding result is presented in appendix D and analyzed using design expert software 11.0.0. The statistical analysis of variance (ANOVA) for the yield of biodiesel obtained using central composite design (CCD) is presented in table 4.2.

Table 4. 2. Statistical analysis of variance (ANOVA)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1143.14	9	127.02	357.23	< 0.0001	significant
A-[alc:oil]	0.0766	1	0.0766	0.2154	0.6525	
B-[cso:jso]	19.28	1	19.28	54.23	< 0.0001	
C-[C]	82.84	1	82.84	233.00	< 0.0001	
AB	1.53	1	1.53	4.31	0.0647	
AC	7.03	1	7.03	19.78	0.0012	
BC	0.0313	1	0.0313	0.0879	0.7729	
A ²	501.85	1	501.85	1411.45	< 0.0001	
B ²	429.49	1	429.49	1207.96	< 0.0001	
C ²	301.68	1	301.68	848.47	< 0.0001	
Residual	3.56	10	0.3556			
Lack of Fit	2.72	5	0.5444	3.27	0.1099	not significant
Pure Error	0.8333	5	0.1667			
Cor Total	3722.67	19				

It was also possible to observe from the table 4.2 above the F-value of the model 357.23 which implies that the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise-values less than 0.0500 indicate model terms are significant. In this case B, C, AC, A², B², C² are significant model terms (less than 0.0001).

It was also possible to observe from table 4.2 in above shows that the p- value of the model coefficient for methanol to oil molar ratio, castor seed oil to jatropha seed oil volumetric ratio and catalyst loading in quadratic form are less than 0.05. This indicates that from the factors studied mixed oil volumetric ratio and catalyst loading significantly affected the yield of biodiesel. In addition, the p- value for the interaction between methanol to oil molar ratio with castor seed oil to jatropha seed oil volumetric ratio (AB), the interaction between castor seed oil to jatropha seed oil volumetric ratio and the catalyst loading (BC) were greater than 0.05. This also indicates that the yield of biodiesel was not significantly affected by the interaction between process variables.

4.2.2. Model adequacy checking (fit statics)

Checking the adequacy of the model developed to describe the variation of the yield of biodiesel as function 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 4.3 as shown below.

Table 4. 3. Table showing the results for model adequacy checking (fit statics)

Std. Dev.	0.5963	R ²	0.9969
Mean	81.70	Adjusted R ²	0.9941
C.V.%	0.7298	Predicted R ²	0.9806
		Adeq Precision	47.9658

From table 4.3 above, it can be observed that The **Predicted R²** of 0.9806 is in reasonable agreement with the **Adjusted R²** of 0.9941; i.e., the difference is less than 0.2. This suggests that the developed model fits the actual response data. The R² (correlation coefficient) value was found to be 0.9969 which is close to unity. This indicates that 99.69% of the total variation of the yield of biodiesel was captured by the developed model. That means, only about 0.31% 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. In this study a ratio of 47.9658

The regression coefficient and corresponding 95% high and low confidence interval (CI) shown in table 4.4 was 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. As shown on the table shows that the regression coefficients for mixed oils volumetric mix ratio and catalyst loading found to be high indicating that the yield of the biodiesel was strongly affected by these two process variables whereas methanol to mixed oil ratio has insignificant or less effect on the yield. In the same manner the indicated values of the regression coefficients for the interaction between methanol to oil molar ratio and catalyst load (AC), and interaction between mixed oil and catalyst loading (BC) were found to be high indicating that the effect of interaction that occurred between them on the yield of the biodiesel has strong effect whereas the regression coefficient of the interaction between methanol to oil molar ratio and the mixed oil (AB) found to be low indicating that the interaction of this two processes variables has less effect on the yield of biodiesel.

The coefficient estimate represents the expected change in response per unit change in factor value when all remaining factors are held constant. The intercept in an orthogonal design is the overall average response of all the runs. The coefficients are adjustments around that average based on the factor settings. When the factors are orthogonal the VIFs are 1; VIFs greater than 1 indicate multi-collinearity, the higher the VIF the more severe the correlation of factors.

Table 4. 4. Summary of the regression coefficients

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	70.82	1	0.2432	70.28	71.36	
A-[alc:oil]	-0.0749	1	0.1614	-0.4344	0.2846	1
B-[cso:jso]	-1.19	1	0.1614	-1.55	-0.8287	1
C-[C]	-2.46	1	0.1614	-2.82	-2.10	1
AB	-0.4375	1	0.2108	-0.9072	0.0322	1
AC	0.9375	1	0.2108	0.4678	1.41	1
BC	0.0625	1	0.2108	-0.4072	0.5322	1
A ²	5.90	1	0.1571	5.55	6.25	1.02
B ²	5.46	1	0.1571	5.11	5.81	1.02
C ²	4.58	1	0.1571	4.23	4.93	1.02

4.2.3. The Regression Model equation

The model equation, in terms of the coded variables which relates the response (yield of FAM/E-E) to the independent variables(factors) is given in equation (3.23). The final equation in terms of coded factors is:

$$\text{YILD \%} = 70.82 - 0.07949(A) - 1.19(B) - 2.46(C) - 0.4375(AB) + 0.9375(AC) + 0.0625(BC) + 5.9A^2 + 5.46B^2 + 4.58C^2 \quad [3.23]$$

Where: A = Methanol to oil molar ratio

B = castor oil to jatropha oil volumetric ratio

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

From the model equation given in (3.23), it can be observed that the yield of biodiesel was linearly decreases with increasing methanol to oil molar ratio, castor oil to jatropha oil

volumetric ratio and catalyst concentration, with the interaction between methanol to oil molar ratio and increases with the interaction between methanol to oil with the catalyst and the interaction of mixed oils with the catalyst. However, the yield of biodiesel increases at higher mixed castor oil to jatropha oil volumetric ratio and molar ratio of methanol and at higher rate of catalyst concentration in a quadratic manner.

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

4.2.4. Graphical analysis (DP)

The adequacy of the developed model can also be checked using graphical analysis of residuals. The following graphical plots were used for checking the model adequacy; by normal probability plot of the standardized residuals to check for normality of residuals. Standardized residuals versus predicted values to check for constant error. Externally standardized 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 standardized residuals is depicted in figure 4.1. 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 throughout the experiment is approximately normal.

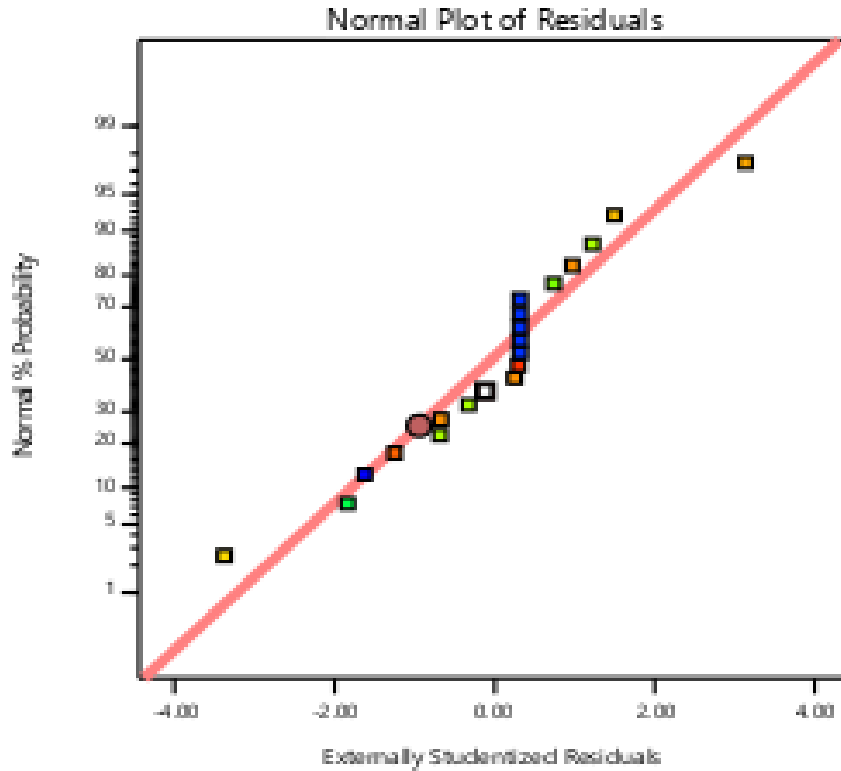


Figure 4.1: Normal probability of residuals

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 versus actual value of this study is shown in figure 4.2. 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.

