ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF MULTIDISCIPLINARY ENERGY CENTER

Characterization and Experimental Analysis of Biodiesel Extracted from Sclerocarya Birrea (Marula) Fruit Using Catalyst

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A Thesis

Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Energy Technology

By

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DECLARATION

Thesis work entitled "**Characterization and Experimental Analysis of Biodiesel Extracted from *Sclerocarya Birrea* (Marula) Fruit Using Catalyst"** has not been presented for master's degree in Addis Ababa University, Addis Ababa Institute of Technology or in any other University.

I have referenced through appropriate referencing and acknowledged for the identified materials for the work of others in this thesis.

The work was supervised under the guidance of Dr. Solomon Kiros instructor in School of Chemical and Bio Engineering.

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Date of Submission: _____

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This is to certify that the thesis prepared by **Bikila Gebeyehu Eticha**, entitled "**Characterization and Experimental Analysis of Biodiesel Extracted from Sclerocarya Birrea (Marula) Fruit Using Catalyst"** and submitted in partial fulfillment of the requirement for the Degree of Master Science in Energy Engineering completes with regulation of the University and meets the accepted standard with respect to originality and quality.

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First of all, I would like to glorify almighty God for his incomparable help until the end of my work. Next, I want to extend my appreciation to my advisor Solomon Kiros (PhD) for his tremendous support to complete my work from the beginning of this work to the end to reach this current level of success. My sincere appreciation also goes to Degaga Kebede from Arba Minch University, who helped me from the basic brotherly during collecting the seed; finally, I want to thank all anybody contributed to my work.

ABSTRACT

The investigation of indigenous resources as alternative energy is the reasonable solution for the diminishing of naturally existing materials for production of fuel from crude oil, environmental concern. Many researchers have been involved in producing a low-price fuel from naturally existing raw materials. Thus, in this specific work biodiesel production was examined from Marula seed. The seeds were collected from *Arba Minch Nech Sar National* Park and the seeds Proximate analysis has been conducted to determine moisture content, ash content, crude fiber content and fat contents. The result found was 5.90%, 4.27%, 11.84% and 47.66% respectively. The extraction of the oil was performed by solvent method using n-hexane as solvent through Soxhlet apparatus and fixing the extraction time.

This study aimed to extract a biodiesel from *sclerocarya birrea* by examining the physio-chemical properties, and the biodiesel production was optimized for pre-determined parameters such as Catalyst Concentration (CC), Reaction Temperature (RT) and Methanol to Oil Ratio (MOR) by implementing Design Expert Software (DES).

The optimum conversion efficiency of marula oil to Fatty Acid Methyl Ether (FAME) was 93.45% at optimal condition of 9:1 methanol to oil ratio for 1.75%of catalyst loading at 60^{o}C of reaction temperature. The properties of sclerocaryabirrea which were determined exist in the recommended standards. The oil content of the seed was found 41.57%. The values of the physiochemical properties of the oil were viscosity 92.8mpas, specific density 0.923, acid value 7.51, Saponification value 229miligrams and free fatty acid 3.8% and the biodiesel were characterized as of its calorific value (CV) which was 42.56 MJ/Kg, viscosity of 11.3mpas, iodine value of 115 I_2/gm, and flash point of 235^{o}C.

In this thesis work, it was concluded that *Sclerocaryabirrea* can be a possible input for biodiesel production which in turn minimize the dependency on fossil fuels.

Key words: **-**Biodiesel, free fatty acid, transesterification and Proximate analysis

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LIST OF ABBREVIATIONS AND NOMENCLATURES

