Addis Ababa Institute of Technology

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Characterization and Process Optimization of Biodiesel Production from Croton Macrostachyus 'besana' Seed using KOH catalyst

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This is to certify that the thesis prepared by **Wondwosen Shiferaw**, entitled: *Characterization and Process Optimization of Biodiesel Production from Croton Macrostachyus 'Besana' Seed Using KOH Catalyst* and submitted in partial fulfilment of the requirement for the Degree of Master Science in Energy Engineering fulfills with regulation of the University and meets the accepted standard with respect to originality and quality.

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Declaration!

I declare that the thesis titled 'Characterization and Process Optimization of biodiesel production from croton seed by using KOH catalyst' original and my blueprint. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due reference to the literature and discussions. Information taken from published and unpublished work of others has been acknowledged in the text and list of references is given. The work was directed under the guidance of *Dr.Solomon Kiros* instructor in School of Chemical and Bio Engineering and Co-adviser *Tewodros Walle* instructor at Center of Energy Technology.

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List of Abbreviations

AEOE ……...Aqueous enzymatic oil extraction

ASE……...Accelerated solvent extraction

ASTM……American standard test method

BBD …….Box-Behnken design

CI engines…….Compression Ignition Engines

CMME……..Croton Megalocarpus methyl ester

CMO……..Croton Megalocarpus Oil

CV…….Calorific Value

FAME……Fatty Acid methyl Ether

FFA……...Free Fatty Acid

GC-MS……..……Gas chromatograph- mass spectrometers

GGGI……Global Green Growth Institute

GHG……..Greenhouse gas emission

GTP II……Growth and Transformation Plan II

IAE……....International Energy Agency

KOH……..potassium hydroxide

IV……..Iodine value

LIDI …….Leather industry development institute

MAE ……microwave-assisted extraction

MME……Ministry of Mines and Energy

RSM…….Response Surface Methodology

SFE ……..supercritical fluid extraction

SG…….specific gravity

SSA……Sub Saharan Africa

SV…….....Saponification value

THF ……..Tetrahydrofuran

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Abstract

Energy security, socioeconomic aspect, and environmental concern are the major arising factor to be considered while selecting the source of energy in today's word including Ethiopia. The rising cost of petroleum fuels, depletion of reserves and strict world protocols on exhaust emissions have also necessitated the need for replacement of petroleum fuels with less polluting, readily available and renewable sources of fuels for automobile and industrial engines. This enforces the worlds to look over the biofuel as a major substitute for mineral fuel sources. Production of biodiesel from non-edible feedstocks is attracting more attention than in the past, for the purpose of manufacturing alternative fuels without interfering with the food chain. Among those non-edible feedstocks, croton macrostachyus seed is another option and which is newly identified feedstock which is indigenous in Ethiopia. The seed was collected from the southeastern part of the country and solvent oil extraction method was selected to extract oil from croton seed. The study aimed at optimizing the biodiesel production process experimentally by varying catalyst concentration, reaction temperature and the molar ratio of methanol to oil. These process parameters were optimized by using design expert software. The optimum conversion efficiency of croton oil to fatty acid methyl ether (FAME) obtained was 96% at the optimal condition of 6:1 methanol to oil ratio, 1% catalyst loading, and 50^{o}C reaction temperature. The properties of croton methyl-ether which were determined fell within the recommended standards. Oil content of the seed was found 53.34% which is beyond estimated value before this study. The main physicochemical properties of biodiesel production from croton oil were characterized and evaluated according to the minimum requirement of international standard (ASTM and EN). It was found that croton biodiesel viscosity 4.613mm^2/s, density 0.854g/cm^3, calorific value 39.889MJ/kg, flash point 220^{o}c, iodine value 107.084mgI/gm and FFA 0.435 mg KOH/gm. The results indicated that the properties of fatty acid methyl ether obtained from Croton macrostachyus seed were agreed with the standard specification of the ASTM and EN. In addition, the oil content of croton seed was observed that 53.34% which is beyond estimated value before. Finally from this study croton seed was discovered as new biodiesel feedstock and extend the choice of feedstock.

Key Words: Croton Macrostachyus, Biodiesel, Transesterification, Homogeneous base catalyst, Surface Response methodology, Design expert software, Box- Behnken.

1. INTRODUCTION

The investigation of indigenous resources as alternative energy is a thoughtful and reasonable solution for the depleting resources of crude oil, environmental concern and many uncertainties in assuring its regular supply with a stable price. Because, Ethiopia endowed with diverse ecological varieties this offer the country to have different potential alternative energy resources such as wind, solar, hydropower, and biomass energy. Amongst various alternative energy source biodiesel fuel has received special attention for this specific study, since it is easy to produce from readily available and renewable sources, safe to handle and use, eco-friendly and completely miscible with mineral fuel at any proportion and used directly on existing diesel engines. Moreover in the case of Ethiopia energy security and sustainable green economic development is a critical issue and also the country's trade deficit due to importing petroleum fuel. Nowadays, all Ethiopia petroleum products imported either through the port of Djibouti or from Sudan. One main issue is that around 65% of the country's export earnings are to pay for the import of petroleum products. Thus, the country is among countries that heavily depend on importing petroleum oil as a source of energy especially for different industries and transport sector (Molla.A & Nigus G, 2014).

Currently, the progressive depletion of conventional fossil fuels with increasing energy consumption and GHG emissions have led to move towards alternative, renewable, sustainable, efficient and cost-effective energy sources with lesser emission. Among much renewable energy source, biodiesel is strategically important sustainable fuel sources in the foreseeable future and which can directly substitute diesel fuel. Biodiesel is non-petroleum fuel consisting of methyl or ethyl esters of fatty acids obtained by transesterification of triglycerides from plant sources. It has a number of environmental benefits over petroleum diesel such as lower overall exhaust emission and toxicity, biodegradability, derived from the renewable and domestic feedstock, negligible sulfur content, superior flash point and higher combustibility due to high oxygen content. These all major factors that have been able to draw much attention to it. It has an appropriate viscosity, completely miscible with conventional diesel fuel and calorific value these all characteristics of biodiesel make it suitable for use with diesel engines without any modification in the design (Singh.V, et al, 2008 and R.K.Singh, Saroj.K, 2009). Since the use of biofuels in place of conventional fossil fuels would slow the progression of global warming by reducing sulfur, carbon oxides and hydrocarbon emissions. So marginal replacement of diesel by biofuel can prolong the

depletion of petroleum resources and abate the radical climate change caused by automotive and industry emission pollutants.

Previously, biodiesel was produced from a range of plants which include: -Jatropha, Croton, Sunflower, soya, Rapeseed, Castor, Palm, Peanut are the most common source of biodiesel. However, it is advisable that the biodiesel should be produced from non-edible plants such as Jatropha, croton, castor, and safflower. This ensures food security and it is cheaper or reduces the production cost of biodiesel since there is no competition for the oil for food. The various plants have different percentages of oil in their seeds e.g. 32% in Croton megalocarpus which is categorized under the same family with Croton macrostachyus 'besana' (native in Ethiopia) and the major focus of this study and 30% in Jatropha (Kurui S and Musyoka R, 2009). The researchers (Dawei.WU, et al, 2013) verified the potential of biodiesel production from Croton megalocarpus oil (CMO) and compared it with another three types of plants, including Jatropha curcas in Ethiopia. The yield rate of croton megalocarpus methyl ester (CMME) from croton megalocarpus oil (CMO) is 94.2%, higher than that of 90.7% from Jatropha curcas oil. They also examined the kinematic viscosity of croton megalocarpus methyl ester, which compared well with that of diesel. Croton megalocarpus seed has the highest raw production potential of 1.8 t ha−1 yr−1 compared with 1 t ha−1 yr−1 of Jatropha curcas. There is another reason why croton seed has much more excellent biodiesel feedstock than jatropha. Since croton megalocarpus tree is categorized under the same family with croton macrostachyus which is native in Ethiopia, the oil content, the yield rate of biodiesel from Croton macrostachyus has estimated to have comparable with croton megalocarpus. Although the oil content of ***croton macrostachyus*** was not well documented in Ethiopia, the study on similar family, ***Croton megalocarpus*** which is a tree indigenous in Kenya showed that the seeds have 40-45% oil content. In Ethiopia, croton macrostachyus occurs in regions between 1300 and 2500m a.s.l (some surveys reporting a range of 500–3400m a.s.l), with annual rainfall ranging between 750 and 2000mm. The tree is common in secondary forests, on forest edges, along rivers, around lakes, in moist or dry evergreen upland forests, woodlands, wooded grasslands or clump bushland and along roadsides. Croton macrostachyus is a member of the family Euphorbiaceae (Kibebaw.W and Legese.N, 2013, Misrak.T, 2007). Thus, this study was the first ground-breaking approach on croton macrostachyus as the new biodiesel feedstock. Croton macrostachyus tree is one of the indigenous trees in Ethiopian and according to this study, it will be another promising new source for production of biodiesel. So far croton macrostachyus

'besana' widely serve as the tool to prevent soil erosion, maintain soil fertility and source of traditional medicine for diseases such as skin diseases and rabies. Finally, this study approved that the oil yields of croton were 53.34% which is beyond the estimated value.

In this study, process variable optimization for conversion of croton oil into biodiesel was carried out under three different reaction parameter. Thus, the three selected process variables were reaction temperature, methanol to oil molar ratio and catalyst concentration. The optimization of these three process variables was analyzed by using response surface methodology (RSM). The optimum biodiesel conversion has been found 96% at optimal combination of process variables of 6:1 methanol to oil ratio, 1% catalyst loading, and 50^{o}C temperature. The properties of croton biodiesel were also tested and compared with recommended ASTM and EN value.

1.2 Statements of Problem

Ethiopia is one of the countries that highly depend on imported fossil fuel as the source of energy in industry and transport sector, as result the country's economy affected by the vulnerable supply of fuel and fluctuation in price. This led the country to deficit foreign currency and unbalance trade which needs great concern to substitute locally available fuel source such as biodiesel. Since biodiesel can substitute mineral fuel directly or bled to any ratio and used with existing compression ignition (CI) engine. Thus, this makes it more valuable alternative fuel and play a great role in minimizing reliance on mineral fuel and diversify energy source of the country. Therefore, self-reliance of energy security and diversifying the source can be attained by utilization of renewable sources of energy, especially the energy from vegetable oils. Exploitation of edible oil for biodiesel production was restricted in the country due to its competition for food resources. Non-edible oil sources possess a clear opportunity as a substitute for fossil fuel in view of economic as well as environmental benefits. So, the discovery of other non-food feedstock and assessment of their propagation potential is a vital solution to avoid food versus fuel interruption. Keeping this in mind there is a lot of potential non-edible biodiesel feedstock in Ethiopia such as castor, jatropha and croton macrostachyus. Despite, Ethiopia has diverse indigenous plants as the source of feedstock plants, the plantation of feedstock in the country only focus jatropha and a lot of researches were done regarding jatropha as a source of biodiesel. Therefore, identifying the feasible and reliable oil-bearing plant for biodiesel from indigenous species is essential for finding

the solution to the above-mentioned problem and to overcome the trade imbalance that the country is facing now and also to stimulate the rural economic development.

According to Moshi, et al, 2010 & Shalini A, 2013, found that the *croton megalocarpus* seed which is categorized under similar family with that of croton macrostachyus 'besana' has equivalent oil contents with castor and jatropha and also have a lot of environmental benefit such as prevent soil erosion, serve as traditional medicine, high yield per acre than jatropha and play great role in maintaining biodiversity. Even though croton macrostachyus seed has higher oil contents and yield per acre than that of jatropha, in Ethiopia so far no research had been done regarding croton seeds as a source of biodiesel feedstocks. Therefore, this paper devised to clearly cover the gap of using potential oil content of croton seed and add additional sources of biodiesel feedstock, propagation of this tree also play a great role in maintaining biodiversity and land degradation which is a critical problem in Ethiopia.

1.3 Objectives

1.3.1 General objective

The major objective of this research was to track potential oil content of the croton seed as new biodiesel feedstock and optimizing the biodiesel production process variables and also evaluate the physicochemical properties of croton biodiesel according to ASTM specification.

1.3.2 Specific objective

This paper is devised to meet the following specific objective:-

- To extract and analyze the physicochemical properties of croton oils.
- To synthesize and optimize biodiesel production process by using response surface methodology (RSM) with help of Design Expert Software under selected reaction parameters (reaction temperature, methanol to oil ratio & catalyst concentration) and identify the best combination.
- To determine the physical and chemical properties of the extracted croton biodiesel.

1.4 Significance of the Study

This study has great significance in terms of assuring the production of an alternative form of energy that is environmentally friendly from Croton macrostachyus which is indigenous, a non-edible and abundantly available and grow on non-arable as well as an arable land without affecting nearby crops. This makes croton macrostachyus eco-friendly plants and promising source of

biofuel than other feedstock and also this study introduce new feedstock that didn't discover so far and also extend the choice of alternative feedstock. In addition, the study was set concrete set up for searching better domestic origin feedstock and tap the potential oil content of croton and also the propagation of this trees will play a great role in preventing land degradation and maintaining underground water table.

Moreover, this study provides environmentally safe, multifunction trees, higher oil content, fast propagation rate and higher yield per acre biodiesel feedstock. Generally, this thesis can be applicable at the specified pilot site and extend to overall region of Ethiopia for both small scale and large scale biodiesel production from croton macrostachyus.

1.5 Scope of the Study and Limitation

The study cover from identifying new feedstock which is croton macrostachyus and collecting, pretreatment of raw materials and proximate analysis of croton seed were the initial activities of this research. The thesis work generally covers croton oil extraction, refining and characterization of croton oil, croton biodiesel production process optimization and purification as well as characterization and standardization of final product (croton biodiesel). Extraction, refining, characterization of croton oil, preparation of FAME and characterization of croton biodiesel (FAME) were done using standard procedures and test methods. Comparison and evaluation of physiochemical parameter of croton biodiesel with an international standard such as ASTMD-6751 and European. Next to characterization of different basic fuel properties of croton biodiesel can be blended with petrol-diesel at different percentage and apply in compression ignition (CI) engine to evaluate the effect of using blend of biodiesel by using different parameter such as engine power, brake thermal efficiency, and specific fuel consumption, exhaust gas temperature and greenhouse gas emission. However, the performance of analysis of blended biodiesel with petrol diesel in CI engine was not done due to lack of laboratory set up and equipment required to measure those parameters.

2 LITERATURE REVIEW

2.1 General Overview of Biodiesel Production

Biodiesel can be derived from a variety of sources including edible oils, non-edible animal fats, and waste cooking oil. It is believed that large-scale production of biodiesel from edible oils may bring global imbalance to the food supply hence the environmentalists started to debate on the negative impact of biodiesel production from edible oil. Hence, as a solution for the competition with food versus fuel crisis, using non-edible oils feedstock are found to be suitable for biodiesel production (Ayhan.D, et al, 2016, and Sirangala.T, et al, 2014). This minimize production cost of biodiesel and also make it competitive without interfering with food supply.

Biodiesel from renewable oil seeds can be used as mixed or pure form with diesel fuels. The advantages of vegetable oils as diesel fuel are their portability, ready availability, renewability, higher heat content (about 88% of Diesel fuel), lower sulfur content, lower aromatic content, and biodegradability. The use of biodiesel instead of the conventional diesel fuel come up with significant reduction in exhaust gas emission such CO_2, SO_x and unburned hydrocarbon (HC). However, the main disadvantages of vegetable oils as diesel fuel are higher viscosity, higher cost (this can be resolve by choice of feedstock), lower volatility, and the reactivity of unsaturated hydrocarbon chains. As result of this using biodiesel affect normal function of engine components such injector coking, engine compatibility and long term storage (Shashi.K, et al 2011, Ahmad.A, 2015 and Obed.Majeed.A, et al, 2016). Overall benefit of biofuel were summarize in table 2.1

Table 2.1 Major Benefits of Biofuels

	Advantage of biofuels
Environmental	• Reduction of GHGs • Reduction of air pollution • Higher combustion efficiency • Easily biodegradable • Carbon neutral
Energy Security	• Domestically manufactured and distributed • Supply reliability • Reducing use of fossil fuel • Renewable • Fuel diversity
Economic Impact	• Source of additional income for rural community • Sustainability • Increases number of rural manufacturing

Source :-(Le.TuThanh, et al, 2012)

2.2 Recent trends in biodiesel production: World versus Ethiopia

I) World

The current world's demand for fossil fuel stands at 84 million barrels per day (bpd) and is projected to increase to 116 million bpd by 2030. Against this demand, peak models for the availability of the fossil oil and natural gas indicate that shortages could occur in the near future. The International Energy Agency (IEA)'s latest analysis indicates that global primary energy demand is set to increase by 55% between 2005 and 2030, at an average annual rate of 1.8%. Fossil fuels will remain dominant, accounting for 84% of the projected increase in primary energy demand (Simonetta.Z, 2008 and Charles.O, et al, 2013). Recent study shows that climate change is currently the most pressing global environmental problem. If the average global temperature increase by more than $2^{o}C$, up to one million species could become extinct and hundreds of millions of people could lose their lives. Worldwide, transportation sector contribute 23% of total

world CO_2 emission (A.E. Atabani et al, 2012). Figure (2.2) shows total world transportation and other sector oil consumption by end-user sector between 2007 and 2035.

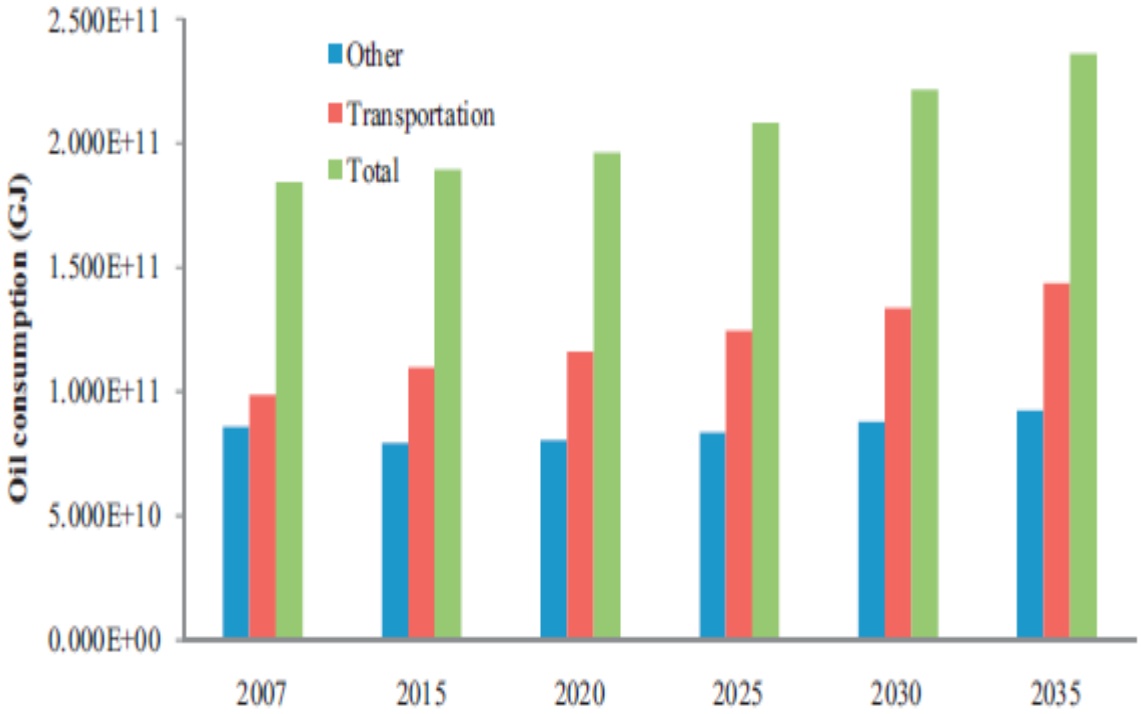


Fig 2.1 Total world oil consumption, transportation oil consumption and other sectors oil consumption (GJ) between 2007 and 2035.

Source: A.E. Atabani et al, 2012.

Recent study show that United States and Brazil were among the largest biodiesel producers in the world, totaling some 5.5 and 3.8 billion liters, respectively in 2016 (figure 2.2). The United States is projected to reach production levels of over 1 billion gallons biodiesel by 2025. After the implementation of the energy policy Act of 2005 which provided tax incentives for certain types of energy, biodiesel production in the U.S began to increase. The volumetric Ethanol Remove Tax Credit is currently one of the main source of financial support for biofuels in the United States. In 2010, the U.S. expected about 85 million gallons of their biodiesel products. Comparatively, Argentina accounted for over half of the world's total exports. The United States has one of the highest bioenergy capacities in the world, totaling 13,764 MW in 2015(St James's Square, 2018).