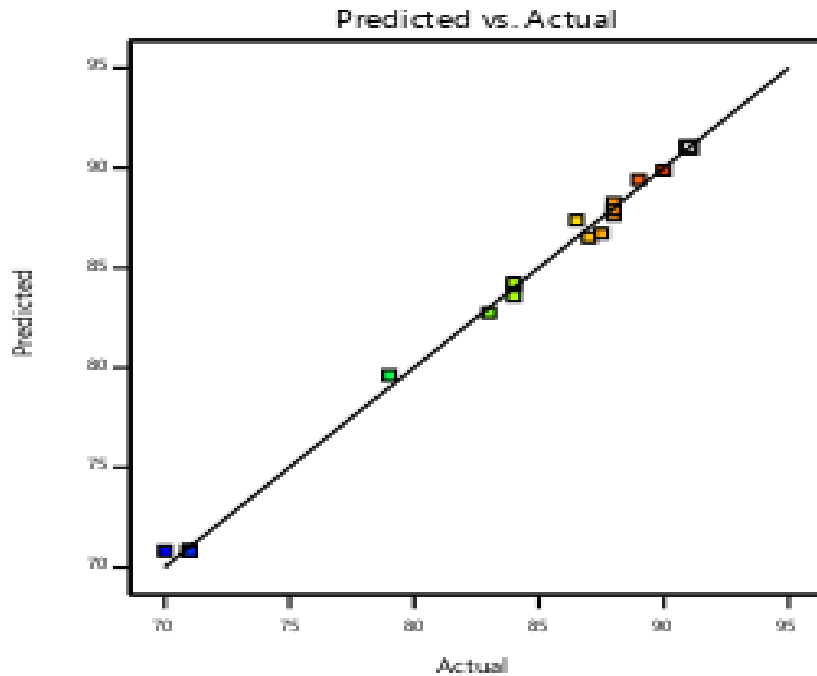


Figure 4.2: Predicted vs actual

4.2.4.3. Residual versus 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 structure less. This graph is used to assess non-linearity, unequal error variances, and outliers. The residual value verse predicted value for this study was shown in figure 4.3. From the graph it was possible to observe that the residual values are not uniquely structured. That means no need of an improvement for minimizing personal error.

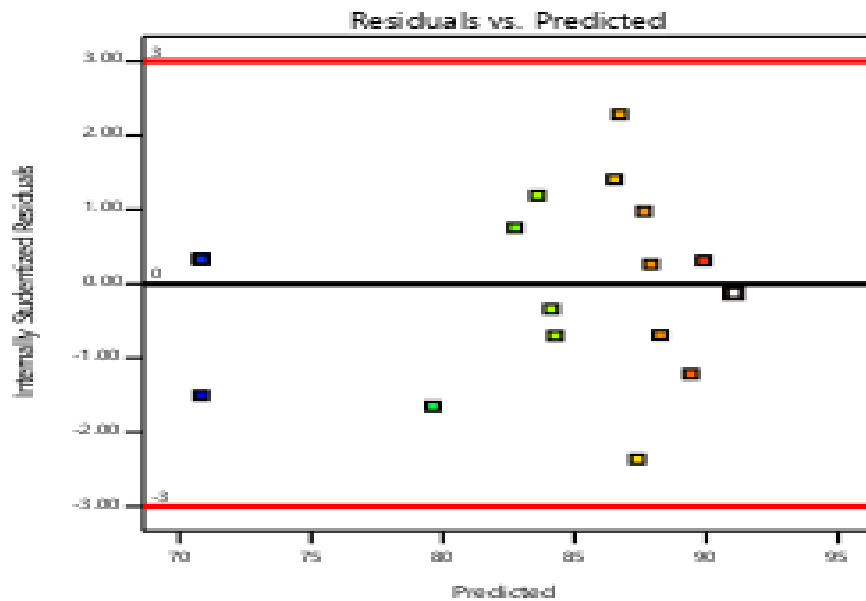


Figure 4.3: Residual versus predicted plot

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 (alcohol to oil molar ratio, mixed castor seed and jatropha seed oils volume ratio and catalyst load) being studied under the specified operating conditions. The interaction effect between this process variable was also highly significant.

4.2.5.1. Methanol to oil molar ratio

From equation (3.23) (regression model equation), the variation of the yield of biodiesel has linear at low methanol to oil molar ratio due to negative coefficient. This indicates that the yield of biodiesel was decreased linearly when the alcohol to oil molar ratio increased at lower ranges. However, the yield was increased with further increasing in molar ratio between alcohol and feed stock (oil). The effect of alcohol to oil molar ratio on the yield of biodiesel is shown in figure 4.4. From the figure the yield of biodiesel was increased with increasing alcohol to oil molar ratio from 4:1 to 6.5:1 and the maximum yield (76%) was obtained at both 4:1 and 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 methanol 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).

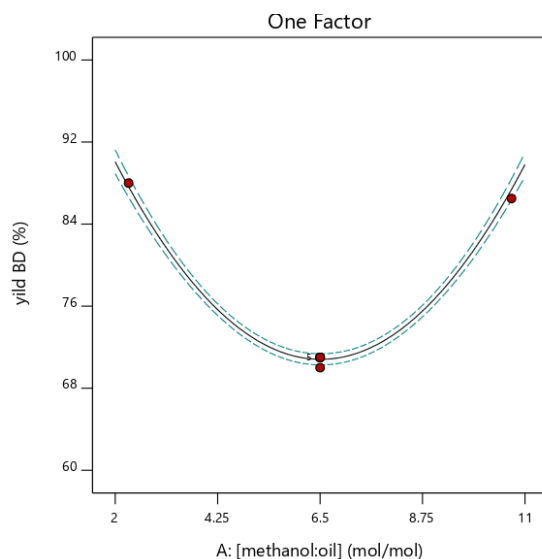


Figure 4.4: Effect of methanol to oil molar ratio

4.2.5.2. Castor seed oil to jatropha seed oil volume ratio

The castor oil to jatropha oil ratio clearly influences the biodiesel yield. The effect of mixed oils castor and jatropha on the yield of biodiesel was presented on figure 4.5. As shown on the figure as mixed oil ratio increases from 25(1:3) to 50(1:1) the yield of biodiesel decreases and minimum yield was achieved at 1:1 mixed castor oil to jatropha oil ratio but as it reaches the minimum point. Further increase of the mixed oil ratio from 50(1:1) to 75(3:1) resulted for the increases of yield biodiesel. The decrease in the yield was may be due to the miscibility problem of mixed oils and methanol resulted from an increase in viscosity due to the high castor oil. Higher ratio of castor oil used could increases the viscosity of oil, which reduces the contact rate of triglyceride molecules with the catalyst's active sites and decrease the catalyst activity.