AL	Aluminum Oxide
AOAC	Association of Official Analytical Chemistry
ASTMD	American Standard Testing Method
CaO	Calcium Oxide
CI	Compression Ignition
CO	Carbon monoxide
CO2	Carbon dioxide
DEE	Diethyl Ether
DME	Dimethyl Ether
DTBE	Ditert butyl Ether
EU	European Union
FAME	Fatty Acid Methyl Ether
FAO	Food Agriculture Organization
FFA	Free Fatty Acid
GHG	Greenhouse gas
H2SO4	Sulfuric Acid
H3PO4	Phosphoric Acid
HCl	Hydrochloric Acid
IFP	French Institute of Petroleum
KOH	Potassium hydroxide
MAE	Microwave Assisted Extraction
MgO	Magnesium Oxide
MJ/Kg	Mega joule per kilogram
NaOH	Sodium hydroxide
oC	Degree Celsius
PM	Particulate Matter
SB	Sclerocarya Birrea
THF	Tetra Hydro Fruran
UAE	Ultrasound Assisted Extraction
USA	United States of America
WO	Tungsten Oxide

1 INTRODUCTION

1.1 General background

In recent days, the instability of petroleum price and diminishing of input material for these fuels initiated scholars searching other resources like non-edible plant seed oils as a substitute for crude petroleum (Mata and Martins 2015).Today biodiesel is the essential alternative diesel fuel in the total production of fuel in European union which accounts around 82% (Bozbas,2008).

For diesel substitution biodiesel is a good option as an alternative energy particularly catalyst involved in the production of biofuel (Mata and martins, 2015)

In fact, in Ethiopia, due to lack of appropriate technology and shortage of detail research finding information on biodiesel, fossil fuels are the important source of energy for domestic and industrial usage. The utilization of petroleum fuels can be the reasons for contamination and results in diminishing of economic growth (Laherrere, 2005). Therefore, fossil fuels became one of the issues which can cause conflict in developing countries due to high price increment every year. The alternative energy source gets high attention particularly for transportation fuel and increasing interest for research in this area leads to be developed independent energy sources.

In acquiring a biofuel with a good quality, searching for recent feed stocks and adaptation measuring technologies have a paramount role (Geissler, 2008).There are a lot of resources which are still not utilized for further studies for biodiesel production (Winayanuwattikun et al. 2008).

These indicates more than 95% of biodiesel that can be produced comes from edible feedstocks which contains oil because the properties of these oils are comfortable in the production of biodiesel in order to replace fuel from the diesel (Gui et al. 2008).

However, the use of edible crops for biodiesel in developing countries like Ethiopia can cause competition with the edible oil market (Kansedo et al. 2009). In order to overcome the above aforementioned challenges, it is timely to search non-edible oil sources which are not suitable for human consumption. Since the cost of raw materials accounts about 60–80% of the total cost of

biodiesel production, choosing a right feedstock is very important (Guiet al. 2009; Singh and Singh, 2009).

Ethiopia is rich in plant biodiversity which can have potential for utilization of biodiesel; Therefore, the present study was tested the suitability of Marula tree, which is the non-edible oil trees commonly available in different parts of the country for the production of biodiesel. Even though, marula tree is widely growing fruit in many parts of the country (Amhara, Southern region, Oromiya and Tigray), there is no research which reveals the suitability of Marula oil as biodiesel.

1.2 Problem of the statement

It is well known that there is high species of biodiversity in Ethiopia. Particularly the very important species can be utilized for different purposes like traditional medicine, for biodiesel production and etc. Marula is one of these species growing in the country can be utilized for biodiesel production (TewoldeBerhane, 1990; Legesse, 2002).

However, the country is utilizing petroleum-based fuels which have negative impacts on environment, global warming and cost of the users. According to trusted sources (National newspaper published on July 7,2019), there is high utilization of imported fossil fuels for different purposes expensing about 81.8-billion-birr (around $2.82 billion) annually, which doesn't in line with the financial capacity of the country. Therefore, this study is devoted to address these problems by producing biodiesel fuel from *Sclerocaryabirrea* which locally available and environmentally friend.

1.3 Objectives

1.3.1 General objective

- Experimentally analyzing biodiesel production from Sclerocaryabirrea seeds for biofuel utilization.

1.3.2 Specific objectives

- To extract biodiesel from Sclerocaryabirrea and analyzing the physicochemical properties of Sclerocaryabirrea oil.
- To optimize the biodiesel Production processes under selected reaction parameters
- To determine Physio-chemical properties of the extracted sclerocaryabirrea biodiesel.

