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Addis Ababa Institute of Technology

School of Graduate

Center of Energy Technology

Process Optimization for Biodiesel Production from Trichiliaemetica Seed 'Luiya' Oil

By: ***Seid Shumet***

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A thesis submitted to the school of graduate studies of Addis Ababa university institute of Technology in partial fulfillment for the degree of masters of Science in Energy of technology

Addis Ababa, Ethiopia
July, 2018

DECLARATION

I, Seid Shumet, I declare that this thesis is the result of my own work and that all source or material used for this thesis have been properly acknowledged. This thesis is submitted in partial fulfillment of the requirement for Master's Degree in Energy Technology at Addis Ababa University and to be made available at the university's Library under the role of the Library. I confidently declare that this thesis has not been submitted to any other institutions anywhere for the award of any academic degree, diploma, or certificate.

Signature: ________________________
Date: ________________________
Seid Shumet

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By: Seid Shumet

Approved by board of Examiners

(Advisor)	Signature	Date
(Internal Examiner)	Signature	Date
(External Examiner)	Signature	Date
(Chairman)	Signature	Date

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ABBREVIATIONS AND ACRONYMS

ASTM	American Society for Testing and Materials
EU	European Union
GTP	Growth and Transformation Plan
CFP	Cold Flow Properties
CFPP	Cold Filter Plugging Point
CP	Cold Point
PP	Pour Point
PH	Potential of Hydrogen
FFA	Free Fatty Acid
FAME	Fatty Acid Methyl Ester
FAEE	Fatty Acid Ethyl Ester
USA	United State of America
USD	United State of Dollar
US	United State
AAiT	Addis Ababa Institute of Technology
AAU	Addis Ababa University
CI	Compression Ignition
AV	Acid Value
ANOVA	Analysis of Variance
CRGE	Climate Resilient Green Economy

CCD	Central Composite Design
CV	Coefficient of Variance
rpm	revolution per minute
RSM	Response Surface Methodology
EN	European committee for standardization
SV	Saponification Value
SG	Specific Gravity
GC	Gas Chromatography
MS	Mass Spectroscopy
SCBE	School of Chemical and Bioengineering

ABSTRACT

The Energy utilization in the whole world has achieved by using the natural resource like coal, natural gas and petroleum diesel for a long period of time. Continuous using up of those nonrenewable energy sources leads to running down the reserve. In addition to this environmental problems are the main issue in the whole world and this leads to search more attractive and environmentally friend energy source. From this biodiesel is the best one to replace petroleum diesel in order to fulfill our energy needs for a sustainable way. The high cost of edible oil seed has increase biodiesel making price. Due to this searching non-edible oil seed has to minimize biodiesel making cost. The major objective for this study work was the optimization process for making biodiesel from the trichiliaemetica oilseed. For transesterification process trichiliaemetica oil, methanol alcohol and calcium oxide catalyst were used. Extraction of oil was undertaken by using manually operated mechanical compress and 75 ml/kg oil was extract. Experimental results of trichiliaemetica oil properties are moisture content (0.43%), density (910 kg/m^3), kinematic viscosity at 40 ^oC (36.4 cSt), saponification value (183.7mgKOH/g oil) and acid value (4.628 mgKOH/g oil). similarly, the experimental result for characterization of biodiesel from trichiliaemetica oil was listed like: density (887 kg/m^3), viscosity at 40 ^oC (6.11cSt), flashpoint (129 ^oC), acid value (0.897mgKOH/g oil) and higher heating value (39.8MJ/kg). The physicochemical properties of trichiliaemetica oil and produced biodiesel were matched with the standard values. Moreover, the design expert software was the tool and implemented five level four-factor central composite designs with response surface methodology to optimize the process. Four process parameter was studied with the range: time (1-2hr), catalyst (1-2 weight %), methanol/oil molar ratio (6:1-12:1) and temperature (55-65^oC). The optimum trichiliaemetica oil conversion was achieved at the time (1.5hr), calcium oxide catalyst (1.5 weight %), methanol/oil molar ratio (9:1) and temperature (60 ^oC). From the analysis of variance result, the experimental percentage of biodiesel yield was 94% and predicted the percentage of biodiesel yield 90.75%. In addition, the result from response surface methodology all parameters except time rendered the high significant influence for biodiesel yield. From the present study, the results show that process optimization from trichiliaemetica oil seed is essential for industrialization and expansion for production of biodiesel.

Keywords: Trichiliaemetica seed oil, Biodiesel, Transesterification, Process Optimization

CHAPTER ONE

1. INTRODUCTION

1.1 Background of Research

Energy is the basic contributing factor to the economic and sustainable growth of the country including Ethiopia. The country's economy growths lead societies have accompanied by an increase in rising energy wants which have been successful by burning of diverse non-renewable materials which considered as nonrenewable fuels, which cause worldwide warming. When the burning of fossil fuel for our energy needs causes global warming by exhaust emission. In addition, numerous of these pollutants have serious significances on human health and the environment [1].

Countries focus on the basic issues like energy to satisfy their needs and requirements for a long period of time. This energy needs to be achieved by burning of natural gas, coal and petroleum diesel. Continuous burning of those natural resources of energy has to be decreased the reserve. In addition to this ecological problem and significant influence on the human health will also the great problems of using fossil fuel for energy needs.

Subsequently, petroleum diesel resources are dropping, growing energy and price crisis and upraised concern about global warming, this leads; the search for a renewable, sustainable and more environmentally friendly fuel source continues. Therefore, biodiesel is the best option that is recommended to substitute a significant percentage of petroleum types of diesel for our energy requirements in the current time. Biodiesel has no the property of petroleum-based fuel that generally consists of fatty acid ethyl esters or, fatty acid methyl esters produced from the transesterification of vegetable oil with alcohols in the presence of the catalyst. Combusts of biodiesel having the extra benefits because of its domestic origin, derivation from a renewable feedstock, biodegradability, non-toxicity, cleaner emissions, more lubricating properties and it burns similarly in diesel engines to petroleum-based diesel fuel [2].

Biodiesel derived from vegetable oil and animal fats is being used in Europe and United States of Americas (USA) and Europe to minimize the effect of burning petroleum diesel and dependence on the non-renewable fuel source.

Due to their extra edible oils, the countries Europe and USA are being used those edible oils as feedstock for the production of biodiesel. Since more than 95% of the biodiesel is produced from edible oil, there are lots of claims that may arise by changing edible oils into biodiesel.

Large-scale production of biodiesel from edible oils may bring global imbalance to the food supply and demand market. In recent times, environmentalists also claimed that the expansion of oil crop plantations for biodiesel production on a huge scale may raise deforestation. In order to overcome the claims researches have been made to produce biodiesel by using renewable feedstock like non-edible oils [3]. Many types of methods have been established to convert vegetable oil into biodiesel. Direct usage of triglycerides or vegetable oil is not applicable to most of the engines as high viscosity would harm by causing coking and trumpet creation. Biodiesel obtained from micro-emulsion and thermal cracking would likely lead to imperfect combustion due to a high density and viscosity. Transesterification is a chemical reaction in which the oil, a triglyceride react with alcohol in the existence of catalyst, producing a mixture of fatty acid (methyl or ethyl ester) and glycerol. It is the best common method for biodiesel production due to its easiness [4].

Presently, the government of Ethiopia has planned and developed the wide range of renewable energy development programs in GTP II to ensure supply of modern energy services, in which biofuel development is one of the priorities given to be implemented. Therefore, Ethiopia government is inviting foreign companies to work on biofuel, but due to lack of skilled human resources, research, and technology, the companies were still export the raw oil seed without any value addition. In addition, various studies have been threatening against the success of biomass energy. The core problems that limit the effective use of biodiesel energy are the high cost of edible oil and there were no mentioned optimization parameters and processes due to the dissimilarity on the type of plant species use, extraction methods and technology used. So that converting non-edible biomass oil into biodiesel must be well studied. This is because physical and chemical properties of biodiesel produced from any feedstock must fulfill with the limits of standard specifications for biodiesel fuel [5, 6].

It is well known to use less costly and non-edible biomass with good fatty acids content to moderate the biodiesel production costs.

In addition, the accessibility and sustainability of adequate supplies of less costly biomass together with well-organized process technology will be a crucial determinant delivering a competitive biodiesel price. The use of non-edible oils as alternative feedstock is picking up as the demand for biodiesel is expected to increase sharply in the near future.

For that reason, Ethiopia has several natural non-edible bio resources that can provide appreciated inputs for biodiesel production which can help both for national and export markets such as Mafura tree, TrichiliaemeticaVahlspecies. At present, however, only very few non edible sources of biodiesel are known compared to the number of non-edible oily plant species identified, so that investigation of low-cost and non-edible sources of biodiesel such as TrichiliaemeticaVahl can help as feedstock to growth the production and use of biodiesel in Ethiopia, as well as to help to expand the plantation of this plant for agro forestry practices for climate change resilience and moisture conservation in the country [7].

In this work, calcined calcium oxide catalyst, trichiliaemetica oil, and methanol alcohol were used as raw materials for biodiesel production. The consequence of different process parameters (reaction time, reaction temperature, methanol/oil molar ratio and catalyst concentration) was studied by using Design-Expert 6.0.8 Trial software program in order to optimize the yield of biodiesel.

1.2 Problem Statement

Obstacles to commercializing non-petroleum diesel are that the feedstock's for the making of biodiesel is substantially expensive than the cost of petroleum diesel. Production of biodiesel will become economically visible only if there was the reduction in the material cost. In addition, there were no mentioned optimization parameters and processes due to the dissimilarity on the type of plant species use, extraction methods and technology used. This indicated that the present study should give due attention to process optimization of biodiesel from trichiliaemetica oil before large-scale commercial biofuel development is encouraged.

Ethiopia is rich in plant biodiversity which can be used for biodiesel production. Therefore, to search a suitable biomass with good fatty acid contents lower the production costs of biodiesel, the use of non-edible biomass can be a potential source of energy. Hence, TrichiliaemeticaVahl (Mafura tree) can be a good candidate due to large availability, non-consumed by human and animal and has oil content [8] that ranges between 58-68% from the whole seed, although there are huge gaps on the scientific information of the Ethiopian TrichiliaemeticaVahl oil content and properties. Recent existing reports dealt with the potential and important feedstock like non-edible TrichiliaemeticaVahl oil for the biodiesel production. However, the result shows that the various sources have different yield due to processes variables.

The yield of biodiesel differs with the feedstock due to physicochemical properties of sources and the process variables. Process optimization study is important and helpful for the industrialization and development of biodiesel production. The traditional technique of optimization studies in biodiesel production is one variable at a time, which is based on the variation of one component at a time, with the responses serving as a function of a single parameter. This method, however, is boring and time-consuming and could not show the overall effect of the related parameters on the procedure. So the end result only can show the good values and effect of variables in the reaction. For that reason, selected methods such as response surface methodology could be working in order to design the experimental work and also to determine the optimum condition for production of biodiesel.

1.3 Objectives of the Research

1.3.1 General Objective

The overall objective of the current research was to carry out the optimization of the biodiesel making process from Trichiliaemetica incorporated with the biodiesel; characterization, and testing.

1.3.2 Specific Objective

- To extract oil from trichiliaemetica seeds incorporated with purification.
- To test the physicochemical properties of crude and purified trichiliaemetica oil.
- To produce biodiesel from trichiliaemetica oil and study the effect of different process parameters (reaction time and temperature, methanol to oil molar ratio and catalyst concentration) on the yield of biodiesel by keeping stirring speed constant at 500 rpm.
- To identify statistically the optimum process parameters to obtain higher biodiesel yield by employing response surface methodology.
- To characterize the physicochemical properties of the optimized biodiesel yields and compare with ASTM/EN standard values.

1.4 Scope of Research

The scopes of this research consist of the following phases:

- Extraction of oil from trichiliaemetica seed and purify the oil.
- Determination of the trichiliaemetica oil properties.
- Design of experiments based on the range of process parameters by design expert software.
- Production of biodiesel through the research laboratory scale and study the effect of different variables on the biodiesel yield.
- Modeling the process and finding the optimum conditions for the process using RSM.
- Analysis of produced biodiesel to find different physicochemical properties of biodiesel.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Overview of Biofuel

A fuel whose energy is derived from biological carbon fixation is termed biofuels. Biofuels refers to solid (bio-char), liquid (ethanol and biodiesel), or gaseous (biogas, bio hydrogen and biosynthetic gas) fuels that are predominantly produced from biomass conversion.

The most popular biofuels such as ethanol from sugar cane, corn, wheat or cassava and biodiesel from sunflower, soybean, and canola are produced from food crops that require good quality land for plantation. However, ethanol can be produced from inexpensive herbaceous and woody plants from agriculture and forestry residues. Therefore, production of bioethanol from biomass is one excellent way to reduce raw material costs. In contrast, biodiesel production is the most popular one because the formation process is faster and the simpler compared with ethanol and methane production. There is also a growing interest in the use of waste cooking oil, and animal fats as cheap raw materials for biodiesel production [9].

Biofuels have been used for years as a way to increase energy self-sufficiency, reduce import costs, carbon dioxide ($CO_{2)}$ emissions from fossil fuel combustion and strengthen domestic agricultural development. In 2015, historical leaders Brazil and the United States produced approximately 70% of the global biofuel supply, consisting primarily of sugarcane-based and corn-based ethanol, respectively. Suppliers in the European Union and Asia represent emergent markets that have developed in the last two decades (Figure 2-1). Among the newer producing regions, the European Union focuses on bio-diesel from waste, soy, rapeseed, and palm. This compares to production in Asia, which centers on sugarcane, corn, wheat, and cassava, with investment also occurring in palm, soybean, rapeseed, and Jatropha. This type of regional and feedstock-based diversification may be conducive to the formation of an international biofuel commodities market [10].

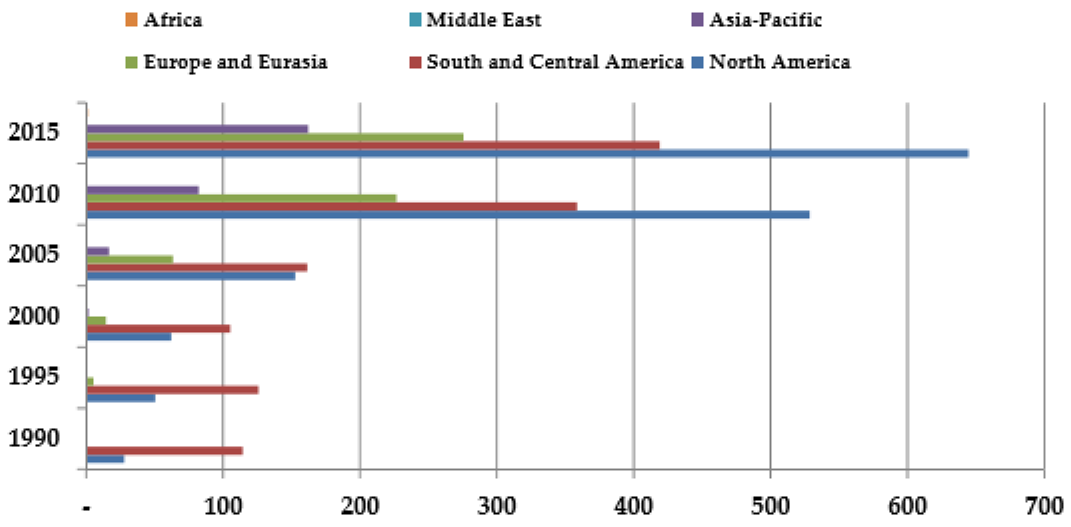


Figure 2-1: Global biofuel production by region (thousand barrels per day) (Source, [10])

Generally, biofuels can be classified in to ‘first-generation’, ‘second-generation’ and ‘third-generation’ biofuels depending on the source of feedstock used for the production.

2.1.1 First Generation Biofuels

‘First-generation’ or conventional biofuels are biofuels made from sugar, starch and vegetable oil. Solid biofuels; liquid biofuels which comprise straight vegetable oil, biodiesel, bioalchol, green diesel, bioethers and gaseous biofuels which are biogas and syngas are included under first-generation biofuels. Wood, sawdust, grass trimmings, charcoal, agricultural waste, non-food energy crops and dried manure are examples of solid biofuels. Study also shown that biomass fuels have significantly less impact on the environment than fossil based fuel. Straight unmodified edible vegetable oil is not often used as a fuel because of its basic use as food and viscosity problems associated with its use in engine [11].

From first generation biofuels food crops are widely used in biofuel industrial production. The raw materials can be divided into three categories which are sugar crops (sugar cane and sugar beet), starch crops (corn, wheat and sorghum) and oil crops (rapeseed, soybean and sunflower). All of these feedstocks can be converted to the biofuel by different techniques. For example, corn is one of the most common use feedstocks are widely grew in the USA and Brazil.

The main product is bio-methanol which can be applied to replace a few part of gasoline in the world currently. But the development of the first generation biofuel is restrained by some problems. Planting crops have not only a longer growing cycle, but also demands large areas of arable land. As the first generation biofuel were produced in a large scale, so that a lot of arable land was occupied by this reason and resulting in a decreased food production problem. Therefore, solving "Energy Crisis" by food crops will increase "Food Crisis" [12].

To solve the problem research establish technology in order to change the three type of first generation biofuel for commercial purpose. Biodiesel is a suitable of diesel and is produced through transestrification of vegetable oil, and residual oils and fats, with minor engine modification. Bioethanol is a substitute of gasoline and it is a full substitute for gasoline in so-called flexi-fuel vehicles. It is derived by the process of fermentation. Biogas, or Bio methane, is a fuel that can be used in gasoline vehicles with slight adaptation.it can be produced through anaerobic digestion of liquid manure and other digestible feed-stock [13].