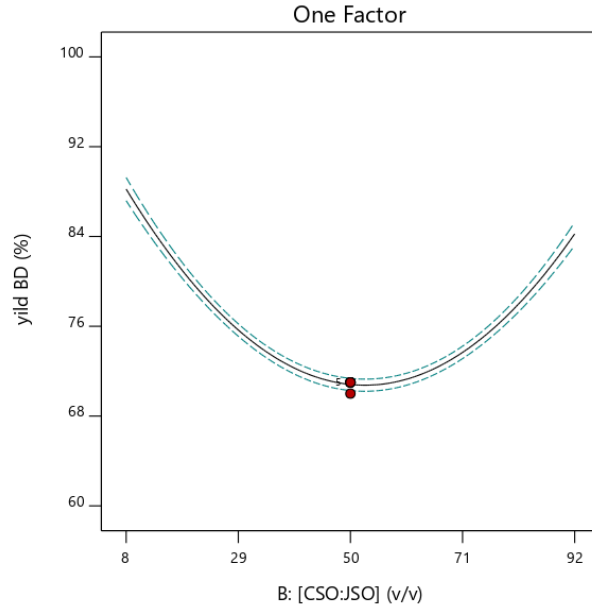


Figure 4.5: Castor seed oil to jatropha seed oil volume ratio

4.2.5.3. Effect of Catalyst loading

The transesterification reaction was strongly dependent upon the amount of catalyst applied. Without the addition of catalyst, the transesterification reaction did not occur. The presence of the catalyst increased the reaction rate. From the figure 4.6 it was possible to observe that the biodiesel yield was higher at the lower range values the catalyst concentration, increasing the catalyst concentration from 0.5 to 1 resulted in decrease in biodiesel yield as it reaches the minimum value at catalyst concentration of 1% further increase of the amount of catalyst resulted in increase in the biodiesel yield. This might be due to the reason that when the catalyst amount was increased the active site of the catalyst also increased thus the transesterification reaction was accelerated and biodiesel yield was increased. But as it reaches the maximum point the yield of biodiesel start to decreases which may be as a result of the formation of an emulsion which led to the formation of gels possibly owing to an increase in soap content this factor hindered the glycerol separation.

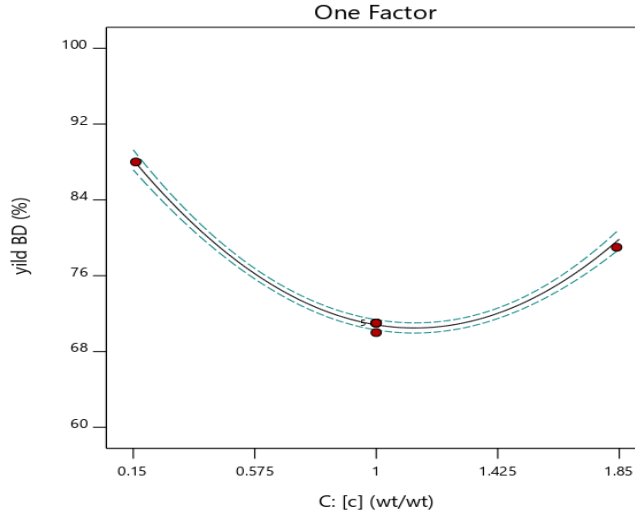


Figure 6.6: Effect of Catalyst loading

4.2.6. Effect of Interaction between process variables

The analysis of variance (ANOVA) as given in table 4.2 shows that the yield of biodiesel was affected by the interaction between Methanol to oil molar ratio and castor seed oil to jatropha seed oil volume ratio (AB), Methanol to oil molar ratio and Catalyst loading (AC) as well as the effect of interaction between castor seed oil to jatropha seed oil volume ratio and Catalyst loading (BC). 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 Methanol to oil molar ratio and castor seed oil to jatropha seed oil volume ratio (AB)

From the analysis of variance (ANOVA), it can be observed that effect of interaction between methanol to oil molar ratio and the volumetric mix ratio of castor seed and jatropha seed on the yield of biodiesel was significant. Figure 4.7 shows the response surface (3D) and contour plots obtained by drawing the yield of biodiesel as function of alcohol (methanol) to oil molar ratio and the volumetric mix ratio of the oils. The catalyst load was held constant at 1%. These figures indicate that the yield of biodiesel was decreased from 83% to 81% with increasing castor seed oil to jatropha seed oil volumetric ratio volume from 25 to 75 at 4:1 alcohol to oil molar ratio. In addition, the yield was also increased from 77.6% to 83% as the alcohol to oil molar ratio increased from 6.5:1 to 9:1 at. Moreover, the yield at higher alcohol

to oil molar ratio (9:1) and low castor seed oil to jatropha seed oil volume ratio volume ratio (25%) was higher than the yield obtained at higher total alcohol to oil molar ratio (9:1) and higher castor seed oil to jatropha seed oil volume ratio volume ratio (75%). This implies that the effect of interaction between methanol to oil molar ratio and mixed oils on the yield of biodiesel was negatively related. This result is also conveyed in the analysis of variance (ANOVA). Figure 4.7 also shows that the yield of biodiesel was more sensitive to the variation in volumetric ratio between castor seed oil to jatropha seed oil volume ratio as compared to the variation of alcohol to oil molar ratio.

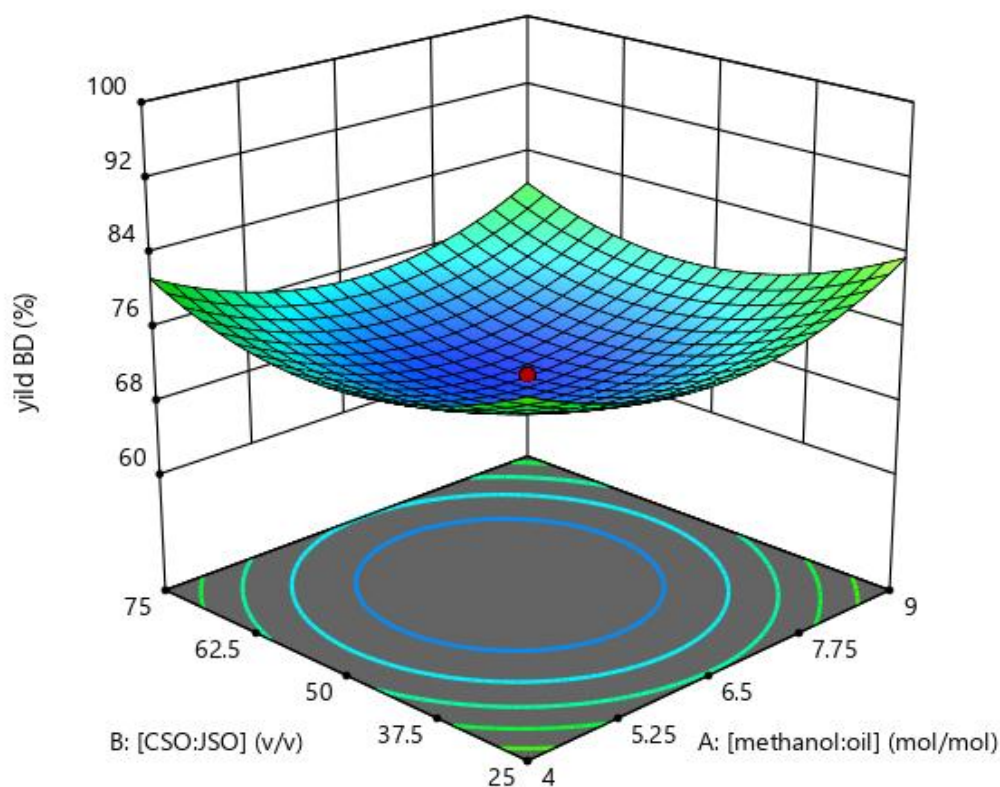


Figure 4.7: 3D plot: representing the Interaction between Methanol to oil molar ratio and castor seed oil to jatropha seed oil volume ratio (AB)

4.2.6.2. Effect of interaction between Methanol to oil molar ratio and Catalyst loading (AC)

The response surface (3D) and contour plots showing the interaction between methanol to oil molar ratio and catalyst concentration on the biodiesel yield are depicted in figure 4.8. These graphs were drawn as function of methanol to oil molar ratio and catalyst loading while

keeping the volumetric mix ratio of castor seed and jatropha seed constant at 50:50(1:1). It was possible to observe from these figures that the yield of biodiesel was increase with increasing both methanol to oil molar ratio and catalyst loading. The yield was increased as the molar ratio of methanol to oil molar ratio increased from 6.5:1 to 9:1. It was decreases with increasing the amount of catalyst used from 0.5 to 1%. 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 methanol to oil molar ratio, 9:1 and 1% catalyst loading. 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).