1.4 Importance of the study

The study has much importance in reducing global warming by producing biodiesel from Sclerocaryabirrea which is indigenous, none edible and abundantly available and grows on non-arable as well as an arable land without affecting nearby crops. This makes *sclerocarya birrea* eco-friendly plants and promising source of biodiesel production.

Biodiesel is the promising alternative fuel by some reasons.

- Decreases reliance on gasoline, although it will not eliminate.
- Minimizes environmental contamination and solve challenges of global warming
- It has low emission as compared to petroleum fuels.

1.5 Scope of the study

This work covered from identifying new feedstock which is *sclerocaryabirrea* and collecting, pretreatment of raw materials and proximate analysis of sclerocaryabirrea fruit was the activities of this research. The thesis work generally covers sclerocaryabirrea oil extraction, refining and characterization of sclerocaryabirrea oil, biodiesel production process optimization and purification as well as characterization and standardization of final product.

The study did not included characterization of different basic characteristics of*sclerocaryabirrea* biofuel (biodiesel) blended at various percentage and not applied in compression ignition (CI) engine to evaluate the effect of using blend of biodiesel by using different constraints.

2 LITERATURE REVIEW

2.1 Definition of Biodiesel

Biodiesel is the result of transesterification (exchange of ester) of oil from vegetables and animal fats. The lipids that exist in the feedstocks used for the production of biodiesel composes 90 up to 98 % (weight) of try glycerides, free fatty acids of 1-5% and some amount of triglycerides trace number of phosphates, carotenes, phospholipids and small amount of water. The quality of biodiesel is explained in terms of its density, viscosity, and composition of fatty acid esters, iodine value, acid value, flash point, calorific value, volatility, water content, carbon residue, ash, and Sulphur (Agarwal, 2007). The flash point of Biodiesel is normally above 170^{o}C and biodiesel contains cetane number of 40 t0 70 and that of diesel is 47 to 55and have the iodine value up to 200 starting from zero based on unsaturation (Mondal *et al.*, 2008).

Biodiesel have higher darkened point, dispense point and thickness than diesel oil, the viscosity of biodiesel is to some extent less in magnitude than that of vegetable oils (Balat, 2008).

Transportation of biodiesel is very easy as compared to petroleum diesel fuel (Agarwal, 2007; Bozbas, 2008; Delucchi, 2003; Canakci and Sanli, 2008).Biodiesel that can be produced from renewable resources is non-aromatic and nearly sulfurless and lubrication property of petroleum diesel is not as good as biodiesel. Very little additive (about 1%) is sufficient for improving conventional diesel fuel's lubricity.

On the average assessment of full life cycle biodiesel greatly minimize the emissions of carbon dioxide as compared to the conservative fossil fuels and also have high contribution in combating global warming.

2.2 Processes of Biodiesel production

The raw materials can be obtained from trivial land because of the increment of production capacity of the soil and many crops can be utilized due to their fixation capacity of nitrogen in the soil and they depend on local climatic conditions and soil type, also, other wastes can be used as in put sources for producing biodiesel. This makes biodiesel easier to be produced at local scale or in farm or industrial production because of availability of broad variety of raw materials for example, for supplying transportation fuels at a regional level or national level. Biodiesel has

high energy as compared to other biofuels, like bio-ethanol from maize and needs less energy, water and other materials.

Currently the availability of the processing units makes simple and easy to implement the technologies connected with reprocessing of raw materials for production of biodiesel. It is convenient for usage almost all conventional diesel engines, provides the same performance and durability of engine as diesel fuel. Therefore, it is not needed to modify or requires new types of engines necessary. The main advantage that pushes the performance the biodiesel production is its possibility of using the existing engine and importance in minimizing environmental pollution. However, vegetable oils have little drawbacks, such as high viscosity which makes the biodiesel impractical of utilization during low temperature and lower input and instabilities of its oxidation and leading to corrosion in the combusting chamber due to the formation of deposits in it (Akohet al., 2007; Agarwal, 2007).