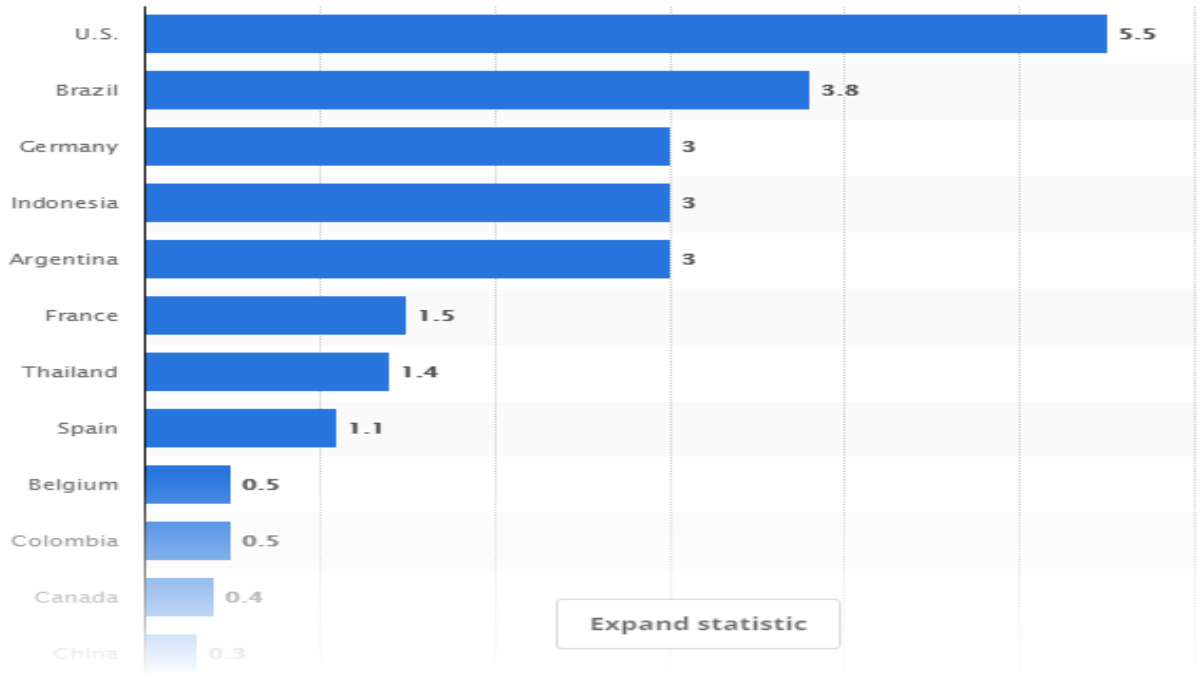


Fig 2.2 Statistical Report of World leading biodiesel producer in 2016

Source: - www.statista.com/statistics/271472/biodiesel-production-in-selected-countries

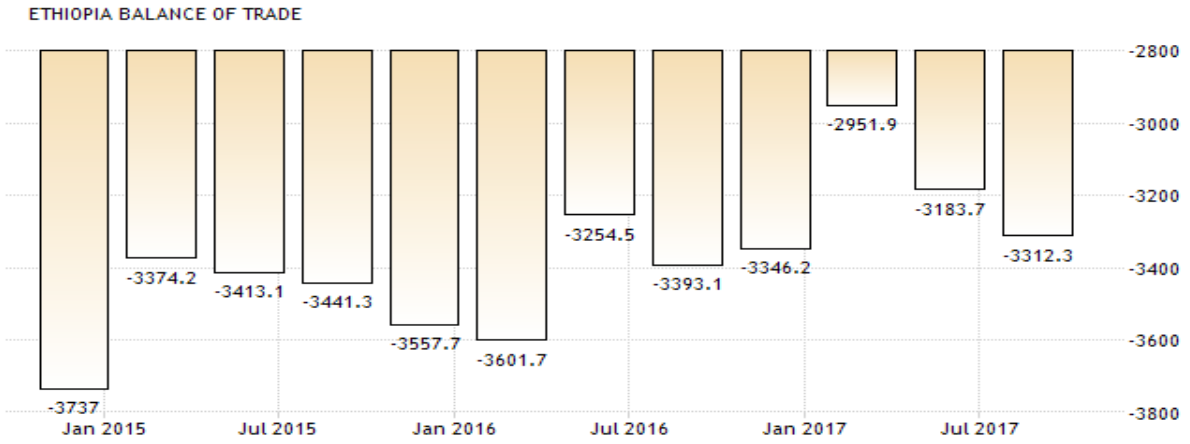
In general the main reason for biofuels and bioenergy development and also their rapid penetration in global and national markets are:-

- The need to reduce greenhouse gas emissions
- Energy security concerns
- Rising in oil prices
- The opportunity to support the countries rural economy (Biniyam Demissie, 2011)

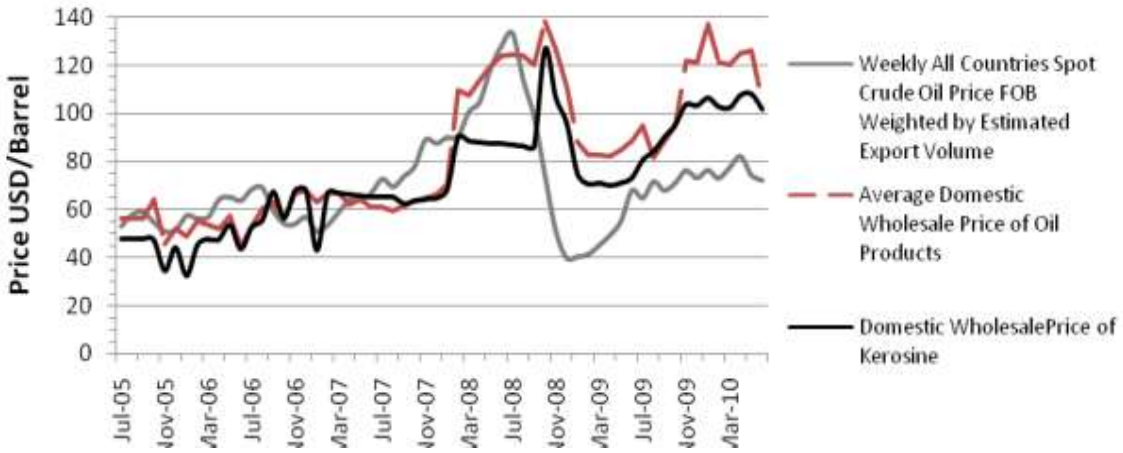
II) Ethiopia

Ethiopia is one the country's which is the large energy consumption rely on imported petroleum product such as Gasoil, Jet/Kerosene, fuel oil and LPG which are the main product of petroleum and also highly depend on traditional biomass that of burning wood. This poses deficit import-export trade balance and different environmental problems such as air pollution, biodiversity loss, soil erosion, as well as health hazards to societies such as breathing problem and some chemicals that are found in wood smoke are found to be cancer-causing due to indoor air pollution. The sector also poses an economic challenge to the country as up to 77% of Ethiopia's total export earning

goes directly to meet nation's fuel demand. As result it is very important to find a way to deal with the situation and reduce the social, environmental and economic challenges of the country by developing different sustainable energy supply systems (Biniyam Demissie, 2011, Manfred Z, Martin G, 2007). Figure 2.3 (a, b) clearly show that how the economy of the country affected by imported petroleum product.



a)



b)

Figure 2.3 Resent Ethiopian cost importing oil (a) Trade deficit of the country from 2015 to 2017 (b) Monthly Price of oil in 2017.

Source: - Trading economics.com/ National back of Ethiopia

Figure 2.3 shows that the country face critical problem in trade balance and foreign currency deficit. This realization made Ethiopia to investigate possibilities of using alternative fuels to petroleum and its derivatives. The essential minimum requirement for biodiesel to be more

sustainable alternative for fossil fuels is that they produced from renewable raw materials, abundantly available non-edible feedstock and that their use has a lower negative environmental impact. Beside hydropower, wind, solar and geothermal energy the country formulated "The Biofuel Development & Utilization Strategy" to facilitate adequate production of biofuels from indigenous trees like croton (Kibebew.W and Legesse.N, 2013). According to the strategy the biodiesel that is to be produced from ***jatropha curcas, castor bean, and palm tree*** aimed to ensure use of biodiesel for transportation ensure a high level of blend Substitute biodiesel for domestic cooking and lighting fuel. In addition to above mentioned feedstock searching for other feedstock that has better oil content and yield per hectare such as **croton macrostachyus or *'besana'*** is major concern of this thesis. Croton macrostachyus is another new potential biodiesel feedstock the main target of this study. Hopefully this trees will extend alternative choice of biodiesel feedstock's and one of the native trees in Ethiopia.

In Ethiopia, blending gasoline with ethanol has been already started with ratio 10:90, since 2011 with two sugar factories and three blender companies (Fincha, Metehara, Nile petroleum, Oil Libya and NOC) and according the government strategy this ratio was increase to 25% by 2015. Thus, with this blending ratio the country save more than 35million USD (Abadi.B & Shimels.A, 2017).

This implies that biofuel (ethanol and biodiesel) are promising substitute of fossil fuel or petroleum oil for the country. Therefore to speed up the development of the country by improving export-import trade balance, the imported quantity or the per-metric price should be curtailed. Since the later is impractical, the only option is minimize the imported quantity and compensate the deficient with appropriate substitute such as biodiesel that can be produced locally.

Ethiopia is endowed with natural resource suitable for bio-diesel development. In this regard, at national level, an estimated area of 23.3 million ha suitable land is available for development of bio-diesel. Regionally, the available land in million ha is : Oromia 17.2, Benishangul-Gumuz 3.1, Gambela 2.8, Somali 1.5, Amhara 1, Southern Nations Nationalities 0.05, Tigray 0.007 (Ministry of Mines and Energy, 2007). It should be noted that there is information gap in some of the regions; nevertheless, the potential is expected to be higher than the available record. Based on the Government development strategy local and foreign private investors have started growing plants for producing bio-diesel. Until recently, the progress shows that over 14 local and foreign investors are undertaking preparations for the development. Among these, about 5 investors already started

implementation. The development of the infrastructure coupled with the high national income has intensified the demand for fuel. In addition to transport, fuel is important for industry, agriculture, households and societal service. Ethiopia imports fuel on average at the expense of 768 USD per annum and this covers 77 % of the total export earnings (Ministry of Mines and Energy, 2007).

So, in order to ensure the country's continued development program and the national fuel security, it is important to increase fuel utilization and substituting the demand by locally produces fuels such as biofuel. In general, the goal of the strategy is to produce adequate bio-fuel energy from domestic resource for substituting imported petroleum products and to export excess products.

2.3 Biodiesel Feedstock's and Its Utilization

Globally, there are more than 350 oil-bearing crops identified as potential sources for biodiesel production. The wide range of available feedstocks for biodiesel production represents one of the most significant factors of producing biodiesel. Biodiesel can be produced from a great variety of feedstock. Common biodiesel feedstock comes from plant oils like rapeseed, soybean, sunflower, palm and some other non-edible oils like Mahua, Neem, Karanja, Jatropha, Castor, Animal fats like beef tallow and used cooking oil can also be used as biodiesel after refining, while new sources like algae is considered to be the third generation of biofuel (A.E. Atabani, et al, 2012). The choice of biomass feedstock is one of crucial steps as it affect the efficiency and quality of biodiesel**.** Selection of feedstock for the production of biodiesel should fulfil two requirements: ***price*** (low feedstock and production costs; more than 75% of the production cost corresponds to the feedstock cost as shown in figure 2.4 and ***local availability*** (large and constant production volume) source. It is also necessary to take into consideration the oil content of the seeds and the yield per hectare. So, in biodiesel production process the choice feedstock is strong function which determine both quantity and quality of biofuels. Since the choice of feedstock is highly influences the biodiesel composition and fuel quality such acid value, oxidation stability, cloud point, cetane number and cold filter plugging point (Arumugam.S, et al, 2009 and Adam.F, 2014).

Therefore non-edible oil like croton macrostachyus, jatropha, and castor oils are become promising alternative feedstock for biodiesel production because of large demand for edible as food vs. fuel competition, the higher prices of edible oils than that of fossil fuels and the lower cost of non-edible oil plant cultivation. From those non-edible oil *croton macrostachyus* is the major focus of this research compare to other especially with jatropha which is currently underproduction and a

lot of effort undertaken in Ethiopia. Croton macrostachyus is native tree in Ethiopia and multi-functional plant. Because, its leaves help as source of traditional medicine such as rabies, skin diseases, its roots maintain soil fertility and prevent land degradation as result it allow practice of agroforestry. Croton seed has also high oil content and higher yield per acre than other feedstock. Despite its multi-functionality of croton seed, there is less concern for this miracle tree.

Therefore this study is designs to tie this gap of knowledge and tap the potential oil of croton macrostachyus. Table 2.2 show some selected oil potential plant species. As shown in table croton has sufficient oil content to be one of best feedstock for biodiesel production.

Table 2.3 Profiles of some selected oil potential plant species.

Species	Habit	Family	Oil content (%)
Croton megalocarpus (native to Kenya)	Tree	*Euphorbiaceae*	47.11 to 57.86%
Jatropha curcas	Shrub	*Euphorbiaceae*	37 to 40%
Excoecari abussei	Shrub	*Euphorbiaceae*	45 to 50%
Croton macrostachyus (native to Ethiopia)	Tree	*Euphorbiaceae*	40 to 45% (estimated from similar family)
Telfairiapedata	Liana	*Cucurbitaceae*	50-55
Ricinuscommunis	Shrub	*Euphorbiaceae*	40-45

Source: - (Moshi, et al, 2010 & Shalini A, 2013)

Biodiesel contains no petroleum, but it can be blended at any proportion with diesel fuel to be used in diesel engines with little or no modification. The advantages of Biodiesel over Diesel fuel are higher combustion efficiency, flash point, biodegradability and less carbon monoxide emissions. Fuel grade biodiesels are produced through the transesterification process conforming to strict specifications such as ASTM D6751 in order to ensure proper performance and quality. Biodiesel is used as a fuel in the form of a blend with the Diesel fuel (Fossil fuel). The Biodiesel can be blended in any percentage. Biodiesel blends from 2% to 20% can be used in most diesel equipment with no or minor modifications. For example blend 'B20' refers 20 volume percent of Biodiesel is present. The properties of the blend change with the amount of fuel blended with the Biodiesel

and hence there is a need for the development of suitable models for the prediction of various properties of the blends (Masjuki.H and Md.Abul.K, 2013, Parag S, et al, 2012).

According to Parag S, et al, 2012 found that the biodiesel quality can be influenced by several factors: the quality of the feedstock, the fatty acid composition of the parent vegetable oil or animal fat, the production process and post-production parameters.

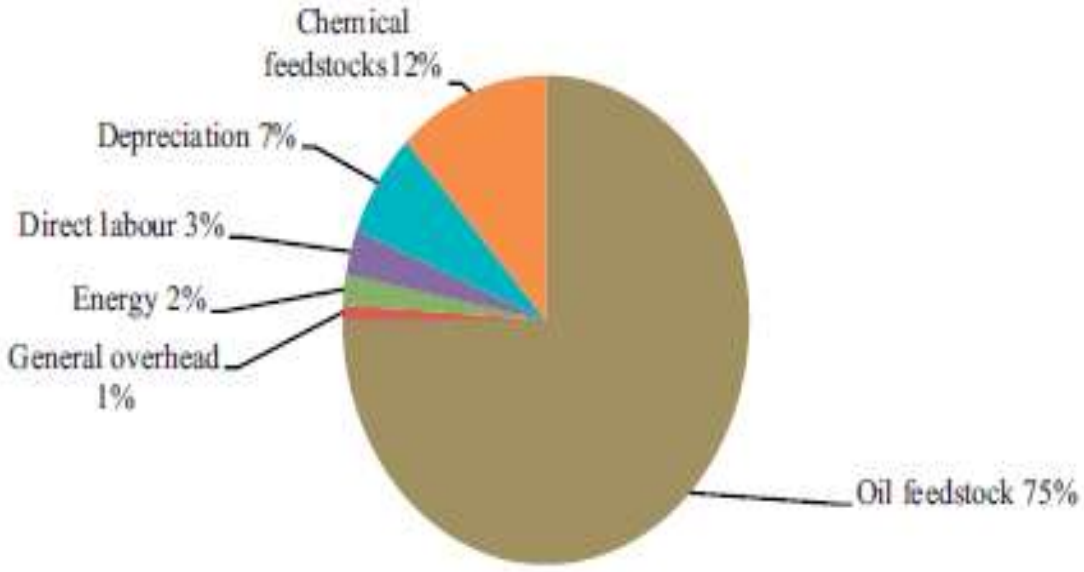


Figure 2.4 General cost breakdown for production of biodiesel

Source: - A.E. Atabani, et al, 2012

However non-edible oil plant have above all listed advantage, there are challenges related to non-edible oil as source of biodiesel. Development of non-edible oilseed as alternative biodiesel feedstock in the transportation sector is critical towards achieving higher self-reliance energy security. This situation offers a challenge as well as an opportunity to look for replacement of fossil fuels for both economic and environmental benefits. Under the existing situation of non-edible oils being of forest origin the problem encountered are;

- Collection from scattered locations, high dormancy and problems in picking and harvesting in avenue and forest plantations.
- Non-availability of quality planting material or seed, limited period of availability, unreliable and improper marketing channels.

- Lack of post-harvest technologies and their processing, non-remunerative prices, wide gap between potential and actual production, absence of state incentives promoting biodiesel as fuel, and economics and cost–benefit ratio (Syers.KJ, et al, 2007).

2.4 Feature of Croton Trees in Ethiopia

Ethiopia, endowed with diverse ecological varieties that have an abundant potential for biofuel production, but little benefit from its wealth. Despite the availability of huge renewable energy resources such as biofuels, the current level of harnessing this energy is very low. This is due to poor socio-economic situation in the country on the one side, a low level of awareness about the potential and technology incubation center to utilize these potential. Castor bean, jatropha and other are among some of non-edible naturally occurring biodiesel feedstocks in the country. Most of the indigenous plants such as *Croton macrostachyus* are not yet exploited or even not identified as biodiesel feedstock so far. In Ethiopia, *Croton macrostachyus* 'Besana' which is indigenous species has expected to be another newly emerged option of biodiesel feedstock. Therefore, this paper was devised to extend alternative feedstock source in addition to castor oil and jatropha on which a lot of research and effort were done and underproduction in parts of the country. Nevertheless, the search for feedstock in addition to jatropha and castor seed are still at its ground level.

(a) (b)

Figure. 2.5 (a) Croton macrostachyus trees and (b) pretreated croton seed.

Croton macrostachyus has repellant chemical ingredients and hence is not attacked by insects. Additionally, it is unpalatable and is therefore not looked by domestic or wild animals, thus

allowing it to grow successfully. It is fast growing trees, high yield rate and grow every parts of Ethiopia including degraded sloppy, marginal areas and also it can be grown in arable land without affecting nearby agricultural crops this allow multi-cropping practice overcome food insecurity that happen during production of jatropha and castor feedstock (figure 2.5). It has significant contribution in traditional agroforestry system in improving physical and chemical properties of soil and crop yield. The bark and buds have several traditional medicinal uses. The sap is used as a common curative traditional medicine for fungal skin diseases .Computed data from "Woody Biomass Inventory and Strategic Planning Project" indicated that *Croton macrostachyus* is the first abundant indigenous tree species of Ethiopia with the total number of 54.1 million trees (Taye.B, et al, 1999).

2.5 Oil Extraction Methods

Following biodiesel feedstocks identification, oil extraction is second step in biodiesel production process. In this process, the oil contained in the croton seeds has to be extracted. The pre-requisite for oil extraction is seed preparation, which involve removal of outer layers of the fruit and drying the kernel to reduce moisture content. According to Jahiru, et al, (2013) has found the moisture content of seed should be less 15% which provide highest oil yields in both mechanical and solvent extraction methods. The seeds are separated from fruits and size reduction or crashing of the seeds takes place after drying. There are three main methods that have been identified for oil extraction: (i) mechanical extraction, (ii) chemical or solvent extraction, and (iii) enzymatic extraction. Mechanical expellers or presses can be fed with either whole seeds or kernels or a mix of both, but common practice is to use whole seeds (Yadesa.G and Jorge.M, 2017, Patel.Sh, et al, 2011). This reduce quality of crude oil and cost of refining process. However, for chemical extraction only kernels are used as feed and extract high quality oil.

2.5.1 Mechanical Extraction

The techniques of oil extraction by mechanical presses is the most conventional one among other methods. In this type, either a manual ram press or engine driven screw press can be used. It has been found that, engine driven screw press can extract 68-80% of the available oil while the ram presses only achieved 60-65%. This broader range is due to the fact that seeds can be subjected to a different number of extractions through the expeller. The oil extracted by mechanical presses needs further treatment of filterization and degumming. One more problem associated with

conventional mechanical presses are. Their design is not suited for some seeds and therefore the yield is affected if used for other seeds. It has been found that, pretreatment of the seeds. Such as cooking, can increase the oil yield of screw pressing up to 89% after single pass and 91% after dual pass (*A.E. Atabani et al, 2012*).

2.5.2 Chemical or solvent extraction

Solvent extraction is the technique of removing one constituent from a solid by means of liquid solvent. There are many factors influencing the rate of extraction such as particle size, the type of liquid chosen, temperature and time. Small particle size is preferable because it allows for a greater interfacial area between the solid and liquid. The liquid chosen should be a good selective solvent and its viscosity should be sufficiently low to circulate freely. The temperature also affects the extraction rate. The solubility of the material will increase with the increasing temperature (A.E. Atabani et al, 2012).

Solvent extraction is economical way of oil extraction, since solvent can be recycled and provide high quality oil this reduce post production cost. For this specific study n-hexane was used as solvent to extract croton oil.

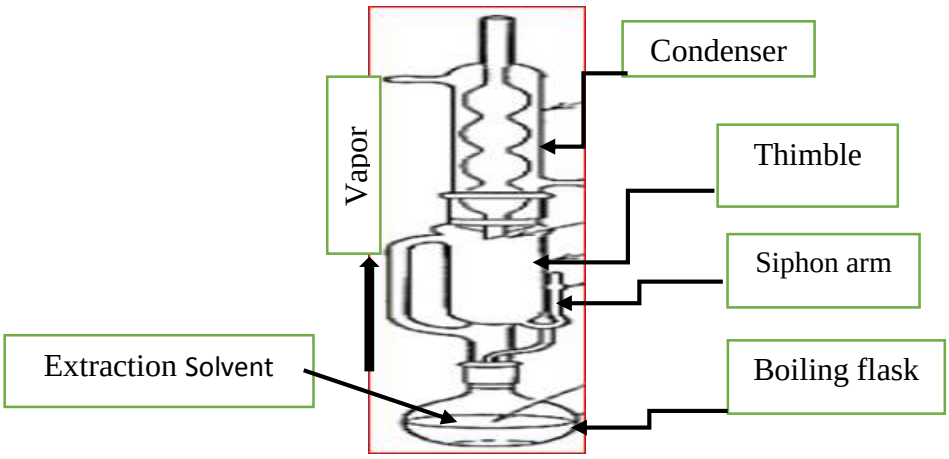


Fig.2.6. Soxhlet oil extraction apparatus

Source: - (Nur'Atiqah M et al, 2015)

2.5.3 Enzymatic Extraction

Enzymatic oil extraction technique has emerged as a promising technique for extraction of oil. In this process suitable enzymes are used to extract oil from crushed seeds. Its main advantages are that it is environmental friendly and does not produce volatile organic compounds. However, long process times and cost are the main disadvantage associated with this technique *(*A.E. Atabani et al, 2012*).* Aqueous enzymatic oil extraction can also be used in combination with other methods of oil extraction. For instance, Shah et al.(2005), used a combination of ultrasonication and aqueous enzymatic oil extraction (using an alkaline protease at pH = 9.0) method to extract oil from *Jatropha curcas* seeds and obtained 74% of the seed oil which is very large compared to the 17–20% oil extracted by aqueous oil extraction alone. Moreover, using of ultrasonication also resulted in reducing the process time from 18 to 6 h.