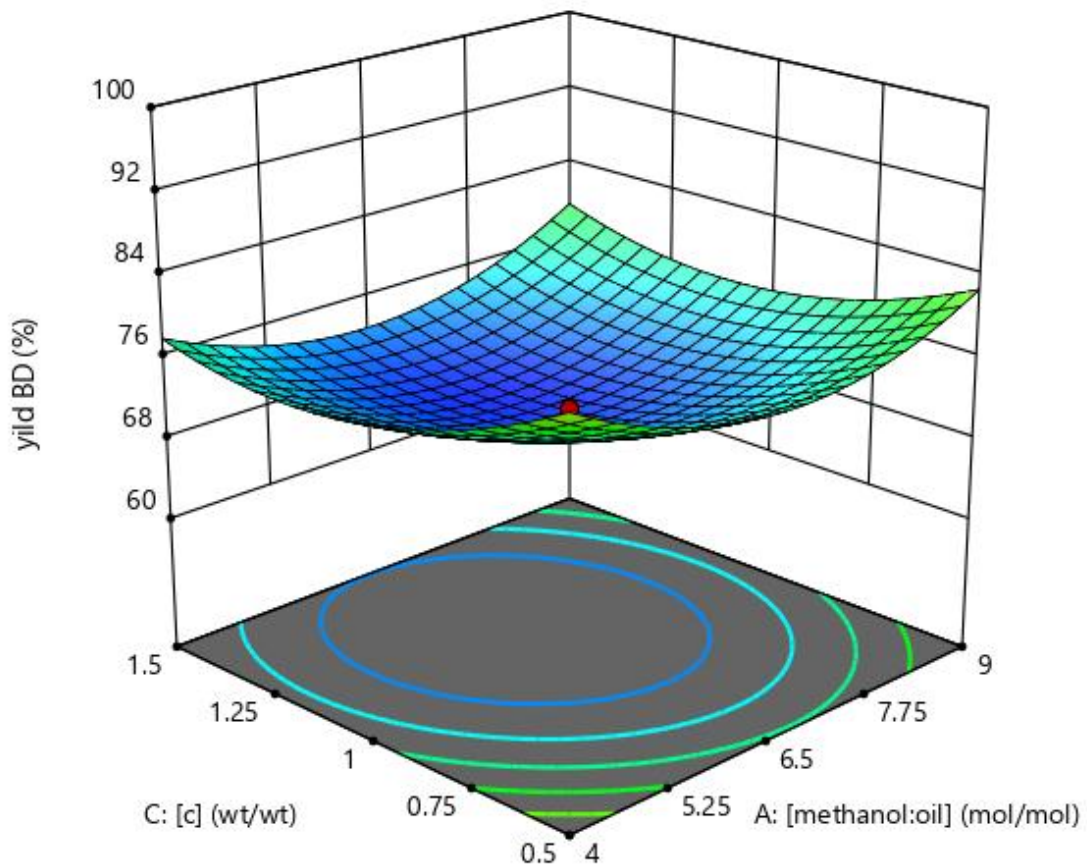


Figure 4.8: 3D plot: interaction between Methanol to oil molar ratio and Catalyst loading (AC)

4.2.6.3. Effect of interaction between CSO to JSO volumetric ratio and catalyst loading (BC)

The effect of interaction between the volumetric mix ratio of castor seed and jatropha seed to oil volumetric ratio and catalyst load on the yield of biodiesel was also analyzed using response surface (3D) and contour plots. The 3D and contour plots representing the effect of interaction between the volumetric mix ratio of castor seed and jatropha seed oil ratio and catalyst loading are depicted in figure 4.9. These plots were drawn keeping the third variable (methanol to oil molar ratio) constant at its center value (6.5:1). The 3D plot shown in figure 4.9 indicates that the yield of biodiesel was increased with increasing the volumetric mix ratio of castor seed and jatropha seed oil volumetric ratio and reached its maximum at 75:25. Similarly, it was also increased with increasing catalyst load from 1 to 1.5%. 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 4.9 which is the contour plot showing interaction between the two factors. It was drawn at constant methanol to ethanol volume ratio of 6.5:1. The figure also shows that, the yield of biodiesel was increased as the amount of catalyst (KOH) increased from 1 to 1.5(%wt of oil used). Similarly, the yield was also increased with increasing the volumetric mix ratio of castor seed and jatropha seed to oil. The maximum yield was obtained at 6.5:1 methanol to oil molar ratio and 1.5% catalyst loading.

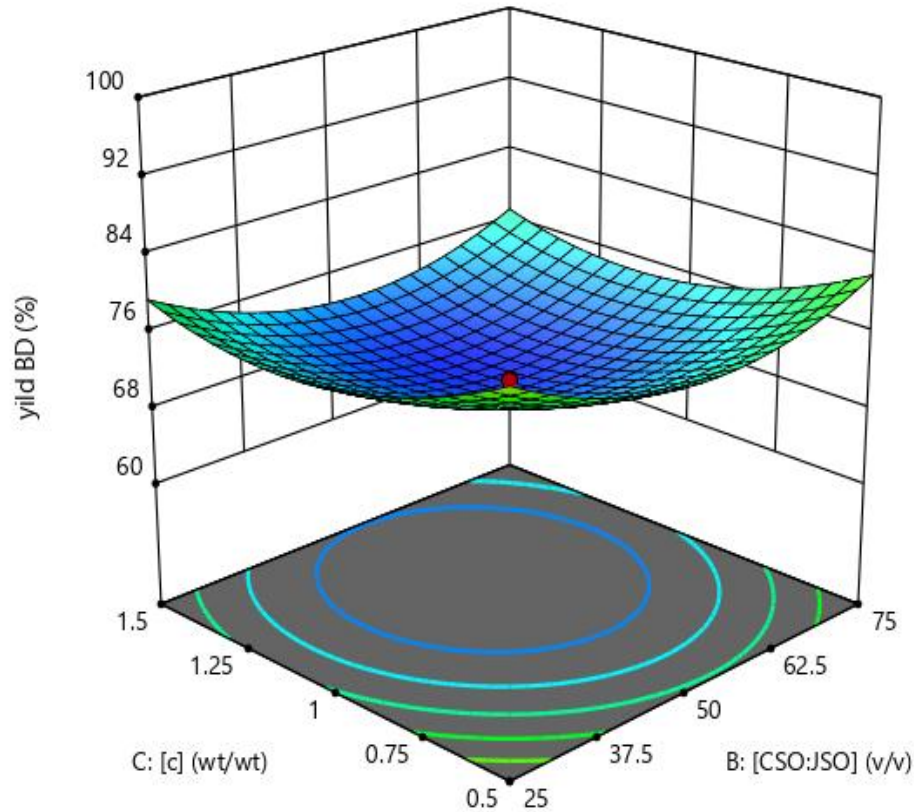


Figure 4.9: 3D plot: interaction between Mixed oil volumetric ratio and Catalyst loading (BC)

4.6 Optimization of process variables

The optimization function in Design Expert 11.1.0.1 software was employed for the optimization of process variables. The goal of the three variables methanol to oil molar ratio, Castor oil to jatropa oil volumetric ratio and catalyst concentration was set in range and the goal of the response was set to maximize.