2.1.2 Second Generation Biofuels

The limited potential of first-generation biofuels to make a significant contribution to displace fossil fuels and reduce GHG emissions highlighted by several studies unleashed a sense of urgency for the transition towards second-generation biofuels.

In general terms, we refer to the first-generation biofuels as those mainly based on sugars, grains, or seeds, and generally requiring relatively simple processing to produce the fuel. In contrast, second-generation biofuels would be generally made from non-edible lignocellulosic biomass, including residues of crops or forestry production (corn cobs, rice husks, forest thinning, sawdust, etc.), and whole plant biomass (e.g. energy crops such as switch grass, poplar, and other fast growing trees and grasses).

Biofuels obtained from vegetable oils produced from sources that do not directly compete with crops for high quality land can also be labeled as second-generation biofuels. As compared to the case of first-generation biofuels, where feedstock, can account for over two-thirds of the total costs, the share of feedstock in the total costs is relatively lower (30% to 50%) in the case of second-generation biofuels [14].

Promotion of second generation biofuels can help provide solutions to multiple issues including energy security and diversification, rural economic development, Greenhouse gas mitigation and help reduce other environmental impacts (at least relative to those from the use of other transport fuels). Policies designed to reward environmental performance and sustainability of biofuels, improving the conversion process as well as to encourage provision of a more abundant and geographically extensive feedstock supply, could see second generation products begin to eclipse first generation alternatives in the medium to longer-term. This ultimately will lead to avoid unwanted consequences and potentially delay commercialization of biofuel trade [15].

2.1.3 Third Generation Biofuels

Microalgae are currently being promoted as an ideal third generation biofuel feedstock because of their rapid growth rate, greenhouse gas fixation ability (net zero emission balance) and high production capacity of lipids (fat). Microalgae are single-cell microscopic organisms which are naturally found in fresh water and marine environment. There are more than 300,000 species of micro algae, diversity of which is much greater than plants. They also do not compete with food or feed crops, and can be grown on non-arable land and saline water.

Because of the second generation biofuels production process requires expensive and sophisticated technologies, the biofuel production from the second generation is not profitable for commercial production. Therefore, the researchers focused on third generation of renewable biofuels like methane, biodiesel and bio-hydrogen [16].

There are several advantages of microalgae biomass for biofuels production: ability to grow out through the year, higher tolerance to high carbon dioxide content and the consumption rate of water is very less in algae cultivation. However, there are several disadvantages of microalgae biomass as feedstock such as the higher cultivation cost as compared to conventional crops.

Similarly, harvesting of microalgae require high energy input, which is approximately about 20–30% of the total cost of production. The conversion technologies for utilizing microalgae biomass to energy sources can be categorized in to three different ways i.e. biochemical, chemical and thermochemical conversion [17]. Microalgae are capable of producing oil all year long. Oil productivity of microalgae is greater compared to conventional crops. The oil content of microalgae is in the range of 20-50% which is greater than other competitors.

Microalgae produce 15-300 times more oil for biodiesel production than traditional crops on an area basis. Microalgae can produce a large variety of novel byproducts. Microalgae biodiesel is not yet economically viable enough to replace petroleum based fuels or compete with other renewable energy technologies such as wind, solar, geothermal and other forms of Bioenergy. Despite their high potential both in terms of productivity and sustainability, most algae based biofuel concepts still require significant investment to become commercially viable [18].

2.2 Historical Background of Biodiesel

It was first suggested to use vegetable oil-derived fuels as a means for motive power by the inventor of the diesel engine himself, Rudolf Diesel. The diesel engine was optimized for the use of petro diesel and the vision of the engine’s inventor to use clean, renewable fuels was all but forgotten. It was not until nearly 60 years after Diesel’s death that the diesel engine’s ability to utilize vegetable oil-based fuels was rediscovered during the oil embargo of 1973. Early work was conducted at the University of Brussels by G.Chavannes on the use of ethyl esters of palm oil in a diesel engine. By 1974, the price for a barrel of oil had risen from $3 to over $12 this leads renewable energy moved into the public eye.

In 1981 and 1982, researchers in South African, Germany, and New Zealand were studying the use of vegetable oil esters in diesel engines. By 1982, a chemist and researcher Martin Mittelbach had begun development of a simplified process for producing fatty acid methyl esters and which resulted in the foundation for the biodiesel industry. By 1988, the term “Biodiesel” had made its way into the global alternative fuels vocabulary [19].

A new technology, i.e. transesterification reaction has been applied to produce a renewable fuel ‘‘biodiesel’’ derived from various raw materials include the edible and nonedible oils, algae, waste cooking oil, etc. In view of the potential properties of the vegetable oils, a large number of investigations have been carried out internationally in the area of vegetable oils as fuel. Some of the vegetable oils from farm and forest origin have been identified. Jamieson listed over 350 oil bearing crops. Few researchers examined the fatty acid profiles of seed oils of 75 plant species having 30 % or more fixed oil in their seed. They reported that the fatty acid methyl esters of oils of 26 species were found most suitable for use as biodiesel and they meet the major specification of biodiesel standards of USA, Germany and Europe [20].

Moreover, the use of non-edible oilseed, microbial oils, oil production with some yeasts, fungi, or bacteria for biodiesel production seems to be very attractive because it does not compete with the food. In general, biodiesel shows lower emissions of particulate matter and carbon monoxide (CO) than regular diesel fuel, but slightly enhanced nitrogen oxides (NOx) production [21].

2.3 Feedstock for Biodiesel Production

A consistent supply of feedstock is being faced as a major challenge by the biodiesel production industry. The problem of high feedstock cost can be mitigated by the selection of non-edible vegetable oil for the production of biodiesel because the cost of feedstocks accounts for about 60–80% of the total cost of biodiesel production. The vegetable oil can be chosen based on non-edibility nature, higher yield, better property, perennial continuous yield for many years, such as from tree and direct use with transesterification. The use of non-edible vegetable oils is of significance because of the great need for edible oil as food. The inedible oils, such as jatropha, karanja, mahua, linseed, rubber seed, cottonseed, and neem oils, and micro algae, are easily available in developing countries and are very economical compared to edible oil [22].

Feedstocks are different and the conversion process is slightly different based on the feedstock, but the basic process remains the same. This allows for biodiesel production to change from one feedstock to another. The main production difference between oil and fat is oil must be extracted from the feedstock and fat must be heated and turned into a liquid form for the reaction process. Depending on the feedstock, different catalysts are used to help with the reaction process [23].

The potential for using oil of non-edible seeds as an alternative fuel for compression ignition engine has vided scope. There are number of non-edible species identified for the production of biodiesel but testing on engine is done with only few of them. Complete understanding of production of biodiesel from non-edible seeds will help in commercializing the product and will also help countries economy by reducing the import of crude oil [24].

2.4 Trichiliaemetica Plant: Renewable Energy Plant

2.4.1 Name and Plant Description

Trichiliaemetica Vahl (Meliaceae), commonly called „Mafura tree‟, „Cape Mahogany‟ or „Natal Mahogany", has significant socio-economic importance, where it is cultivated for protection around home yards and farm lands. The tree grows wildly along coastal low lands and is also intensively cultivated by farming communities. The fruits of the mafura tree are pear-shaped containing 3-6 shiny black seeds with a bright coloured fleshy aril almost covering the seed. The fruits are usually ripe for picking from December/January to March [7].

Trichiliaemetica plant is grown in Tepi, south west of Ethiopia for possible development and use. The plant is an evergreen tree; usually up to 21 m tall but occasionally reaching up to 30m in height. The seed contains high oil concentrations as most oil-rich dicotyledonous seeds. Fresh seed yield approximately 64.7 ml oil/kg, using a simple ram press (yield from the whole seed is 58-68%). It is a fast-growing species; up to 1 m/year in colder areas and 2 m in warmer areas. It should be planted in groups near water in shade or full sun. Not resistant to frost and is therefore more suited to warmer areas, but can survive long periods of drought. Ethiopia is among the country that the plant native species distributions area (Figure 2-2) [8].

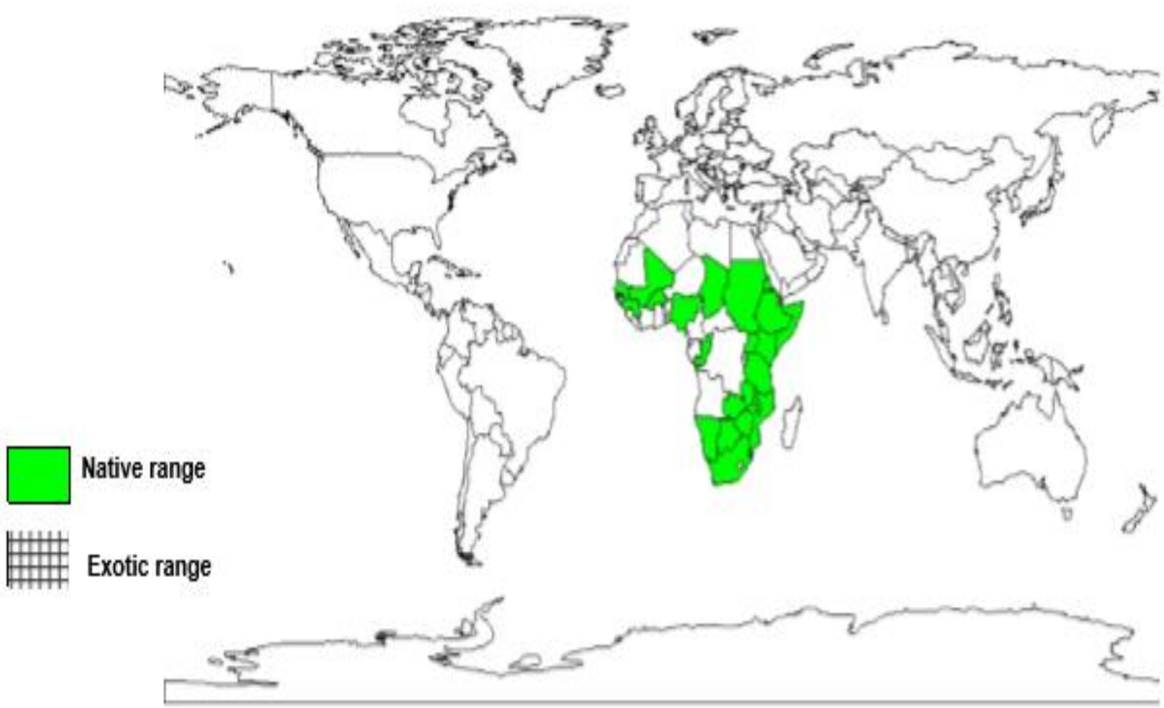


Figure 2-2: The Distribution of Trichiliaemetica Species around Africa (Source, [8])

2.4.2 Potential use of Trichiliaemetica

Trichiliaemetica is commonly used for firewood, candle making, medicine, soil conservation, shade or shelter, soil improvement, Ornamental and the high oil yields of the trichiliaemetica seeds, together with the favorable characteristics of the oils, make all the variants of the species attractive for commercial development for non-food uses such as feedstock for the production of biodiesel [8].

The physicochemical properties of trichiliaemetica seeds have been studied for their domestic and commercial applications. The seeds have been found to have good oil yield of 65.81%(w/w) which is comparable to the oil yield of some selected commercial seed oils such as cottonseed, safflower, soybean and olive oil. The acid value of trichiliaemetica seeds oil is higher than the maximum permissible acid level of fat or oil and therefore it is necessary to purify the oil to make suitable for consumption and biodiesel production [25].

Study indicated that trichiliaemetica seeds used for biodiesel production by in-situ transesterification and yielded 84% biodiesel. The physicochemical parameters of the biodiesel copper strip corrosion, kinematic viscosity, cloud point, ash content satisfy the quality criteria of biodiesel set by ASTM D6751. However, the flash point and the acid values of biodiesel don’t meet the quality criteria set by ASTM D6751, due to the presence of unreacted (residual) alcohol and mineral acids from the production process respectively. Hence, pretreatment of the seeds is necessary to increases the quality of biodiesel [26].

2.5 Biodiesel in Ethiopia

Ethiopia’s vision for greening its economy, or Climate-Resilient Green Economy (CRGE) strategy, is based on its national Growth and Transformation Plan (GTP), which seeks to enable the country to reach middle-income status by 2025. Launched in 2011, the CRGE aims to support improvement of agriculture, sustainable management of natural resources and poverty reduction. The ambitious CRGE strategy rests on four pillars: (1) improving agricultural practices to increase food security; (2) protecting and re-establishing forests for direct economic benefit and for ecosystem services, including enhanced carbon stocks; (3) expanding electricity generation from renewable sources; and (4) leapfrogging inefficient technologies and instead implementing modern, energy-efficient technologies in transport, industry and infrastructure.

Included in the fourth pillar of the CRGE strategy are efforts toward decarbonizing transport fuel, as well as producing biodiesel and ethanol. The planned implementation of 5% biodiesel and 15% ethanol blends by 2030 would mean replacing 0.28 billion liters of diesel and 0.09 billion liters of gasoline [27].

As Indicated in the bio-fuel development strategy, Ethiopia has suitable land for bio-fuel (bioethanol and bio-diesel) development. The Ethiopian government aims to increase its annual production of biodiesel to 1.6 million liters by 2015 through involvement of Private investors, farmers, etc. In general, the development of bio-fuel will generate 1 billion dollar foreign currency [28].

The second Growth and Transformation Plan (2015/16-2019/20) for biodiesel development in Ethiopia, it was planned to identify 23 million hectares of land for Biofuel development. Thus, 16.6 million hectares of land is partly planted and being planted with biodiesel seeds such as Jatrofa and caster, etc. Regarding the construction of blending facilities at fuel stations and the supply of biofuel products, eight facilities were planned to be constructed and four facilities (50% of the plan) have been constructed. As a result, 77.38 million liters of ethanol was produced and earned 51.8million USD. About 41million USD has been saved through the production of 50.6 million liters of ethanol and blending it with Benzene [29].

2.6 Biodiesel Production Technology

There are still some problems that hinder the use of vegetable oil for substitute of petro diesel. Vegetable oils have about 10% less heating value than diesel for the oxygen content in the molecule and the viscosity of vegetable oil is several times higher than that of mineral diesel due to large molecular weight and complex chemical structure. This high viscosity of vegetable oil leads to problem in pumping and spray characteristics (atomization and penetration etc.). The inefficient mixing of oil with air contributes to incomplete combustion.

Viscosity is the main barrier that presents the use of direct vegetable oils in conventional diesel engine. Because of these problems, vegetable oils must be chemically modified to a more suitable and compatible fuel for existing engines. This fuel modification is mainly aimed at reducing the viscosity to get rid of flow and combustion-related problems. This can be done in either of the following ways [30]:

- Dilution
- Pyrolysis (thermal cracking),
- Micro-emulsion
- Transesterification

2.6.1 Dilution

Dilution of vegetable oils can be accomplished with such materials as diesel fuels, solvent or ethanol. The vegetable oil is diluted with petroleum diesel to run the engine. The main advantages of dilution are its liquid nature portability, heat content (80% of diesel fuel) and renewability. In contrast higher viscosity causes problem of using in engines as coking and trumpet formation, Carbon deposits and gelling of the lubricating oil.

Caterpillar Brazil, in 1980, used pre-combustion chamber engines with the mixture of 10% vegetable oil to maintain total power without any alteration or adjustment to the engine. It has been reported that substitution of 100% vegetable oil for diesel fuel is not practical, but a blend of 20% vegetable oil and 80% diesel fuel was successful. Some short-term experiments used up to a 50/50 ratio [31].

2.6.2 Pyrolysis (thermal cracking)

Pyrolysis is the heating of organic matter in the absence of air to produce gas, a liquid and a solid. Heat or a combination of heat and catalyst is used to break vegetable oils or animal fats into smaller constituents. Studies on effects of feedstocks size showed that the product yield is independent of the oilseed particle size. The maximum temperature range for conversion of bio-oil is 400°C to 450°C.

The viscosity, flash and pour points and equivalent calorific values of the oil are lower than diesel fuel. However, cetane number of the pyrolyzate was lower compared to diesel fuel. Apart from reducing the viscosity of the vegetable oil, pyrolysis enables decoupling of the unit operation equipment in shorter time, place and scale. It produces clean liquids which needs no additional washing, drying or filtering. Product of pyrolysis consists of heterogeneous molecules such as water, particulate matter, sulfur, alkanes, alkenes and carboxylic acids [32].

The equipment for thermal cracking and pyrolysis is expensive for modest biodiesel production particularly in developing countries. Furthermore, the removal of oxygen during the thermal processing also removes any environmental benefits of using an oxygenated fuel. Another disadvantage of pyrolysis is the need for separate distillation equipment for separation of the various fractions. Also the product obtained is similar to gasoline containing sulphur which makes it less eco-friendly.

Pyrolytic chemistry is difficult to characterize because of the variety of reaction path and the variety of reaction products that may be obtained from the reaction occur. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The first pyrolysis of vegetable oil was conducted in an attempt to synthesize petroleum from vegetable [33].

2.6.3 Micro emulsion

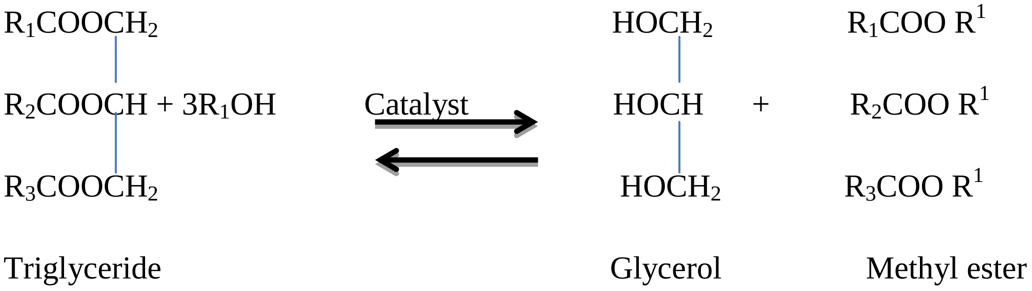
The micro emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the1-150 mm range formed spontaneously from two immiscible liquid mixtures of oil, water and surfactant (compounds that lower the surface tension of a liquid, the interfacial tension between two liquids); this process will solve the problem in viscosity and some other atomization properties of oil [34].