2.6 Biodiesel Production Technologies

Globally, there are many engineering efforts were developed and improve vegetable oil properties in order to proximate the properties of diesel fuels. It has been remarked that high viscosity and polyunsaturated characters are the mostly associated problems with crude vegetable oil. These problem can be overcome by four methods: pyrolysis, dilution with hydrocarbons blending, micro-emulsion and transesterification process (Fukuda.H, et al, 2001 & A.E. Atabani et al, 2012). In this study transesterification process was employed, due to its simplicity, cost and effective way conversion of croton oil to biodiesel. So, specifically transesterification reaction process discussed in detail from different literature prospective.

2.6.1 Transesterification (Alcoholysis) and Its Process Optimization

Transesterification process is one the best methods of reducing viscosity vegetable oil. Form all above list biodiesel production technology transesterification is low cost, simple and efficient technique employed to reduce viscosity of vegetable oil. Transesterification is described as the best choice as it is relatively simple and produces a product with properties close to diesel fuel. For these reason this research paper employed this method in order to convert croton oil to biodiesel by considering different parameters those affect the production process of biodiesel. This reaction process has been widely used to reduce the viscosity of vegetable oil and conversion of the triglycerides into ester. Basic definition of transesterification is one of thermochemical biomass conversion and define as chemical reaction in which the vegetable oil a triglyceride react with

alcohol (methanol or ethanol) in the presence of catalyst (homogenous or heterogeneous), producing a mixture of fatty acid (methyl or ethyl ester and glycerol. Different parameters considered during the transesterification reaction are: Molar ration (vegetable oil to alcohol), reaction time, reaction temperature, stirring speed, catalyst (homogenous and heterogeneous) and catalyst concentration (%w/w of oil). Transesterification process can be classified into catalytic and non-catalytic methods (Zakir.T, 2016, Prusty.B, et al, 2011, Alemayeh.G and Alemu.L, 2014 and Parmjit.S, et al, 2015).

i) Catalyst Transesterification methods

The transesterification of vegetable oils by heating with an alcohol and using catalyst is carried out in the process of conversion of vegetable oil to biodiesel. Two types of catalysts are used in catalytic technique, one is homogenous catalysts and the other one by heterogeneous catalyst.

In the catalytic methods the selection of suitable catalyst is more important to reduce the cost of production. The homogenous catalytic methods are again sub divided into two, one is homogenous base catalytic transesterification and the other, homogenous acid catalytic transesterification.

Methanol and ethanol are used most frequently during transesterification reaction; especially methanol is preferred because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). It can quickly react with triglycerides and KOH gets easily dissolved in it Ethyl ester and methyl ester almost has same heat content.

Homogenous base catalytic transesterification: At present, this process is the most employed in commercial sectors. It uses homogenous catalysts such as an alkaline metal alkoxides and hydroxides, as well as sodium or potassium carbonates. In the method of basic methanolysis, 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.T, 2016). The reasons these catalysts preferred are best operative conditions, high conversion rate in minimum time, good catalytic activity and economical.

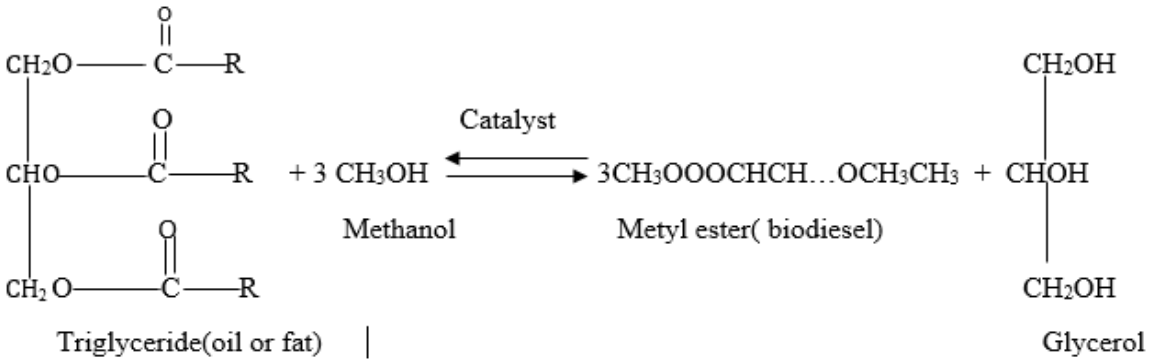


Fig.2.8 Biodiesel conversion process (catalyst transesterification reaction process)

The maximum amount of free fatty acids acceptable in homogeneous base catalytic biodiesel production process is below 2.5 wt. % FFA. If the oil or fat feedstock has a FFA content over 2.5 wt. %, a pretreatment step is necessary before the transesterification process (Birhanu A, 2014).

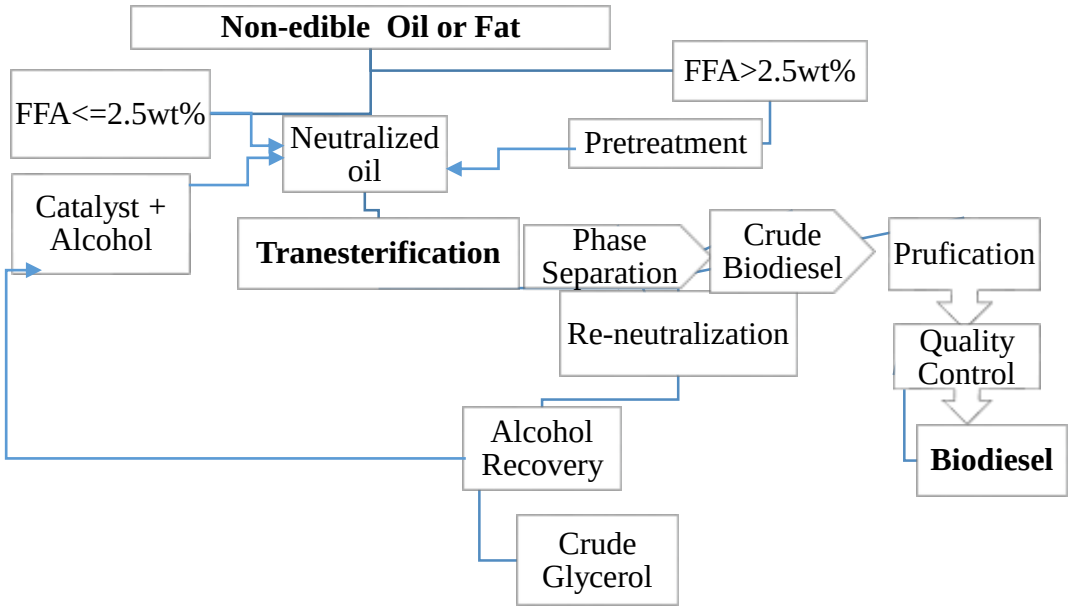


Fig 2.9 Flow path of Biodiesel production process.

The alcohol reacts with fatty acids to form the mono-alky ester or biodiesel and crude glycerol. In most production methanol or ethanol is used. If methanol used as alcohol methyl esters while ethanol used ethyl esters will produced in presence of catalyst (homogenous or heterogeneous).

Chemical transesterfication process for methyl ester biodiesel shown in figure 2.7. The reaction between the fat or oil (non-edible or edible) and alcohol is a reversible reaction and so the alcohol must be added in excess to drive the reaction towards the right and ensure.

In general homogenous base catalyst has the following advantage over acid catalyst:-

- The transesterfication reaction is very fast
- Consumption of alcohol is less
- The catalyst is less corrosive
- Methanol to oil molar ratio and catalyst concentration requirement is low as compared to acid catalyst process.

Homogeneous acid catalytic transesterification: 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.

Heterogeneous catalytic transesterification: These catalysts can act in different phases which can help in easy separation. The expensive method of homogeneous catalysts has called for heterogeneous methods. No soap formation takes place in heterogeneous processes. The whole is shown in the figure below.

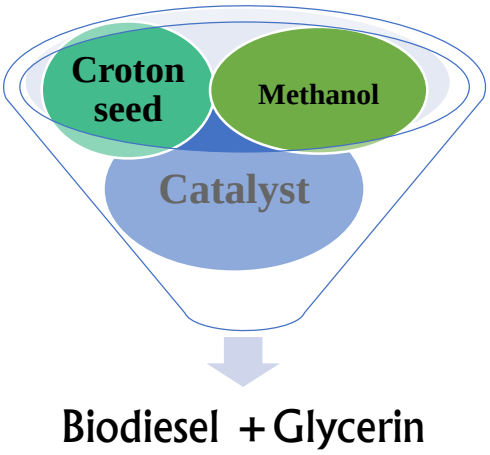


Fig 2.10 Catalytic Transesterification process

There are two more divisions in heterogeneous catalyst run reactions, they are heterogeneous solid base catalysts and heterogeneous solid acid catalysts. The former catalysts are base or basic oxides coated over large surface area. Solid-base catalysts are more active than solid-acid catalyst. The most common solid-base catalysts are Basic zeolites, alkaline earth metal oxides and hydrotalcites. Solid base can leads to the heterogeneous catalytic process, which promises the cost reasonable biodiesel production (Kouzu.M and Hidaka.J-S, et al, 2011).

Heterogeneous solid acid catalysts have different acid sites with varying strengths of Bronsted or Lewis acidity, compared to the homogenous acid catalysts. Heterogeneous Solid acid catalysts, such as Nafion-NR50, sulphated zirconia and tungstated zirconia have been chosen to catalyze biodiesel forming transesterification due to the presence of sufficient acid site strength (Dalai.A and Meher.LC. 2006).

ii) Non-catalyst Transesterification methods

There are few non-catalytic methods too. These process render production of biodiesel through a conventional transesterification system complicated, thus giving a reason to investigate the production of biodiesel from triglycerides via non-catalytic reactions. There are two basic routes to produce biodiesel by non-catalyzed transesterification. These are BIOX co-solvent process and supercritical alcohol process (Ahmad.A, et al, 2012, Ayhan, et al 2016). BIOX co-solvent process uses either tetrahydrofuran (THF) or methyl tert-butyl ether as a co-solvent to generate a one-phase system. The result is a fast reaction, on the order of 5–0 min, and no catalyst residues in either the ester or the glycerol phase (Ayhan, et al 2016). Non-catalyst is insensitive to free fatty acid and water content of feedstock and thus enable to use wider feedstock types, and produces more biodiesel per unit mass of oil. However, it requires higher temperature and pressure and consumes more methanol so that it is not economically profitable due to its high operating cost (Shemelis N and Jorge M, 2017).

Non-catalyst transesterification process require advanced technology and BIOX co-solvent not available in market. So, catalyst transesterification was employed due to low cost and availability of base catalyst like KOH. And also the amount of catalyst required per batch is too much small and the cost incur for catalyst is not that much significant compare to non-catalyst methods (appendix C).

From previous research catalyst transesterification has been established as most document and universally accepted method to use vegetable oils for diesel engine application. However,

transesterification process can produce biodiesel that have very similar properties with mineral fuel, the conversion rate of triglycerides or vegetable oil in to mono-alky esters vary due to different reaction parameter such as: reaction temperature, molar ratio of methanol to oil, catalyst concentration, types of catalyst, reaction time, free fatty acid of oil, water content oil and mixing intensity. The effect of each reaction parameter on yield of biodiesel discussed in section 2.6.1. Therefore, optimization of process variable is must to minimize cost of production and to have maximum yields of final product. Response surface methodology (RSM) were employed in transesterification process optimization. Because, response surface methodology is good tool of process optimization with more three independent variables.

2.6.1 Effect of Different Reaction Parameters on the Biodiesel Yield

The process of transesterification brings about a drastic change in the viscosity of the vegetable oil. The high viscosity component, glycerol, is removed and hence the product has low viscosity like the fossil fuels. The biodiesel produced is totally miscible with mineral diesel in any proportion. Flashpoint of the biodiesel is lowered after transesterification and the cetane number is improved. The yield of biodiesel in the process of transesterification is affected mainly by several process parameters which include; the presence of moisture and free fatty acids (FFA), reaction time, reaction temperature, catalyst and molar ratio of alcohol and oil (Alemayehu.G, et al, 2015). The effect of each parameter discussed in detail as follows. So, optimization of these parameters must be done in order to increase yields of biodiesel and with a minimum corresponding cost of production.

Temperature

Reaction temperature is the important factor that will affect the yield of biodiesel. For example, higher reaction temperature increases the reaction rate and shortened the reaction time due to the reduction in viscosity of oils. However, the increase in reaction temperature beyond the optimal level leads to decrease of biodiesel yield, because higher reaction temperature accelerates the saponification of triglycerides and causes methanol to vaporize resulting in decreased yield. Usually the transesterification reaction temperature should be below the boiling point of alcohol in order to prevent the alcohol evaporation. The range of optimal reaction temperature may vary from 50°c to 60°c depends upon the oils or fats used. Therefore, the reaction temperature near the boiling point of the alcohol is recommended for faster conversion by various literatures. At room

temperature, there is up to 78% conversion after 60 minutes, and this indicated that the methyl esterification of the FFAs could be carried out appreciably at room temperature but might require a longer reaction time (Mathiyazhagan, M.Ganapathi.A, 2011 and Ogbu, et al, 2013).

Methanol to Oil Molar ratio

One of the most important parameters affecting the yield of biodiesel is the molar ratio of alcohol to triglyceride. Theoretically the ratio for transeterification reaction requires 3mol of alcohol for 1mol of triglyceride. To produce 3mol of fatty acid ester and 1mol of glycerol. An excess of alcohol is used in biodiesel production to ensure that the oils or fats will be completely converted to esters and a higher alcohol triglyceride ratio can result in greater ester conversion in a short time (Alemayehu.G, et al, 2015 & Birhanu Ayalew, 2014). One 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. Freedman et al, 1984, studied the effect of molar ratio (from 1:1 to 6:1) on ester conversion with vegetable oils. Soybean, sunflower, peanut and cottonseed oils behaved similarly and achieved highest conversions (93-98%) at 6:1 molar ratio. However, increasing the molar ratio beyond the 6:1 may interfere with separation of glycerol because there is an increase in glycerol solubility. When glycerin remains in solution it will drive equilibrium back to the left, lowering yield of esters (Gupta, 2008).

Reaction time

Reaction time is another factor which affect the transesterification process of biodiesel production. The increase in fatty acid esters conversion observed when there is an increase in reaction time. The reaction is slow at the beginning due to mixing and dispersion alcohol and oil. After that the reaction proceeds very fast. However the maximum ester conversion was achieved within less than 90min (Alemayehu.G, et al 2015). Further increase in reaction time does not increase the yield product i.e. biodiesel. Beside, longer reaction time leads to the reduction of end product (biodiesel). Due to the reversible reaction of transesterification resulting in loss of esters as well as soap formation.

Type and Amount of Catalyst

Biodiesel formation is also affect by the types of catalyst (homogeneous or heterogeneous) and the concentration of catalyst. Most commonly used catalyst for transesterification is sodium hydroxide (NaOH) or Potassium hydroxide (KOH) (Mathiyazhagan, M.Ganapathi.A, 2011). 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 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.

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

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. The effect of mixing on the kinetics of the transesterification process forms the basis for process scale-up and design.

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. The resulting soaps can induce an increase in viscosity, formation of gels and foams and made the separation of glycerol difficult (Ayna.D et al, 2016). In the conventional transesterification of fats and vegetable oils for biodiesel production, FFAs and water always produce catalyst, reduces its catalytic effectiveness which results a low conversion in biodiesel production. FFAs react with the alkaline catalyst to produce soaps that inhibit the separation of the ester, glycerin and wash water.

In general, from the previous 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. So, these threes parameters were employed in reaction process optimization throughout the production of croton biodiesel, by varying one parameter at a time and keeping other variables constant.

2.7 Storage and Handling of Biodiesel

As already discussed before in this research biodiesel can be used for blending with petroleum in any percentage but the standard storage and handling procedures used for biodiesel are the main issue due to the biodiesel fuel specification and reactivity of unsaturated hydrocarbon chain, the biodiesel should be stored in a clean, dry and dark environment. Fuel grade of biodiesel must be produced to strict industry specifications (ASTM-D6751) in order to insure proper performance (Hanis Z et al, 2014). The key issue in using vegetable oil-based fuels is oxidation stability, stoichiometric point, bio-fuel composition, antioxidants on the degradation and much oxygen with comparing to diesel.

All fuels degrade after a certain period of time. The shelf life of biodiesel varies significantly but if manage properly, biodiesel can last long. A lot of articles are discussed about what is biodiesel its benefit, the factor affecting shelf life of biodiesel and how to store biodiesel. Here the main factors that influence the storage of biodiesel from different literature summarized as follow;-

- Temperature
- Microbial contamination
- Additives
- Light exposure
- Air exposure
- Chemical contamination

- The kind of feedstock

If biodiesel is contaminated by a microbe, the growth of the organism will render it unusable in a few hours. To prevent such a reaction, biodiesel storing tanks should always ensure the tank is air tight. If biodiesel has suffered microbial contamination, use a biocide to kill the microbes.

Oxidative damage also spoils biodiesel fuel at a fast rate. A question that most people ask is how is biodiesel stored to prevent oxidation. Oxygen attacks the chemical composition of biodiesel molecules. The oxidative attack causes acidic compounds to be formed and the fuel becomes acidic and lets out a rancid odor. As oxidation continues, the biodiesel becomes viscous and more corrosive and even starts to form sediments. Some of the factors that affect how long oxidative damage takes to render your fuel unusable include:

- The free oxygen content of biodiesel. Most biodiesel companies keep their fuel under nitrogen to prevent oxygen damage. A small company can extend the life of their fuel by keeping it in sealed biodiesel tanks. In actuality, the common place plastic diesel tanks that can be acquired cheaply will do if you're storing it for some time.
- Exposure to light: Oxidation can be facilitated by sunlight. To test the effects of sunlight on oxidation, take a small ration of oil and put it directly under the sun and in the open air for a few days. The oil becomes rubbery plastic. This is caused by the formation of polymers during the oxidation of the fuel. Practice storing biodiesel away from direct sunlight.
- Temperature: Cool temperature is good in preserving the life of biodiesel. Oils form polymers when under high temperature and this leads to their degeneration.
- Chemical contamination: Oxidation can be strengthened by trace metals mainly iron, copper and zinc. Biodiesel acts corrosively towards copper, brass and bronze. Therefore, you should ensure that the plumbing, valves and storage of biodiesel is done in containers that are not made of copper, brass or bronze.

2.8 Compatibility of Biodiesel with Petroleum Diesel Engines

The major disadvantages of biodiesel are its higher viscosity, lower energy content, higher cloud point and pour point, higher nitrogen oxide (NOx) emissions, lower engine speed and power, engine compatibility, and high price. So, before using biodiesel as substitute of diesel fuels a number of factors to be considered regarding compatibility engines.

Logically, the effect of biodiesel on engines and after treatment systems depends on the blend level used. While in many cases the most significant effect would be expected with pure B100 or high level blends, intermediate level blends can be most prone to the precipitation of fuel insoluble and filter plugging. Some cumulative effects can be also caused by prolonged operation with low biodiesel blends (Hannu.J and W.Addy.M, 2017).

Biodiesel advocates, including manufacturing groups and those environmental organizations that support the use of biodiesel, often that biodiesel can be used in exiting diesel engines without modifications. While it may be true that most diesel engines can be started and operated for a number of hours with biodiesel fuel (at least under mild weather conditions), engine manufacturers limit the use of biodiesel in many engine models to ensure no adverse effects over the entire life of the engine. The restrictions on the use of biodiesel fuels are typically imposed through new engine warranties that become void if the engine is operated with a fuel that does not meet the manufacturer's specifications, such as B100 or high level biodiesel blends. Another common issue is the lack of standard specifications for neat biodiesel and/or higher biodiesel blend fuels. Even if the engine is designed for an average B100 fuel, problems may arise due to the variability of a non-standard fuel without a widely accepted and enforced quality specification (Hannu.J and W.Addy.M, 2017).The potential issues with biodiesel fuels may be grouped as follows:

- Material compatibility
- Oil dilution
- Fuel injection equipment
- Emission control system

Therefore whenever the fuel composition is changed in the fuel system, material compatibility is a major concern. Fuel system designers incorporate materials based on laboratory testing and the available historical data. Thus, changes in fuel composition and the introduction of alternative fuels often create unforeseen problems in seals, gaskets, oil-rings, and metallic components in the fuel system.

Generally the use of biodiesel in existing engines may cause a number of issues related to materials compatibility, lubricating oil dilution, fuel injection equipment, and exhaust after treatment

devices. To minimize these potential impacts and ensure engine longevity, engine manufacturers often limit the use of biodiesel to low level blends.

Material compatibility: - Depending on the engine make model and model year, the engine components that come in contact with the fuel can be made from incompatible materials.

Oil dilution: - a possibility exists with all engines that some fuel will make its way into the engine's crankcase and dilute the lubricating oil. Over time, the accumulated fuel can amount to a significant proportion of the engine's oil capacity. What happens to the lubricating oil and engine components that come into contact with the oil/fuel mixture can have an impact on engine durability and longevity.

Fuel injection equipment: - Impacts on fuel injectors, filters and other fuel system components can cause a significant deterioration in engine performance.

Emission control system: - Emission after treatment systems, including catalysts and particulate filters, can be negatively affected by biodiesel fuels. Increased engine emissions or shortened durability of emission components can result.

2.8.1 Technique of Modifying Biodiesel Properties

Some of the properties of biodiesel fuel are not ideal from an engine performance point of view. Thankfully, additives can be used to counteract these problems and improve the overall quality of the fuel (Hancsok.J, et al, 2008). The selection of biodiesel additive is mainly depends on different properties of additives such as flash point, viscosity, density, calorific value and solubility.

Cold-flow improvers: these additive improve the cold weather performance of biodiesel by limiting its ability to gel. They tend to only improve the operating range by about 5 degrees.

Fuel stabilizers: these additives act as antioxidants to reduce the possibility of oxidation degradation of the biodiesel.

Antimicrobial additive: It is possible for microbes to grow in biodiesel resulting in clogged lines and fouled equipment. Antimicrobial additives prevent this by killing off any existing microbes and preventing them from regeneration.

Detergent additives: these help reduce the formation of deposits on engine parts by forming a protective layer on the parts and dissolving existing deposits from the surfaces within the engine.

Corrosion inhibitors: these also protect the engine by forming a protective layer on the components, thus preventing corrosive chemicals from reaching the surface.