Table 4.5. Summary of optimum solution in transesterification reaction to produce biodiesel

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
A: [AL:OIL]	is in range	4	9	1	1	3
B: [CSO:JSO]	is in range	25	75	1	1	3
C: [C]	is in range	0.5	1.5	1	1	3
YILDE	maximize	70	93	1	1	3

The possible optimum solution in transesterification reaction to produce biodiesel was presented in table 4.5 above. The predicted optimum yield of biodiesel was 91% (27.9 ml), it was obtained at 4 methanol to oil molar ratio, 0.5%(wt/wt) catalyst concentration and 25 (which is 1:3) castor oil to jatropha oil volume ratio.

4.3. Characterization of biodiesel (Physicochemical Properties of Biodiesel)

The physicochemical properties of the biodiesel such as acid value and saponification value were determined by using titration method and the rest physicochemical properties of the biodiesel such as heating value, Iodine number, flash point and cetane number were determined by using empirical formulas suggested by previous studies. The obtained results were summarized in table 4.6.

4.3.1 Density

The density of biodiesel was obtained with the same procedure as the density of oil. Thus, it was found to be 880 kg/m^3 . Through the production processes the density of the feed stock oil decreased, the decrease in the density values obtained shows the effectiveness of the transesterification reaction processes. The ASTM D6751 standard for biodiesel indicates that the biodiesel fuel should have a density within the range of 870 and 900 kg/m^3 the obtained result for the density value was within the acceptable limit. This property is important mainly in airless combustion systems because it influences the efficiency of atomization of the fuel (Ryan *et al.*, 1984).

4.3.2 Viscosity

Viscosity of biodiesel was determined by the same procedure as viscosity of oil determination that was explained in Sections 3.7.3. Kinematic viscosity of biodiesel was found to be $2.2 \text{ mm}^2/\text{s}$. It is worth mentioning that the extent of the reaction, as well as the experimental conditions used in the biodiesel production processes, greatly influenced the fuel properties and especially its viscosity. Transesterification reaction is responsible for minimizing the viscosity of vegetable oil in order to apply it as a fuel for engines. The result shows that the value was in agreement with standard specification limit of ASTM D6751 with maximum limit of $1.9\text{-}6.0 \text{ mm}^2/\text{s}$.

4.3.3 Acid Value

The acid value measures the content of free fatty acids in biodiesel, the presence of free fatty acids influences fuel aging. The same procedure was conducted to determine the acid value of biodiesel as it was done for the oils. The average acid value of the biodiesel was calculated using the equation 3.9 and the result was found to be 0.561mg KOH/g oil, which was in agreement with the standard specification limit of ASTM D6751 with maximum limit of 0.8 mg KOH/g oil. The experimental result of the acid values for biodiesel was attached on annex A-3.

4.3.4 Saponification Value

The same procedure was done to determine the saponification value of biodiesel as it was conducted for oil. The titration was done three times and the average observation of the result was taken. The obtained result of saponification value the mixed castor and jatropha seed biodiesel was 230 mg of KOH per gram oil.

4.3.5 Heating Value

The heating value of biodiesel was determined by empirically from the titration result of saponification value and Iodine value of biodiesel. The obtained result of heating value was 41.42MJ/kg. This result indicates that the obtained biodiesel has great potential to be used as fuel. The heating value result reported by Graboski et al. (1999) was 40.39 and 40.37 MJ/Kg for methyl rape and methyl soy, respectively. The result of this study was beyond the results of this author but it was in agreement with the standard specification limit of EN14214 >35MJ/kg.

4.3.6 Flash point

Flash point was determined by empirical formula depending on the calculated result of heating value and result was found to be 133.33^oc, which was in agreement within the lower limit of standard specification of EN14214 >120^oc and ASTM D6751 >130^oc. Flash point is used in safety regulations to define “flammable” and “combustible” materials, this higher value indicate that the biodiesel is less likely to ignite accidentally.

4.3.7 Cetane number

Better ignition quality of the fuel is always associated with higher cetane number (CN). This is one of the important parameters, which is considered during the selection of methyl esters for use as biodiesel. Generally, methyl esters with higher CN are favored for use as biodiesel; however, an increase in CN will lead to the solidification of methyl esters at higher temperature. To avoid this situation, the upper limit of CN (65) has been specified in US biodiesel standards. The cetane number was determined by empirical formula depending on the titration result of saponification value and iodine value of biodiesel and the result was found to be 55 and the result was a little beet lesser than standard specifications of both ASTM D6751 and EN14214 which stated that a minimum amount of 47 and 51, respectively.

4.3.8 Moisture content

Determination of moisture contents of biodiesel was conducted in the same procedures and methods with that of oil moisture content determination as discussed in Sections 3.7.1. Moisture content of the biodiesel was determined using equation 3.3 and the result was found to be 0.027%. Fuel contaminated with water can cause engine corrosion or react with the glycerides to produce soaps and glycerol. Therefore, EN14214 (2003) imposes a maximum content of 0.05% of water in fuels. The result was in agreement within the limit of standard specifications of ASTM D6751 and EN14214 which stated that a maximum content of 0.03% and 0.05% of water in fuels, respectively.

4.3.9. Iodine value

Iodine value of the biodiesel were determined using empirical formula suggested by (Demibras, 1998). The heating value (content) of the produced biodiesel was obtained to be 41.42MJ/kg while the. This result indicates that the obtained biodiesel has great potential to be used as fuel. Similarly, the iodine value was obtained to be 67 g I₂/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 stability. This implies that the obtained biodiesel can be stored for long time without being deteriorated (Barabás & Todoru, 2011).

4.4. Comparison of the parameter characteristics of the obtained biodiesel with ASTM Standard Biodiesel

The physio-chemical properties of the biodiesel being produced from mixed castor seed and jatropha seed oil were summarized in table 4.6.

Table 4.6. Physio-chemical properties of the biodiesel produced

Property	unit	Experimental	ASTMD standard
Density at room temperature ⁰ c	(Kg/cm ³)	880	820–900
Dynamic Viscosity at 40 ⁰ c	mg/mm.s	2.8	1.9 – 6.0 @40 °C
Kinematic viscosity	mm ² /s	2.2	1.9 – 6.0 @40 °C
Acid value	(mg KOH/g oil)	0.561	≤ 0.8
% FFA		0.2805	≤ 0.4
Moisture content	%	0.027	<0.03
Saponification value	(mg KOH/g oil)	230	≤ 215.99
Iodine value	(mg KOH/g oil)	67	-
Cetane number		55	-
Heating value (MJ/kg)	(MJ/kg)	41.42	-