The components of a biodiesel micro-emulsion include diesel fuel, vegetable oil, alcohol, and surfactant and cetane improver in suitable proportions. Alcohols such as methanol and ethanol are used as viscosity lowering additives, higher alcohols are used as surfactants and alkyl nitrates are used as cetane improvers.

All micro-emulsions with butanol, hexanol and octanol met the maximum viscosity requirement for diesel fuel. The micro emulsion method is characterized by a simple and direct reduction in viscosity of biodiesel. However, continuous use of micro-emulsified diesel in engines causes problems like injector needle sticking, the deposition of a large amount of carbon, increased viscosity of lubricating oils and incomplete combustion [35, 36].

2.6.4 Transesterification

Transesterification is a reaction of a lipid (triglycerides from fat or oil) with an alcohol to form esters and a byproduct glycerol. Generally, this reaction is produce in the presence of catalyst to improve the reaction rate and yield. Transesterification is a reversible reaction and thus excess alcohol is needed to shift the equilibrium to the product side [37].



$$\begin{array}{lcccc} R_1COOCH_2 & & HOCH_2 & & R_1COO\,R^1 \\ | & & | & & \\ R_2COOCH + 3R_1OH & \underset{}{\overset{\text{Catalyst}}{\rightleftharpoons}} & HOCH & + & R_2COO\,R^1 \\ | & & | & & \\ R_3COOCH_2 & & HOCH_2 & & R_3COO\,R^1 \\ \text{Triglyceride} & & \text{Glycerol} & & \text{Methyl ester} \end{array}$$

Figure 2-3: General Equation of Transesterification Reaction R_1, R^1, R_2 and R_3 Indicate Alkyl groups

Transesterification as an industrial process is usually carried out by heating an excess of the alcohol with vegetable oils under different reaction conditions in the presence of an inorganic catalyst. The alcohols that can be used in the process are methanol, ethanol, propanol, butanol and amyl alcohol, with methanol and alcohol being frequently used.

Several catalysts have been investigated for the purpose of transesterification by many researchers. Examples are magnesium, calcium, sodium oxides and carbonates of basic and acidic macro-reticular organic resins, alkane alumina, and phase transfer catalysts, sulphuric acids, p-toluene sulphuric acid, sulfonic acids, hydrochloric acids and dehydrating agents are the usual acid catalysts. However, basic catalysts are usually favored over acid catalysts because of the higher reactivity and the milder process conditions such as the lower temperature required.

A successful transesterification reaction produces ester and crude glycerol. Though esters are the desired products of transesterification reactions, glycerin recovery is also important due to its numerous applications in daily products. The reactions are often catalyzed by an alkali and acid to improve the reaction rate and yield [38, 39].

Alkali-Catalyzed Transesterification

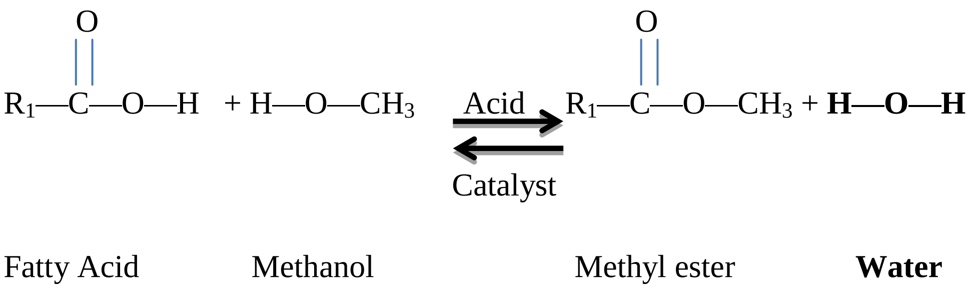
Alkali used for transesterification includes Sodium Hydroxide (NaOH), Potassium Hydroxide (KOH), carbonates, and alkoxides such as sodium methoxide, sodium propoxide, and sodium butoxide. Alkali catalyzed transesterification proceeds approximately 4000 times faster than that catalyzed by the same amount of an acidic catalyst [40].

Alkaline catalyst is more commonly used in commercial biodiesel production because it does not form water during transesterification reaction. Numbers of research have been conducted on heterogeneous catalysts to overcome the problems caused by homogeneous catalyst in biodiesel production. Most of the heterogeneous catalysts developed for production of biodiesel are either alkaline oxide or alkaline earth metal oxide supported over large surface area.

Heterogeneous basic catalysts are more active than heterogeneous acid catalyst, similar to their homogeneous counterparts. In addition, solid alkaline catalysts, for instance, calcium oxide (CaO) provide many advantages such as higher activity, long catalyst life times, and could run in moderate reaction condition. Nonetheless, CaO as catalyst can also slow down the reaction rate of biodiesel production. Most of the literature reported on heterogeneous base catalyst used lower reaction temperature (<65 ^{o}C). As a matter of fact, temperature above 70˚C will result in lower yield as methanol evaporates at 65˚C [41].

Acid- Catalyzed Transesterification

Acid-catalyzed transesterification process in biodiesel production is conventionally carried out with excess of a short chain alcohol as methanol or ethanol, and in the presence of an acid catalyst such as sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4) or hydrochloric acid (HCl).Converting the FFA in to biodiesel governs the stoichiometry as shown in Figure 2-4.



$$R_1—\overset{\overset{O}{||}}{C}—O—H \ + H—O—CH_3 \ \underset{\text{Catalyst}}{\overset{\text{Acid}}{\rightleftharpoons}} \ R_1—\overset{\overset{O}{||}}{C}—O—CH_3 + \mathbf{H—O—H}$$

Figure 2-4: Esterification of FFA

These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring typically, temperatures above 100 ^{o}C and from 3-48 hour to reach complete conversion. Reaction rates in acid-catalyzed processes may be increased by the use of larger amounts of catalyst. Homogeneous acid-catalyzed reaction is slower than the homogeneous base-catalyzed reaction. However, acid-catalyzed transesterification holds an important advantage with respect to base–catalyzed ones; the performance of the acid catalyst is not strongly affected by the presence of free fatty acids in the feedstock. Thus, a great advantage with acid catalysts is that they can directly produce biodiesel from low-cost feedstocks, generally associated with high free fatty acid concentrations [42].

Biodiesel is conventionally produced from expensive high-quality oil by transesterification that hardly occur if the FFA content in the oil is more than 3%. Consequently, much research work has been reported for the use of high acidity raw materials with a first reaction step in which the acid esterification is carried out, followed by an alkali-transesterification step in which the triglyceride portion is transformed into biodiesel. The content of free fatty acid raw materials are found in Table A -1 Appendices A [43]

2.7 Biodiesel Production Process

Biodiesel is the name of a clean burning mono-alkyl ester-based oxygenated fuel made from natural, renewable sources such as vegetable oils (e.g., soybean, cottonseed, palm, peanut, rapeseed/canola, sunflower, safflower, coconut, jatropha) and animal fats as well as waste oils (e.g., used frying oils) [44].

The resulting biodiesel is quite similar to conventional diesel in its main characteristics. Since biodiesel is miscible with petro-diesel in all ratios, in many countries, this has led to the use of blends of biodiesel with petro diesel instead of neat biodiesel. The level of blending with petroleum diesel is referred as Bxx, where xx indicates the amount of biodiesel in the blend (i.e. B20 blend is 20% biodiesel and 80% diesel).

The biodiesel production is comprises of two main sub processes namely oil extraction & purification and transesterification processes. The details of the processes are discussed here after.

2.7.1 Oil Extraction and Purification

Oil extraction

There are three main methods that have been identified for the extraction of the oil: (i) mechanical extraction, (ii) solvent extraction and (iii) enzyme extraction. Mechanical pressing and solvent extraction are the most commonly used methods for commercial oil extraction. Before oil extraction takes place, seeds have to be dried. Seed can be either dried in the oven (105 ^{o}C) or sun dried (3 weeks).Mechanical expellers or presses can be feed with either the whole seed or kernels or a mix of both, but common practice is use whole seeds. However, chemical extraction only kernels are used as feed [30, 45, and 46].

Mechanical extraction

Extracting oil using mechanical press is the most conventional practice by using manual ram press or an engine driven screw press. Engine driven screw press can extract 68-80% of the available oil while the ram presses only achieved 60-65%. However oil extracted by mechanical press needs further treatment of filtering process and degumming. Another problem associated with conventional mechanical press is that the design of mechanical extractor is suited for some particular seed and that affect the oil yield [30].

Solvent extraction (chemical extraction)

Solvent extraction is the technique of removing one constitution from a solid by means of liquid solvent. There are many factors influence the rate of extraction such as particle size, the type of liquid chosen, temperature and agitation of the solvent. The small particle size is preferable as 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. Temperature also affects the extraction rate. The solubility of the material will increase with increasing temperature. Solvent extraction with n-hexane can be used to extract the oil from jatropha and pmgamia pinnata seeds. It is reported that this method could produce about 41% and 95-99% of oil yield respectively [46].

Enzymatic oil extraction

This technique has emerged as a promising technique for extraction of oil. In this process suitable enzyme are used to extract oil from crushed seeds. Its main advantages are that it is emission friendly and does not produce volatile organic compounds. However, this type consumes much more time compared to other types. It has been found that the chemical extraction using n-hexane method resulted in the highest oil yield which makes it the most type. Furthermore n-hexane solvent extraction has a negative environmental impacts as a result of the waste water generation, higher specific energy consumption and higher emissions of volatile organic compounds and human health impacts. Using aqueous enzymatic oil extractions greatly reduce thus problems [30, 46].

Oil Purification

The oil extracted from the seed can be purified by the following means:

- Sedimentation: This is the easiest way to get clear oil, but it takes about a week until the sediment is reduced to 20-25% of the raw oil volume.
- Boiling with water: The purification process can be accelerated tremendously by boiling the oil with about 20% of water. The boiling should continue until the water has completely evaporated (no bubbles of water vapor anymore). After a few hours the oil then becomes clear.
- Filtration: Filtration of raw oil is a very slow process and has no advantage in respect of sedimentation. It is not recommended.

2.7.2 Transesterification process

Since transesterification is the major process in production of biodiesel researchers will concentrate on the details of the process as follows:

Oil Heating

In order to speed up the reaction as well as remove any water residue, as an example jatropha oil should be boiled at 105-110 ^{o}C for at least 30 min. Heating should be stopped if there is no more water bubbles in the oil. When water is present, particularly at high temperatures, it can hydrolyze the triglycerides to diglycerides and form a free fatty acid.

It is important to stir the oil as it is heated. This will result in a more even heating and reduce the temperature of oil exposed directly to the heating element. After the entire water residue is removed from the oil it should be cooled to a temperature a little lower than boiling temperature of alcohol [47].

Mixing of alcohol and catalyst

Suitable alcohols that used for transesterification include methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol and ethanol are utilized most frequently, because of their low cost and its abundance in local market. The reactions are often catalyzed by an acid or a base, since the alcohol is sparingly soluble in the oil phase. The purpose of mixing alcohol and the catalyst is to make the reaction for the two substances to form Methoxide or Ethoxide. The catalyst promotes an increase in solubility to allow the reaction to proceed at a reasonable rate. Methanol and Ethanol is preferred for its abundance in local market [48].

Transesterification Reaction

In the transesterification reaction, the reactants initially form a two phase liquid system. Hence the reaction is diffusion controlled and poor diffusion between the phase results in a slow rate. Therefore in order to speed up the reaction between the mixture of Methoxide or Ethoxide and the oil, a mixing mechanism should be there. Experiment conducted by [49] reveals that transesterification of vegetable oils and animal fats into methyl ester or ethyl ester was function of mixing intensity. Best reaction rate in this experiment is observed for a rotational speed above 200 rpm. However this mixing effect is most significant during the slow rate region of the reaction. As the single phase is established, mixing becomes insignificant and the reaction rate is primarily influenced by the reaction temperature.

Although the crude oils could be transesterified, ester yields were reduced because of gums and extraneous material present in the crude oils. These parameters (60°C reaction temperature and 6:1 methanol to oil molar ratio) have become a standard for methanol-based transesterification.

Draining of Glycerol

After the transesterification reaction, one must wait for the glycerol to settle to the bottom of the container. This happens because glycerol is heavier than biodiesel.

The settling will begin immediately, but the mixture should be left a minimum of eight hours (preferably 12) to make sure all of the glycerol has settled out. There will be a difference in viscosity and color between the two liquids. Glycerol looks very dark compared to the yellow biodiesel. The viscosity difference is large enough between the two liquids that the difference in flow from the drain can be seen.

Biodiesel Washing and Drying

The purpose is to wash out the remnants of the catalyst and other impurities. There are three main methods:

- Water wash only (a misting of water over the fuel, draining water off the bottom)
- Air bubble wash (slow bubbling of air through the fuel)
- Air/water bubble wash (with water in the bottom of the tank, bubbling air
- through water and then the fuel

Which method works the best is dependent on the quality of the fuel. The mostly used method is a combination of water washing and air bubble washing. Warm water, usually from 49-60ºC [50], is misted above the fuel.

The use of warm water prevents precipitation of saturated fatty acid esters and retards the formation of emulsions with the use of a gentle washing action. The amount of wash water should equal from 25-100% of the volume of oil [51, 52] and can be drained throughout the washing process. After the water is drained, the air washing process can start. At this point, the biodiesel is usually a pale yellow color. Air should be bubbled through the biodiesel mixture for approximately 8 hours. The bubbling should be just enough to agitate the biodiesel surface. A final drain of accumulated contaminants is done immediately after the air bubble wash is finished. The fuel is now ready for use.

During the washing process, gentle agitation is required to avoid the emulsion. After the biodiesel is washed, it should be dried until it is crystal clear. This can be done by letting the biodiesel sit uncovered in a sunny location for a few days, or it may be heated to about 49 ^{o}C for a few hours. Another popular technique is recirculating the biodiesel from the bottom of the drying tank through a shower head or sprayer suspended above the top of the open tank.

This increased contact with air will dry biodiesel in about an hour, depending on humidity. It should have a pH of close to 7, or chemically neutral and it should have no methanol left in it [52].

2.8 Variables Affecting the Yield of Transesterification

The yield of biodiesel in the process of transesterification is affected by several process parameters/variables. The most important variables affecting the yield of biodiesel from transesterification are:

- ✓ Molar ratio of alcohol and oil
- ✓ Reaction time
- ✓ Catalyst concentration
- ✓ Temperature

2.8.1 Effect of Molar Ratio

Molar ratio is variable affecting the yield of ester is the molar ratio of alcohol to vegetable oil. The Stoichiometry of the transesterification reaction requires 3 mol of alcohol per 1 mol of triglyceride to yield 3mol of fatty esters and 1 mol of glycerol. Alcoholysis of beef tallow oil was carried out with different molar ratio of alcohol to beef tallow from 6:1-12:1 with different times from 60-120 minute in reaction temperature of 55 ^{o}C and amount of catalyst 3 %(w/w).According to the experimental studies, the best conditions for alcoholysis of beef tallow waste oil is 3% of catalyst in oil, methanol to oil molar ratio 9:1, reaction temperature 55 ^{o}C for a period of 1.5 h. The yield of methyl ester is 82.43%. The biodiesel properties like methyl ester content, density, kinematic viscosity and flash point was evaluated and fallen within the scope of the biodiesel specification ranges [53].

The molar ratio of methanol to oil increased from 3:1 to 6:1, the production yield also increased. Further increase resulted in lower yield. The optimum molar ratio of methanol to oil was determined as 6:1 for maximum yield (75.4%) of biodiesel fuel from chicken fat using calcium oxide catalysts. Therefore, we concluded that to elevate the biodiesel yield and excess methanol feed was effective to a certain extent. The molar ratio of alcohol to triglyceride is the most important variable affecting the biodiesel yield.

However, transesterification is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction to the forward direction. In addition, the high molar ratio of alcohol to vegetable oil interferes with the separation of glycerin because of the increase in solubility. When glycerin remains in solution, it helps to drive the equilibrium back to the left, lowering the yield of esters [54].

The maximum conversion was achieved at methanol to oil molar ratio have obtained above 98% yield using 1:9 Jatropha oil to methanol molar ratio and heterogeneous solid catalyst used was Sodium or Silicon Dioxide (Na/$SiO_{2)}$.The work carried out by [55] shows that with molar ratio of oil to methanol of 1:12, maximum conversion was achieved in 30 minutes only and after that it almost a constant over an extended reaction time. Molar ration of 1:3 and 1:6 are not showing good results. One of the reasons for the same may be the predominance of esterification reaction at the initial phase, to transesterify the FFA present in the Jatropha oil, of transesterification which can consume methanol present in the reaction mixture and hence, the amount of methanol available for transesterification may not be sufficient to drive the reaction forward for longer time.

2.8.2 Effect of Reaction Time

To study the effect of reaction time on yield and characteristics of biodiesel, it was prepared from different oils and samples were collected at different reaction time from the batch reactor. The trend of yield with respect to reaction time biodiesel increases with increase in reaction time at beginning. The yield of biodiesel reaches a maximum at 15-30 min. and then remains relatively constant with further increase in reaction time. Similar trend was obtained for all oils under consideration. The yield slightly decreases with increase in reaction time after 80 min.