A wide array of additives is available on the market today, and they can be purchased at an automotive shop or on the Internet. Often, a single product can be purchased that combines many or all of the above additives. Therefore, the use of additives in biodiesel also solves many technical problems which limits the acceptability of biodiesel as an alternative fuel in all conditions.

2.9 Benefits of Using Biofuels in Ethiopia

Biodiesel have several environmental and socioeconomically benefit here some of the benefit gained from biodiesel as substitute of diesel fuel are discussed as follow.

Improve social well-being; - A huge part of Ethiopia's population, mostly in rural areas, does not have access to modern energy services. The greater use of renewable (mainly biofuels) in rural areas is carefully linked to poverty reductions because greater access to energy services can:

- Allow lighting or rural electrification which improve life standard of rural community.
- Decrease the time spent by women and children on basic survival activities (congregation firewood, fetching water, cooking, etc.)
- Diminish indoor pollution caused by firewood use, together with a reduction in deforestation.

Enhancing energy security and reducing dependency imported oil: - Ethiopia is among the countries those heavily depend on importing diesel fuels as source of energy in transport and industry sector. More than 87% of export earning goes to purchase oil and 95% of the country's energy demand is met by traditional energy sources (Melis T, 2007). These result in negative trade balance and cause of different social problem such as health due to indoor air pollution, deforestation and loss of biodiversity. Therefore, using biodiesel from local feedstock can be resolve those problem in addition to energy security regenerating native plants for biodiesel feedstock play great role in maintaining biodiversity. In general, using biofuel as alternative source of energy lower exposure to the price volatility in international oil market.

3. METHODOLOGY

3.1 Site Description

The samples for biodiesel production were collected from Arsi Robe which is located in the south-eastern part of Ethiopia. It is named after the nearby Robe River. It is one of the administrative woreda in the Arsi Zone of the Oromia Region, this town located at a latitude and longitude of 09°36′N 39°08′E respectively, with an elevation of 2435 meters above sea level. Among many reasons why this specific place was selected: - the potential availability of croton trees, critical land degradation in the area (figure 3.1), and cost wise decision.

Fig 3.1 Map and geographical overview of pilot site.

3.2 Materials and Chemicals used

During the works of this research different laboratory equipment and chemical were employed for preparation of raw material, extraction and characterization of the *croton* oil and biodiesel production process (table 3.1).

Table 3.1 Summery of materials and chemicals used

Materials needed	Croton seed
	Crusher
	Oven dry, furnace , desiccators
	Chiller , Soxhlet, condenser, filter paper and round flacks
	Pipet, burette, beaker, crucible, digital balance
	Vibro-viscometer
	Pycnometer
	Stirrer
Chemicals	n-hexane
	Ethanol and methanol
	Diethyl ether, phosphoric acid and distilled water
	Phenolphthalein
	hydrochloric acid (HCl), potassium hydroxide (KOH)

3.3 Croton Seed Collection and Preparation

Croton macrostachyus seed was collected from Robe site and transported to the School of Chemical and Bioengineering laboratories. The seed was exposed to sun and dried for five days then decorticated manually to remove the outer shell of the seeds then dry it further for one day (figure 3.2). Crushing or size reduction is a crucial step in Croton seed preparation and can drastically change the physical properties such as specific surface area, cellulose crystallinity index and degree of polymerization, moisture and lignin content of the seed.

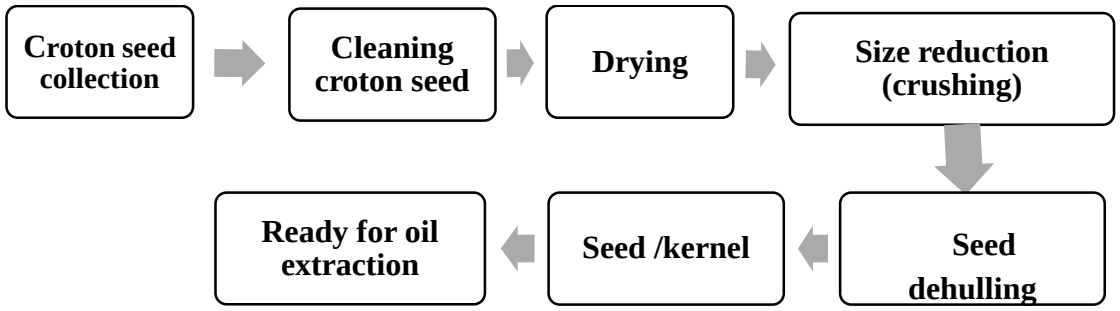


Fig.3.2 flow chart of raw material preparation procedures.

3.3.1 Characterization of Raw material (Croton Seeds)

The proximate analysis of the raw material (moisture content, volatile matter, fixed carbon and ash content) was determined using ASTM D1762. These are the basic physical properties of biodiesel feedstocks need to determine for a rough approximation of the final product quality.

Moisture Content: - Since moisture content affects the combustibility of the final product, it decreases the heat content per kg of croton oil. Moreover, it introduces formation glycerol and decreases yields of biodiesel during transesterification. Typical range is 0.5 to 10% Moisture (A.K.Shaha, 2011). Increases heat loss due to evaporation and superheating of vapors.

Thus, the raw croton kernel crushed to desirable size was put into a crucible. The crucible was weighted with and without croton kernel. The crucible with crashed croton kernel was dried in an oven at 105°C for 7h. The sample weight was recorded every 2 hours until constant weight obtained and once constant weight obtained then place crucible in the desiccator for 30 minutes to cool. Finally, the weight was taken and compared with the initially recorded weight of the sample.

The percentage weight in the croton kernel was calculated using the formula:

$$moisture\ content, \% = \left(\frac{w_1 - w_2}{w_1}\right) * 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.1)$$

Where; w_1=is the original weight of the sample before drying and

w_2= is the weight of the sample after drying

Volatile matter: - The amount volatile matter is one important factor to determine easy ignitability of biofuels extracted from plant oils. Determined by using the high-temperature furnace. The muffle furnace was heated until it reaches a temperature of 925^{o}C. Then, the crucible and its cover were weighed with and without of the croton kernel. Then, the samples were heated at 925°C in a closed crucible for 8 minutes. The weight of the sample before heating and after heating was used to determine the amount of volatile matter present in the sample. The percentage of volatile matter in the sample was calculated using the formula:

$$Volatilematter, \% = \left(\frac{b-a}{b}\right) * 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.2)$$

Where; b is weight of sample before drying and

a is weight of sample after drying at 925^{o} C

Ash content: - indicate the impurities that will not burn. The presence of high ash content affects the combustion efficiency of fuels and cause slagging and clinkering. Typical ranges of ash content should be 3% to 10% (A.K.Shaha, 2011) and the variation range is extended due to the origin of solid biofuels, species, climatic condition and specific part of the selected plant. It was determined as follow; the muffle furnace was heated until it reaches a temperature of 650℃. The dry crucible was weighed with and without of the crushed croton kernel. 2g of croton seed sample was heated at 650°C in an open crucible for 1 hour 30 minutes in a furnace. The weight of the sample before heating and after heating was used to determine the amount of ash content present in the sample. In this test, the amount of residual substance is equal to the ash present in the sample.

The percentage of ash in the sample was calculated using the formula:

$$Ash, \% = \left(\frac{W_1 - W_2}{W_1}\right) * 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.3)}$$

Where W_1 is weight of the sample before heating and W_2 weight of after combustion

Fixed Carbon Content: - it consists typically of carbon but also contains some hydrogen, oxygen, and nitrogen not driven off with the gases. Fixed carbon gives a rough estimate of the heating value of fuels. Proportionately increases the flame length and helps in the easier ignition of fuels.

The fixed carbon content was determined by subtracting the sum of percentage compositions of moisture content, volatile matter content, and ash content form 100. The value obtained is the amount of fixed carbon present in the sample expressed in percentage.

$$F.C, \% = 100 - (A_{sh}, \% + M_{c}, \% + V.M, \%) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.4)}$$

Where F.C is fixed carbon content,

A_{sh} is ash content,

Mc is moisture content, and

V.M is volatile matter

3.4 Extraction of Croton Macrostachyus Oil

The extraction of oil was carried out in the laboratory of the School of Chemical and Bio-Engineering, by using the method described by (Nur'Atiqah M et al, 2015). The extraction was done with a soxhlet apparatus of 1000ml capacity using n-hexane of analytical grade as the solvent. In the process, crushed (powder) croton (100g) was packed into filter paper and placed in the soxhlet extractor. 1000ml Round bottom flask containing 500ml n-hexane to its mark was attached to the lower part of the extractor which in turn attached to the condenser (fig 3.2). The solvent used was recovered after the completion of every experimental run by using simple distillation process, and the actual oil obtained was weighed. The average oil yield of croton seed was determined by using the equation;

$$\text{Oil yield, \%} = \left(\frac{Vo*\rho}{Ms}\right) * 100 \quad \text{..... (3.5)}$$

Where; Vo is volume of extracted oil and ρ is density of croton oil

Ms is mass of sample

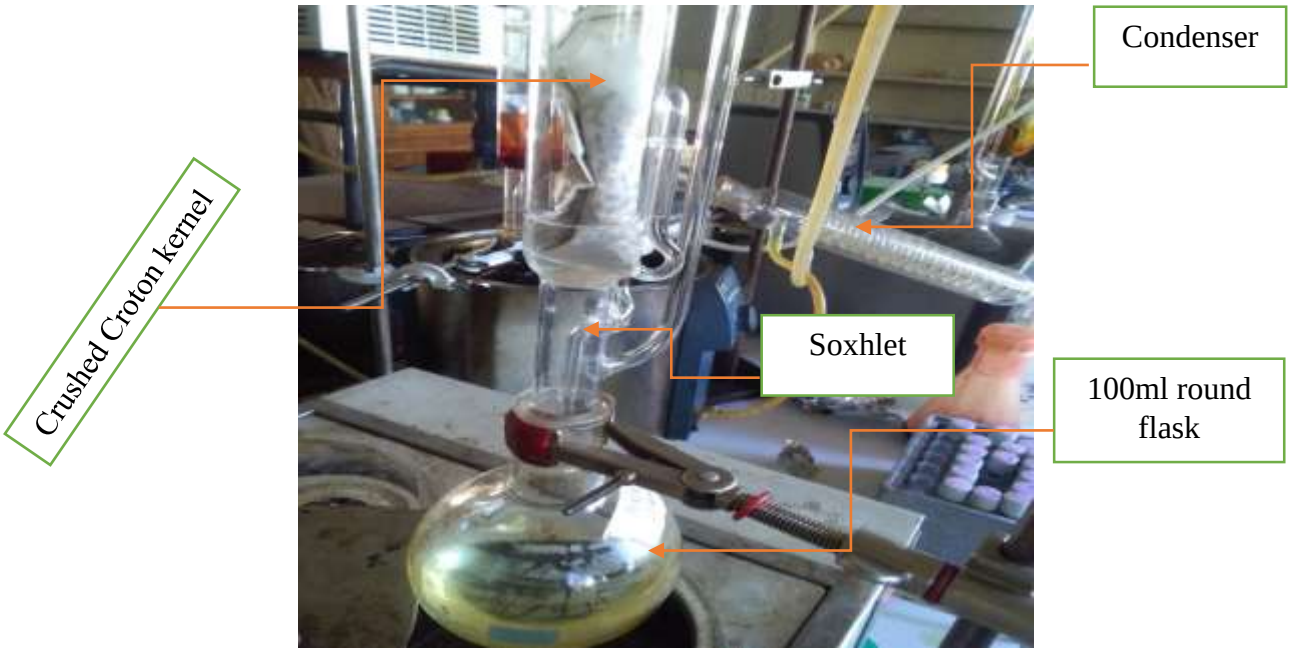


Figure 3.3 experimental set up soxhlet oil extraction

3.4.1 Purification of Crude Croton Oil

After croton oil extraction the purification process is a significant activity before proceeding to biodiesel production as the gum, phospholipids FFA, moisture and other undesirable compounds such as wax substances were contained in the crude croton oil which can reduce the biodiesel quality and these should be removed prior to the biodiesel production. As these undesirable mixture increase formation of soap during the transesterification process. Furthermore, the biodiesel produced from the refining oil affects the yields as well as the quality of the biodiesel.

There are several types of treatment methods such as degumming, neutralization, bleaching, and deodorization. However, degumming refining process was selected because of its simplicity and cost-effective methods of crude oil refining. Thus, the unwanted components in the crude croton oil were removed by means of degumming.

Degumming: - Different degumming processes are used during refining crude oil in order to separate gum, wax, minimize FFA and other impurities incorporate in the mixture. The extracted oil contains a considerable quantity of gums so that the oil was subjected to the water degumming process immediately the following extraction. In the degumming process, the oil was heated up to 70^{o}C and 3% of distilled water was added to the oil. Acid degumming and water degumming of crude oil were conducted. Acid degumming was performed by adding 4%wt of the phosphoric acid solution. The bleached oil was then mixed with water systematically and heated again to 70^{0}C, stirred vigorously for 30 min. After half hour the hydrated gums was separated by decantation (settling). In this process step a large part of hydratable and even a small proportion of the non-hydratable gums were removed.

In order to remove remaining trace moisture from the oil, dry the oil by using 105^{o}C oven dry until all moisture is removed completely. This can be achieved by continues weighting of the oil each half-hour interval until the weight of the oil become constant.

3.5 Characterization of Purified Croton Oil (Physicochemical Properties)

The physicochemical properties of croton oil were analyzed such as specific gravity, kinematic viscosity, acid value, the percentage of FFA content, and moisture content. These parameters directly or indirectly affect the quality of the biodiesel and also determine next reaction process and types of catalyst to be used.

3.5.1 Moisture Content of croton oil Determination

The empty dish was weighed with and without the croton oil and dried in an oven at 105ºC for 7hr, weighing each 2hr till constant weight is obtained and finally the weight was taken and compared with the initially recorded weight. The percentage weight in the oil was calculated using the formula:

$$\text{Moisture content, \%} = \left(\frac{w_1 - w_2}{w_1}\right) * 100 \quad \text{..... (3.6)}$$

Where, w_1=original weight of the sample before drying

w_2= weight of the oil sample after drying

3.5.2 Determination of Specific Gravity

Specific gravity was determined using empty pycnometer bottle that was weighed, then filled up with water and reweighed. The water was poured out and dried the bottle. The bottle was filled up with the oil and the weight was recorded. The specific gravity was then calculated using the following equation.

$$\text{Specific gravity} = \frac{w_2 - w_1}{w_3 - w_1} \quad \text{..... (3.7)}$$

Where; w_1 is weight of empty pycnometer

w_2 is weight of bottle with oil sample

w_3 is weight of bottle with water

$$\text{Density of oil } (\rho) = (specific\ gravity * density\ of\ water) \quad \text{..... (3.8)}$$

3.5.3 Determination of Kinematic Viscosity

The kinematic viscosity of biodiesel was determined using vibro-viscometer and compare with ASTM-D6751. Vibro-viscometer was used to determine the viscosity of the oil, and the sample was kept in the water thermostat bath until it reaches the equilibrium temperature of 20^{o}C. After maintaining the equilibrium temperature, the Vibro-viscometer tip was inserted into the sample and the reading was taken from the controller.

Viscosity depends on temperature and decreases as the temperature increases. The kinematic viscosity is then equal to the ratio of dynamic viscosity to the density of the oil.

$$\mu = \frac{\nu}{\rho} \quad \text{……..……} \quad (3.9)$$

Where μ=kinematic viscosity, mm^2/s

ν=dynamic viscosity of oil, mg/mm.s (measured by using vibro-viscometer) and

ρ=density of oil, g/cm^3

3.5.4 Determination of Acid Value or Acid Number (AV)

Acid value or acid number is the quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample to a specified end point. The acid number is direct measure of free fatty acids in B100 (Gerpen, 2004). The free fatty acids can lead to corrosion and may be indicator of presence of water in the fuel. The acid value is often a good measure of the breakdown of the triacylglycerol into free fatty acids, which has an adverse effect on the quality of final product.

To determine the Acid value, alcoholic KOH solution (0.1 N) was prepared by dissolving KOH with ethanol. The solution was filtered and stored in brown bottle for five days. Furthermore, a mixture of 95% ethanol and diethyl ether in a ratio of 1 to 1 by v/v was prepared by mixing 25ml diethyl ether and 25ml of ethanol. A weighed quantity of the oil sample (m=2g) was dissolved in 25 ml of 1 to 1 mixture of ethanol and diethyl ether. The solution was titrated with 0.1N ethanolic KOH standard solution in presence of 5 drops of phenolphthalein as indicator until the end point (colorless to pink) is recognized. The volume of 0.1 N ethanolic KOH (V) for the sample titration was noted.

The total acidity (acid number) in mg KOH/gm was calculated using the following equation:

$$\text{Acid Number} = \left(\frac{V*N*56.1}{m}\right) \quad \text{(3.10)}$$

Where V is the volume expressed in milliliter of 0.1N solution of ethanolic KOH

m is mass in gram of the test portion

N is concentration of ethanolic KOH

The free fatty acid, FFA of the oil was calculated empirically from the acid value previously determined using the equation.

$$FFA = \frac{Av}{2} \quad \text{(3.11)}$$

3.5.5 Determination of Saponification Number (SN)

The Saponification Number determination was conducted by dissolving the oil in an ethanolic KOH solution. This solution is then heated for half an hour so that the oil completely dissolves in the ethanolic KOH solution.

Saponification number was determined by the weighted amount of oil (m=2.5gm) was added to 25 mL of 0.5N solution of ethanolic potassium hydroxide and the reflux condenser was attached to the flask. The mixture was heated, and as soon as the ethanol boils, the flask occasionally agitated using a magnetic stirrer until the oil was completely dissolved, and then the solution was boiled for half an hour. After the oil was completely dissolved, 5 drops of phenolphthalein indicator were added and the hot soap solution obtained was slowly titrated with 0.5N hydrochloric acid up to the end point (colorless to pink) (volume Va was recorded). Then a blank determination was carried out in the same quantity of potassium hydroxide solution at the same time and under the same conditions (and volume Vb was recorded). The final result was calculated using the following equation.

$$\text{Saponification number} = \frac{N*56.1*(Vb-Va)}{m} \quad \text{(3.12)}$$

Where m= mass of oil taken in gram.

N= normality of HCL solution

Va= volume of HCL solution used in the test in milliliter.

Vb= volume of HCL solution used in blank in milliliter.

3.6 Experimental Design for Biodiesel production and Process Optimization (Transesterification)

Response surface methodology has been used to study the optimization of chemical processes and products. Thus, response surface methodology was used in this study to investigate the optimum process variables for the transesterification of biodiesel from croton oil. The process variables considered for this study were methanol to oil ratio, temperature and catalyst concentration. The Box-Behnken design (BBD) method was employed using Design Expert 6.0.8 software to examine the optimum conditions of the biodiesel production process. Seventeen possible combinations of process variables (experimental runs) were generated by Box-Behnken design (BBD) and the actual result of each run was investigated (table 3.3). The experiments were studied for nonlinear conditions using Response Surface Methodology (RSM) and the results analyzed by using the commercially available software program, Design Expert 6.0.8 software.

In this work, the main objective was to identify the optimum combination of the selected parameter at which the maximum yield of biodiesel achieved by using design expert software. Thus, different reaction parameter such as alcohol to oil molar ratio, reaction temperature, and catalyst loading was employed in order to observe the effect of those parameters on the response variable and select the best combination. The biodiesel production was conducted by using a purified croton oil, methanol, and analytical grade potassium hydroxide.

Transesterification reaction process commonly employed for non-edible oil are homogeneous base catalyzed or acid catalyzed, but for this specific study based catalyzed transesterification was selected because the maximum amount of free fatty acid of croton oil was less than 2.5% as discussed in section 2.6.1, Thus, in this work KOH catalyzed transesterification was employed to convert the purified and pretreated oil.

The catalyst (KOH) and the alcohol (CH3OH) were mixed with vigorous stirring, 20ml of purified croton oil was charged to three neck reactor and preheat the oil for 30min at 80oC to remove trace moisture and minimize parallel saponification reaction. The alcohol-catalyst mixture was fed to the reactor containing dehumidified pure oil. Then the alcohol-catalyst-oil mixture was agitated at

500rpm using overhead motor stirrer for an hour. The reaction temperature, catalyst loading, and alcohol to oil ratio were the three independent variables selected in process optimization and varied to obtain the optimum yields of biodiesel.

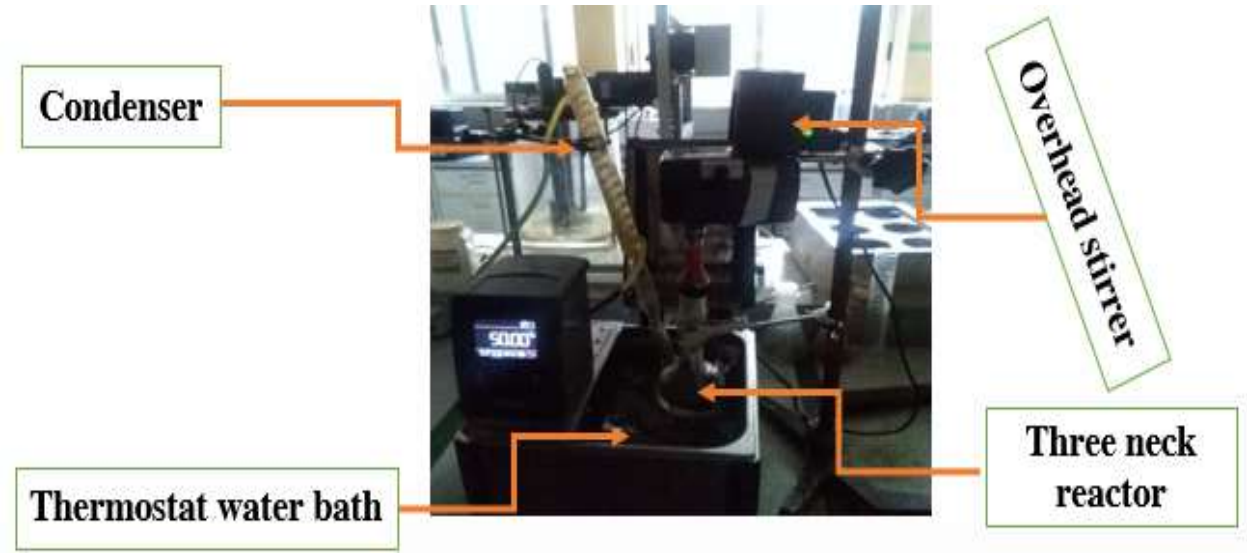


Fig.3.4. Experimental Set Up for Transesterification Process

a) Experimental set-up

The transesterification reaction process was done as shown in figure 3.4. The experimental set up consists of a 500ml three-necked batch reactor which is equipped with an overhead motor stirrer (max 2000rpm) fitted with stainless steel rod stirrer provided the mixing requirement and condensing coil. The reactor was submerged into a thermostat water bath heater.