4.5 Analytical FTIR analysis

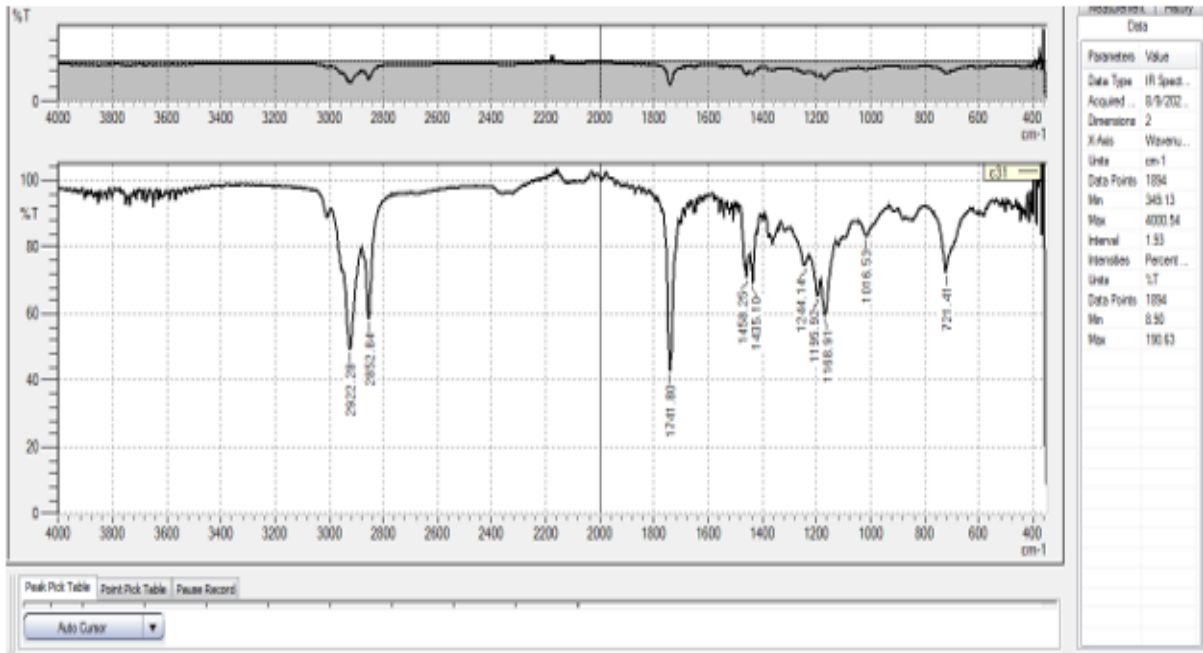
Fig.4.10 and 4.11 shows the IR spectra of two different seed oils of mixed castor and jatropha oils and their biodiesels. Based on the infrared spectrum of mixed oils, mixed castor and jatropha biodiesel and conventional diesel Figures 4.10 and 4.11, both mixed oils, mixed castor and jatropha biodiesel and conventional diesel showed the alkane C–H bond which lies on the wave numbers range from 2800 cm⁻¹ to 3000 cm⁻¹ and alkene C–H bond at 1400 cm⁻¹ to 1500 cm⁻¹. Thus, it could be confirmed that both conventional diesel and castor biodiesel had the same functional group of C–H. Thus, it could be confirmed that both conventional diesel and the mixed oil and the mixed oil biodiesel had the same functional group of C–H.

It was found that the absorption peaks of many major functional groups from oil and biodiesel are almost identical. The obvious absorption at 1745 (1741.8) cm⁻¹ is assigned to the

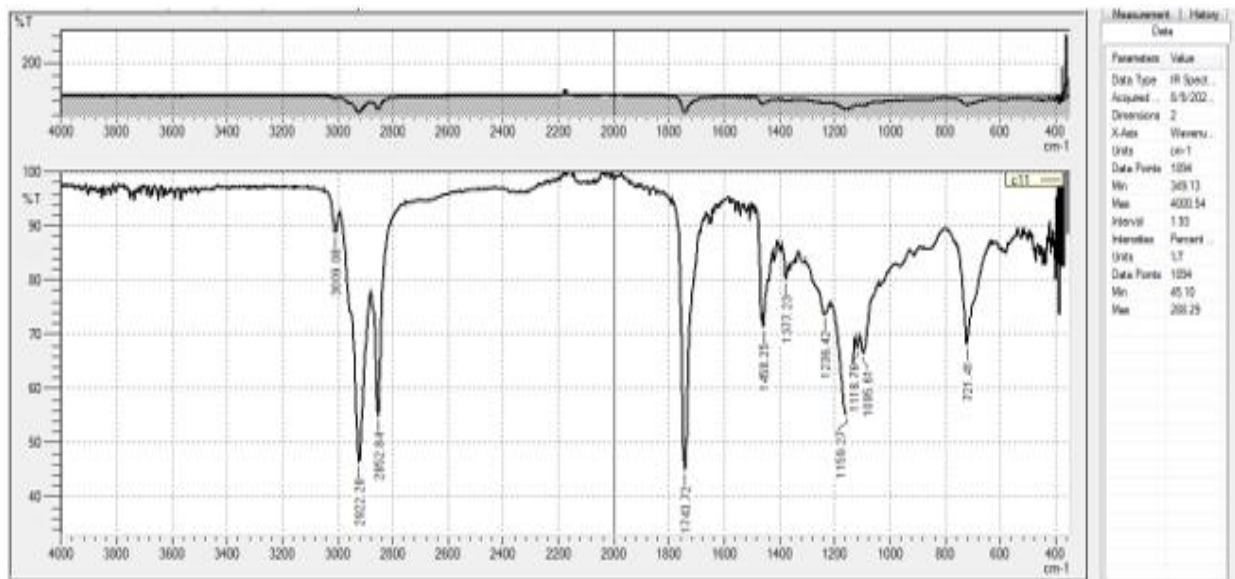
vibrations of -C=O in -COOG (G means the glyceryl) or -COOCH_3 . The strong absorptions at 2855 (2852.84) cm^{-1} and 2926 (2922.28) cm^{-1} are attributed to the stretching and asymmetric stretching vibrations of $\text{-CH}_2\text{-}$. The peaks at 1458 cm^{-1} and 1375 cm^{-1} are due to the stretching and asymmetric deformation vibrations of $\text{-CH}_2\text{-}$.

The small absorption at 3010 (3009) cm^{-1} is from the stretching vibrations of C-H in -C=C-H . However, through the considerable observation, it is found that the absorptions range from 1000 to 1500 cm^{-1} of seed oil and biodiesel are significantly different, although they have the same absorption at 1171 cm^{-1} (1168 cm^{-1}) which is attributed to the symmetric stretching vibration from C-O of C-O-G or C-O-CH_3 (Siatis *et al.*, 2006). In the biodiesel, the absorption at 1196 (1196) cm^{-1} is attributed to the stretching vibration from O-CH_3 in FAME and that at 1436 cm^{-1} (1435) is attributed to the asymmetric bending vibration from C-H of O-CH_3 .

However, the conventional diesel had no oxygen group, whereas mixed castor and jatropha biodiesel showed oxygen functional group of ester C-O bond at 1000 cm^{-1} to 1300 cm^{-1} and ester C=O bond at 1735 cm^{-1} to 1750 cm^{-1} . The presence of oxygen in biodiesel promotes cleaner and complete combustion. On the other hand, the conventional diesel without any oxygen component produced more black smoke and incomplete combustion during burning. These data from the IR spectra can conveniently testify. The FTIR spectra of mixed oils biodiesels was attached on annex G.



a) Mixed oil (MCJSO)



B) Biodiesel produced from mixed oil (MCJSME)

Figure 7: FTIR spectra of the mixed oil and biodiesel produced from mixed oils of castor and jatropha seed oil.