This decrease may be due to the hydrolysis of esters at longer time causing more fatty acid to generate to form soap. Thus reaction time is also a controlling factor of product yield; extending might have negative effect on yield [56].

2.8.3 Effect of Catalyst Concentration

Recently, the application of heterogeneous catalyst has attracted considerable interest in biodiesel production compared to homogenous catalyst because of its reusability in successive reactions runs and easier to separate from the reaction mixture.

Thus, attempts have been directed to develop supported catalyst to improve the efficiency and recovering ability of the prepared catalyst. It is observed that the increase in catalyst dosage from 1 to 3 wt% resulted in corresponding increase in methyl ester yield from 70 to 87.5%. As reported by Leung and Guo (2006), low loading of catalyst (2 wt %) is insufficient to drive the reaction for completion and the yield of biodiesel was only less than 75% after 2 hours. An addition of 4 wt% of catalyst content however had deterioration effect for methyl ester yield as a decrease was observed from 87.5 to 82.5%. Then, the yield of the methyl ester decreased slowly from 82.5 to 80% along with an increase in catalyst content from 4 to 5 wt%. Based on the study result, 3 wt% of catalyst amount was selected as the optimum amount [57].

Base catalysts (NaOH and KOH) were used. These reactions are relatively fast but are sensitive to water content and free fatty acids. Typical base concentrations are 0.3 to 1.5% based on the weight of oil. When sodium methoxide is used, the concentration can be 0.5% or less. Most researchers use NaOH as the catalyst. The effects of KOH and NaOH on the transesterification of the oils were investigated with the concentration kept constant at 1%. The result showed that both NaOH and KOH catalysts exhibited the appreciable behavior especially at the ratio of 6:1, where NaOH also gave the best yield (97%) while it was poor at 4:1. Increase in reaction time from 5 minutes to 30 minutes did not improve the yields and viscosities. It also has no significant effects on specific gravity. Alcohol/oil molar ratio and the nature of catalyst can be thought to be responsible for the variation in yields, viscosity and specific gravity [58].

2.8.4 Effect of Reaction Temperature

The study showed that the mean yield from Soybean Oil increased when the reaction temperature increased from 55 to 60^oC. Higher reaction temperature can improve the efficiency of transesterification, which in turn enhances the mean yield. On the contrary, the mean yield decreases significantly when the reaction temperature is higher than 60 ^oC. One reason may be offered to explain why the reaction temperature at 55 ^oC resulted in a lower mean yield than at 60 ^oC. The boiling temperature of methanol is about 65 ^oC. The methanol started volatilization when the reaction temperature exceeded 65 ^oC. The volatilization of methanol might reduce the yield. In short, the optimal level of reaction temperature should be less than 65 ^oC and 60 ^oC might be the optimal level of reaction temperature.

The result was consistent with earlier findings that reaction temperature (Colucci et al., 2005; Hanh et al., 2009b; Koc, 2009; Tan and Lee, 2009) is the significant factor on the yield of vegetable oil, and the optimal reaction levels should be around 60 ^{o}C .The optimal reaction levels were catalyst amount of 1.0 wt%, reaction temperature at 60 ^{o}C, and methanol/oil molar ratio of 6:1. The mean yield achieved was 97.49 % [59].

2.9 Biodiesel Quality and Specifications

The standards that are developed to determine the quality of biodiesel depends on variety of factors which vary from region to region. The factors may include: availability of feedstocks for production of biodiesel; characteristics of the diesel fuel standards existing in each region, which are different and the predominance of the types of diesel engines most common in the region and the emissions regulations governing those engines.

The current standards for biodiesel in Brazil and the United States of America are applicable for both fatty acid methyl esters (FAME) and fatty acid ethyl esters (FAEE), whereas the current European Union biodiesel standard is only applicable for fatty acid methyl esters (FAME).

In Brazil and the United States of America, biodiesel is perceived primarily as a blend stock for fossil diesel fuel, and so some parameters are set on the understanding of a certain percentage of biodiesel being present in the finished fuel.

In the European Union, the standard for biodiesel describes a product that may be used as a stand-alone fuel or as a blending component in conventional hydrocarbon based diesel fuel, therefore some EU limit values are set to different levels to those of Brazil and USA, and the specification is more extensive. This difference in usage of biodiesel represents in some cases a considerable difficulty in achieving the eventual establishment of a common specification. Biodiesel specification according to the United States of America, European Union and Brazilian standards are given in Table 2-1.

The fuel specification defines and sets the quality standards based on the standard ASTM and EN FAME (biodiesel) property specifications. Generally, the major fuel properties are defined as follows [61-64];

Table 2-1: Biodiesel Specifications Compilation

Property	**Test method**			**Limits**			
	USA	EU	Brazil	Units	USA	EU	Brazil
	ASTM D6751	EN14241	ANP42		ASTM D6751	EN14241	ANP42
Acid Number	D664	EN 14104	ABNT NBR 14448/EN 14104/ASTM D664	mgKOH/g	0.50 max	0.50 max	0.80 max
Carbon Residue(on 100% Sample)	D4530	EN10370	EN 10370/ASTM D4530	% mass	0.050 max	-	0.10 max
Flash Point	D93	EN 3679	ABNT NBR 14598/EN 3679/ASTM D93	°C	130 min	120 min	100 min
Density @ 15°C		EN 3675/ EN 12185	-	kg/m3	-	860 – 900	-
Cetane Number	D 613	EN 5165	EN 5165 / D613	-	47 min	51.0 min	Report
Kinematic viscosity(40^{o}C)	D445	EN ISO 3104	ABNT NBR 10441/EN 3104/D445	mm2/s	1.9-6.0	3.5-5.0	Report

2.9.1 Flash Point

The flash point is defined as the "lowest temperature at which application of an ignition source causes the vapors of a specimen to ignite under specified conditions of test. The flash point is a determinant for flammability classification of materials.

The typical flash point of pure methyl esters is > 200 °C, classifying them as "non-flammable". However, during production and purification of biodiesel, not all the methanol may be removed, making the fuel flammable and more dangerous to handle and store if the flash point falls below 130ºC. Flash point is used in safety regulations to define "flammable" and "combustible" materials. Higher values indicate materials that are less likely to ignite accidentally.

2.9.2 Cetane Number

The cetane number of a fuel describes its propensity to combust under certain conditions of pressure and temperature. The European specification is more stringent; requiring a minimum cetane number of ≥51.The cetane number of diesel fuel in the USA is specified at ≥47. The higher the cetane value the better the ignition properties. The cetane number affects a number of engine performance parameters like combustion, stability, white smoke, noise and emissions of Carbon monoxide (CO) and hydrocarbons.

Biodiesel has higher cetane value than conventional diesel fuel, which results in higher combustion efficiency. But with the increase of cetane number the iodine value decreases which means that the degree of unsaturation decreases. This situation leads to solidification at higher temperature. It means that biodiesel with a very high cetane number may have higher melting point, cloud point and pour point and that it can solidify at or above 0^{o}C depending on the value of the cetane number or the iodine number of the biodiesel.

2.9.3 Viscosity

The kinematic viscosity of biodiesel is an important factor as it controls the characteristics of the injection from the diesel injector. The kinematic viscosity of biodiesel is higher than that of fossil diesel, and in some cases at low temperatures becomes very viscous or even solid. A minimum viscosity is required for some engines because of the potential for power loss caused by injection pump and injector leakage.

This is not an issue for B100, and the minimum is set at the same level as for petroleum diesel. The maximum viscosity is limited by the design of engine fuel injection systems. Higher viscosity fuels can cause poor fuel combustion that leads to deposit formation as well as higher in-cylinder penetration of the fuel spray, which can result in elevated engine oil dilution with fuel.

2.9.4 Density

Density is mass of the substances occupying unit volume at a temperature. Hydrometers are used to evaluate the density of liquids. The values depend on their fatty acid composition as well as on their purity. Density increases with decreasing chain length and increasing number of double bonds, or can be decreased by the presence of low density contaminants such as methanol.

If the fuel is of higher density large mass of fuel is injected and hence more power and emissions. The densities of biodiesels are generally higher than those of fossil diesel fuel.

2.9.5 Acid Number

The test measures the amount of potassium hydroxide as mg KOH needed to neutralize 1 gram of fuel. It is expressed as mg KOH required neutralizing 1g of FAME. Acid number or neutralization number is a measure of free fatty acids contained in a fresh fuel sample and of free fatty acids and acids from degradation in aged samples. Acid numbers higher than 0.80 milligram potassium hydroxide per gram (mg KOH/g) have been associated with fuel system deposits and reduced life of fuel pumps and filters.

2.9.6 Carbon Residue

Carbon residue is defined as the amount of carbonaceous matter left after evaporation and pyrolysis of a fuel sample under specific conditions. Although this residue is not solely composed of carbon, the term carbon residue is found in all biodiesel standards depending on the region because it has long been commonly used. The parameter serves as a measure for the tendency of a fuel sample to produce deposits on injector tips and inside the combustion chamber when used as automotive fuel. Studies showed that for FAME, carbon residue correlates with the respective amounts of glycerides, free fatty acids, soaps and remaining catalyst or contaminants. For these reasons, carbon residue is limited in the biodiesel specifications

CHAPTER THREE

3. METHODOLOGY

3.1 Materials and Chemicals/Reagents Used

a) Materials used

The following materials were used during the study period:

- Weight balance
- Vibro Viscometer
- Moisture analyzer
- Pycnometer
- Dropper
- Reflux condenser
- Boiling water bath
- Conical flask, of alkali resistance glass, 250 ml capacity
- Burette graduated in 0.1 ml
- Electric Oven
- Water bath reactor with circulating thermostat and condenser
- Stirrer motor with a capacity of 1000 rpm
- Furnace
- Separating funnel
- Thermometer

b) Chemicals/Reagents Used

The following chemicals/reagents were used through the study period:

- Ethanol (C_2H_5OH): Two liters of Ethanol alcohol with the concentration of about 97% was supplied by Neway P.L.C. import and commission agent.
- Methanol (CH_3OH): One liter of Methanol alcohol with the concentration of about 99.6 % was supplied from AAiT lab.

- Sodium hydroxide (NaOH), Concentrated Hydrochloric acid solution (HCl), phosphoric acid (H_3PO_4), Calcium oxide (CaO): are supplied by Atomic Educational Materials Supply P.L.C.
- Trichiliaemetica seed: It was purchased at the local market in Tepi, South-west of Ethiopia.
- Trichiliaemetica Oil: Extracted by using a manually operated mechanical pressing machine: supplied from AAiT lab.
- Phenolphthalein: for color indication
- Diethyl ether: for acid value determination
- Potassium Hydroxide (KOH): for acid value determination

3.2 Methods

In this Part, The most important methods used for process optimization of biodiesel production of the whole research work were described. Laboratory scale batch production of biodiesel was carried out from trichiliaemetica oil by using methanol alcohol and calcium oxide (CaO) catalysis through transesterification methods. The different methods used were mainly focused on tested and identified the effects of different process parameters for biodiesel production and found the optimum conditions to maximize the yield of biodiesel.

Among the main activities, trichiliaemetica seed preparation, oil extraction and purification for physicochemical analyses, as well as heating to high temperature in air or oxygen(calcination) of calcium oxide, biodiesel production and characterization of the quality of the biodiesel produced from trichiliaemetica oil and determined the optimum biodiesel yield were conducted at, Addis Ababa Institute of Technology (AAiT), AAU.

The reaction parameters considered in the present study were; alcohol to oil molar ratio, the catalyst to oil molar ratio (wt/wt), reaction temperature and time. The values of reaction parameters used in the present research were selected based on referring to previous works done by different researchers.

The physicochemical parameters considered for crude and purified trichiliaemetica oil during the present study include; specific gravity, density, moisture content, kinematic viscosity, saponification value, acid value and % FFA, whereas, for the optimized biodiesel yields; specific gravity, density, kinematic viscosity, acid value, saponification value and flash point.

Fatty acid composition (%) of trichiliaemetica biodiesel where conducted at Research and Testing Directorate Laboratory, Ethiopia Leather Industry Development Institute, Addis Ababa. In conclusion, the results were compared to the standard specifications of ASTM/EN/ Brazil. The optimization processes were determined using Design-Expert 6.0.8 Trial software program was used for the purpose of optimization.

3.2.1 Sample Preparation and Oil Extraction

The most important feedstock used in this work was Trichiliaemetica seeds, locally accessible in Ethiopia. The seeds were paid for at the local market in Tepi town, South-west of Ethiopia and directs of 7o 12′ 0″ N, 35o 27′ 0″ E. The collection was done for the period of the month of January through March, 2018and washed with tap water to get rid of impurities.

The moisture content of trichiliaemetica seeds concentration affects biodiesel production yield. Therefore trichiliaemetica seed was sun-dried on the open floor for 6 days to get rid of the moisture from the seeds. Then trichiliaemetica seed sample was randomly selected to determine moisture content in the seed. At that time11.935 gm of each seed, the sample was oven-dried at 105 ^{o}C for 18 h at School of Chemical and Bioengineering (SCBE) laboratory, Addis Ababa Institute of Technology (AAiT).

The dry sample was well-ventilated at room temperature and re-weighed to determine the weight loss. The value of the dried seed was 11.246 gm. From now, the moisture content of the seed was calculated by using equation 3.1[65]. The tests were replicated three times and the average moisture content of the trichiliaemetica seed was found about 5.77 %.

$$\%\ \text{moisture} = \frac{Wi - Wf}{Wi} \text{x } 100\% \qquad (3.1)$$

Where:

Wi = Initial weight of seed before oven dried

Wf = Final weight of seed after oven dried

Trichiliaemetica seed was used without size reduction for mechanical press machine that is available in SCBE laboratory, AAiT. To end, the dried seeds were feed into manually manipulated mechanical pressing machine for extraction of rough oil.

Mechanical pressing is low cost oil extraction method and produces a large amount of oil from trichiliaemetica seeds yield approximately 75 ml oil/kg.

3.2.2 Purification of the Crude Trichiliaemetica Oil

Degumming

Crude oil obtained by mechanical pressing machine extraction of trichiliaemetica oilseed has a deposit of so-called gums. The effect of the existence of gums in the biodiesel production process has decrease biodiesel yield and quality. In addition to this, the negative effects of gums on biodiesel form in injector pump affect the performance of the engine. When % the weight of oil is used in the following it has to be understood as wt. % (w/w). To solve this problem mass of crude trichiliaemetica seed oil in grams was heated to 70°C under the constant string at 1000 rpm in a beaker. At that time 3% of hot distilled water which was heated to 90°C with string and 0.2% phosphoric acid to reduce the phospholipids solubility and removed the non-hydratable phospholipids, respectively [66].

Studies indicated that increasing mixing time and as a result of prolonged reaction time, it is logical to expect that the phosphatide removal efficiency will also be increased. In the case that a mixture of water and phosphoric acid is used instead of water for a phosphatide recovering method, a relatively high-speed process with better efficiency will be followed. Hence the mixture was stirred for 1 hour. The black formed precipitate was separated by centrifuging for 5 min at 6000 rpm. The degummed oil was dried at 105 ^{o}C for 30 min using oven [67, 68].

Neutralization by Caustic Treatment

Neutralizing the acid value and FFA of crude trichiliaemetica oil was done by adding 0.5 N NaOH to the degummed trichiliaemetica oil and heated the reaction mixture to 70 ^{o}C while stirring at 1000 rpm to break any emulsion that might have formed during neutralization. In addition, Sodium chloride (10% of the weight of oil) was also added to help settle out the soap formed. After one hour mixing the mixture was transferred into a separating funnel and allowed to stand for one hour; the soap formed was separated from the oil. In conclusion, the neutralized oil was passed through hydration process by the addition of 30% hot distilled boiled water in which the mixture was stirred for 2 minutes and allowed to stand in the separating funnel until two clear phases were observed.

The neutralized oil was then drawn off into the beaker and dried at 100 ^{o}C for 30 min using the oven. The appropriate amount of alkaline solution (NaOH) required to neutralize the free fatty acid was calculated in equation 3.2 [69].

$$L = \frac{\rho \; of FFA * 1000}{M * N} \qquad (3.2)$$

Where:

Where L   appropriate volume of 0.5 N-molar aqueous NaOH solution

ρ- density of the oil
M -average molecular weight of the fatty acids
N -concentration of the aqueous NaOH solution (mol/l)

3.3 Physicochemical Analysis Method

Certain physicochemical properties of the (Trichiliaemetica oil and Biodiesel)were determined prior to the biodiesel production process (Table 3-1).

The feedstock status determination helps not only to know the condition of the oil but also helps to make a certain decision on whether it requires further treatment or not, as well as to select treatment methods.

The key physicochemical properties that were determined for trichiliaemetica oil included density, specific gravity, moisture content, kinematic viscosity, acid value and saponification value. In addition to this flash point and calorific value excluding moisture content were determined for trichiliaemetica biodiesel using the test methods defined below.

All determinations excluding moisture content and flash point were done three times and the average values were noted down. These parameters directly or indirectly affect the final product/biodiesel quantity and quality.

Table 3-1: Physicochemical Parameters Analyzed

Characteristics	**Trichiliaemetica oil**	**Biodiesel**
Specific gravity	X	X
Density at 25 ^{o}C	X	X
Moisture content	X	-
Kinematic viscosity at 40 ^{o}C	X	X
Saponification value	X	X
Acid value	X	X
Higher Heating Value	-	X
Flash point	-	X

3.3.1 Determination of Specific Gravity

A Specific gravity of trichiliaemetica oil at a given temperature is the ratio of the mass in air of a given volume of the oil at that temperature to that of the same volume of water. This can influence the efficiency of the fuel atomization for the airless combustion system. Density is the relationship between the mass and volume of a liquid and can be expressed in units of mass per unit volume (i.e.kg/m3).