A three-variable Box-Behnken design for response surface methodology was used to study the combined effects of catalyst concentration, methanol to oil molar ratio and reaction temperature on the amount of biodiesel yield over three levels. The range and levels of the variables used for optimization are shown in table 3.2.

The Box-Behnken design is suitable for the exploration of quadratic response surfaces and generates a second-degree polynomial model, which in turn is used in optimization process using a small number of experimental runs.

Table 3.2 Independent variable and levels used in transesterification process

Variables	Unit	Level	
		-1	1
Methanol to oil ratio	-	3	9
Catalyst loading	Wt%	1	2.5
Reaction temperature	^{o}C	50	65

The combination of three independent variable and the results of 17 experimental runs and yields of each run was investigated using the selected levels for reaction temperature, molar ratio of methanol to croton oil and KOH concentration. The amount of croton oil used per test was 20ml and by keeping reaction time (1hr) and string speed (500rpm) constant.

Table 3.3 Box Behnken Design matrix of transesterification process

Run	Factor 1 A: molar ratio of methanol to oil	Factor 2 B:Temperature	Factor 3 C:Catalyst loading	Response %
1	6.00	57.50	1.75	
2	3.00	57.50	2.50	
3	9.00	57.50	2.50	
4	3.00	65.00	1.75	
5	3.00	50.00	1.75	
6	6.00	57.50	1.75	
7	6.00	57.50	1.75	
8	6.00	65.00	2.50	
9	6.00	50.00	1.00	
10	3.00	57.50	1.00	
11	9.00	50.00	1.75	
12	6.00	57.50	1.75	
13	9.00	57.50	1.00	
14	6.00	57.50	1.75	
15	6.00	65.00	1.00	
16	9.00	65.00	1.75	
17	6.00	50.00	2.50	

b) Feed Material Requirement for Biodiesel Production

20ml of purified croton oil was used for each run. Hence, the amount of methanol and catalyst loading was calculated as follows using the process parameters.

The amount of methanol required when the molar ratio of methanol to oil ratio 6:1,

$$\frac{n\ of\ methanol}{n\ of\ oil\ sample} = 6 \quad \text{.....3.13}$$

Where n is number of mole methanol in given ratio

Number of mole (n):- can be expressed in terms of mass

$$n = \frac{\rho * V}{M} \quad \text{.....3.14}$$

Where ρ is density of given methanol or oil in the reaction mixture

M is molecular weight of methanol or oil the reaction mixture

V is volume of methanol

Therefore in order to calculate the volume of methanol required for each run substitute equation (3.13) in place of n as follow:-

$$\frac{\rho meoH * Vmeo H / MmeoH}{\rho oil * Voil / Moil} = 6 \quad \text{.....3.15}$$

The amount of catalyst required when the ratio of catalyst weight to is ranges from 0.5% to 2.5% and can be calculated as follow:

$$Moil = Voil * \rho oil \quad \text{... ... ...3.16}$$

=0.889*20ml

=17.78gm

$$Mcatalyst = catalyst, \% * Moil \quad \text{... ... ...3.17}$$

Similarly, the amount of methanol and catalyst loading required for each experimental run was calculated and the result for different processes parameter was given under ***Appendix-C (table-3).***

c) Optimization Process

Biodiesel was prepared from croton oil through a transesterification process in a biodiesel reactor. An optimization for percentage yield of biodiesel was designed for three selected factors. The optimum reaction conditions were determined by varying preselected parameters such as reaction temperature, methanol to oil ratio and catalyst loading (Jahirul MI, 2013). Accordingly, the reaction parameters were set as follows: reaction temperature ranges in between 50oC to 65oC which is below the theoretical boiling point of methanol and catalyst concentration vary from 1% to 2.5% of the weight of croton was investigated. In addition, molar ratio was varied from 3:1, 6:1 and 9:1, then the effect of each variation was evaluated. The reaction time and mixing intensity were fixed at 1hr and 500rpm respectively for all experimental runs. The optimal value of each parameter was determined, whereas 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 croton biodiesel.

Ester yield results (given as a percentage) were related to the weight of oil at the start (weight of ester/weight of oil). The biodiesel yield was determined as:

$$Yields\ \% = \frac{Total\ wieght\ of\ FAME}{Total\ wieght\ of\ oil\ in\ the\ sample} * 100 \quad \text{..... (3.18)}$$

3.7 Croton Biodiesel Purification

In biodiesel production, downstream purification is an important step in the overall process. The purification of crude biodiesel is the first step usually employed to recover biodiesel after the transesterification reaction. The purification of crude biodiesel is achieved via two notable techniques (I.M.Atadashi et al, 2011);

- Wet washings (low cost and effective way of removing excess alcohol)
- Dry washings (high cost and environmentally friendly)

The mixture of fatty acid methyl esters (FAME) obtained from the transesterification process must be purified in order to comply with established quality standards for biodiesel. Therefore, FAME must be washed, neutralized and dried.

Conventionally wet washing the most employed techniques to remove impurities such as soap, catalyst, glycerol and residual alcohol from biodiesel. In this study, wet washing of biodiesel was employed because of two reasons. The first reason was low cost and easy methods of washing glycerol and another by-product. The second reason was an efficient way of removing excess methanol than the dry wash. Normally washing of crude biodiesel carried out after phase separation. The reaction mixture was stored in the funnel until biodiesel light layer completely separated from the glycerin heavy layer. The complete separation of light biodiesel and glycerin layer formed after twenty-four hour (Fig 3.5).

Care must be taken (gentle shake and warm water) to avoid the formation of the emulsion during the washing steps since they would reduce the efficiency of the process. The first washing step was carried out with acidified water, to neutralize the mixture of esters.

Fig.3.5 Phase separation of biodiesel and post separation of wet washing biodiesel

The biodiesel layer was separated by removal of the glycerin layer. Afterward, the biodiesel was prepared for the washing procedure. For the washing process, 50% (related the biodiesel volume) of water was added to the biodiesel in order to extract contaminants. The gentle mix was allowed to separate, forming a top biodiesel layer and bottom aqueous layer, due to the difference in

densities and immiscibility. After complete separation, the aqueous layer was removed and the washing process was repeated until pure water or aqueous layer shows no contamination. The next step was the drying process. The drying process carried out by heating the biodiesel sample to a temperature ranges of 105^{o}C-110^{o}C. The temperature should not be less than 105^{o}C and higher than 110^{o}C. Biodiesel was heated for about half an hour until the water evaporates and removed from the sample.

3.8 Physicochemical Properties Analysis of Biodiesel

Characterization of Croton biodiesel crucial step which was used in standardizing and ensuring the quality of final product and also evaluating the measured value of selected parameters with installed international standard (ASTM and EN).Thus, the international standard set ground on biodiesel quality and ensure better criteria of biodiesel storage and successful commercialization of biodiesel. So, it is necessary to compare croton biodiesel with the installed international standard of fuel quality before using it as a diesel fuel substitute in CI-engine. According to (M.C.G. Albuquerque et al, 2009) the quality of biodiesel fuel can be influenced by various factors including the quality of feedstock, the fatty acid composition of the feedstock, type of production and refining process employed and post-production parameters.

Currently, the properties and qualities of biodiesel must adhere with the international biodiesel standard specifications. These specifications include the American Standards for Testing Materials (ASTMD-6751 or the European Union (EN14214) standards for biodiesel fuel. The properties of biodiesel are characterized by physicochemical properties such as percentage free fatty acid and acid value (mg KOH/g-oil), density (g/cm^3), viscosity (mm^2/s), caloric value (MJ/kg), Cetane number, cloud and pour point (^{o}C), flash point (^{o}C), ash content (%), water content and iodine value (A.E. Atabani, et al, 2012).

These parameters describe the physical and chemical characteristic of biodiesel produced from both non-edible and edible of oil resource, consequently, the present study was also selected some significant parameters which can directly or indirectly affect the quality of the final product/biodiesel. Therefore, the variables or parameters that mainly determine physicochemical properties of biodiesel were a percentage of FFA content, density, calorific value, acid value, kinematic viscosity, specific gravity, saponification number, iodine value and flash point.

Specific gravity

The procedure described in section 3.5.2 was used to determine the specific gravity and density of croton biodiesel.

Determination of Kinematic viscosity

As indicated in Figure 4.6 show the value dynamic viscosity of both croton oil and biodiesel. Instrument used to measure dynamic viscosity is known as vibro-viscometer.

The procedure described in section 3.5.3 was used to determine the kinematic viscosity of biodiesel.

(a) (b)

Fig 3.6 viscosity measuring instrument (vibro-meter).

a) Dynamic viscosity of croton oil and b) Dynamic viscosity of croton biodiesel.

Determination of Acid value and percentage of FFA

The procedure described in section 3.5.4 was similarly used to determine the Acid value and FFA of biodiesel.

Determination of saponification value

Saponification is the process of breaking down a neutral fat into glycerol and fatty acids by treatment with alkali and measure of the average molecular weight of triacylglycerol in a sample. The smaller the saponification number the larger the average molecular weight of the triacylglycerol present saponification value is inversely proportional to the mean molecular weight of fatty acids.

Therefore, the procedure described in section 3.5.5 was used to determine the saponification value of biodiesel.

Flash point

The flashpoint of the biodiesel was determined using open cup method. The cup was partially filled with the biodiesel about (35ml) and the cup was heated by a Bunsen burner. A small open flame was maintained from an external supply. Periodically, the flame was passed over the surface of the oil when the flash temperature was reached the surface of the oil catch the flame. Therefore the temperature at which the surface of the oil catches the flame was noted and reported as flash point temperature.

Calorific value

Calorific value is one the most important properties of a fuel, it is the thermal energy released per unit quantity of the fuel when the fuel burned completely and the products of combustion are cooled back to the initial temperature of the combustible mixture. Four essential parts are required in any bomb calorimeter: (1) a bomb or vessel in which the combustible charges can be burned, (2) a bucket or container for holding the bomb in a measured quantity of water, together with a stirring mechanism, (3) an insulating jacket to protect the bucket from transient thermal stresses during the combustion process and (4) a thermometer or other sensor for measuring temperature changes within the bucket.

An oxygen bomb calorimeter (Model C5000, Adiabatic Calorimeter, IKA®-Werke, Staufen, Germany) was used to determine the calorific value of the grind. The bomb calorimeter and the metal container surrounding it form the kernel of the calorimetric system, which is placed in a thermally insulated jacket. A primary temperature transducer, placed inside the unit, records the change in the system temperature due to the combustion of the fuel in the bomb. The calorimeter also contains a cooling system. The bomb calorimeter enables a rapid analysis to be carried out, the basic time of which cannot be reduced since it is related to the fuel combustion process itself. Calorific value can be defined as the amount of energy released by a mass unit of combustible mass. Two calorific values are the gross calorific value (GCV) and net calorific value (NCV). The gross calorific value (GCV) is the amount of energy released by complete combustion of a mass unit of sample at constant volume in an oxygen atmosphere, assuming that the final products of combustion consist of O2, CO2, SO2 and N2 in gas phase together with that of the sample contains and that generated from the combined hydrogen, in a liquid form. The net calorific value (NCV) can be calculated from GCV assuming that water in the product in the products remains in the form of vapor. NCV (net calorific value) is the quantity of heat produced by combustion when the

water produced by combustion remains gaseous or vapor. Since water releases heat when it condenses, GCV is clearly bigger than NCV. GCV is also called HHV (higher heating value) and the value measured for this case. NCV is also called LHV (lower heating value) can be calculated by using the following formula:

$$NCV = GCV - H_2O * 24.41 \quad \text{.....3.19}$$

Where: - NCV is net calorific value

GCV is gross calorific value

Calorific value of croton biodiesel was done in Ethiopia Geological Survey Laboratory, the method employed to determine calorific value of croton biodiesel was known as adiabatic calorimeter analysis. The original scanned result of calorific value report attached under ***Appendix-D.***

Iodine Number

The iodine value (IV) of the biodiesel was determined using the empirical formula suggested by Dembirbes (2008) for determination of calorific value. After rearrangement the iodine value (IV) was calculated from equation…

$$IV = \frac{49.43 - NCV - 0.041SN}{0.015} \quad \text{... ... ... 3.20}$$

Where IV is iodine value

NCV is net calorific Value

SN is saponification number

3.9 Gas Chromatography mass spectrometer (GC-MS) Analysis

The properties of biodiesel depend on many factors, such as the source of feedstock, method of esterification and fatty acid content. Being significantly different from diesel, the properties of biodiesel required to be estimated before application to a particular combustion system.

The properties of the triglyceride and the biodiesel fuel are determined by the amounts of each fatty acid that are present in the molecules. Chain length and a number of double bonds determined the physical characteristics of both fatty acids and triglycerides. According to (Samir A et al, 2015) found that transesterification does not alter the fatty acid composition of the feedstock, and this composition plays an important role in some critical parameters of biodiesel such as flash point, calorific value, and cold flow properties. So, determination of the fatty acid composition critical issue in biodiesel characterization.

Gas chromatography (GC-MS) analysis was employed to determine the fatty acid composition of croton biodiesel. It is an elemental analysis of biodiesel characterization and used to determine fatty acid composition in FAME. Biodiesel characterization by using GC-MS analysis showed that major fatty acid components in all FAME were saturated and unsaturated fatty acid. It provides an accurate qualitative and quantitative analysis of biodiesel (Zakir T, 2016).

Therefore GC-MS analysis is used to determine the structure of carbonyl group, the length of the carbon atom and degree of saturation of fatty acid. Since, the feature structure, the length of the carbon atom and the degree of saturation of fatty acids determine the physical properties of biodiesel such as viscosity, flash point, density, high heating values (Onkar S et al, 2010). The method also allows an assessment of the quality of biodiesel based on fatty acids composition. So, gas chromatography has been the most widely used method for the analysis of biodiesel owing to its generally higher accuracy in quantifying minor components.

GC-MS analysis was carried out in ***Ethiopia Leather Industry Development Institute and Research Laboratory Directorate***. The abundant Fatty Acid Methyl Ester of croton biodiesel was recorded and summarized in table 4.8 and the scanned original result is attached in Appendix E.

4. RESULT AND DISCUSSION

4.1 Characterization and oil content of Croton Macrostachyus Seeds

This study verifies that the average oil content of croton seed was achieved 53.34%, whereas the free fatty acid content of croton oil was 2.244%. Since the free fatty acid of croton oil is less 2.5% one step transesterification is possible without the requirement of pretreatment production steps. So, the homogeneous based catalyst was selected. In this work, a maximum of 96% biodiesel yield was obtained at an optimum point of input process variables (temperature, catalyst loading, and methanol to oil ratio). The rate of conversion of croton oil to biodiesel via transesterification process of each experimental run was recorded and at optimal point mass production of croton biodiesel was carried out by increasing the amount of input parameter (***Appendix C***).

Table 4.1 Proximate Analysis of Croton Macrostachyus Seeds.

Parameters	Yields (%)	Contents (%)[a]	Max. limit (ASTM D1762-84)[b]
Moisture content		6	3% to 10%
Ash content		2.5	0.3 % to 10%
Volatile matter		84.62	70% to 80%
Fixed carbon		6.88	-
Oil content	53.34		
Croton Biodiesel	96		

[a] present study **[b]** B.M. Jenk et al, 1989

The characteristics of raw material as described in table 4.1; Moisture content 6%, ash content 2.5%, volatile matter 84.62% and fixed carbon content 6.88% had been recorded. The result indicated that moisture content of croton seed moisture content was in the recommended ranges, whereas rich in a volatile matter (84.62%) and low ash content; this implies that biodiesel extracted from croton seed can easily ignitable with low ash. The presence of higher moisture content than specified ranges causes spontaneous hydrolysis reaction and deteriorate croton oil during storage, increase heat loss due to evaporation and add the cost of pretreatment. Thus, this study indicates that determination and characterization of the physicochemical properties of feedstock before biodiesel production would help to know the physical condition of feedstock and to make a certain

decision on whether it requires further treatment and what types of oil extraction methods employed.

4.1.1 Croton Oil Extraction and Purification

Solvent oil extraction was carried out with n-hexane as solvent. 100g of flour sample was placed into filter paper and the filter was placed in the soxhlet extraction apparatus. The optimum croton powder to the solvent ratio (1:5), temperature and extraction time were found 1:5, 70oC and 4hr respectively (Nur'Atiqah M et al, 2015). After 4 hour of the extraction period, the trapped oil was separated from the solvent by simple distillation methods and the solvent (n-hexane) was recycled. According to this extraction method, 100gm of crushed croton seed by using 500ml of solvent (n-hexane) and 60ml of crude oil was obtained. Thus, the oil content of croton seed was calculated numerically as follow;

$$yields\ of\ oil\ \% = \frac{mass\ of\ extracted\ oil}{wieght\ of\ in\ put\ sample} \quad \text{.....4.1}$$

Finally oil content of croton seed has been found 53.34% which is really make croton seed competitive and best future promising feedstock (table 4.1). Purification was done as discussed session 3.4.1.

4.1.2 Characterization of Croton oil and Compare with Jatropha Oil

Initially checking physicochemical properties of croton oil very import, because parameter such as free fatty acid, moisture content are highly affected next transesterification reaction and yields of biodiesel. This was the major properties of oil that help in decision making for next process such what types of transesterification appropriate, types of catalyst and to estimate oil quality as well as oil content of given feedstock. In the conventional transesterification of fats and vegetable oils to biodiesel, the presence of free fatty acids and moisture content always result in negative effects due to soap formation, excess catalyst consumption and low production of the biodiesel. Therefore, physicochemical properties (free fatty and moisture content) croton oil should be determined prior to biodiesel production.

Hence, it was observed that the free fatty acid of croton oil is less than 2.5% or acid value is less 5 mg KOH/g, which allow single step transesterification reaction process to produce biodiesel. So, one step homogeneous base transesterification process was selected as discussed in section 3.6.

Thus, The high FFA content (>2.5 %w/w) will cause soap formation, and the separation of products will be exceedingly difficult; as a result, it has a low yield of biodiesel product.

Moisture content is one of the basic important properties of oil that should be determined before transesterification process take place because transesterification reaction (conversion of oil to biodiesel) is the most sensitive reaction process to moisture.

The moisture content of croton oil was obtained 1.23% which reveal allowable ranges for biodiesel production. Many researchers recommend moisture content of oil should be less than 8% gives the optimum yield of biodiesel (Abbah E et al, 2016). So, this study result shows the moisture content of croton oil was confirmed as too small and can be used without pretreatment for next transesterification.

Viscosity is the most important characteristic in the storage and use of fuel oil. It influences the handling, storage, and satisfactory atomization. If the oil is too viscous, it may become difficult to pump, hard to combust and tough to operate CI engine. Poor atomization of the oil results in the formation of carbon deposits in the combustion chamber or on the walls. The result of this study was verified 43.98 mm^2/s, which implies the croton oil is too viscous in order to use for CI engine directly that is why next process was required to reduce the viscosity of croton oil. Therefore, among different methods of minimizing viscosity of vegetable oil transesterification process was employed.

Table 4.2 Physicochemical properties of croton oil verses castor and Jatropha oil

Parameters	Units	Croton oil [a]	Castor oil [b]	Jatropha oil [c]
Oil content	%	53.34	40 to 60	35 to 40
Free fatty acid	mg KOH/gm	2.244	1.2	1.7
Acid value	mg KOH/gm	4.488	2.4	3.38
Saponification number	mg KOH/gm	195.885	199	-
Viscosity	mm^2/s	43.98	222	49.93
Density	g/cm^3	0.889	930	907
Moisture Content	%	1.23	-	-

[a] present study [b, c] Aldo Okullo et al, 2012 & Madhu A, 2017

The FFA content of crude croton oil 2.244 mg KOH/gm which was less than 2.5mg KOH/gm and usually, base catalyzed transesterification process can be employed in croton biodiesel production. The free fatty acid value after biodiesel production will be low since the base catalyst will strip the available free fatty acids. After croton oil characterization, biodiesel production and process optimization were conducted experimentally.

4.2 Biodiesel Production and Analysis of Process Variables Optimization

4.2.1 Transesterification Process

The transesterification process was carried out using the method described in section 3.6. The biodiesel yield was investigated mainly for the three major reaction parameters namely methanol to oil ratio, temperature and catalyst concentration. In this investigation, the reaction time and mixing intensity kept constant for all experimental runs (1hr and 500rpm) respectively (Mathiyazhagan, M, 2011). The biodiesel was synthesized using batch wise transesterification process. Since soxhlet extraction oil produces high-quality oils, degumming was enough to reduce the acid values or no need for esterification process in order to reduce the acid values. So, after oil purification direct transesterification reaction was done. Twenty milliliters of degummed croton oil was used for each run under given constraint. The statistical analysis of the biodiesel yields and the effect of selected parameters were discussed in the next session.

4.2.2 Statistical Analysis on Different Process Variable Optimization

The experimental design selected for this study is Box Behnken design and the response measure is the yields of biodiesel as discussed in session 3.6. The three transesterification process variables studies were reaction temperature, the molar ratio of methanol to oil and catalyst concentration. The experimental data obtained by the above procedure was analyzed by the response surface regression using a second-order polynomial equation.

The Design-Expert 6.0.8 software was used in the regression analysis of variance (ANOVA). The statistical software was used to generate surface plots, using the fitted equation obtained from the regression analysis, holding of the independent variables constant. The equation was also validated by carrying out confirmatory experiments. The actual results obtained from every 17 experimental runs and predicted value generated by design expert was recorded in table 4.3 below.

Table 4.3 Box Behnken arrangement and response for alkali transesterification reaction processes.