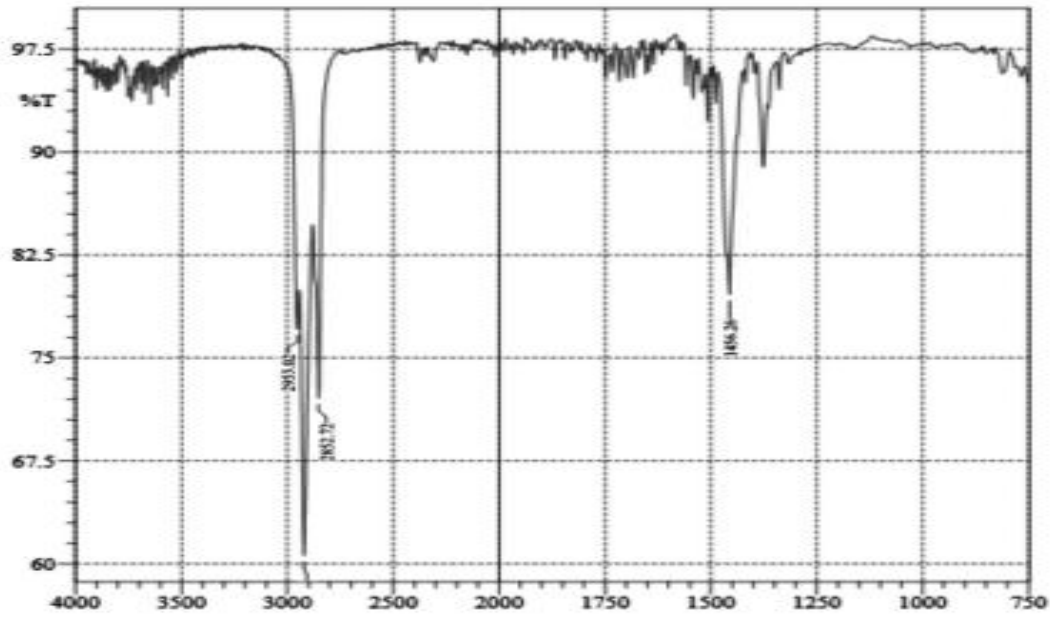


Figure 4.10: FTIR spectra of conventional diesel.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the current research work it was possible to indorse the following conclusions. Solvent extraction using normal hexane as a solvent gives beater result for extraction of oil from castor and jatropa seeds with the oil yield of 34.71% and 52% respectively. The investigated physio-chemical properties of the oil extracted from castor, jatropa seed oil and mixed oils revealed that the suitability of this feed stocks for the production of biodiesel. Mixing of the two oils greatly affect the characteristics properties of the individual oil feed stocks this in turn helps for the optimal feedstock allocation (economic utilization) and improvement quality from each mixed oil. An increase concentration of jatropa oil in mixed oil greatly increased the density and acid value of the resultant mixed oil.

The effect of interaction between the volumetric mix ratio of castor and jatropa seed oil to catalyst load (BC) has a significant effect on the yield of biodiesel.

Increasing castor seed oil to jatropa seed oil volumetric ratio from 25 to 75 at 4:1 alcohol to oil molar ratio resulted in decrease of yield of biodiesel from 83% to 81%. As the alcohol to oil molar ratio increased from 6.5:1 to 9:1, the yield was of biodiesel increased from 77.6% to 83%. The yield at higher alcohol to oil molar ratio (9:1) and low castor seed oil to jatropa seed oil volume ratio volume ratio (25%) was higher than the yield obtained at higher alcohol to oil molar ratio (9:1) and higher castor seed oil to jatropa seed oil volume ratio volume ratio (75%).

The interaction between mixed oil and catalyst loading (BC) were found to be high indicating that the effect of interaction that occurred between them on the yield of the biodiesel has significant effect. Whereas the regression coefficient of the interaction between methanol to oil molar ratio and the mixed oil (AB) and interaction between methanol to oil molar ratio and catalyst load (AC) found to be low indicating that the interaction of these two processes variables has less effect on the yield of biodiesel.

The optimum yield of biodiesel was 91 % (27.9 ml), this value was obtained with the production conditions of methanol to oil molar ratio 4, catalyst concentration 0.5% (wt/wt) and at castor oil to jatropha oil volume ratio MCJSO (which is 1:3).

The physicochemical properties of the biodiesel density were 880 kg/m^3 Kinematic viscosity of biodiesel $2.2 \text{ mm}^2/\text{s}$, the acid value 0.6 mg KOH/g oil , the saponification value $230 \text{ mg of KOH/ gram oil}$, water content 0.027% and heating value was 41.42 MJ/kg . The physicochemical analysis result shows that the majority of the parameters fall within the range of values established by ASTM-D 6751.

5.2 Recommendations

The following points are recommended in order to step up the mixed oils of castor and jatropha seed commercial feedstock: -

- Further Engine test could be done in order to determine torque/ power out, basic fuel consumption efficiency, brake thermal efficiency and emission of exhaust gas to get results that show a reduction of emissions and power develop when using mixed castor and jatropha oils biodiesel.
- The used catalyst could be further optimized in addition to the homogeneous base catalyst; optimization of the catalyst might bring benefits in biodiesel production yields.
- Non-catalyst transesterification of biodiesel production can be employed for further study and to compare the response variable with catalyst transesterification.
- The effect mixing intensity, reaction time and temperature on the yield of biodiesel should be investigated.

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APPENDICES

Appendix A-1: Oil extraction process



Appendix A-2: Biodiesel production process



Appendix A-3: phase separation



Appendix- B: characterization of the feed stock Castor seed and jatropha seed oil properties

B-1. Moisture content of the feed stocks

Time(hr)	Castor seed			Jatropha seed		
0	50	50	50	50	50	50
2	48.9	48.92	48.39	49.95	49.9	49.92
4	47.6	47.67	47.62	49.12	49.14	49.16
6	47.58	47.55	47.58	48.8	48.85	48.9
Difference	2.42	2.45	2.42	1.2	1.15	1.1
% m.c	4.84	4.9	4.84	3.4	3.3	3.2
average	4.86			3.3		
var	0.0012				0.1	
s.d	0.035				0.01	

Appendix B-2. Acid value test

B-2-1. Castor seed oil

Run no	mass	normality	Volume of KOH	Acid value	FFA
1	2.5	0.1	2.26	5.07	2.535
2	2.5	0.1	2.25	5.049	2.52
3	2.5	0.1	2.24	5.02	2.51
average	2.5	0.1	2.25	5.04	2.52
variance				0.44	0.111
s.d				0.67	0.333

Appendix B-2-2. Jatropha seed oil

Run no	mass	normality	Volume of KOH	Acid value	FFA
1	2.5	0.1	7.2	16.12	8.06
2	2.5	0.1	7.16	16.1	8.05
3	2.5	0.1	7.15	16.1	8.05
average	2.5	0.1	7.17	16.1	8.05
variance				0.22	0.056
s.d				0.47	0.236

Appendix B-2-3. mixed castor and jatropha biodiesel oil

Run no	mass	normality	Volume of KOH	Acid value	FFA
1	20	0.1	1.8	0.5049	0.252
2	20	0.1	2	0.561	0.2805
3	20	0.1	2.2	0.6171	0.308
average	20	0.1	2	0.561	0.2805
variance				0.22	0.056
s.d				0.47	0.236

Appendix- C: summary of Physicochemical properties of castor, Jatropha oil and mixed oil

para	unit	CSO	JSO	15	25	50	75	85
density		950.00	960.00	951.50	952.50	955.00	952.50	958.50
WC	%	0.005	0.003					
AV	mg KOH/g	5.04	16.1	14.44	13.335	10.57	7.805	6.7
SV	mg KOH/g	180.00	160.00	185.00	178.60	178.60	163.00	162.00
FFA	mg KOH/g	2.77	8.05	7.22	6.67	5.285	3.9	3.34
Iv	mg KOH/g	267.05	350.46	257.69	278.06	285.25	320.70	340.68
CN	mg KOH/g	16.54	1.56	17.82	14.30	12.68	7.63	3.34
HHV	(MJ/kg)	38.04	37.61	37.98	37.94	37.83	37.94	37.68
MW	gm/mol	965.05	1175.40	947.03	988.88	1005.44	1129.62	1145.94

Appendix- D: Experimental Processes (Transesterification reaction) of each run and loading of selected parameters.