The density of diesel oil is important because it gives an indication of the delay between the injection and combustion of the fuel in the diesel engine (ignition quality). The samples were filled into Pycnometer (0.05 m^3) and its weight was recorded at room temperature. Hence, the specific gravity was calculated by using equation 3.3[70].

$$\text{Specific Gravity} = \frac{\rho \text{ of the oil}}{\rho \text{ of water}} \qquad (3.3)$$

Where: - ρ - Density

Density of oil was calculated by using the correlation:

$$\text{Density} = \frac{Mass\ of\ oil}{Volume\ of\ oil} \tag{3.4}$$

3.3.2 Determination of Moisture Content

During the transesterification reaction existence of moisture decreases the conversion of triglycerides to biodiesel fuel. The moisture content of biodiesel produces the heat of combustion and will cause corrosion of vital fuel system components: fuel pumps, injector pumps, and fuel tubes. For that reason, it is necessary to minimize the moisture content in the feedstock prior to the transesterification process. Hence, the moisture content of trichiliaemetica oil was determined by moisture analyzer at SCBE laboratory, AAiT. Trichiliaemetica oil weighting 2.78 gm were placed in the moisture analyzer set at 100 ^{o}C 15 min. The reading was reached the required time then moisture content of oil recorded. Finally, the moisture content of the trichiliaemetica seed oil was recorded from moisture analyzer [71].

3.3.3 Determination of Kinematic Viscosity

Viscosity is defined as the opposition of liquid to flow. It refers to the thickness of the oil. Kinematic viscosity is the most important property of biodiesel. Subsequently, it affects the operation of fuel injection equipment's, particularly at low temperature when an increase in viscosity affects the fluidity of the fuel. High viscosity may lead to the formation of soot and engine deposits due to inadequate fuel atomization. Therefore, the viscosity of trichiliaemetica oil was determined by Digital Vibro viscometer at SCBE laboratory, AAiT and the oil was kept in the water thermostat bath until it reaches the equilibrium temperature of 40 ^{o}C.

After maintaining the equilibrium temperature, the Vibro viscometer tip was inserted to 50 ml of trichiliaemetica oil and the reading was taken from the controller as dynamic viscosity. The kinematic viscosity is then equal to the ratio of dynamic viscosity to the density of the oil as mentioned in equation 3.5 [72, 73].

$$\mu = \frac{V}{\rho} \tag{3.5}$$

where:

μ=kinematic viscosity, mm2/s

ν=dynamic viscosity, mPa.sec and ρ=density, kg/m

3.3.4 Determination of Saponification Value (SV)

Saponification value is used to determine the total acid content of the oil. The saponification value is, therefore, a measure of oil quality. The saponification value of trichiliaemetica oil determined the biodiesel production yield. Therefore to determine the saponification value of trichiliaemetica oil potassium hydroxide solution of 0.5 M, in 97% (v/v ethanol) was prepared. Thirty-five (35) grams of potassium hydroxide pellet were dissolved in 20 ml of water, and the solution mixed with 1000 ml of 97% ethanol. The solution was allowed to stand for 12 hours at room temperature and the clear supernatant solution decanted off. The filtered solution was then kept in the dark for storage. Hydrochloric acid of 0.5 M and 0.5 mol/liter was accurately standardized and a 2% phenolphthalein indicator prepared.

Two grams of the oil was correctly weighed into a 250 ml conical flask and 25 ml of alcoholic potassium hydroxide solution was measured into the flask. The flask was connected with a condenser and refluxed continuously for 1 h, swirling intermittently until complete saponification. The flask was removed and the content titrated against the 0.5 N HCl, using phenolphthalein as an indicator. The endpoint was reached when pinkish coloration changed to colorless. The blank determination was conducted along with that of the sample, using the same reagents minus sample. Saponification value was calculated and articulated as the number of the milligram of KOH required to saponify two-gram oil. The last result was calculated using equation 3.6 [74].

$$\mathrm{SaponificationValue} = \frac{(\mathrm{Vb} - \mathrm{Va}) * \mathrm{N} * 56.1}{\mathrm{W}} \tag{3.6}$$

Where:

W - Weight 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 black in milliliter

Molecular weight of KOH = atomic mass of H + atomic mass of O +atomic mass of K

= 1.00794 + 15.9994 + 39.0983

= 56.1

The same procedure will be used to determine the SV of biodiesel as discussed above.

3.3.5 Determination of Acid Value

The acid value is the measure of the number of carboxylic acid groups in a chemical compound, such as fatty acid, or in a mixture of compounds. Acid value can provide an indication of the level of lubricant degradation while the fuel is in service. Therefore the acid value of the oil was calculated by preparing standard alcoholic KOH solution (0.1 N) dissolving 1.4 gm of KOH pellet to 250 ml of (97%) ethanol. The solution was filtered and stored in the brown bottle for five days. A phenolphthalein 1 gm per 100 ml of 97% v/v ethanol was used our indicator. A mixture of ethanol 97% v/v and diethyl ether was prepared by mixing 50 ml diethyl ether and 50 ml of ethanol. The solution was neutralized in a presence of 0.3 ml of indicator per 100 ml of the mixture by means of ethanolic KOH solution. A weighed quantity of the sample five gm was dissolved in 50 ml of the mixture of ethanol and diethyl ether previously neutralized. The solution was titrated with 0.1N ethanolic KOH solution in presence of phenolphthalein indicator. The volume of 0.1 N KOH for the sample titration was noted. The total acidity (acid number) in mg KOH/ gm was calculated using equation 3.7 [75].

$$\text{Acid Value} = \frac{Volume\ of\ KOH\ used * 0.1 * 56.1}{Weight\ of\ sample} \tag{3.7}$$

Where:

0.1= Normality of aqueous solution of KOH

56.1= Molecular weight of KOH

Free Fatty Acid Determination: The amount of free fatty acid (FFA) was calculated according to [4], as being equivalent to half the value of acid value,

$$\text{Free Fatty Acid Value} = \frac{Acid\ Value}{2} = \text{mgKOH/g} \tag{3.8}$$

3.3.6 Determination of Flash Point

Flashpoint is one more important property for biodiesel fuel. Flashpoint of a fuel is the temperature at which it will ignite when exposed to a flame or a spark. Therefore, the flash point of the biodiesel was determined using an open cup method at SCBE laboratory, AAiT. The cup was filled with the biodiesel up to the mark (about 50 ml) and the cup was heated by a Bunsen burner. A small open flame was maintained from an external supply of natural gas. Periodically, the flame was passed over the surface of the oil. When the flash temperature has reached the surface of the oil catch flame, the temperature at the moment was noted and reported as flash point temperature [3].

3.4 Laboratory Scale Biodiesel Production

The biodiesel produced in this work was prepared using purified Trichiliaemetica oil together with methanol alcohol (approximately 99.6% purity) and calcined calcium oxide catalyst. Different reaction parameters, such as reaction time, reaction temperature, methanol to oil molar ratio and catalyst concentration were considered while producing the biodiesel.

3.4.1 Experimental Design

The 5-level-4-factor experimental design was employed in this study requiring 30 experiments, consisting of 6 central points. Central Composite Design experiment (CCD) was applied for carrying out the optimization studies to maximize the yield of biodiesel in the transesterification process. The mixing speed was fixed at 500 rpm for all experimental runs.

The reaction time A (hour), reaction temperature B (^oC), methanol to oil ratio C (w/w) and the catalyst concentration D (weight %) were the independent variables selected for the study. The study indicated that the four factors are the major factors that affect biodiesel yield [76]. The coded and uncoded levels of the independent variables used for the transesterification of biodiesel were given in Table 3-2.

Table 3-2: Experimental Range and Levels of the Independent Variables

Variables	**Symbols**	**Level**				
		-2	-1	0	1	+2
The reaction time (hours)	A	0.5	1	1.5	2	2.5
Reaction temperature (^oC),	B	50	55	60	65	70
Methanol/oil molar ratio (w/w)	C	3	6	9	12	15
Catalyst loading wt. (%)	D	0.5	1	1.5	2	2.5

3.4.2 Experimental Set-up

The transesterification reaction system employed in this work was displayed in Figure 3-1. The experimental set up consists of a 500 ml two-necked water batch reactor which is equipped with a motor (IKA WERKE, max 1000 rpm) fitted with stainless steel rod stirrer provided the mixing requirement and condensing coil.

The reactor was immersed into a constant temperature water bath equipped with a thermostatically controlled heater. Thirty reactions were carried out over the entire duration of experimental work.

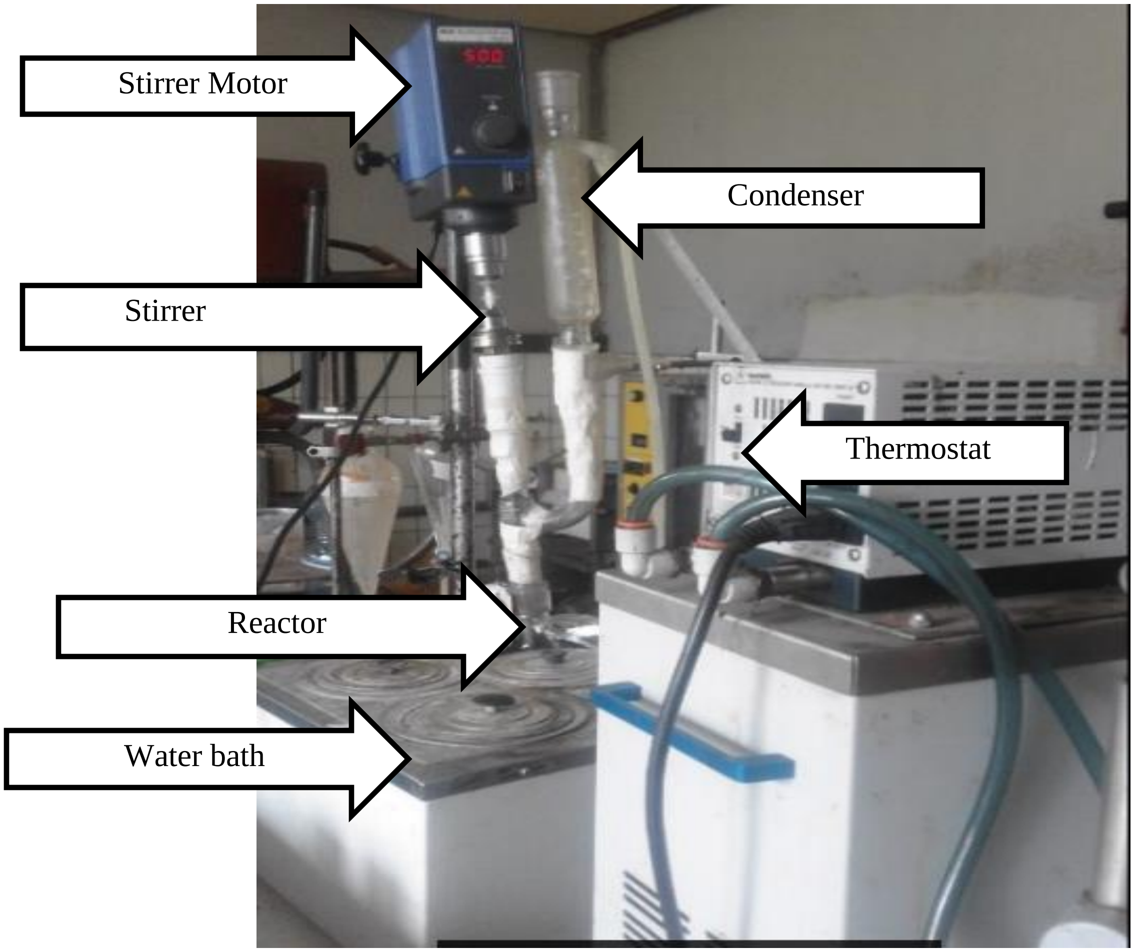


Figure 3-1 Experimental Set-Up Used

3.4.3 Production Procedure

In place, of biodiesel production process catalysts are either homogeneous or heterogeneous. Homogeneous base transesterification processes have a number of drawbacks due to difficulty in the purification step of biodiesel. In the case of heterogeneous catalyst calcium oxide is one of the most studied systems for biodiesel production due to high activity, availability at mild temperature, long life activity, its low cost and its simple recovery from the final products of transesterification (Biodiesel and Glycerol)[77].

For the transesterification process, the purchased calcium oxide was calcined by using furnace in SCBE, lab AAiT at 550 ^{o}C for 4 hours. Methanol and calcined calcium oxide mixture were prepared as per the requirement. This mixture was agitated continuously until all the calcined calcium oxide dissolved completely.

Trichiliaemetica oil was heating up in order to remove the remains moisture content from the oil. The reactor was then charged with the required amount of trichiliaemetica oil and the methoxide solution as per the design. Then the reactor assembly was heated to the desired temperature by using the circulating thermostat. Mixing, assisted with mechanical stirrer motor, was started immediately by gradually increasing the intensity to 500 rpm. After the required time was reached the mixture was transferred to a clean separating funnel and allowed to separate.

After the separation is completed the biodiesel layer was collected and transferred to another separation funnel for washing. The biodiesel layer was purified by washing with warm water to remove methanol, residual catalyst, and soaps. During the washing process, gentle agitation was applied to avoid the emulsion. After separation of the layer for 30 minutes, the wash water layer was drained off from the bottom of the separating funnel. The washing process was repeated until the biodiesel layer became clear. The washing was continued until most of the unreacted oil, catalyst, alcohol, and trace glycerin are washed away. After the washing process, the biodiesel was allowed to stay in an oven for several hours at 50 ^{o}C.

The quantities of the obtained rough biodiesel, after purification of the samples, were evaluated by measuring their final yield of biodiesel by using equation 3.9. The biodiesel quality attributes were measured by conducting the physicochemical properties analysis techniques as described in subtopic 3.3 above.

$$\text{Biodiesel Yield}=\frac{Mass\ of\ Biodiesel}{Mass\ of\ raw\ trichiliaemetica\ oil}*100 \qquad (3.9)$$

3.4.4 Statistical Analysis

The design-expert program was used in the regression analysis and analysis of variance (ANOVA). The statistical software program was used to generate surface plots, using the fitted quadratic polynomial equation obtained from the regression analysis, holding one of the independent variables constant [78]. The design-expert 6.0.8 trial software was used for the regression and graphical analysis of the data. For optimizing the factors, maximum biodiesel content was selected as the goal of optimization. The experimental data obtained by the above procedure was analyzed by the response surface regression using the following second-order polynomial equation 3.10.

$$y = \beta_{\circ} + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=j}^{K} \sum_{j}^{K} \beta_{ij} x_i \, x_j + \mathrm{e} \tag{3.10}$$

Where; y is the biodiesel content (response), i and j are the linear and quadratic coefficients respectively, x_i and x_j are the uncoded independent variables (reaction time, reaction temperature, methanol to oil molar ratio and catalyst concentration, i.e., A, B, C and D respectively), and βo, βi, βii and βij are the intercept, linear, quadratic and interaction constant coefficients respectively, k is the number of factors studied and optimized in the experiment and e is the random error. The performances and appropriateness of RSM models were statistically measured by F-and p-values of the model and the lack of fit, as well as the coefficient of determination (R^2) [79].

CHAPTER FOUR

4. RESULTS AND DISCUSSIONS

4.1 Physicochemical Properties and Yield of Trichiliaemetica Oil

The amount of oil yield obtained from trichiliaemetica seed was 75 ml oil/kg. This showed that all the non-conventional seeds including trichiliaemetica were considered economical for commercial production of oil in Ethiopia.

Trichiliaemetica oil ought to comply with the standard norm to minimize the chance of engine damage and emission. Therefore, to eliminate the problem due to the occurrence of phospholipids, gums and other complex colloidal compounds from oil should subsequently remove by the degumming and neutralizing process. Then, purification processes were continued to change the color of the oil from the dark red to dark yellow due to the reduction of phosphatide, free fatty acid, and coloring compounds.

Finally, transesterification of trichiliaemetica oil was carried out with methanol in the presence of the base a catalyst for biodiesel production purpose. The present study has used calcium oxide catalyzed transesterification reactions for the production of biodiesel because it provides better conversion rates and efficiencies and easier handling and recovery.

The characterization was performed for the following properties namely specific gravity, density, moisture content, kinematic viscosity, saponification value, acid value, and %FFA. These properties were selected because they are the describing properties of biodiesel oil and also due to the limitation of resource to perform other tests in SCBE, lab AAiT.

The crude and purified trichiliaemetica oil was determined in triplicate and the average results were recorded in Table 4-1.

Table 4-1: Physicochemical Properties of Crude and Purified Trichiliaemetica Oil

Experimental Results			
Properties	**Crude Trichiliaemetica Oil**	**Purified Trichiliaemetica Oil**	**Unit**
Moisture content	-	0.43	%
Specific gravity	912	910	-
Density at 25 ^{o}C	912	910	kg/m^3
Kinematic viscosity at 40 ^{o}C	43.5	36.4	cSt
Saponification value	198.6	183.7	mgKOH/g oil
Acid value	8.738	4.628	mgKOH/g oil
% FFA	4.369	2.314	%

4.1.1 Specific Gravity (SG)

Specific gravity (SG) is defined as the ratio of the density of the substance, ρ, to a reference density, ρref. (water- kg/m^3), (SG = ρ/ρref). The specific gravity of vegetable oil is lower than that of water and the differences between vegetable oil are quite small, particularly amongst the common vegetable oils. As results are shown in Table 4-1, the density of crude and purified trichiliaemetica oil was found to be 912 kg/m^3 and 910 kg/m^3 respectively. These results indicated that there was a different value in the density of crude and purified trichiliaemetica oil which was due to the purification processes (degumming and neutralizing). The density of refined trichiliaemetica oil was in agreement with the ASTM/EN standard specification.