Run	Factor			% Biodiesel	Yields	Residuals
	Temperature ^{o}C	Methanol to oil ratio	Catalyst concentration	Actual value	Predicted value	
1	57.50	3.00	2.50	75	72.63	-2.63
2	57.50	6.00	1.75	83.5	75.13	-0.13
3	57.50	6.00	1.75	83.5	59.88	0.12
4	50.00	6.00	2.50	85	67.38	2.62
5	50.00	3.00	1.75	70	63.88	1.12
6	65.00	6.00	2.50	75	86.38	-1.38
7	50.00	9.00	1.75	75	73.63	1.37
8	65.00	9.00	1.75	70	61.13	-1.13
9	57.50	6.00	1.75	83.5	94.50	1.50
10	57.50	3.00	1.00	65	81.25	-1.25
11	65.00	3.00	1.75	60	83.75	1.25
12	50.00	6.00	1.00	96	76.50	-1.50
13	57.50	9.00	2.50	60	83.50	0.000
14	57.50	6.00	1.75	83.5	83.50	0.000
15	57.50	9.00	1.00	85	83.50	0.000
16	65.00	6.00	1.00	80	83.50	0.000
17	57.50	6.00	1.75	83.5	83.50	0.000

As discussed in session 3.6 the yield of the transesterification processes have been calculated by dividing the weight of biodiesel (FAME) produced for the sample of croton oil used, multiplied by 100. The result of the transesterification process of each run from croton oil is presented in table 4.3. The yield for each run of the experiment was determined using equation 3.19. The varying biodiesel yield values were indicated that the extraction parameters considerably affect the transesterification process. It was observed that the actual yield well confirmed with the predicted value generated by the Design Expert software (BBD).

The maximum biodiesel yield of croton oil was 96% at optimal combination of the process variable. From the actual investigation of each run verified that the optimum conditions at which maximum yield was found @6:1 methanol to oil ratio, @50^{o}C reaction temperature, and @1% KOH concentration of the oil in transesterification. Therefore, at this optimum combination mass production of croton biodiesel were made to obtain the required amount of biodiesel for this study. Using Design expert the value of biodiesel yields was predicted as well as possible combination process variable was selected. Analysis of variance (ANOVA) process evaluation by using Box-Behnken Design (BBD) methods, the selected design point of optimum yield 96.0164% was found at 6.72:1 of alcohol, 50.12^{o}C of reaction temperature and 1% catalyst loading which is nearly equivalent with the actual experimental process variable combination (table 4.6). Thus, a little deviation in the selection of optimum process variable condition between actual and software generated is a result of lack of precision measurement or error might occur in the laboratory.

Table 4.4 Analysis of variance (ANOVA) for response surface quadratic model of alkali Transesterification process.

Source	Parameters	Sum of squares	DF	Mean square	F-value	Pro>F	Remark
Model		1512.31	9	168.03	42.39	< 0.0001	Significant
	A	50.00	1	50.00	12.61	0.0093	
	B	210.13	1	210.13	53.00	0.0002	
	C	120.13	1	120.13	30.30	0.0009	
	A^2	796.05	1	796.05	200.81	< 0.0001	
	B^2	4.21	1	4.21	1.06	0.3370	
	C^2	9.47	1	9.47	2.39	0.1661	Not significant
	AB	6.25	1	6.25	1.58	0.2495	
	AC	306.25	1	306.25	77.25	< 0.0001	
	BC	9.00	1	9.00	2.27	0.1756	
Residual		27.75	7	3.96			
	Lack of Fit	27.75	3	9.25			
	Pure Error	0.000	4	0.000			

The statistical analysis for transesterification process variable was done using analysis of variance (ANOVA). From Table 4.4 the ANOVA results of transesterification process parameters. The model F-value of 38.83 implies the model is significant. There is only a 0.01% chance that "Model F-Value" this large could occur due to noise. The value of "pro>F" or P-value less than 0.0500 indicate the model terms are significant and the value greater than 0.100 indicates the model terms are not significant. In this case, A, B, C, A^2, and AC are significant model terms.

The multiple regression analysis of the experimental data gives a second-order polynomial equation, which was modified to discard the insignificant parameters model terms. The reduced quadratic model developed depicts the interaction between the dependent biodiesel yield (Y) and the coded values of the independent variables A, B and C (molar ratio of methanol to oil, temperature, and catalyst concentration). This is shown in the regression equation 4.2 and 4.3.

Final Equation in Terms of Coded factors:

Yields, % = +83.5 + 2.50*A – 5.13*B – 3.88*C - 13.75*A^2 – 1.00B^2 + 1.5*C^2 + 1.25*A*B -8.75*A*C + 1.5*B*C…….. (4.2)

Final Equation in Terms of Actual Factors:-

$$Yields, \% = +26.38889 + 22.77778 * molar\ ratio\ of\ methanol\ to\ oil + 0.56111 * temperatur - 6.50 * catalyst\ concetration - 1.52778 * molar\ ratio\ of\ methanol\ to\ oil^2 - 0.017778 * temperature^2 + 2.66667 * catalyst\ concetration^2 + 0.055556 * molar\ ratio\ of\ methanol\ to\ oil * temperature - 3.88889 * molar\ ratio\ of\ methanol\ to\ oil * catalyst\ concentration + 0.26667 * temperature * catalyst\ concentration \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.3)$$

The significance and adequacy of the model were tested using ANOVA. It was observed from the table that the linear interaction effects are due to the Code Factor A, corresponding to the molar ratio of methanol to oil, which is a significant factor. The quadratic effects of molar ratio A^2, linear effects of temperature B, catalyst concentration C and molar ratio & catalyst concentration AC are all significant since the value of each variable is less than 0.05, while the values greater

than 0.05 means not significant. The ANOVA result shows that the process variables B^2, C^2, AB, and BC are not significant.

Table.4.5 shows the assessment of experimental errors and the confidence interval (CI) of the experimental variables. The standard errors are analyzed from the differences between the predicted biodiesel yields and the experimental values recorded of each run as shown in table 4.3.

Table 4.5 Regression coefficients and significance of response surface quadratic model for the KOH catalyzed

Factor	Coefficient Estimate	DF	Standard error	95% CI Low	95% CI High	VIF
Intercept	83.50	1	0.89	81.39	85.61	
A-molar ratio of methanol to oil	2.50	1	0.70	0.84	4.16	1.00
B-temperature	-5.13	1	0.70	-6.79	-3.46	1.00
C-catalyst concentration	-3.88	1	0.70	-5.54	-2.21	1.00
A^2	-13.75	1	0.97	-16.04	-11.46	1.01
B^2	-1.00	1	0.97	-3.29	1.29	1.01
C^2	1.50	1	0.97	-0.79	3.79	1.01
AB	1.25	1	1.00	-1.10	3.60	1.00
AC	-8.75	1	1.00	-11.10	-6.40	1.00
BC	1.50	1	1.00	-0.85	3.85	1.00

Table 4.6 Design Expert numerical evaluation of process optimization within a given constraint

Name of parameters	Goal	Lower limit	Upper limit	Lower limit weight	Upper limit weight	Importance
molar ratio of methanol to oil	is in range	3	9	3	4	3
Temperature	is in range	50	65	1	6	3
catalyst concentration	is in range	1	2.5	1	5	5

Yields %	maximize	60	96	1	1	5

Possible solution generated by Design Expert software and selected process parameters

No.	Molar ratio	Temperature(°C)	Catalyst concentration	% Yield	Desirability	Remarks
1	**6.72**	**50.12**	**1.00**	**96.0164**	**1.000**	**Selected**
2	7.49	50.04	1.00	96.0068	1.000	
3	7.07	50.28	1.01	96.0127	1.000	
4	7.21	50.41	1.00	96.0289	1.000	
5	7.54	50.00	1.00	96.0028	1.000	
6	7.10	50.15	1.00	96.201	1.000	
7	7.28	50.05	1.00	96.211	1.000	
8	7.31	50.23	1.01	96.0109	1.000	
9	7.13	50.21	1.01	96.1009	1.000	
10	7.42	50.18	1.00	96.0022	1.000	
11	6.97	50.20	1.01	96.0211	1.000	
12	7.29	50.21	1.01	96.0538	1.000	
13	7.37	50.09	1.00	96.1102	1.000	
14	6.79	50.08	1.01	96.056	1.000	
15	7.31	50.64	1.00	95.8929	0.997	
16	6.11	50.00	1.00	94.8351	0.968	
17	7.73	52.83	1.00	94.0733	0.946	

4.2.3 Diagnosis of Model Adequacy Test

After the development of models using the RSM, the significance tests using ANOVA were carried out in order to validate the model and its precision. The model was tested for adequacy by variance analysis.

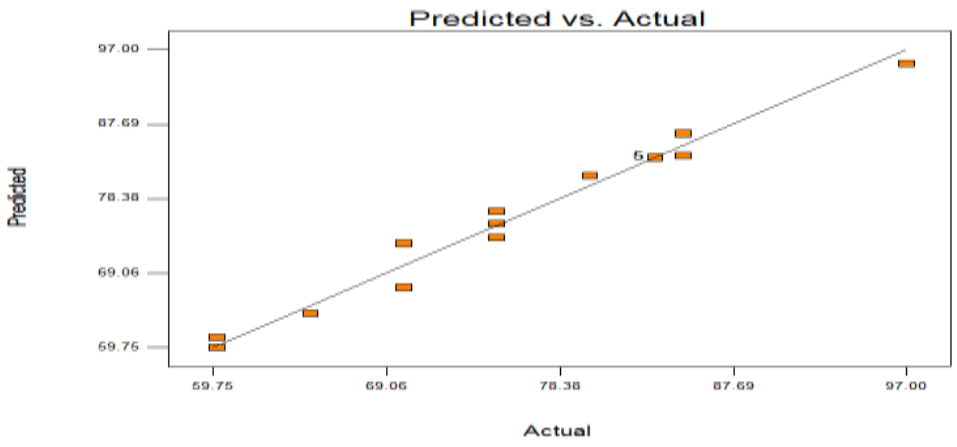


Fig.4.3 Predicted versus Actual value of response (yields of biodiesel)

The graph of the predicted values obtained using the developed correlation versus actual values forms a line of unit sloped correlation versus actual values forms a line of a unit slope, i.e. the line of a perfect fit with points corresponding to zero error between predicted values and actual values as shown in figure 4.3. The results in figure 4.3 demonstrated that the regression model equation provided a very accurate description of the experimental perfect fit. This result indicates that it was successful in capturing the correlation between the three transesterification process variables to the yield of biodiesel.

Table 4.7 Model adequacy validation using Standard deviation, Mean and CV

Std. Dev.	1.99	R-Squared	0.9820
Mean	77.26	Adj R-Squared	0.9588
C.V %	2.58	Pred R-Squared	0.7117
PRESS	444.00	Adeq Precision	22.674

The low value of the coefficient of variation (CV=2.58%) indicates that the result of the fitted model is reliable. The quality of the model fit was evaluated by the coefficient of determination (R2), this value is calculated to be 0.9820 for the response, indicating that the developed model

equation successfully capture the correlation between the process parameters to the yield of biodiesel. The value of R-square (R^2) was 0.9820, this indicates that 98.2% of the total variation in biodiesel yield was attributed to the experimental variables studied. The closer the R2 value to unity, the better the model will be as it will give predicted values which are closer to the actual optimum values for the response.

From table 4.7 the regression model was found to be highly significant with the correlation coefficients of determination of R-squared (R^2), adjusted R-squared and predicted R-squared having values of 0.9820, 0.9588 and 0.7117 respectively. The adjusted coefficient of determination (R^2adj=0.9588) is also very high, supporting the significance of the model. As the fitted model Eq.4.3 provides a good approximation to the experimental condition, the model is used to find the values of the process parameters for optimum yield of biodiesel.

It can be observed that the variable with the largest effect on biodiesel yield is the linear term of A-methanol to oil ratio and followed by quadratic terms of methanol to oil ratio, a linear term of C-catalyst concentration, linear terms of temperature and cross product of methanol to oil ratio and catalyst concentration (AC). However, quadratic terms of temperature, quadratic terms of catalyst concentration and cross product of methanol to oil ratio and temperature (AB) are found to be insignificant ($p>0.05$). Regression analysis of the experimental data also shows that methanol to oil ratio and catalyst concentration of reaction variables has positive and negative linear effects respectively on biodiesel yield. Both variables are strong linear effects of 22.7778 and -6.5000 respectively on biodiesel yield (Equation 4.3).

4.3 Effect of Different Process Variables on Biodiesel Yields

The individual and the interaction effect of three process variables (molar ratio of methanol to oil, temperature and catalyst concentration) on the biodiesel yields were studied using the interaction plot and 3D surface plot of RSM by using Design Expert.

a) Effect of methanol to oil ratio on biodiesel (FAME) yields

The transesterification process consists of the sequence of three consecutive reversible reactions where the triglyceride is successively transformed into diglyceride, monoglyceride and finally into fatty acid methyl esters (FAME) and glycerin as discussed in session 2.6. Methanol to oil ratio is

one of the parameters highly affect the production process of biodiesel (transesterification). It plays a great role in transesterification reaction by converting the triglycerides to FAME.

The percentage yields of biodiesel increase as methanol to oil ratio increase, however increasing methanol beyond optimum or excess methanol result in marginal decreasing in biodiesel yields and increase the cost of post-production treatment. The maximum percentage yield of biodiesel obtained during the transesterification process was obtained at methanol volume of 25ml which corresponded to methanol to oil ratio approximately 6:1. Further increase in the volume of methanol added to the reaction mixture led to a decrease in percentage yield of biodiesel. In this work, the methanol to oil ratio of 6:1 was found the optimum point and increasing above this point was not increase conversion efficiency rather slight decrease in yields of biodiesel and also excess methanol increase cost of post-treatment and makes phase separation of biodiesel and glycerol difficult result in the increase in soap formation. On another hand, the experimental run at lower methanol volume increased formation emulsion and incomplete transesterification reaction. Figure 4.1 shows the variation of the mean percentage yield of croton biodiesel with the volume of methanol used for transesterification.

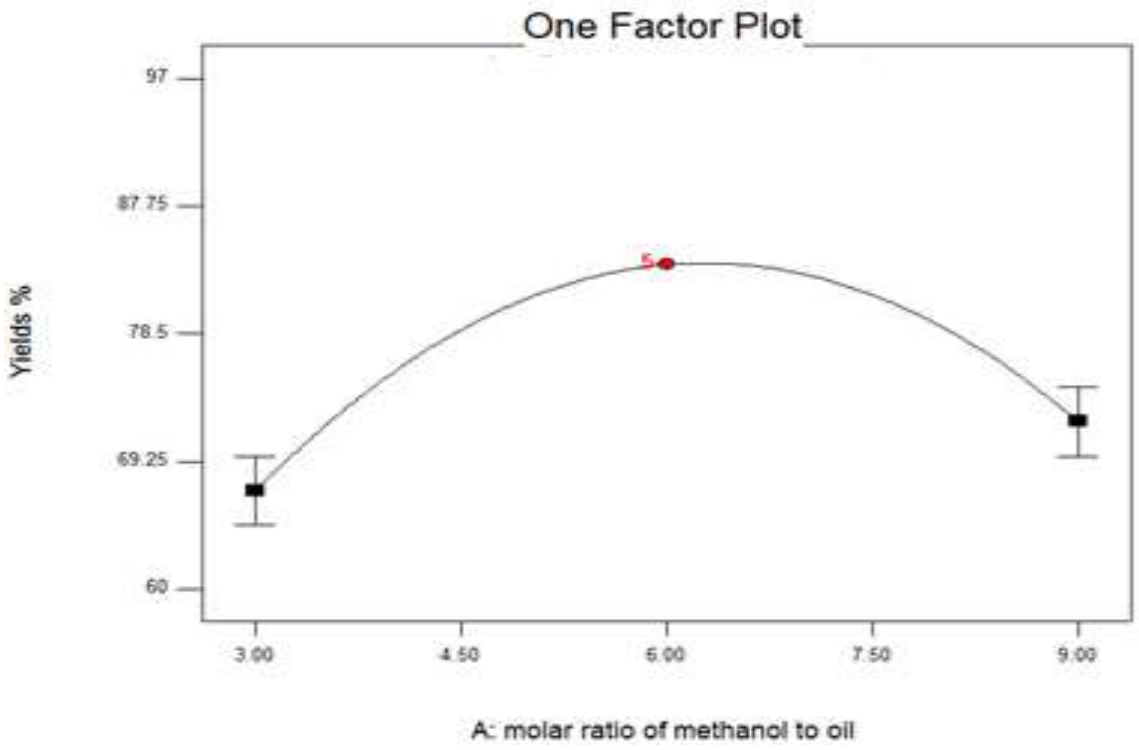


Fig 4.5 Effect of methanol to oil ratio on biodiesel yield

b) Effect of Temperature on Biodiesel Yield

The effect of temperature on the transesterification of croton oil is presented in figure 4.2. The results have shown that an increase in temperature decreases the rate of reaction. The optimum temperature was found at 50^{o}C and the corresponding highest conversion of 96% was observed at this temperature at 1hr reaction time. At 65^{o}C, the maximum conversion was 80% after 1hr with corresponding optimum methanol to oil ratio. At a temperature above the boiling point of methanol, evaporation of methanol occurred and it may also accelerate saponification of triglycerides by alkaline catalyst before completion of transesterification process as discussed in session 2.6.1.

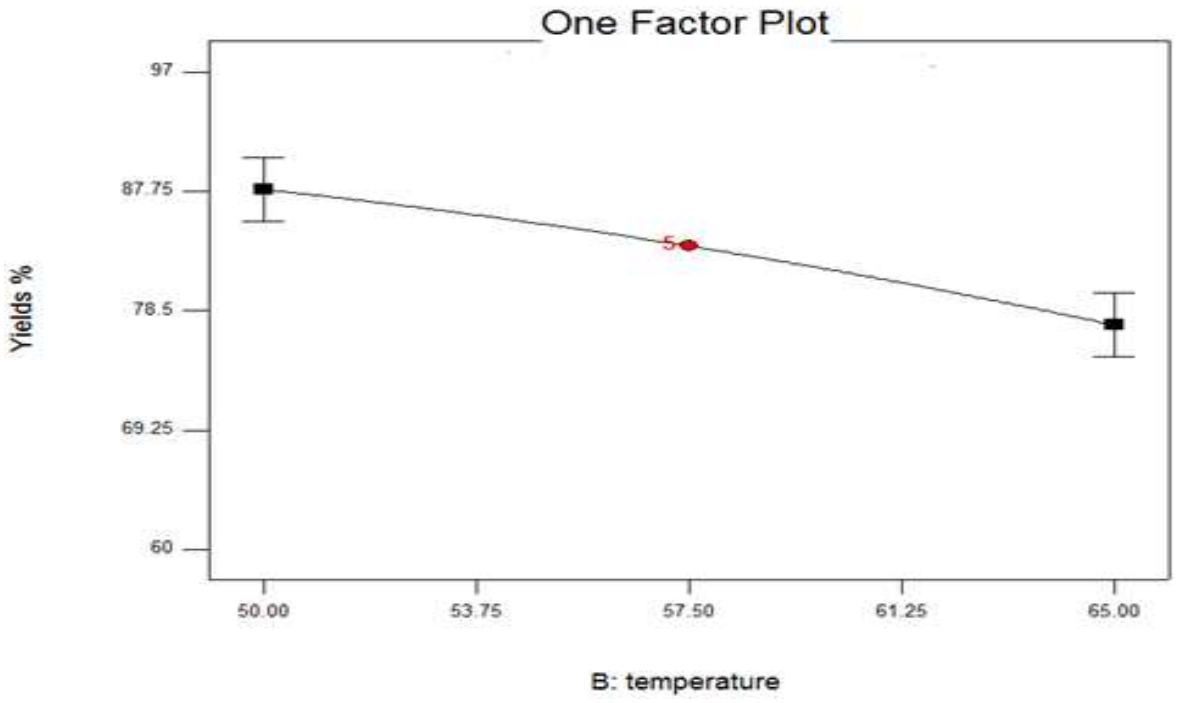


Fig.4.6. Effect of temperature on biodiesel yield

c) Effect of catalyst concentration on biodiesel yield

The percentage yield of biodiesel marginally decrease with increase in mass of base catalyst. The maximum yield of biodiesel was found at a base concentration of 1% w/w of croton oil. Further increase in mass of base catalyst added to the reaction mixture led to drastically decrease in percentage yield of biodiesel.

At higher concentration greater than 2% both soap and emulsion formation occurred and a lower yield of biodiesel was obtained and separation phase was difficult for higher catalyst concentration. Figure 4.3 shows the effect of mass of KOH added on the percentage yield of biodiesel.