2.3 Conventional Processes (CP) basedbiodiesel production

2.3.1 Homogenous Catalyzed Processes (HCP) for Biodiesel Production (BP)

A lot of routes used to obtain biodiesel from lipid raw materials. The very essential process mostly is transesterification of triglycerides through batch process in the attendance of uniform catalysts of Acid or base with alcohol of low molecular weight (Demirbas, 2008). This procedure has a vital importance due to being easy to put in to practice, monitor and activate it and the occurrence of liquid phase reaction is under softconditions of heat and pressure, due to this case base catalyzed ester-exchange is much faster by arrangement enormity when compared with acid-catalyzed ester –exchange, the widely used base catalyst is sodium hydroxide (Agarwal, 2007; Demirbas, 2008; Aranda*et al.*, 2009; Han*et al*., 2009).

The proportion or ratio of the resources of the collection input and alcohol output is about 1:1. This due to the reversible ester-exchange procedures to assure the complete transformation of triglycerides a surplus alcohol is needed to swing the balance to the yield side.

Normally, thebiodiesel yield increases with the overload of the fuel, but yield price, in meticulous due to increment requirement of volume for the reactor and the partition of glycerol that becomes more difficult. When the alkalis catalyst isused some emulsification occurs due to saponification reaction (Atayaet al. 2008). As the procedure involves the creation of two

immiscible phases, thereactors vessels are extremelystimulated to endorse mass convey (Ataya, 2008). Then, any surplusalcohol that did not react and catalyst are detached from both phases (of esters and glycerol) and cast-off back to the reactor. The elimination andrecycling of the catalyst and unreacted surplus alcohol raisethe difficulty and in-service costs of the procedure (Fig. 2.2)

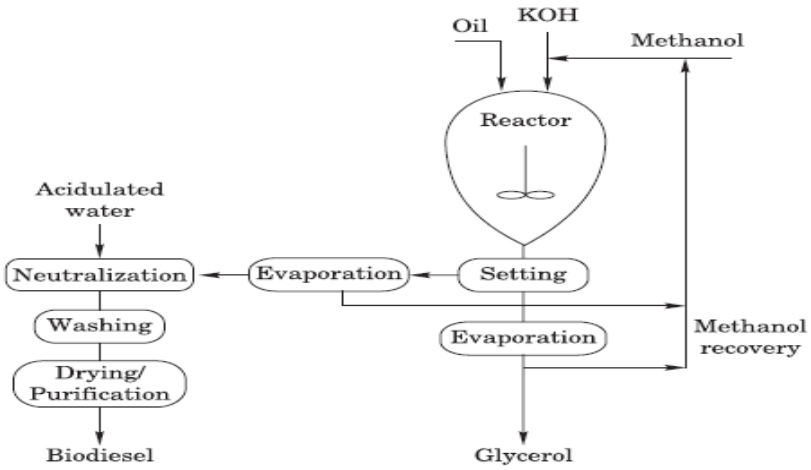


Figure 2-1: Alkaline catalysis based typical biodiesel production process diagram

2.3.2 Biodiesel production process by heterogeneous catalysts

The manipulation of uniform catalysts in which the catalyst has to be detached from the end yield and recycled back to the reactor, adds difficulty and function prices, and environmental impacts.

The usage of the homogenous catalysts is very essential in minimizing difficulty of heterogeneous catalysts and ensures in great reduction of complexity of purification steps and helps in obtaining pure product, minimizing cost of production and making it easier to activate in continuous mode.

It is a natural, step in providing and improving existing processes. Wide-ranging and simplifiedevaluation of the presentpositionon the usage of alkali catalysts is given by Liu *et al*. (2007).

An additionalassessof the status of the performance of acid and base catalysts for biodiesel production are being recognizedthrough scientific and exclusive rights literature, has been indicated by Di Serio*et al*. (2008). The general usage of non-liquid activation chemicals for ester

exchange to generate different ester-made compounds (Otera, 2003), its consumption in the transesterification reaction for biodieselproduction is almost inexistent at industrial level.