Therefore, the result indicated that the value of the density of trichiliaemetica oil was important for biodiesel quality because of it gives an indication of the delay between the injection and combustion of the fuel in the diesel engine (ignition quality).

4.1.2 Moisture Content

Moisture content is one more important quality characteristic for oils and fats for biodiesel production. The moisture content of biodiesel produces the heat of combustion and will cause corrosion of vital fuel system components. Therefore it is essential to minimize the moisture content in the feedstock prior to the transesterification process. As the point in Table 4-1, the average value of trichiliaemetica oil moisture content was very low (0.43 %). Therefore, the value of the moisture content of trichiliaemetica oil does not affect biodiesel yield and quality.

4.1.3 Kinematic Viscosity

Viscosity is the opposition of a substance to flow or measure of the resistance of a fluid to deformation under shear stress. Kinematic viscosity is the resistance to the flow of a fluid under gravity. Vegetable oils have the higher viscosity than the viscosity of diesel fuel. The higher value of viscosity causes a decrease in injection rate; consequently lower the efficiency of the engine. Therefore, the high viscosity of trichiliaemetica oil (Table 4-1) should not be used directly as engine fuel, often results in operational problems such as carbon deposits, fuel atomization, proper combustion, oil ring sticking, and thickening and gelling of lubricating oil. Hence, the pretreatment method and methanol transesterification with calcium oxide catalyst were used to reduce the viscosity and make them suitable for engine applications. As indicated in Table 4-1, the kinematic viscosity of the crude trichiliaemetica oil was 43.5 cSt whereas 36.4 cSt of the purified at 40 ^{o}C temperatures during degumming.

4.1.4 Saponification Value (SV)

The saponification value is expressed as the value of milligrams of potassium hydroxide (KOH) required to saponifying 2 gm of trichiliaemetica oil. As results presented in Table 4-1, the saponification value of the crude and purified trichiliaemetica oil was 198.6 and 183.7 mg KOH/gm respectively. Saponification value of purified trichiliaemetica oil was in agreement with the ASTM/EN standard specification.

4.1.5 Acid Value

The acid values of crude and purified trichiliaemetica oil, expressed in mgKOH/gm of oil, are shown in Table 4-1.

The acid value of oil determines indirectly the total acidity of the oil due to the presence of free fatty acids (carboxylic acids). Therefore, the acid value of crude trichiliaemetica oil was found to be 8.738 mgKOH/g of the oil which is higher than the recommended value. However, purification (degumming and neutralizing) of crude trichiliaemetica oil reduced and purified acid value was 4.628 mgKOH/gm; this showing the efficiency of purification processes.

The catalyst used in this work will have a potential to tolerate the acid value of the purified trichiliaemetica oil for biodiesel production.

The percentage of FFA value was also calculated from the AV relation using Equation (3.8) and determined as 4.369 % and 2.314 % for crude and purified trichiliaemetica oil respectively. Therefore, the percentage of FFA value in purified oil was slightly approaching to the literature

4.2 Transesterification of Trichiliaemetica Oil into Biodiesel

Transesterification of trichiliaemetica oil and methanol was carried out using calcium oxide as a solid base catalyst. One interesting feature of calcium oxide catalyst is the effect of water in the reaction system. While the presence of water has an adverse effect on the yield of biodiesel for most catalyst systems, calcium oxide performs better in the presence of a small amount of water. Amount of methanol and calcium oxide catalyst required for biodiesel production has to be listed in Appendix C.

4.2.1 Interaction Effect of Variables on Biodiesel Yield

T The results obtained from 30 experimental runs conducted to observe the effect of the four biodiesel factors (Reaction time (A), Reaction temperature (B), Methanol to oil molar ratio(C) and Catalyst concentration (D), using calcined CaO catalyze transesterification are presented in Table B -1(Appendix B).

In this case Reaction temperature (B), Methanol to oil molar ratio(C), Catalyst concentration (D), A^2, B^2, C^2, D^2, AB, AC, and CD are the important model. On the other hand, Reaction time (A), AD, BC, and BD have less effect (Prob>F more than 0.05) on the biodiesel yield from trichiliaemetica oil. In this section, the interaction effects of AB, AC and CD of the four factors on the biodiesel (% biodiesel yield) are discussed in detail. The analyses are supported by the 3D plot for the interaction effects of the four factors on the percentage biodiesel yield.

4.2.1.1 Interaction effect between reaction time and methanol to oil molar ratio on biodi1esel yield

The effect between reaction time and methanol to oil molar ratio on the biodiesel yield percentage is shown in the form of 3D plots in Figure 4-1. The reaction temperature and catalyst loading were fixed at 60 ^{o}C, 1.5 %wt respectively. The maximum biodiesel yield was achieved when the molar ratio is close to 9:1 since the higher molar ratio of ester formation and could ensure complete reaction within 1.5 hours reaction time. However, it was observed that molar ratio above 9:1 brought about the significant decrease in yield. Too much methanol reduces the flash point thus eroding an important advantage of biodiesel. As the reaction time increase from 1 hour, the biodiesel yield starts to increase and maximum yield of 91% in 1.5 hours at a molar ratio 9:1 in Figure 4-1. This result points out that both biodiesel factors have the significant effect on the % biodiesel yield.

The ANOVA analysis also indicated the interactions effect of reaction time and methanol to oil molar ratio have “Prob.>F” value of 0.0460, which indicates the significance of the factors on the percentage of biodiesel yield.

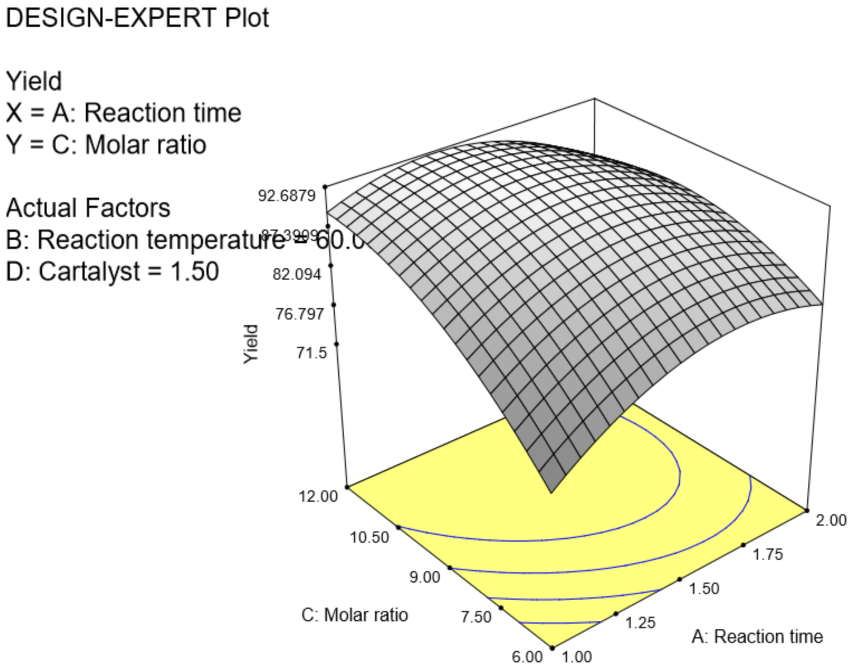


Figure 4-1: The Interaction Effect between Reaction Time (A) and Methanol to Oil Molar Ratio (C) On Biodiesel Yield 3D Plot

4.2.1.2 Interaction effect between reaction time and reaction temperature

Figure 4-2 showed the 3D plot for the interaction effect between reaction time (A) and reaction temperature (B) towards biodiesel yield for calcined calcium oxide catalyzed transesterification reaction. The methanol to oil molar ratio (C) and catalyst concentration (D) was fixed at 9:1 and 1.5 wt. % respectively.

The center points showed in the middle of Response Surface Methodology (RSM) 3D surface plot point out the designed center point that replicated for six times to show good certainty in the middle of the design space.

The interaction between reaction time and temperature showed a curved effect, in which the biodiesel yield showed a slight decrement when the temperature and reaction time reached the high level. This was due to the reaction reach equilibrium at the optimum time and started to shift the equilibrium to reverse the reaction.

Reaction temperature played a crucial role to initiate and enhance the catalytic activity of the calcined calcium oxide catalyzed transesterification reaction. With the increase of reaction temperature (55-65 ^{o}C), the high content of biodiesel was found at 1.5 hours reaction time.

On the contrary, the increase of reaction time does not improve the biodiesel yield at the high reaction temperature. On the other hand, the biodiesel content was raised apparently to 87.89 % at the high-level reaction temperature (62.5 ^{o}C) with at the time of the high or intermediate level. The maximum percentage of biodiesel yield 90 % was obtained at a reaction temperature of 60 ^{o}C and with the reaction time of 1.5 hours.

The ANOVA analysis also showed the interactions effect of reaction time and temperature have “Prob.>F” value of 0.0121, which indicates the significance of the factors on the percentage of biodiesel yield.

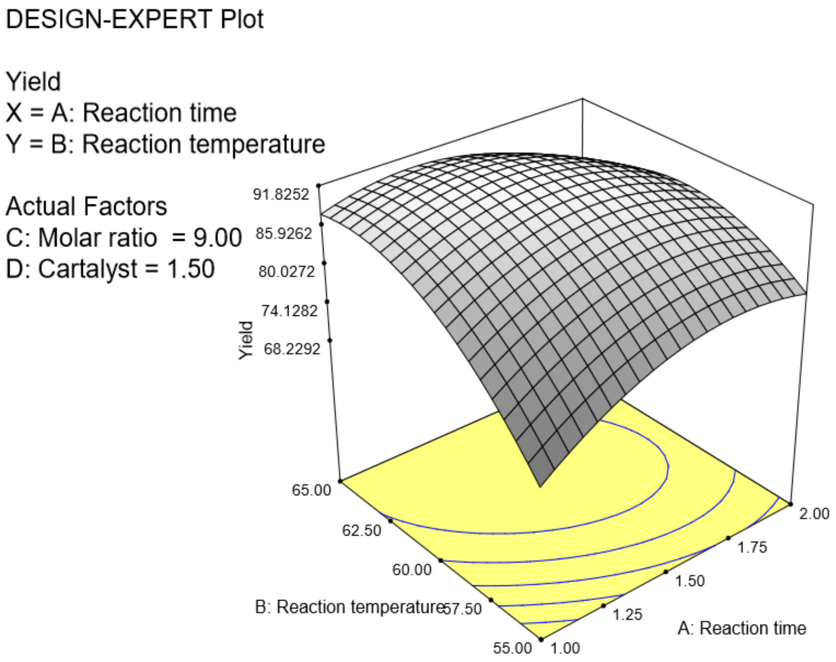


Figure 4-2: The Interaction Effect between Reaction Time (A) and Reaction Temperature (B) On Biodiesel Yield 3D Plot

4.2.1.3 Interaction effect between methanol to oil molar ratio and catalyst

Figure 4-3 presented the interaction effects of methanol to oil molar ratio and catalyst on the % biodiesel yield. The reaction time and reaction temperature were fixed at 1.5 h and 60 ^{o}C respectively. From the Figure 4-3, it can be understood that increases in both methanol's to oil molar ratio and catalyst give rise to an increased biodiesel yield.

At low methanol to oil molar ratio and catalyst concentration, the biodiesel yield was low. In addition to this, too much methanol to oil molar ratio and catalyst concentration beyond 9:1 and 1.5 wt % respectively decreases biodiesel yield.

The ANOVA analysis also indicated the interaction effects of the amounts of methanol to oil ratio and catalyst concentration have “Prob.>F” value of 0.0247, which indicates that the significance of the factors on the percentage of biodiesel yield.

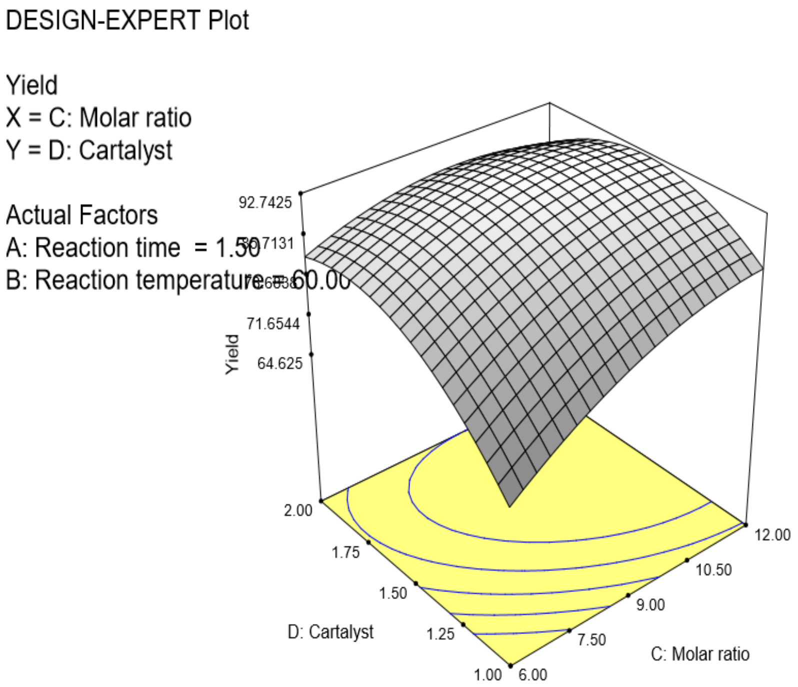


Figure 4-3: Interaction Effect between Methanol to Oil Molar Ratio(C) and Catalyst (D) on Biodiesel Yield 3D Plot

4.2.2 Statistical Analysis of Biodiesel Process using RSM

The statistical analysis of biodiesel experiments conducted using calcined calcium oxide catalyze transesterification was carried out using the response surface methodology. The biodiesel yield was used as a response in the design layout given in Table B -1(Appendix B).

The major statistical analysis of the biodiesel process (i.e. model generation, model fitness test and ANOVA analysis) are presented and discussed as follows.

Table 4-2: ANOVA for Response Surface Quadratic Model

Analysis of variance table [Partial sum of squares]

Source	**Sum of Squares**	**DF**	**Mean Square**	**F Valu**	**P-Value Prob > F**	
Model	5847.26	14	417.66	10.65	< 0.0001	significant
A	*14.26*	*1*	*14.26*	*0.36*	*0.5555*	
B	*656.26*	*1*	*656.26*	*16.74*	*0.0010*	
C	*731.51*	*1*	*731.51*	*18.66*	*0.0006*	
D	*546.26*	*1*	*546.26*	*13.93*	*0.0020*	
A^2	*800.13*	*1*	*800.13*	*20.41*	*0.0004*	
B^2	*1213.34*	*1*	*1213.34*	*30.95*	*< 0.0001*	
C^2	*472.63*	*1*	*472.63*	*12.05*	*0.0034*	
D^2	*1658.52*	*1*	*1658.52*	*42.30*	*< 0.0001*	
AB	*319.52*	*1*	*319.52*	*8.15*	*0.0121*	
AC	*185.64*	*1*	*185.64*	*4.73*	*0.0460*	
AD	*102.52*	*1*	*102.52*	*2.61*	*0.1267*	
BC	*4.52*	*1*	*4.52*	*0.12*	*0.7390*	
BD	*47.27*	*1*	*47.27*	*1.21*	*0.2895*	
CD	*244.14*	*1*	*244.14*	*6.23*	*0.0247*	
Residual	588.10	15	39.21			
Lack of Fit	*572.23*	*10*	*57.22*	*18.02*	*0.0026*	*significant*
Pure Error	*15.87*	*5*	*3.17*			
Cor Total	6435.37	29				

Table 4-3: ANOVA for Response Surface Quadratic Model

Std. Dev.	6.26	R-Squared	0.9086
Mean	71.57	Adj R-Squared	0.8233
C.V.	8.75	Pred R-Squared	0.4843
PRESS	3318.90	Adeq Precision	12.596

4.2.3 Biodiesel Modeling and Model Analysis

Biodiesel production experiments were carried out using calcined calcium oxide catalyzes transesterification according to the Central Composite Design procedure (CCD) of the response surface methodology.

The outcomes (% biodiesel yield) from the interaction of the four processes factors (reaction time, reaction temperature, methanol to oil molar ratio and catalyst concentration), were used for the model generation.

A second order quadratic regression was performed to estimate the response function as a second order polynomial after the examination of the model fit summery shown that a quadratic model was statistically significant for the response (% biodiesel yield).

The resulting biodiesel model equation which expresses the relationship between the interactions of the biodiesel factors and the response (% biodiesel yield) is given in equation 4.1 in terms of coded values and equation 4.2 in terms of significant coded factors.

The regression equation 4.1 in terms of coded factors for the determination of predicted values of output parameter (i.e. biodiesel yield) is given as follows:

$$\text{Yield} = +90.75+0.77A+5.23B+5.52C+4.77D-5.40A^2-6.65B^2-4.15C^2-7.78D^2-4.47AB-3.41AC-2.53AD+0.53BC-1.72BD-3.91CD \quad (4.1)$$

By removing the insignificant model terms that have a p-value higher than 0.05 (Table 4.2), Equation 4.1 can be simplified as follows:

$$\text{Yield} = +90.75+5.23B+5.52C+4.77D-5.40A^2-6.65B^2-4.15C^2-7.78D^2-4.47AB-3.41AC-3.91CD \quad (4.2)$$

From ANOVA results obtained from calcined calcium oxide catalyzed transesterification; the model F-value of 10.65 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob> F" less than 0.0500 indicate model terms are significant.

Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), the model reduction may improve the model.