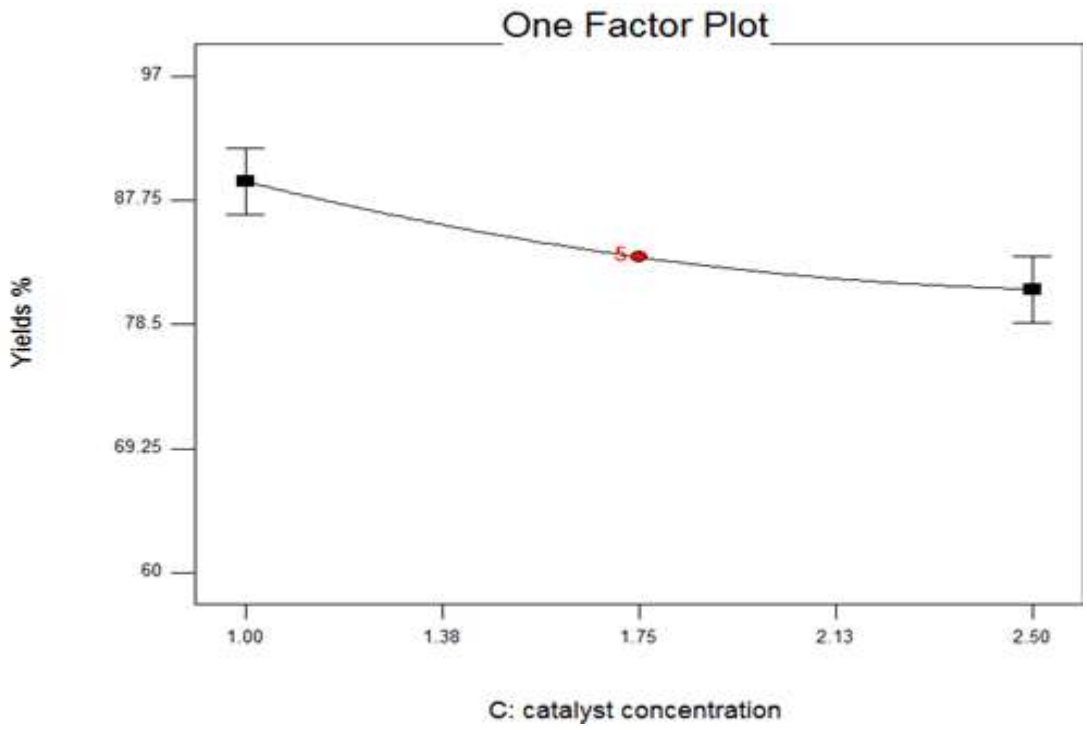
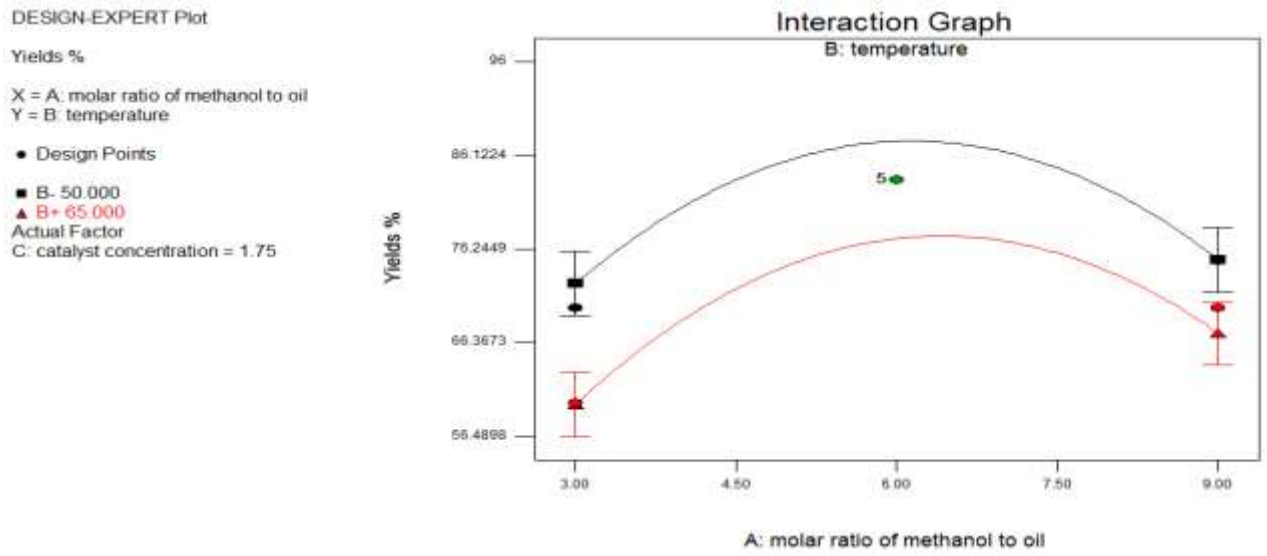


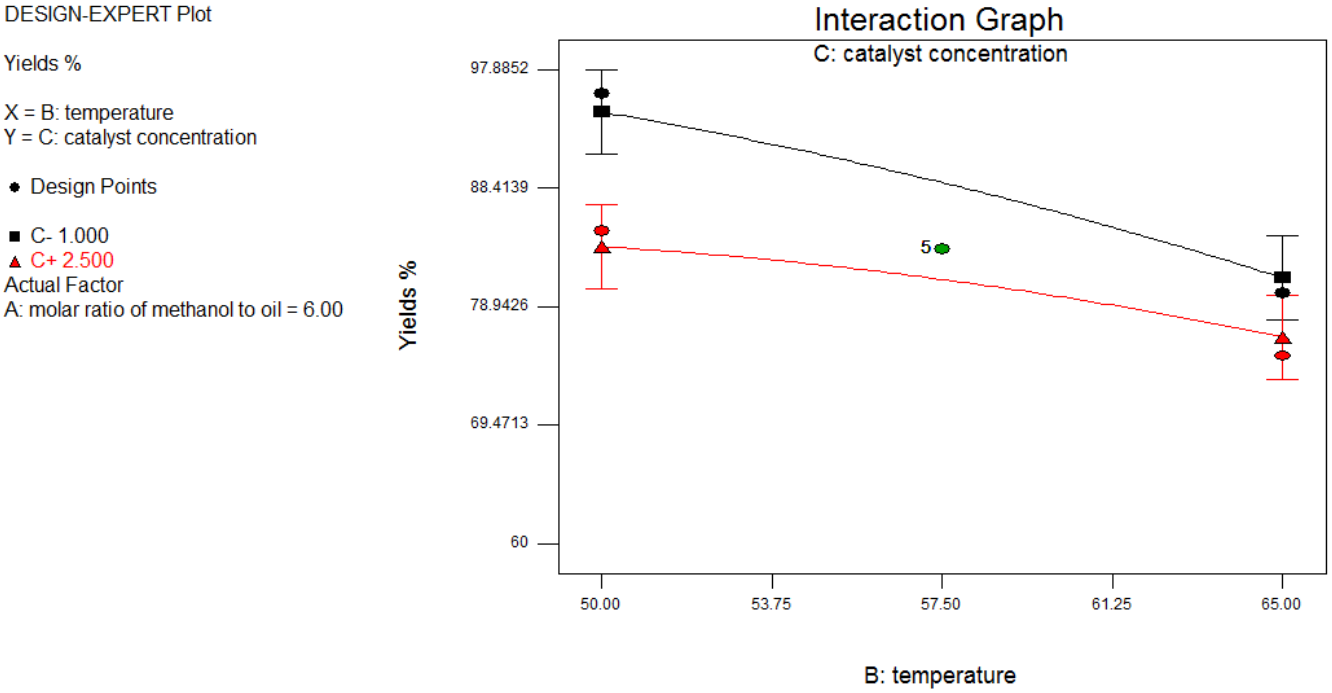
Fig 4.7. Effect of catalyst concentration on biodiesel yield

d) Interaction effect of different process variable on biodiesel yields

In the previous section the effects of individual process parameters on biodiesel were discussed. From ANOVA analysis interaction between molar ratios of methanol to oil with catalyst concentration has significant effect on the yield of FAME. But the interaction between temperatures versus reactant molar ratio, catalyst concentration versus temperature shows linear relationship on triglyceride conversion as shown on figure 4.8 (a, b). The effect of significant interactions is discussed below.



(a)



(b)

Fig 4.8.linear interaction between process variable (a) Temperature versus reactant ratio, (b) Temperature versus catalyst concentration.

e) Effect of interaction between catalyst concentration and methanol to oil molar ratio on biodiesel yield

Figure 4.5 show the interaction effect between catalyst concentrations with methanol to oil molar ratio on percentage yield of biodiesel. This interaction effect was carried out by keeping the reaction temperature constant or at optimum temperature.

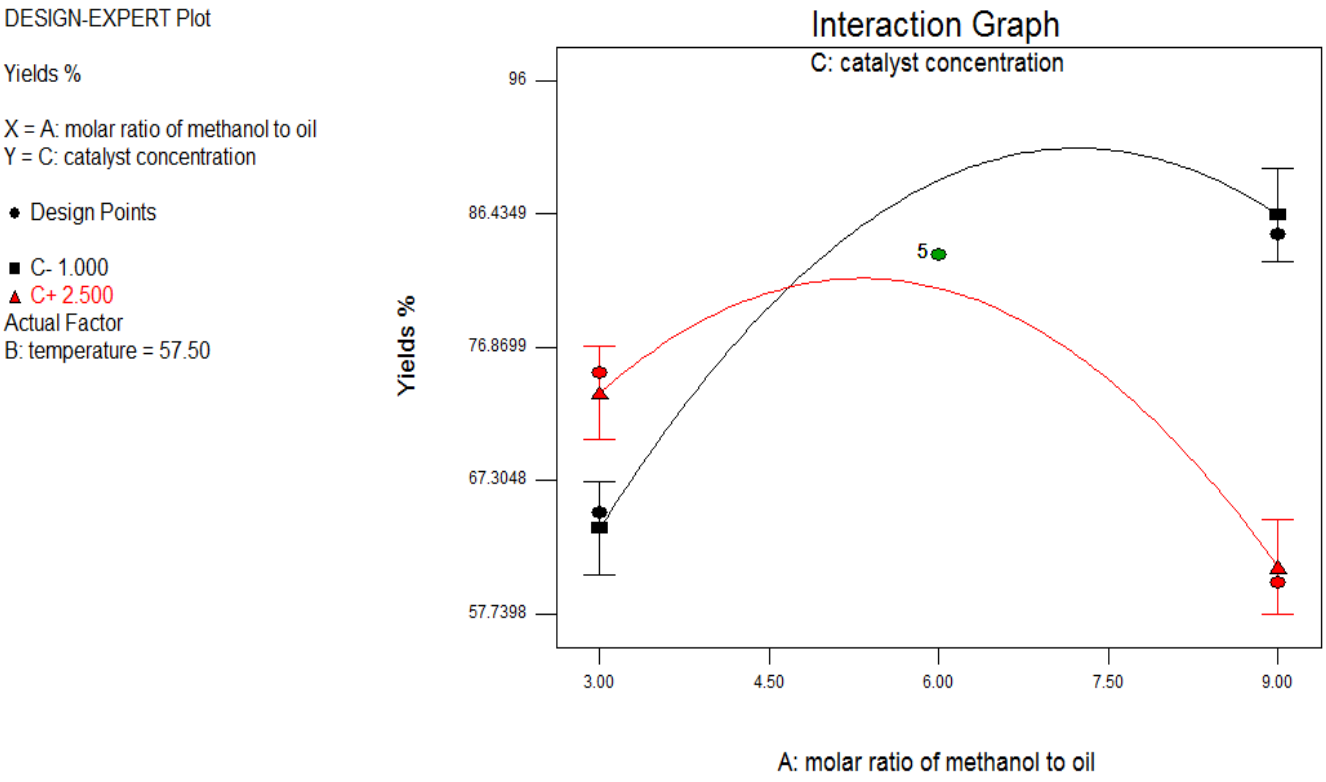


Fig.4.9. Interaction effect of reactant ratio versus catalyst concentration.

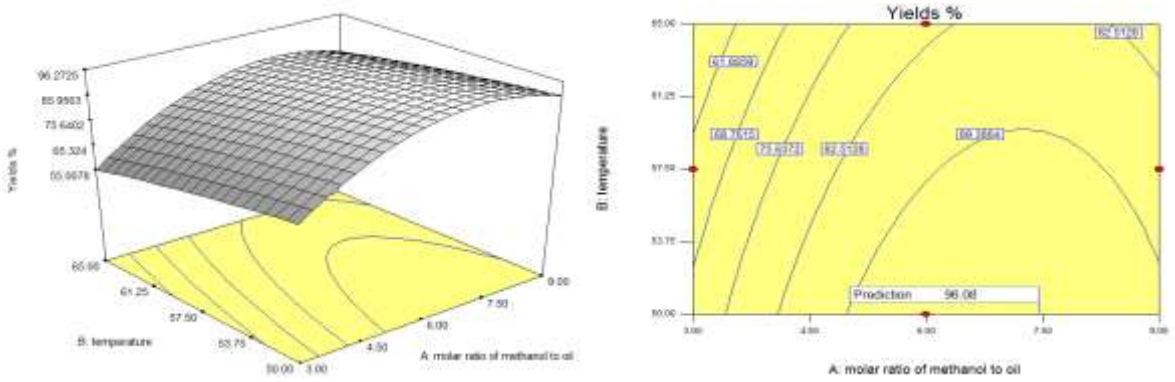
As easily observed from figure 4.5 the effect of both process variable had a positive effect on the biodiesel yield up to optimal point, then after this point further increase in methanol or catalyst loading were not increase biodiesel yield rather causes the marginal decrease in biodiesel and result in the formation of soap and increase the cost of post-reaction.

The graphical description of the regression equation (4.3) i.e. response surface plots were taken by using the design expert software. The plots describing the impact of the dependent and independent variables for selected parameters were shown in Figure 4.10. Surface and contour plots figure 4.10 (a-c) show the relationships between interaction process variables of the developed model. Each contour curve presented the effect of two variables on the methyl ester yield, holding the third

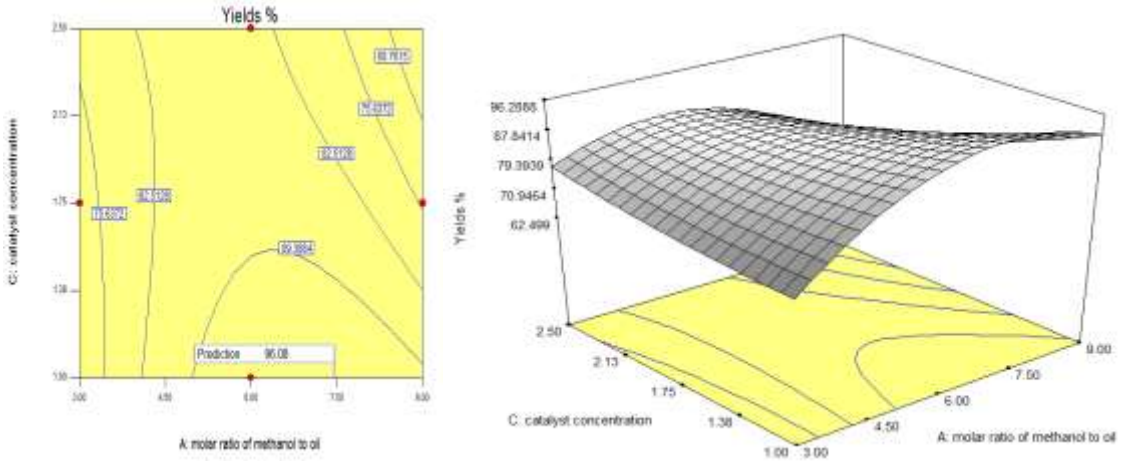
variable at a constant level. The third variable is held at the selected zero level. However, the interaction factor also must be considered since the individual effect plot does not give information regarding the significant interaction involved. A remarkable interaction between the independent variable could be observed if the contour plots had an elliptical profile. The relationship between independent and dependent variables of the developed model in the response surface plots at the stationary value of 6:1, 1.02% catalyst concentration and 50.15oC of the reaction temperature are shown in figure 4.10.

Figure 4.10(a) shows the 3D plot and contour plot for the interaction effect of methanol to oil molar ratio versus reaction temperature towards biodiesel yield. It can be seen that the yield of FAME increases with increase in temperature toward 50oC up to 6:1 alcohol to oil ratio and after that there is no substantial increase in yield with an increase in the amount of alcohol and temperature. The shape of contour plot revealed that more than 96% of croton biodiesel was obtained at 6:1 alcohol and 50oC temperature. However, there is a reduction yield at higher alcohol concentration and temperature. This is because of increase in the solubility of glycerol leading to difficulties in separation of ester layer at higher alcohol concentration and temperature.

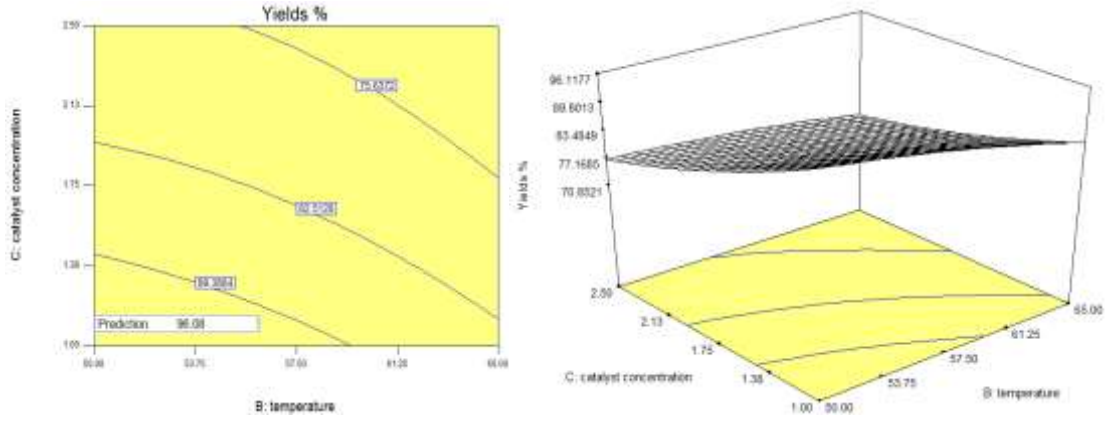
Figure 4.10 (b) shows the response for the interactive factors of catalyst concentration and alcohol to oil molar ratio. It is observed that at a high level of alcohol to oil molar ratio, the yield increases with catalyst concentration. The increasing rate of biodiesel yield changes slowly with the decrease in catalyst concentration at the other alcohol molar ratio. However, at higher catalyst concentration and alcohol molar ratio, a reduction in the yield can be observed due to the formation of soap that makes the separation of ester difficult in washing step.



a) Methanol to oil ratio verses temperature @ 1.02%w/w catalyst concentration



b) Methanol to oil ratio catalyst concentration @50.12ºC temperature



c) Temperature verses catalyst concentration @ 6:1 methanol to oil ratio

Figure 4.10 Contour (to the left) and Response surface (3D) (to right) plot of biodiesel Yield (%) in terms of coded factors (a,b & c)

Contour plots of figure 4.10 (b) show that more than 90% yield of croton biodiesel was obtained between at intermediate to high level of catalyst concentration and alcohol molar ratio. Figure 4.10 (c) indicate the effects of temperature and catalyst concentration on the biodiesel yield. The result shows that at a low level of catalyst concentration, the yield increases from 77.1685% to 83.48 with the temperature. The increasing rate of biodiesel yield changes slowly with the temperature at the other catalyst concentration.

4.4 Physicochemical Properties of Croton Biodiesel

Various physiochemical parameter which defines the quality croton oil and biodiesel are acid value, free fatty acid (FFA), viscosity, density, specific gravity, flash point, calorific value, Iodine number and moisture content are the most significant parameters used to describe the physical and chemical characteristics of biodiesel produced from both non-edible and edible oil resources, which also used to standardized final product (table 4.7). So, these parameters directly or indirectly affect the quality of biodiesel. All alternative biodiesel fuels should meet the international standard specification of biodiesel such as ASTM. Since biodiesel is produced from vegetable oils of varying origin and quality, the pure biodiesel must meet this standard before being used as a pure fuel or blended with conventional diesel fuels.

Table 4.7 Comparison of Croton Methyl Ester (biodiesel) with standard specification of biodiesel: - [USA and European]

Parameter	Unit	CME or Biodiesel [a]	ASTM D6751 [b]	EN14214 [c]	Tested Methods
Specific gravity	-	0.854	-		
Viscosity at 20^{o}C	mm^2/s	4.613	1.9 – 6.0 @40 ^{o}C	3.5-5.0 @40^{o}C	ASTM D445
Acid value	mg KOH/gm	0.87	≤ 0.8	≤ 0.5	ASTM-D664
Free fatty acid	mg KOH/gm	0.435	≤ 0.4	≤0.25	
Saponification value	mg KOH/gm	193.53	≤ 215.99	≤ 218.79	
Moisture content	%	0.053	<0.03	-	
Density	g/cm^3	0.854	0.82–0.90	0.86 – 0.90	ASTM D445
Caloric value	MJ/kg	39.889	-	-	
Flash point	^{o} C	220	≥ 120	≥ 130	ASTM D93
Iodine value	mg iodine/g	107.084	-	120	

[a] present study [b] A.E. Atabani et al, 2012 [c] Roseli A et al, 2011

So, those parameters can help in the decision to what extent croton biodiesel will apply for, either blended or pure form. Here, I discussed each parameter with corresponding value and what it implies about properties of croton biodiesel.

Density

Fuel density measurement has crucial importance for biodiesel quality because density can directly affect engine performance of fuel injection system (pumps and injector) must deliver precise amount of fuel and under high pressure (atomized form) in order to have proper combustion and some of the fuel properties, such as cetane number, heating value and viscosity is strongly connected to density. The density of the fuel also affects the quality of atomization and combustion. Thus, the present result of biodiesel has the density of 0.854g/cm^3 (Table 4.7), which is in range of international standard requirement value of 0.86 – 0.90 g/ cm^3 set by EN14214. The present result is similar to the result of biodiesel obtained from Jatropha and castor oil reported by Aldo et al. (2011). Additionally, similar to the present result, Evangelos (2013) has reported that biodiesel fuels are characterized by higher density than conventional petroleum diesel, which means that volumetrically-operating fuel pumps will inject a greater mass of biodiesel than conventional diesel fuel. Densities of biodiesel obtained from crude and degummed oil are very close; this may be due to the density of methanol used in their production since the density of biodiesel is affected by fatty acid composition and purity (Adekunle et al., 2016). Similarly, According to (Samir Abd, 2015) the density of the biodiesel varied from 0.878 to 0.883 g/cm^3 depends upon the raw materials used for biodiesel production and the biodiesel methyl ester profile.

So, Croton biodiesel can be used as a blend form or pure fuel in CI-engine. The higher density of biofuels than that of specification cause the delay time between the injection and combustion of the fuel in the diesel engine (ignition quality) and the energy per unit mass. Thus, this result in poor atomization and consequently incomplete combustion takes place.

Acid Value

Determination of acid value is an important test to assess the quality of a particular biodiesel. The acid value of the starting material can play an important role on the % FAME of the final product and also used to determine the number of carboxylic acid groups in a chemical compound such as

a fatty acid or in the mixture of compounds. Acid number can provide an indication of the level of lubricant degradation while the fuel is in service. Higher acid content can lead to severe corrosion in the fuel supply system and the internal combustion engine.

Considering that the presence of free fatty acids influences fuel aging due to hydrolytic cleavage of the ester bond, the American and European Standards specify a maximum value of 0.8mg of KOH/g and 0.5mg of KOH/g of acid value respectively. In this study (table 4.7), the acid value croton biodiesel was found to be 0.87mgKOH/g and the free fatty acid value of 0.435 mg KOH/g which was a little higher than the maximum requirement and this can be improved by different additive as discussed in section 2.9.1.

Kinematic Viscosity

Another parameter characterized the croton biodiesel was kinematic viscosity, and this limits are present both in ASTMD 6751 (1.9 - 6.0 mm^2/s @ 40°C) and EN 14214 (3.5-5.0 mm^2/s @ 40°C), respectively for biodiesel fuels (Table 2). Viscosity is a key fuel property because it persuades the atomization of a fuel upon injection into the diesel engine ignition chamber and ultimately, the formation of engine deposits. Thus, the present result of kinematic viscosity of biodiesel was 4.613 mm^2/s @ 20^oC respectively (Table 2) at room temperature and both values of kinematic viscosity fall within the scope of both the ASTMD 6751 and EN 14214 biodiesel specification ranges. The result has shown that the viscosity croton oil decreases sharply after transesterification processes of biodiesel. The viscosity of biodiesel will even drop below the value recorded here if preheating (40^oC) was applied. Because, from basic fluid mechanics, it is already known that viscosity decreases with an increase in temperature of the fluid.