2.4 Biodiesel production process through Biological catalysis

One of the interesting alternative indications for future utilization for producing biodiesel is biological catalysis (enzymes and living organisms).This biological catalysis can be utilized either in solution or supported especially, through biological films in packed beds.

Even though an intensive research has been attracted to natural catalysis for production of biodiesel, no reasonable practical implementation is not visible in a mean time (Ming*et al*., 1998; Dossatet al., 1999; Shimadaet al., 2002; Oliveira and Rosa, 2006; Akohet al.2007; Rathore and Madras, 2007; Ibrahimet al.2008;2008; Shaw et al.2008).

In ester exchange of oils, many enzymes can be involved in biological catalysis, especially, lipase that available in many different living cells. These enzymes, when reacted as catalyst it is more selectable, effective and needs less energy and temperature, it also, produces less by product and waste as compared to other types of catalyst processes.

The manipulation of enzymes or living organisms modifies not only the improvement of its elasticity and its performance; italso, in capacitates the functions of enzymes in hard situations.

Currently, manyresearchershave been focused on the usage of lipases that exists in different natural resources for executing ester exchange. For preserving the oil to methanol oil ratio, it needs addition of enzymes step by step to the mixture at normal conditions in order to protect hang-up and inactivation of enzymes (Shimada *et al*. 2002). it activates the regulation of enzymes function for the long duration of time. From the report, enzymes have different functions and abilities especially lipase that gained from several varieties of microorganisms requires high water and methanol gradients.

If the methanol is used in an appropriate way, it speeds up the reaction rates and causes some co-solvents to be added for positive regulation of stability of enzymes (Al-Zuhair,2007; Akohet *al*.2007). Thus, an intensive work should be done to discover the best solvents and their effects on the future reactions.

2.4.1 Sequences of Biodiesel production

The sequences of biodiesel production can be described by simple steps as indicated below.

- . Production of feed stock
- Processing of feedstocks-treatment and oil extraction
- production of biodiesel
- post-treatment of biodiesel and its unification

2.4.2 Feedstocks Production

Biodiesel is the essential part of liquid fuels, which can be obtained from waste raw materials, waste cooking oils, feedstocks that contains lipids and other vegetables produced from the collection of crops that comparatively stick to topographical sites. Among these crops located in temperate regions is corn, sunflower, rape seeds are very useful in production of biodiesel. There are also other resources or feedstocks in tropical regions includeJatropha, Palm oil, soya beans and etc. and also, other feed stocks utilizable free of climate and geographical locations being accepted such as microalgae and cellulosic biomass. The speculation of the world production as chief oil seeds for both biofuel companies and for the consumption indicated in 2007/2008.included (FAO, 2009). Till to date Europe is the dominating continent through biodiesel production from rape seeds as chief feedstock. The best explanation and farming practices for the crucial production sources indicated (FAO, 2008; Kurkiet al., 2006). but to ensure the eminence requirements for biodiesel production, different measures for preprocessing should be recognized (Canakci and Sanli, 2008).

During the extraction of biofuels, the selection of feed stocks has the reflective influence and becomes environmental concerns and some commodities or goods used as human feed that leads to the increment of the price of the crops either in various ways. This may be the cause for deforestation of the land and degradation of different species, on the other hand which minimizes the production capacity of human utilization (Bickel and Dros, 2003).

Lately it has been emphasized on microalgae, which could be as a raw material in production of biodiesel minimizes problems concerned with vegetable crops. The cultivation of microalgae requires small acres of land as compared to other feedstocks (Chisti, 2007) and its ability to grow in hard situations less requirement of price. This leads in reducing the competition with human consumption and brings best opportunity for areas affected by drought and salinity (Schenk et al., 2008).The growth rate of microalgae and its oil content is high as compared to other biodiesel feedstocks. They can multiply themselves in a few days and plays a vital role in

minimizing environmental contamination by absorbing carbon dioxide from air and eliminates phosphorus and nitrogen from environment during producing of high value chemicals (Murakami et al., 1998; Hodaifaet al., 2008)