Thus the model proposed that terms which might significantly influence the biodiesel yield response were reaction temperature (B), methanol to oil molar ratio (C), catalyst concentration(D) and in addition, the interaction between reaction time with reaction temperature (AB), reaction time with methanol to oil molar ratio (AC) and methanol to oil molar ratio with catalyst concentration(CD) and the square of reaction time (A^2), reaction temperature (B^2), methanol to oil molar ratio (C^2) and catalyst concentration (D^2) are significant model terms to contributed more to the biodiesel yield while model term reaction time (A) and interaction between reaction time and catalyst concentration(AD), reaction temperature and methanol to oil molar ratio (BC) and reaction temperature and catalyst concentration(BD) insignificant model terms to contribute the biodiesel yield.

The "Lack of Fit F-value" of 18.02 implies the Lack of Fit is significant. There is only a 0.26% chance that a "Lack of Fit F-value" this large could occur due to noise. Significant lack of fit is bad--we want the model to fit.

The "Pred R-Squared" of 0.4843 is not as close to the "Adj R-Squared" of 0.8233 as one might normally expect. This may indicate a large block effect or a possible problem with the model and/or data. "Adeq Precision" measures the signal to noise ratio. A ratio greater than four (4) is desirable. The ratio of 12.596 indicates an adequate signal.

This model can be used to navigate the design space. Moreover, from the ANOVA analysis, the lower value of the coefficient of variation (C.V. =8.75) indicates the better precession and reliability of the experiments carried out.

The C.V. as a ratio of the standard error of the estimate to the mean value of the observed response (as % biodiesel yield) is the measure of reproducibility of the model and as the general rule, a model can be considered reasonably reproducible.

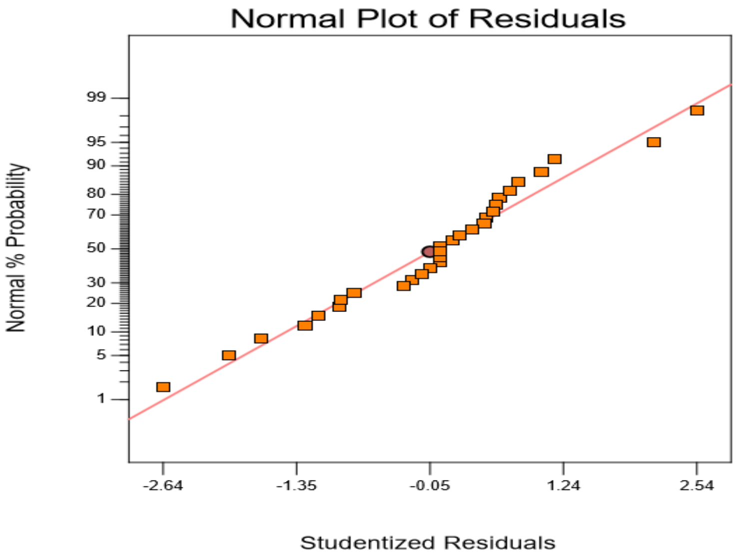


Figure 4-4: Normal Plots of Residuals

To identify the statistical properties of the model, the Central Composite Design (CCD) normal probability plot of the residuals shows the normality of the model. Figure 4-4 shows the normal probability plot of the residuals indicates that the errors are distributed normally in a straight line. The data points should be approximately linear. A non-linear pattern indicates an abnormality in the error term which may be corrected by transformation. From figure 4.4 there is no any sign of any abnormality in the model.

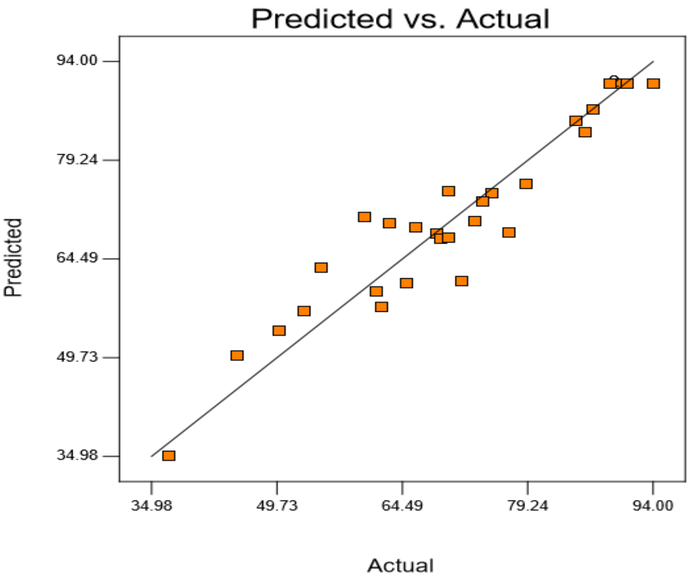


Figure 4-5: Predicted Versus Actual Biodiesel Values

The relationship between the predicted and experimental biodiesel yield shown in Figure 4-5. It can be seen that there is the high correlation (R^2=0.9086) between the predicted and experimental biodiesel yield. The predicted values and experimental values were in reasonable agreement (the R^2 value close to unity), which means that the data well with the model and influentially good estimation of response for the system in the ranges studied.

4.2.4 Numerical Optimization

The optimum conditions for four factors (reaction time, reaction temperature, methanol to oil molar ratio and catalyst concentration), were determined using the numerical optimization feature of the Design expert software. The software examined for a combination of factors that simultaneously fulfilled the requirements placed on the response and each of the factors.

Table 4-4 shows the optimum working conditions (ultimate goals, high and low limits) of the response (% biodiesel yield)) and factors (reaction time, reaction temperature, methanol to oil molar ratio and catalyst concentration), employed during the optimization analysis.

In observation of the best condition was maximized for % biodiesel yield while the values of reaction time, reaction temperature, methanol to oil molar ratio and catalyst concentration, were set in the ranges studied.

The optimum conditions obtained were then evaluated by the composite desirability, which has a value from 0 to 1, to determine the degree of satisfaction of the optimum conditions for the ultimate goal of response.

Table 4-5 presents the optimum conditions in uncoded units (reaction time, reaction temperature, methanol to oil molar ratio and catalyst concentration), which give the highest composite desirability (1.0) from the Design expert software.

The predicted (90.75 %) and experimental (94 %) values of % biodiesel yield under the optimum conditions are also presented. The very small deviation, i.e., 0.0914 %, between the predicted and experimental values of % biodiesel yield point out that the model (Eq. 4.2) is suitable and sufficient to predict the biodiesel yield process using calcined calcium oxide catalyzed transesterification in the range of parameters studied.

Table 4-4: Working Conditions of Response and Factors for Optimization

Variables	Ultimate Goal	Experimental region	
		Lower limit	Upper limit
Reaction time (hours)	In the range	1.00	2.00
Reaction temperature (^oC)	In the range	55.00	65.00
Methanol to oil molar ratio	In the range	6.00	12.00
Catalyst concentration wt.%	In the range	1.00	2.00
% biodiesel yield	Maximize	37.00	94.00

Table 4-5: Optimum Conditions and Model Validation

Variables	Optimum result
Reaction time(hours)	1.50
Methanol to oil molar ratio	9.00
Reaction temperature(^oC)	60.00
Catalyst concentration (wt. %)	1.50
Predicted % biodiesel yield	90.75
Desirability	1.00
Experimental % biodiesel yield	94.00
% deviation	0.0914

4.2.5 Biodiesel (FAME) Quality Evaluations

Once the optimum conditions for the heterogeneous transesterification using calcium oxide as the catalyst have been determined (1.5 h, 9:1 methanol to oil molar ratio, 60 ^oC and 1.5 % wt catalyst) and 94% biodiesel yield was obtained. The physicochemical properties of optimization studies were summarized in Table 4-6. Among 30 experiments optimized result were selected in order to measure the physicochemical properties of biodiesel yield and results were presented in

Table 4-6. The quality parameters quantified were: specific gravity, density, kinematic viscosity, saponification value, higher heating value, acid value and flash point.

Table 4-6: Physicochemical Properties of Optimized Biodiesel Yield

Properties	**Value**	**Unit**
Specific gravity	887	-
Density	887	kg/m^3
Viscosity at 40˚C	6.11	cSt
Flash Point	129	^{o}C
Acid value	0.897	mgKOH/g
Saponification value	183.76	mgKOH/g
Higher Heating Value	39.8	MJ/kg

In gene In general, biodiesel has the higher density than petroleum diesel. The density of the optimized biodiesel yield was found to be between 887 kg/m^3 which are well within the range specified by EN 14241 (860–900 kg/m^3) and the biodiesel is acceptable.

Viscosity is the most important property of biodiesel since it affects the operation of fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. High viscosity leads to the improper atomization of the fuel spray and less accurate operation of the fuel injectors.

As the result was presented in Table 4-6, The optimized biodiesel yield was observed to have viscosity 6.11cSt at 40 °C and the result is somewhat approached to the ASTM/EU range for the requirement of biodiesel kinematic viscosity. This variation of kinematic viscosity was occurred due to the conversion of biodiesel yield which means the higher the conversion the lower the viscosity.

In general, the kinematic viscosity of biodiesel was higher compared to that of fossil diesel the implication was that biodiesel has lubricating effect in engines which will be an added advantage to the users since it will reduce wear and tear in the engine.

Acid value or neutralization number is a measure of mineral acids and free fatty acids contained in a fuel sample. It is expressed in milligrams of KOH required to neutralize mass of fatty acid methyl esters and it sets to a maximum value of 0.5 and 0.8 mg KOH/g in the ASTMD6751 and EN14241 specifications respectively. As the results were presented in Table 4-6, the acid value of the optimized biodiesel produced was 0.897 mgKOH/g. This result showed that the acid value of the biodiesel slightly increased from the standard value due to residual mineral acids from the production process. These results showed that the acid value of the biodiesel reduced significantly after the transesterification reaction. The acid value was somewhat approaching to the standard specification limit.

The flash point is the minimum temperature at which fuel gives momentary flash on ignition under specified test conditions. It is an important property for storage, handling, and safety of the fuel. The result is shown in Table 4.6, the flash point of optimized biodiesel yield was found to be 129 ^{o}C. The result was in agreement with the lower limit of standard with 120 ^{o}C (EN 14241) and slightly approach to 130 ^{o}C (ASTM D6751).

The minimum value of the flashpoint for conventional diesel fuel is about 35 ^{o}C. Based on the results, the produced biodiesel was considered to be safe for storage and handling purposes when compared to the conventional diesel.

Heating value is the ability of heat generated by the unit mass of fuel. As the results presented in Table 4-6 the optimized biodiesel yield was observed to record the calorific value of 39.8 MJ/kg. This value was slightly lower than the conventional diesel. However, trichiliaemetica biodiesel result was in agreement with the standard specification limit.

4.2.6 Fatty Acid Compositions of Trichiliaemetica Biodiesel

Gas Chromatography-Mass Spectroscopy Analysis: In this present study, quantification of Fatty Acid Methyl Esters present in Trichiliaemetica oil biodiesel is categorized using Gas Chromatography (GC) and Mass Spectroscopy (MS) at Leather Industry Development Institute Research and Testing Directorate at Addis Ababa.

The major FAME’ present in biodiesel sample are tabulated in Table 4-7 below.

Table 4-7: Chemical Composition of Fames of Trichiliaemetica Oil by GC-MS Analysis

No	Name of the compound	Area (%)
1	9-Hexadecanoic acid, Methyl Ester	0.46
2	Pentadecanoic acid, 14-Methyl Ester	25.7
3	9, 12-octadecanoic acid Methyl Ester	28.4
4	9-octadecanoic acid, Methyl Ester	39.3
5	Methyl stearate	5.9
6	2-Naphtylene-sulphonic acid	0.1
7	Eicosenoic acid Methyl Ester	0.09
8	1, 13-Dimethylcyclotridecene	0.09

Analysis of fatty acid methyl ester composition of the biodiesel produced from trichiliaemetica oil was done with the help of GC-MS and 8 fatty acid methyl esters were identified. The results showed that the major component of Trichiliaemetica biodiesel was 9-octadecanoic acid, Methyl Ester (39.3%), followed by 9, 12-octadecanoic acid Methyl Ester (28.4%) and Penta decanoic acid, 14-Methyl Ester (25.7%). The other fatty acids were minor in concentrations.

In general, the quality of the biodiesel fuel can be significantly influenced by several factors. The fatty acid composition of the vegetable oil, quality of feedstock, type of production and refining process employed, and purification steps are the major factors.

Property like viscosity is mostly depending upon the fatty acid composition of the raw oil. Other properties: flash point, viscosity, and acid value highly depend on to the purification process. To get clear of these contaminants, several purification techniques such as distillation, evaporation, and washing with distilled water has been employed to ensure the achievement of highly refined biodiesel.

CHAPTER FIVE

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The study presented in this thesis aimed process optimization for biodiesel production from trichiliaemetica oil. Biodiesel was prepared at different reaction parameters from Trichiliaemetica oil and methanol alcohol with calcined calcium oxide catalyst on a laboratory scale. Under this investigation, process optimization was accomplished by five level-four-factorial Central Composite Design (CCD) using Response Surface Methodology (RSM). Transesterification reaction was carried out with four important parameters (reaction time, reaction temperature, methanol to oil molar ratio and catalyst concentration) to optimize biodiesel yield.

According to data from the Analysis of Variance (ANOVA) table, methanol to oil molar ratio (C) is an important parameter in this optimization and has a large and positive influence on biodiesel yield. After methanol to oil molar ratio (C), reaction temperature (B) is the most effective parameter and it has the positive effect on the biodiesel yield. Catalyst concentration (D) is also the third most effective parameter and it has the positive effect on biodiesel yield. Reaction time (A) is the insignificant parameter and it has no any effect on the biodiesel yield. The interaction effect of reaction time with reaction temperature (AB), reaction time with methanol to oil molar ratio (AC) and methanol to oil molar ratio with catalyst concentration (CD) has the significant positive effect on the biodiesel yield.

The second-order model equations were obtained to predict the biodiesel yield as a function of input parameters and a quadratic model was statistically significant for the response (% biodiesel yield). From the experimentation it was found that maximum biodiesel yield of 94 % was obtained under following optimized reaction conditions; methanol to oil molar ratio (9:1) using calcined calcium oxide as catalyst (1.5 % w/w) in 1.5 h time and 60 ^{o}C temperature. 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. The optimized biodiesel yield was found within the ASTM and EN standards specifications.

5.2 Recommendations

Transesterification reaction is a relatively a new technology in biodiesel production. Therefore, there are many aspects of the technology that need to further development in the near future to improve and develop the process. Following are some recommendations for upcoming works.

- Blending the biodiesel with diesel and engine tests has to be carried out with biodiesel produced from trichiliaemetica oil.
- Preliminary design of the pilot plant, process development, and scale-up has to be performed on the transesterification process.
- Full exploitation of all physicochemical properties of biodiesel from trichiliaemetica oil is also needed to be conducted and compared with other results obtained from various oil and catalyst types.
- Study of biodiesel production from trichiliaemetica oil using non-calcined and calcined calcium oxide catalyst with ethanol.

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APPENDICES

Appendix A: Standard Specification of Biodiesel

Table A- 1: The Content of FFA in the Acidic Raw Materials

Materials	**FFA content(%w)**
Recycled oil	0.4_3.3
Crude palm oil	3.0_10.0
Waste frying oil	>10
Coconut oil	12
Residues from several industries	11.5_22.4
Jatropha seed oil	15
Mahua oil	19
Animal fats	7.0_50.0
Cotton seed oil	85.3
Palm fatty acid distillate	93

Table A- 2: Trichiliaemetica Biodiesel Literature Physicochemical Parameter

Property	**Test method ,ASTM**	**Test ASTM 6751 limit**	**Biodiesel**
Flash point (PMCC), ^{o}C	D 93	Min. 93	49
Cloud point, ^{o}C	D 2500	Report	18
Kinematic viscosity, mm2/s	D 455	Min. 1.9 Max. 6	5.44
Conradson carbon residue	D 189	Max.0.05	0.33
Total acidy, mgKOH/g	D 974	Max.0.5	6.28
Ash content	D 482	Max.0.02	0.062
Copper strip corrosion	D 130	Max.No.3	1a

Source: Bizuneh Adinew, 2013

Table A- 3: Fatty Acid Composition (%) Of Trichiliaemetica Seed Oil from Tepi Area

Peak	**RT(min)**	**Fatty acid composition**	**Amount (%)**
1	44.41	Palmitic acid (C16:0)	52.36
2	49.874	Oleic acid (C18:1)	36.70
3	49.617	Linoleic acid (C18:2)	7.59
4	50.627	Stearic acid (C18:0)	1.99
5	49.995	Cis-vaccenic acid(C18:1)	1.36

Source: Bizuneh Adinew, 2015

Appendix B: Experimental Results

Table B- 1: Results of Central Composite Design (CCD) Showing Observed for Optimization of Parameters for Biodiesel Production from Trichiliaemetica Oil

		Factor 1	**Factor 2**	**Factor 3**	**Factor 4**	**Response**
Std	**Run**	**A:Rxn time**	**B:Rxn Temperature**	**C:Molar ratio**	**D:catalyst**	**Yield**
		Hrs	**^{o}C**	**%wt/wt**	**%**	**%**
10	1	2.00	55.00	6.00	2.00	74
18	2	2.50	60.00	9.00	1.50	60
28	3	1.50	60.00	9.00	1.50	91
27	4	1.50	60.00	9.00	1.50	90
8	5	2.00	65.00	12.00	1.00	75
29	6	1.500	60.00	9.00	1.50	91
17	7	0.50	60.00	9.00	1.50	70
16	8	2.00	65.00	12.00	2.00	69
13	9	1.00	55.00	12.00	2.00	63
11	10	1.00	65.00	6.00	2.00	79
12	11	2.00	65.00	6.00	2.00	73

19	12	1.50	50.00	9.00	1.50	50
23	13	1.50	60.00	9.00	0.50	45
1	14	1.00	55.00	6.00	1.00	37
4	15	2.00	65.00	6.00	1.00	71.5
24	16	1.50	60.00	9.00	2.50	66
3	17	1.00	65.00	6.00	1.00	53
2	18	2.00	55.00	6.00	1.00	62

		Factor 1	Factor 2	Factor 3	Factor 4	Response 1
Std	Run	A:Rxn time	B:Rxn temperature	C:Molar ratio	D:Catalyst	Yield
25	19	1.50	60.00	9.00	1.50	94
21	20	1.50	60.00	3.00	1.50	55
6	21	2.00	55.00	12.00	1.00	68.5
15	22	1.00	65.00	12.00	2.00	87
26	23	1.50	60.00	9.00	1.50	89.5
20	24	1.50	70.00	9.00	1.50	70
9	25	1.00	55.00	6.00	2.00	65
7	26	1.00	65.00	12.00	1.00	86
30	27	1.50	60.00	9.00	1.500	89
5	28	1.00	55.00	12.00	1.00	61.5
22	29	1.50	60.00	15.00	1.50	85
14	30	2.00	55.00	12.00	2.00	77

Appendix C: Calculations for biodiesel Production (%Yield)

Transesterification reaction is a reversible reaction:

3 alcohol (Methanol) + 1 Oil (Triglyceride) = 3 biodiesel + Glycerol

Amount of oil volume for each run = 100 ml in each experiment

Oil molecular weight = 886 g / mol.