The experimental result verifies that the value of kinematic viscosity of croton biodiesel was 4.613mm^2/s which can fulfill the international standards requirement for biodiesel. Higher viscosity above-specified range highly affect the operation of fuel injection equipment, particularly at low-temperature operation an increase in viscosity affects the fluidity of the fuel. Moreover, high viscosity may lead to the formation of soot and engine deposits due to insufficient fuel atomization. At low temperature, it may even compromise the mechanical integrity of the injection pump drive systems.

Iodine Value

Iodine value is one of the crucial property of biodiesel that greatly influences the oxidation stability, polymerization of glycerides and unsaturation degree. This can lead to the formation of deposits in diesel engines injectors. The iodine number of biodiesel is set to a maximum value of 120mgI_2/g according to EN14214. In this sense, methyl ether obtained from Croton macrostachyus can meet the specification. In the present study, the iodine value of biodiesel of croton oils was 107.084 mg I_2/g, which was closer to 120 mg I_2/g which is the set standard given by EN14214. The Iodine value is also helping to understand the quality of biodiesel because Iodine value is directly correlated to biodiesel viscosity, cetane number and cold flow characteristics (cold filter plugging point).

The iodine value can provide information on degree unsaturation of the oil, which directly affects its stability with regards to oxidation. The reason for autoxidation is the presence of double bonds in the chains of the fatty compounds. The autoxidation of unsaturated fatty compounds proceeds with the different rate depending on the number and position of double bonds.

Calorific Value

Calorific value is another important parameter in the selection of biofuel. It is already known that the caloric value of biodiesel is lower than diesel because of its higher oxygen content. As indicated in table 4.7 the croton biodiesel calorific value has been found 39.889MJ/kg which is in the range of the requirement set by the ASTM standard for the calorific value of biodiesel 37-42.5MJ/kg. In addition, the present calorific value was lower than the diesel fuel (44.123MJ/kg) because of the higher oxygen content of the biodiesel. Thus, based on the croton biodiesel calorific result, the croton biodiesel can be potential supplement or alternative to petroleum diesel. Similarly, Ioannis G et al, (2016) confirm that the calorific value of different agroforestry species and residues ranges from 14.3 to 25MJ/kg. The highest calorific value was obtained by seeds and kernels due to higher unit mass and higher lipid content.

Flash point

Flashpoint is the most important properties of biodiesel which determine easy flammability of the fuel. It is used as a regulation for categorizing the transport and storage of fuels, with different thresholds from region to region. The flash point of petrol diesel fuel is only about half the value

of those for biodiesels, which therefore represents an important safety asset for biodiesel. The flash point of pure biodiesels is considerably higher than the prescribed limits but can decrease rapidly with increasing amount of residual alcohol. As these two aspects are strictly correlated, the flashpoint can be an indicator of the presence of methanol in the biodiesel. According to this study croton biodiesel spark at 220oC temperature (table 4.7). The figure of the flame temperature of croton biodiesel is higher than the standard value, however, it is not as much higher than the combustion chamber surface temperature. Because literature thought that flame temperature can reach up to 2500oC at the instant of combustion takes place in CI-Engine. This temperature only happens at a local point and the flame temperature distribution around or surface temperature of the cylinder head and piston can reach up to 260oC (Jani L et al, 2013). So, the result shows the flash temperature of croton biodiesel is less than the surface temperature of the combustion chamber.

In summary physiochemical properties of the biodiesels, namely; Density, Kinematic Viscosity, flash point, Acid No. Iodine value, moisture content, saponification value and Caloric value were summarized and analyzed in comparison with the standards as depicted in table 4.7. It is clearly observed that croton macrostachyus derived biodiesel well agree with all the standard specification of ASTM D 6751. It also compromises with the European standard EN14214.

In general physiochemical properties of the croton biodiesel present in table 4.7 are all directly or indirectly determine fuel consumption, power developed and performance of CI-engine and also determine the quality of biodiesel and to recommend extent at it can be blended with diesel fuel. Overall, the current results indicate that almost all physicochemical properties of croton biodiesel meet international standard.

4.5 Fatty Acid Composition of Croton Biodiesel

Fatty acid composition determination was another important characteristic carried out in this study (table 4.8). The properties of the triglyceride and the biodiesel fuel are determined by the amount of each fatty acid that is present in the molecules.

Gas chromatography-mass spectrometer (GC-MS) was employed to determine the fatty acid composition of croton biodiesel as discussed in session 3.9. The investigations of content and distribution of fatty acid methyl esters (FAMEs) in biodiesel were carried out in LIDI laboratory. The composition of fatty acid methyl esters (biodiesel) of croton oil is presented in table 4.8. Both

saturated and unsaturated components were detected, besides some unknowns. All obtained croton biodiesel samples were analyzed by qualitative methodology using FAME areas (%). Transesterification does not alter the fatty acid composition of the feedstocks and this composition plays an important role in some critical parameters of the biodiesel of the biodiesel, as cetane number and cold flow properties.

The major fatty acids in croton oil were the linoleic, oleic, methyl isohexadecanoate and methyl stearate (table 4.8). Linoleic acid showed the highest percentage of composition of 41.1% followed by oleic acid with 35.8%. Thus, croton seed oil can be classified as a linoleic-oleic oil. The scanned original result of LIDI was attached in Appendix-E

Table 4.8. Fatty Acid Composition of Croton biodiesel (FAME)

Systematic name	Synonyms name	Area (%)
Dodecanoic Acid, Methyl Ester	Lauric acid	0.06
Methyl tetradecanoate	Myristic Acid,	2.31
9-Hexadecanoic acid, Methyl Ester	Palmitoliec	0.4
Pentadecanoic acid, 14-Methyl Ester	Methyl Isohexadecanoate	14.4
9-octadecanoic,(Z) Methyl Ester	Stearic acid	0.14
Heptadecanoic acid, Methyl Ester	Margaric Acid	0.23
9, 12-octadecanoic acid, (Z,Z) Methyl Ester	Linoleic	41.1
9-octadecanoic acid ,Methyl Ester	Oleic	35.8
Methyl stearate	Stearic acid methyl ester	4.0
9,12-octadecanoic acid ethyl Ester	9, 12-diemoic acid	0.08
Cis-11-Eicosenoic acid Methyl Ester	-	1.1
Eicosenoic acid Methyl Ester	-	0.5

In this study, the composition of FAMEs of croton biodiesel was found to be in agreement with the general distribution pattern of fatty acids in jatropha (Emil A et al, 2009). According to Emil A et al, 2009, variation in fatty acid concentrations is determined by many factors including species, maturity level of the seeds and extraction method.

4.6 Comparison of Croton Biodiesel with Jatropha and Castor Bean

This thesis was steered on croton seed characterization, oil extraction and production process optimization and characterization of croton biodiesel and finally discover croton seed as a new biodiesel feedstock. According to this study results, croton biodiesel fulfills the minimum requirement of international biodiesel specification as discussed and presented in table 4.7. Here in this session I clearly show a comparison of basic physiochemical properties of croton biodiesel with the previously studied oil-bearing plant, which is jatropha and castor. Thus, regarding these two feedstocks, a lot of research was done so far both at worldwide and Ethiopian level.

Table 4.9. Comparison of physiochemical properties of Croton biodiesel with Jatropha, Castor and Diesel fuel form different literature.

No.	Parameters	Unit	Croton[a] biodiesel	Jatropha[b] biodiesel	Castor[c] biodiesel	Diesel fuel[d]
2.	Acid value	mg KOH/gm	0.87	0.32	0.35±0.02	0.02
3.	Viscosity	mm^2/s	4.613 @20^oC	4.8–4.9 @40^0C	10.75±0.27	2.5–5.7
4.	Density	g/cm^3	0.854	0.878-0.880	0.900 ±9.16	0.821
5.	Caloric value	MJ/kg	39.889	38.5–42	30.40±0.90	42–45.9
6.	Flash point	^{o} C	220	158	160±1.53	50–86
7.	Iodine value	mg iodine/g-sample	107.084	76.7	-	84

[a] Present study , [b] Kumar et al, 2013 , [c] Aldo Okullo et al, 2012 , [d] T. Ganapathy et al, 2011

Heats of combustion of biodiesel from croton seed, jatropha and castor oils were found to be high. Biodiesel from croton oil was more competitive substitute fuel than castor and jatropha due to higher oil content and low viscosity compares with the two feedstock, especially castor biodiesel is not suitable for use in diesel engine due to high viscosity value. As seen from table 4.8 Castor biodiesel has lower heating value than croton and jatropha biodiesel. Moreover according to this study croton macrostachyus seed more competitive source of biodiesel. Biodiesel from croton seed was convinced international standard which make this feedstock more appropriate and suitable for use in the diesel engine.

5 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

From the experimental work carried out in this study concluded that biodiesel of acceptable quality can be produced from Croton macrostachyus seed. Croton macrostachyus oil was extracted using chemical extraction methods and chemically converted to biodiesel via transesterification reaction to fatty acid methyl ester in the presence of KOH as a catalyst. In this study different reaction parameters (temperature, methanol to oil molar ratio and catalyst concentration) were employed in order to investigate biodiesel production process optimization. The experimental study investigated and optimized the effect of those process variables on the biodiesel production from croton oils using RSM. The three selected reaction parameter and their interaction effects on transesterification were studied. The optimum conditions were evaluated using design expert 6.0.8 software. A full factorial Box-Behnken was successfully employed for 17 experiments and results were analyzed. An optimized study reveals that the impact of methanol to oil ratio was the most important factor that affects the biodiesel yield compare to other parameters.

The optimum condition for biodiesel production from croton oils was found as follow: the molar ratio of methanol to oil 6:1, the reaction temperature of 50^{o}C, and catalyst concentration 1%w/w, with 96% corresponding optimum yields of biodiesel. After the production is completed the physicochemical properties of biodiesel prepared were tested to check whether the products could satisfy the international standard or not. For this test, only the major physicochemical properties were selected only to minimizing cost and time and the value of selected properties was found density 0.854g/cm^{3}, kinematic viscosity 4.613mm^{2}/s, flash point 220^{o}C, iodine value 107.084mg iodine/g and calorific value 39.889MJ/kg. The physicochemical analysis result shows that the majority of the parameters fall within the range of values established by ASTM-D 6751 and EN.

Generally speaking, this research concluded that croton macrostachyus seed was approved as potential biodiesel feedstock and competitive source with previously discovered feedstock such as jatropha.

5.2 Recommendation

Since Ethiopia has the potential of growing croton macrostachyus seed and can be grown over all the country climate condition. It is highly recommended to use these resources in producing a biodiesel so far, an eco-friendly fuel that can substitute a fossil-based diesel. This research confirmed the possibility of producing biodiesel from Croton macrostachyus. Even though the result of this study was remarkable, on the basis of producing biodiesel from those local resources and meeting an international standard, the scattered population of the Croton tree make difficult the seed collection phase and integrated data regarding this feedstock was not available and also in this study biodiesel quality parameters (density, viscosity, FFA, Iodine value, calorific value, saponification number, fatty acid composition and flash point) were determined, But the experimental procedure adopted in present research work can be extended up to engine performance analysis.

Therefore the following points are recommended in order to step up the croton seed commercial feedstock:-

- Aware farmer community in order to grow croton trees and deny removing this trees as a weed from their agricultural farm and encourage agroforestry practice since it never affects normal agricultural practice.
- Further experiments of biodiesel analytics could be done to get other fuel properties cloud point, cetane number, pour point, ash content, etc.
- 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 croton biodiesel.
- The used catalyst could be further optimized in addition to the homogeneous base catalyst, however, it might bring benefits in croton biodiesel production yields.
- Non-catalyst transesterification of biodiesel production can be employed for further study and to compare the response variable with catalyst transesterification.

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Appendix –A

Table 1. Proximate analysis (fixed carbon, volatile matter and ash content) of different biomass (B.M. Jenk et al, 1989).

	Alfalfa stems	Wheat straw	Rice hulls	Rice straw	Switch-grass	Sugar cane bagasse	Willow wood	Hybrid poplar
Proximate analysis (% dry fuel)								
Fixed carbon	15.81	17.71	16.22	15.86	14.34	11.95	16.07	12.49
Volatile matter	78.92	75.27	63.52	65.47	76.69	85.61	82.22	84.81
Ash	5.27	7.02	20.26	18.67	8.97	2.44	1.71	2.70
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Appendix-B

Table 2. Biodiesel Standard EN 14214 (Europe, 2017) (www.intechopen.com)

Property	Test method	Limits		Unit
		min	max	
Ester content	EN 14103	96.5		% (m/m)
Density, 15°C	EN ISO 3675 EN ISO 12185	860	900	kg/m³
Viscosity, 40°C	EN ISO 3104 EN ISO 3105	3.5	5.0	mm²/s
Flash point	EN ISO 3679	120		°C
Sulfur content	EN ISO 20846 EN ISO 20884		10.0	mg/kg
Carbon residue (10% dist. residue)	EN ISO 10370		0.30	% (m/m)
Cetane number	EN ISO 5165	51		
Sulfated ash	ISO 3987		0.02	% (m/m)
Water content	EN ISO 12937		500	mg/kg
Total contamination	EN 12662		24	mg/kg
Copper strip corrosion (3hr, 50°C)	EN ISO 2160		1	
Oxidative stability, 110°C	EN 14112	6.0		hr
Acid value	EN 14111		0.50	mg KOH/g
Iodine value	EN 14111		120	g iodine/100g
Linolenic acid content	EN 14103		12	% (m/m)
Content of FAME with ≥4 double bonds			1	% (m/m)
Methanol content	EN 14110		0.20	% (m/m)
Monoglyceride content	EN 14105		0.80	% (m/m)
Diglyceride content	EN 14105		0.20	% (m/m)
Triglyceride content	EN 14105		0.20	% (m/m)
Free glycerol	EN 14105, EN 14106		0.02	% (m/m)
Total glycerol	EN 14105		0.25	% (m/m)
Alkali metals (Na + K)	EN 14108, EN 14109		5.0	mg/kg
Earth alkali metal (Ca + Mg)	prEN 14538		5.0	mg/kg
Phosphorus content	EN 14107		10.0	mg/kg

Appendix- C

Material loading for each experimental run was carried out by using equation discussed in session and 20ml of croton oil were used for each run.

Volume Methanol required for different experimental run within a given ratio: ranges from (3:1, 6:1 and 9:1)

$$\frac{\rho meoH * Vmeoh / MmeoH}{\rho oil * Voil / Moil} = 6$$

$$Moil = \frac{56.1 * 1000 * 3}{S.V - A.V} = \frac{879.347g}{mol}$$

M_{meoH} = 32.04g/mol and ρ_{meoH} =0.79g/mol

Volume of methanol for run#1= 4.917ml ≈5ml

Catalyst loading with respect to percentage of catalyst concentration which ranges from (1 to 2.5%) and respective temperature ranges (50 to 60) of each run.

$$Mcatalyst = catalyst, \% * Moil$$

M_{oil} = ρ_{oil}*V_{oil}=0.889*20ml=17.78g

Table 3 Experimental Processes (Transesterification reaction) of each run and loading of selected parameters.

Reaction Parameter	Run#1		Run#2		Run#3		Run#4	
Methanol volume	3:1	2.5ml	6:1	5ml	6:1	5ml	6:1	5ml
Catalyst loading %w/w	2.5	0.445g	1.75	0.315g	1.75	0.315g	2.5	0.445g
Reaction Temperature ^oC	57.5	57.5	57.5	57.5	57.5	57.5	50	50
Biodiesel yields	15ml		16.7ml		16.7ml		17ml	
	Run#5		Run#6		Run#7		Run#8	
Methanol volume	3:1	2.5ml	6:1	5ml	9:1	5ml	9:1	5ml
Catalyst loading %w/w	1.75	0.315g	2.5	0.445g	1.75	0.315g	1.75	0.315g
Reaction Temperature ^oC	50	50	65	65	50	50	57.5	57.5
Biodiesel yields	14ml		15ml		15ml		14ml	

	Run#9		Run#10		Run#11		**Run#12**	
Methanol volume	6:1	5ml	3:1	2.5ml	3:1	2.5ml	**6:1**	**5ml**
Catalyst loading %w/w	1.75	0.315g	1	0.178g	1.75	0.315g	**1**	**0.178g**
Reaction Temperature ^{o}C	57.5	57.5	57.5	57.5	57.5	57.5	**50**	**50**
Biodiesel yields	16.7ml		13ml		12ml		**19.2ml**	
	Run#13		Run#14		Run#15		Run#16	
Methanol volume	9:1	7.34ml	6:1	5ml	9:1	7.34ml	6:1	5ml
Catalyst loading %w/w	2.5	0.445g	1.75	0.315g	1	0.178g	1	0.178g
Reaction Temperature ^{o}C	57.5	57.5	57.5	57.5	57.5	57.5	57.5	57.5
Biodiesel yield	12ml		16.7ml		17ml		16ml	

Run#17		
Methanol volume	6:1	5ml
Catalyst loading %w/w	1.75	0.315g
Reaction Temperature ^{o}C	57.5	57.5
Biodiesel yields	16.7ml	

Appendix-D

GEOLOGICAL SURVEY OF ETHIOPIA (***hydrocarbon laboratory Analysis Result Report***)

Calorific value of croton biodiesel (cal/g).

The relationship between calorie and joule expressed as follow:

$$1cal = 4.1868 \text{ Joule}$$

	GEOLOGICAL SURVEY OF ETHIOPIA	Doc.Number: GSE/F 5.10-2	Version No: 1
	GEOCHEMICAL LABORATORY DIRECTORATE		Page 1 of 1
Document Title:	Hydrocarbon Laboratory Analysis Report	Effective date:	May, 2017

Issue Date: - 04/05/2018
Request No: - GLD/0285/18
Report No: GLD/TR/0279/18
Sample Preparation: - 60 Mesh
Number of Sample: -One (1)

Customer Name – Wondwosen Shiferaw
Sample type: - Biofuel
Date Submitted: - 02/05/2018
Elements to be determined: Calorie.
Method of analysis: Adiabatic Calorie Metter.

Collector's Code	Calorific Value cal/gm
FAME	9527.33

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

Analysts	Approved By	Quality Control
Hayimanot Bayeh Shashie Hailie	Alemnesh Abate	Awash Yirga

Geochemical Laboratory Directorate
Tell: +251113204161

Appendix E

Laboratory result of Gas Chromatography mass spectrometer (GC-MS)

LIDI

LEATHER INDUSTRY DEVELOPMENT INISTITUTE
TESTING & RESEARCH LABORATORY
DIRECTORATE

Title: TEST REPORT — Page : 1 of 2

Test date(s) : 01/06/18 — **Report No :** C-14369 & C-14370/18

Lab. Desg .Code No : C-14369 & C-14370 — **Test order No:** ETC/066/2010

Type of Sample: OIL
Sample Identification: --
Sampling: By Customer
Conditioning: Room temperature,
Sample extraction ; By Customer

Sampling date & place: _____
Sampling location: _____
Sample receiving date: 18/05/18
Sampled by: Customer
Report date: 05/06/18

Environmental test condition: Temp.(°C) 22.5 R/H (%) 46.3

ORIGINAL

Name of Customer: ADDIS ABABA INSTITUTE OF TECHNOLOGY,
ADDIS ABABA UNIVERSITY, SCHOOL OF CHEMICAL AND BIO-ENGINEERING

Address of customer: Tel.(251)1232417
Fax 011-1239480
P.O.Box 385
Email:info@aau.edu.et

Used equipment/ instruments:- Gas Chromatograph (GC-MS)

Customer Code: see the attachment

S/No	Type of test	Lab code	Customer code	Unit	Test Result	Uncertainty	Test method	Standard Requ.	Remark
1.	Oil	C-14369	Wondowesen shiferaw	%	Attached	-	By customer	-	
2.		C-14370	Seid shumet	%	Attached	-		-	

Note: **1. Batch no** C-14369 & C-14370 **Sample was diluted 50 times prior to analysis.**

The test results relates only to the item tested
This test report is for technical information of the client only. Not for the advisement, promotion, publicity litigation or legal purpose.

Tested By: Samuel.A Signature — Chemical analysis Expert IV
Checked By: Meron M. Signature — Lead Chemical Analysis Expert (Team Leader)
Authorized By: Director,Research & Testing Laboratory Directorate

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AKAKI -KALITY KEBELE KETEMA, ADDIS ABABA

LIDI	LEATHER INDUSTRY DEVELOPMENT INISTITUTE TESTING & RESEARCH LABORATORY DIRECTORATE	
Title	**ATTACHED** TEST REPORT	Page : 2 of 2

Customer code	Lab designation code	Name of the compound	Area (%)
Wonowsen shiferaw	C-14369	Dodecanoic acid ,methyl ester	0.06
		Methyl tetradecanoate	2.31
		9-Hexadecanoic acid ,Methyl Ester	0.4
		Pentadecanoic acid ,14-Methyl Ester	14.4
		9-octadecanoic acid, (Z)Methyl Ester	0.14
		Heptadecanoic acid Methyl Ester	0.23
		9,12-octadecanoic acid, (Z,Z)Methyl Ester	41.1
		9-octadecanoic acid, Methyl Ester	35.8
		Methyl sterate	4.0
		9,12-octadecanoic acid ethyl Ester	0.08
		Cis-11-Eicosenoic acid Methyl Ester	1.1
		Eicosenoic acid Methyl Ester	0.5
Seid Shumet	C-14370	9-Hexadecanoic acid ,Methyl Ester	0.46
		Pentadecanoic acid ,14-Methyl Ester	25.7
		9,12-octadecanoic acid Methyl Ester	28.4
		9-octadecanoic acid, Methyl Ester	39.3
		Methyl sterate	5.9
		2-Naphtylene-sulphonic acid	0.1
		Eicosenoic acid Methyl Ester	0.09
		1,13-Dimethylcyclotridecene	0.09

Tested By: Samuel.A Signature
Chemical analysis Expert IV

Checked By: Meron M. Signature
Lead Chemical Analysis Expert (Team Leader)

Authorized By: Berhanu Negate Baraki
Director,Research & Testing Laboratory Directorate

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