		Factor 1	Factor 2	Factor 3	methanol	catalyst	Response 1
Std	Run	A:[methanol:oil]	B:[CSO:JSO]	C:[c]	ml	g	yield BD
		mol/mol	v/v	wt/wt			
12	1	6.5	92	1	9.4	0.3	84
6	2	9	25	1.5	11.4	0.4	87.5
20	3	6.5	50	1	8.3	0.3	71
19	4	6.5	50	1	8.3	0.3	71
2	5	9	25	0.5	11.3	0.1	90
8	6	9	75	1.5	13.0	0.5	84
7	7	4	75	1.5	5.8	0.5	83
5	8	4	25	1.5	5.0	0.4	84
10	9	10.7	50	1	13.7	0.3	86.5
17	10	6.5	50	1	8.3	0.3	71
13	11	6.5	50	0.16	8.3	0.0	88
4	12	9	75	0.5	13.0	0.2	87
18	13	6.5	50	1	8.3	0.3	70
15	14	6.5	50	1	8.3	0.3	71
16	15	6.5	50	1	8.3	0.3	71
11	16	6.5	8	1	7.9	0.3	88
3	17	4	75	0.5	5.8	0.2	89
1	18	4	25	0.5	5.0	0.1	91
9	19	2.3	50	1	2.9	0.3	88
14	20	6.5	50	1.84	8.3	0.6	79

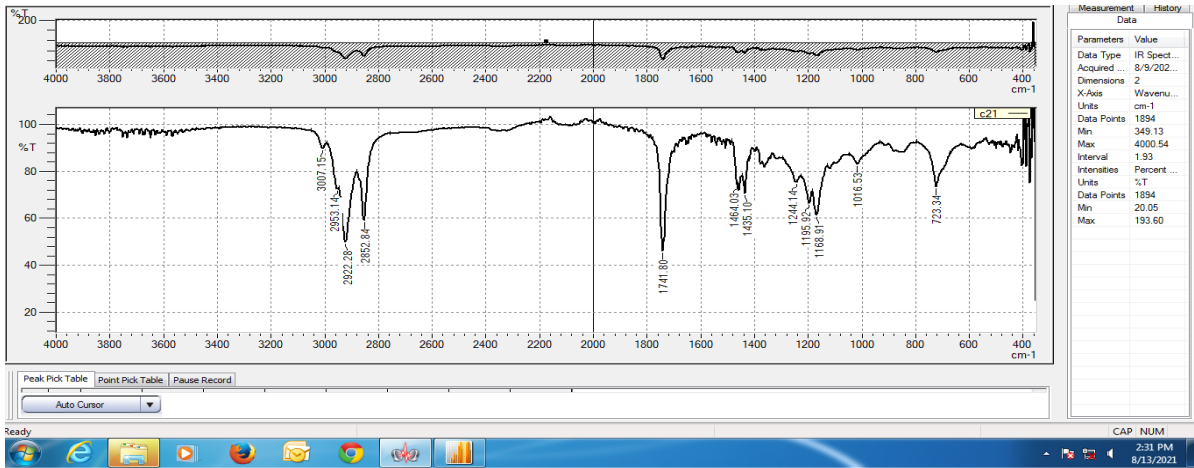
Appendix E: Actual (Experimental) and predicted Yield of biodiesel

		Factor 1	Factor 2	Factor 3	Response 1		
Std	Run	A:[methanol:oil]	B:[CSO:JSO]	C:[c]	yild BD	perdicted	residual
		mol/mol	v/v	wt/wt			
12	1	6.5	92.0	1.00	84	84.26	-0.2611
6	2	9.0	25.0	1.50	87.5	86.72	0.7830
20	3	6.5	50.0	1.00	71	70.82	0.1815
19	4	6.5	50.0	1.00	71	70.82	0.1815
2	5	9.0	25.0	0.50	90	89.89	0.1071
8	6	9.0	75.0	1.50	84	83.59	0.4095
7	7	4.0	75.0	1.50	83	82.74	0.2597
5	8	4.0	25.0	1.50	84	84.12	-0.1167
10	9	10.7	50.0	1.00	86.5	87.38	-0.8834
17	10	6.5	50.0	1.00	71	70.82	0.1815
13	11	6.5	50.0	0.16	88	87.90	0.0984
4	12	9.0	75.0	0.50	87	86.52	0.4836
18	13	6.5	50.0	1.00	70	70.82	-0.8185
15	14	6.5	50.0	1.00	71	70.82	0.1815
16	15	6.5	50.0	1.00	71	70.82	0.1815
11	16	6.5	8.0	1.00	88	88.26	-0.2577
3	17	4.0	75.0	0.50	89	89.42	-0.4162
1	18	4.0	25.0	0.50	91	91.04	-0.0426
9	19	2.3	50.0	1.00	88	87.64	0.3647
14	20	6.5	50.0	1.84	79	79.62	-0.6172

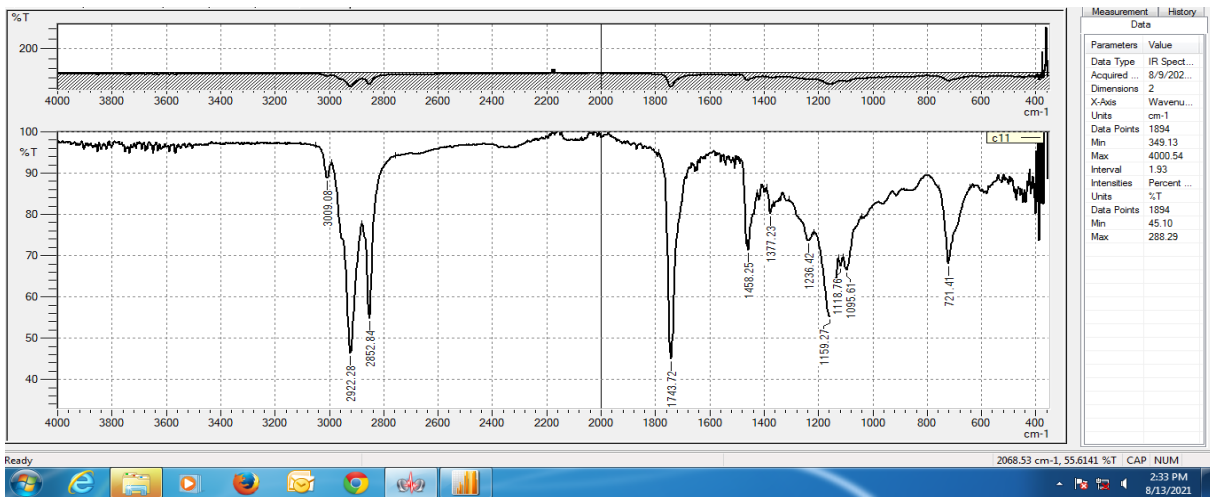
Appendix F: experimental results of biodiesel properties

Property	unit	Experimental	ASTMD standard
Density at room temperature c(g/ml)	(kg/m ³)	880	820–900
Dynamic Viscosity at 40° c(mm ² /sec)	mg/mm.s	2	1.9 – 6.0 @40°C
Kinematic viscosity	mm ² /s	2.2	1.9 – 6.0 @40°C
Acid value (mg KOH/g oil)	(mg KOH/g oil)	0.561	≤ 0.8
% FFA		0.2805	≤ 0.4
Moisture content	%	0.053	<0.03
Saponification value (mg KOH/g oil)	(mg KOH/g oil)	230	≤ 215.99
Iodine value	(mg KOH/g oil)	67	-
Cetane number		52.095	-
Heating value (MJ/kg)	(MJ/kg)	41.42	-
Molecular weight			-

Appendix G: FTIR spectra of mixed oil and biodiesel produced from mixed oils



a) infrared spectrum of mixed (CJSME) biodiesel oils



b) infrared spectrum of mixed (CJSME) biodiesel oils