Oil density = 0.9100 g/ml

Methanol density= 0.79 g/ml

Methanol molecular weight= 32.04 g/mol.

The theoretical amount of biodiesel which can be obtained assuming 100% conversions, are calculated and becomes:

Oil weight = Oil Volume x Oil density = 100 ml x 0.9100 g / ml = 91 g (C.1)

Oil mole = Oil weight / Oil molecular weight (C.2)

= 91g / 886 g / mol. = 0.1027 mol.

According to stoichiometry of the reaction, one mole of oil produces three mole of biodiesel.

Theoretical yield of biodiesel = 3 x 0.1027 mol. = 0.308 mol of biodiesel. Hence, the amount of methanol and catalyst were calculated as follows using the process parameters.

The amount of methanol required when the molar ratio of methanol to oil ratio 9:1;

$$9 = \frac{mole\ of\ methanol}{moleof\ TEO} \quad \text{(C.3)}$$

Thus from equation C.2, mole of TEO= 0.1027 mol

$$9 = \frac{\frac{\text{ρof Methanol}*\text{Volume of Methanol}}{\text{Molecular wt.of Methanol}}}{\text{mole of TEO}} \qquad \text{(C.4)}$$

Substituting the known values in equation C.4 and becomes;

$$9 = \frac{\frac{0.79\mathrm{g/ml} * \mathrm{Volume\ of\ Methanol}}{32.04 g/mol}}{0.1027\mathrm{mol}} \qquad (C.5)$$

After rearrangement and solving equation C.5, the volume of methanol required for 9:1 molar ratio becomes;-

Volume of Methanol= 37.48 ml

Similarly the volume methanol required for all experiment:

3:1 = 12.49 ml

6:1 = 24.98 ml

12:1 = 49.97 ml

15:1 = 62.47 ml

The amount of catalyst required when the ratio of catalyst loading weight to oil is 1.5%;

Since the mass of the oil= 91 g (C.6)

Mass of the catalyst= 1.5%*mass of the oil (C.7)

= 0.015*91= 1.365 g

Similarly the weight of calcium oxide catalyst required for all experiment:

0.5 % = 0.455 g

1% = 0.91 g

1 =1.365 g

2% = 1.8 g

2.5% = 2.275 g

Appendix D: Calculation of Biodiesel Yield

Calculation of optimized biodiesel yield:

Mass of biodiesel = 85.6 g

Mass of trichiliaemetica oil = 91 g

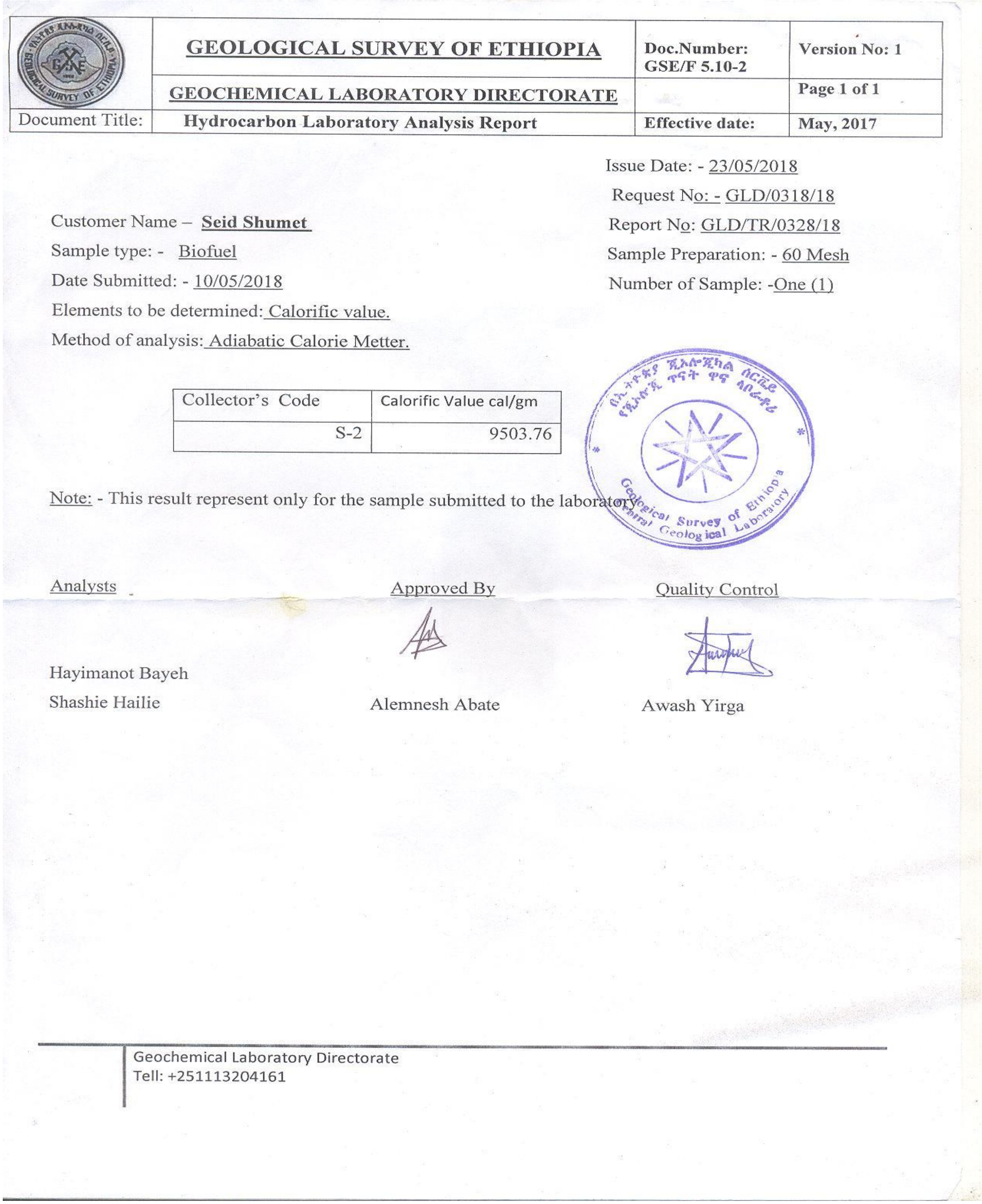
Biodiesel Yield=$\frac{Mass\ of\ Biodiesel}{Mass\ of\ raw\ trichiliaemetica\ oil}$ *100

Biodiesel Yield=$\frac{85.6\ g}{91\ g}$ *100

Biodiesel Yield = 94 %

Similarly, the amount of biodiesel yield was calculated for all experiments.

Appendix E: Certificate of Test Report



	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: - 23/05/2018
Request No: - GLD/0318/18
Report No: GLD/TR/0328/18
Sample Preparation: - 60 Mesh
Number of Sample: -One (1)

Customer Name – **Seid Shumet**
Sample type: - Biofuel
Date Submitted: - 10/05/2018
Elements to be determined: Calorific value.
Method of analysis: Adiabatic Calorie Metter.

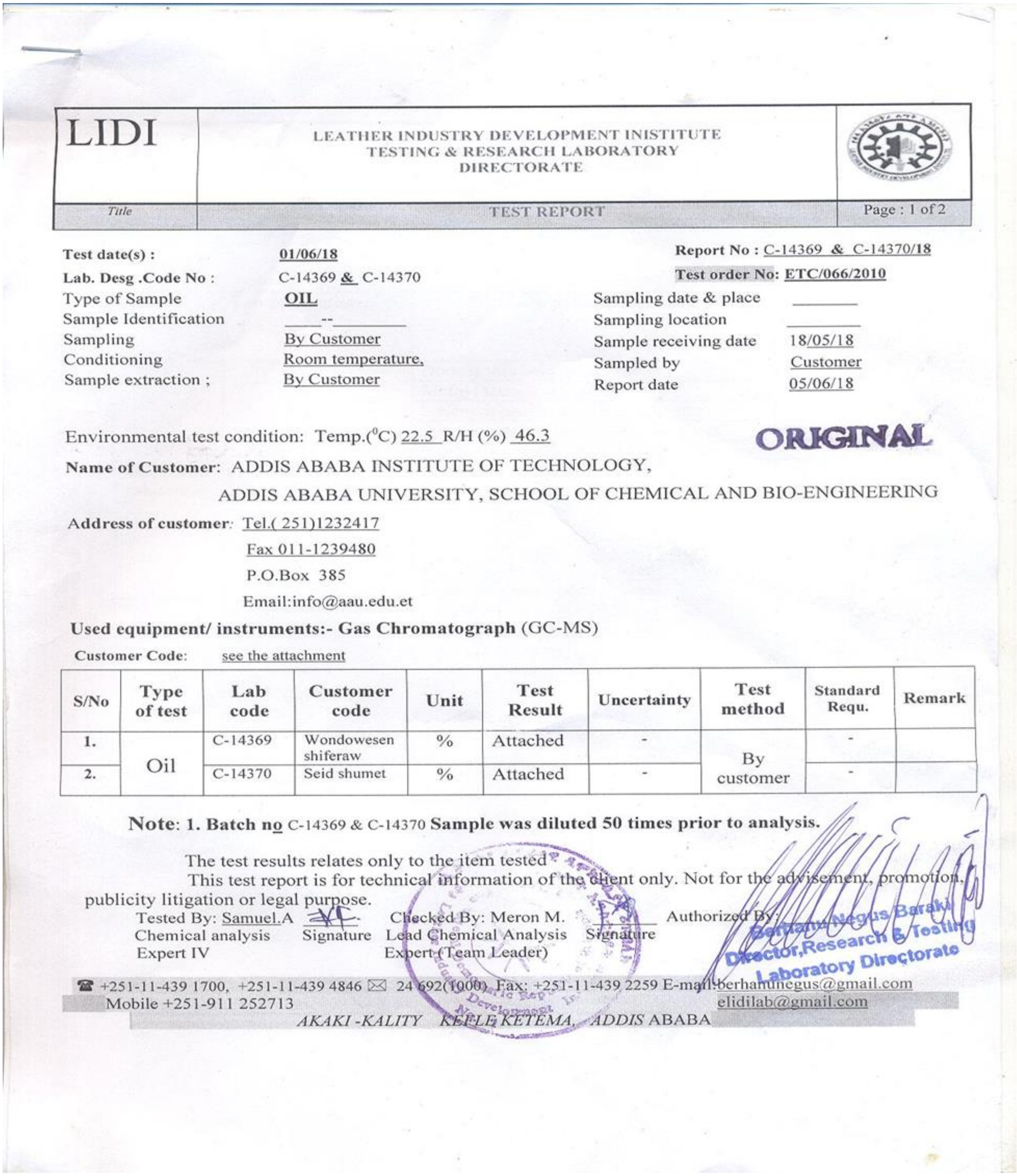
Collector's Code	Calorific Value cal/gm
S-2	9503.76

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

Figure E- 1: Calorific Value of Trichiliaemetica Biodiesel



LIDI	LEATHER INDUSTRY DEVELOPMENT INISTITUTE TESTING & RESEARCH LABORATORY DIRECTORATE	
Title	TEST REPORT	Page : 1 of 2

Test date(s) : **01/06/18**
Lab. Desg .Code No : C-14369 & C-14370
Type of Sample **OIL**
Sample Identification --
Sampling By Customer
Conditioning Room temperature,
Sample extraction ; By Customer

Report No : **C-14369 & C-14370/18**
Test order No: **ETC/066/2010**
Sampling date & place
Sampling location
Sample receiving date 18/05/18
Sampled by Customer
Report date 05/06/18

Environmental test condition: Temp.(^{0}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

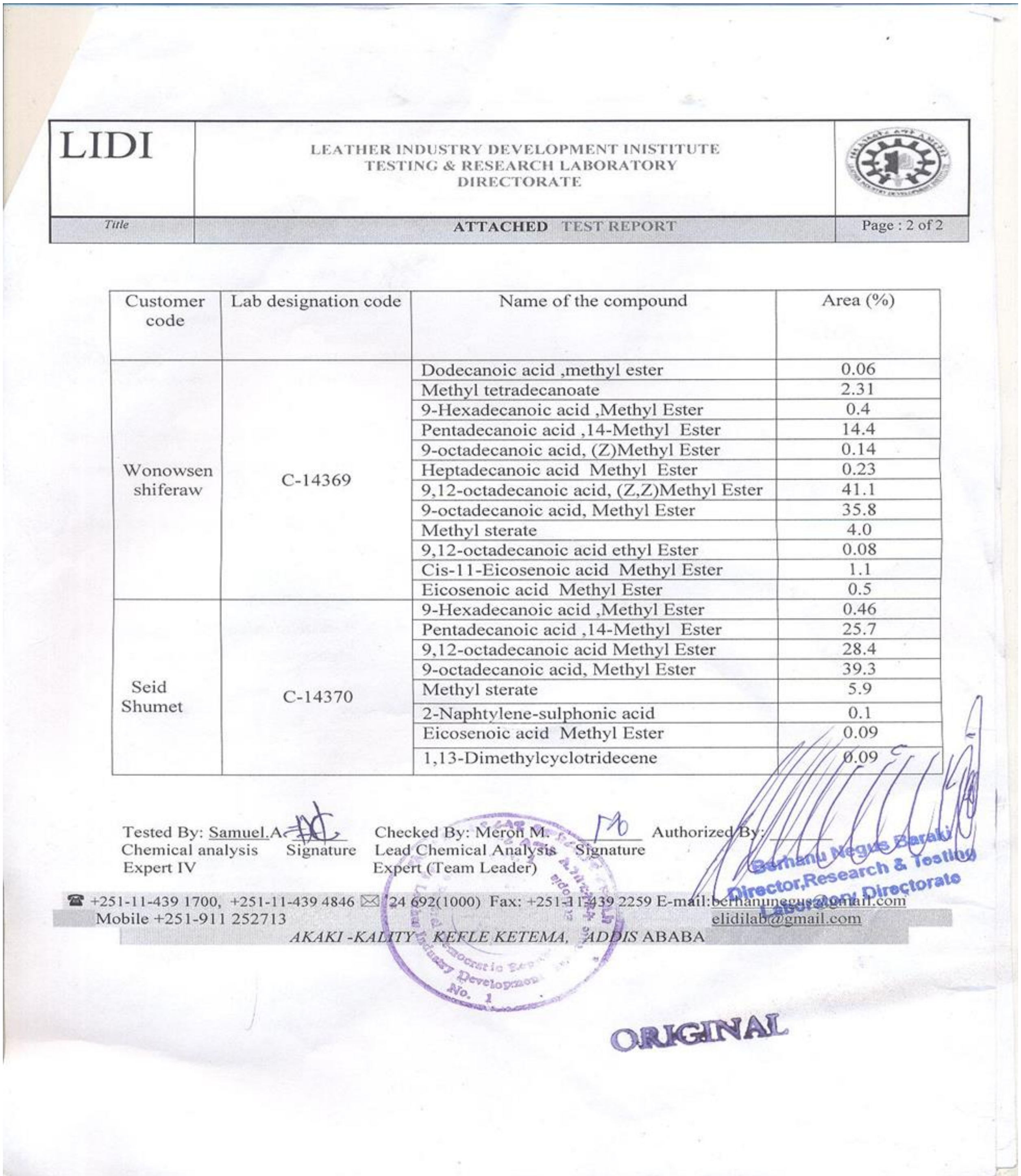
Checked By: Meron M. Signature
Lead Chemical Analysis Expert (Team Leader)

Authorized By:

Berhanu Negus Baraki
Director, Research & Testing
Laboratory Directorate

☎ +251-11-439 1700, +251-11-439 4846 ✉ 24 692(1000) Fax: +251-11-439 2259 E-mail:berhanunegus@gmail.com
Mobile +251-911 252713 elidilab@gmail.com
AKAKI -KALITY KEFLE KETEMA, ADDIS ABABA

Figure E- 2: Test Report Letter



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 ______ Checked By: Meron M. ______ Authorized By: ______
Chemical analysis Expert IV Signature
Lead Chemical Analysis Expert (Team Leader) Signature

Berhanu Negus Baraki
Director,Research & Testing
Laboratory Directorate

☎ +251-11-439 1700, +251-11-439 4846 ✉ 24 692(1000) Fax: +251-11-439 2259 E-mail:berhanunegus@gmail.com
Mobile +251-911 252713 elidilab@gmail.com
AKAKI -KALITY KEFLE KETEMA, ADDIS ABABA

No. 1

ORIGINAL

Figure E- 3: Free Fatty Acid Composition of Trichiliaemetica Biodiesel