2.5 Processing of Feedstocks

2.5.1 Extraction of Oil

There are several methods used for extraction of oils from feed stocks, among these mechanical press extraction and solvent extraction are the dominant methods. In the mechanical press extraction, the seeds should be heated up to fifty degree Celsius and compressed by screw press to obtain oil from feedstocks. The solvent Extraction is different from mechanical extraction because of the presence of solvents in solvent extraction, like hexane, methanol and other solvents can be used for extraction of oil. The solvents can be recycled and utilized in the next process and solvent oil separated by simple Distillation. For microalgae the oil extraction is highly different from supplementary raw materials (Grimaet al., 2003). In order to elongate the life span of microalgae different methods engaged such as freeze drying, drum drying and sun drying (Richmond, 2004). Other essential methods useful in extraction of oil from vegetable feedstocks are ultrasound-assisted extraction and microwave-assisted extraction (Cravotto*et al*., 2008; Deshmane*et al*., 2009)

2.5.2 Pre-treatment

The ester-exchange requires pre-treatment prior to produce biodiesel. The oils that can be obtained from feedstock like wastes and animal fats should be pre-treated before any transesterification processes. This ensures to produce quality biodiesel and the impurities must be removed, which leads high by product generation and minimizes the reaction rates (Canakci,2007).And also creates complex separation phase during the production of biodiesel (Aranda*et al*.,2008).The normal composition of free fatty acid of wastes from animals and other wastes is in the range of 2%w/w to40%w/w (Watanabe *et al*., 2001; VanGerpen*et al*., 2004; Canakci, 2007).In other case the physical cleansing of some chemical industries during the production of biodiesel is in the range of(4-8)% out of the total production(Watanabe *et al*., 2007).The improvement of the free fatty acid is complicated and not practicable in economic

wise(Arandaet *al*., 2008). Thus, searching for other sources as feedstocks for production of biodiesel is hopeful to vary free fatty acid based up on carbon chain contents (Allen et al., 1999).

2.6 Sclerocaryabirrea (Marula)

2.6.1 The Marula tree and its fruit

Sclerocaryabirreais usuallyrecognized as marulain southern Africa but other names are used in other countriesalso. It composes various species like birreaand *gillettii (*Shackletonet.*al.* 2004). AccordingtoShackletonet.*al.* (2004), it was found that about three (3) main species namely *Birrea*, *Caffra*and *Multifoliolata*

Figure 2-2: Marula tree, Source: GadissaHundessa (2014)

2.6.2 The use of marula

Sclerocaryabirrea is the interesting tree which can generate profits for societies living in African Continent (du Plessis, 2002) and frequently useful asnativenaturalcrop in different African countries (Shackletonet *al.*, 2001).

Marula is cherished tree due to its importance for preparation of alcohol, juice and utilized as edible sources (Nerd & Mizrahi, 1993 and Mizrahi & Nerd, 1996).And also, needed for several issues (du Plessis, 2002; Mojeremane&Tshwenyane, 2004).

In addition to this the tree is useful for different purposes like preparation of traditional medicine, treating cough and dysentery, preparing various house utensils and etc

3 Materials and Methods

3.1 Study sample

Raw materials, ripened fresh fruits, ofMarulatrees (Sclerocaryabirrea) were collected from*Arba Minch, NechSar National Park*andtransported to laboratory (School of Chemical and Bioengineering), Addis Ababa Institute of Technology, Addis Ababa University for further analysis.

3.2 Equipment and chemicals used

Equipment used	Drying oven,
	Weighing balance,
	a Soxhlet apparatus,
	Round flask
	Water bath
	viscometer
	condenser
	Three neck flasks
	Burette
	Dense meter
	Beaker
	Holding clamp
Chemicals used	potassium hydroxide
	Phenolphthalein
	Diethyl ether
	Ethanol
	Hydrochloric acid
	Sodium hydroxide
	Methanol

Table3.1: Equipment and chemicals utilized

3.3 Methodology

Biodiesel production procedures were described in fig 3-1

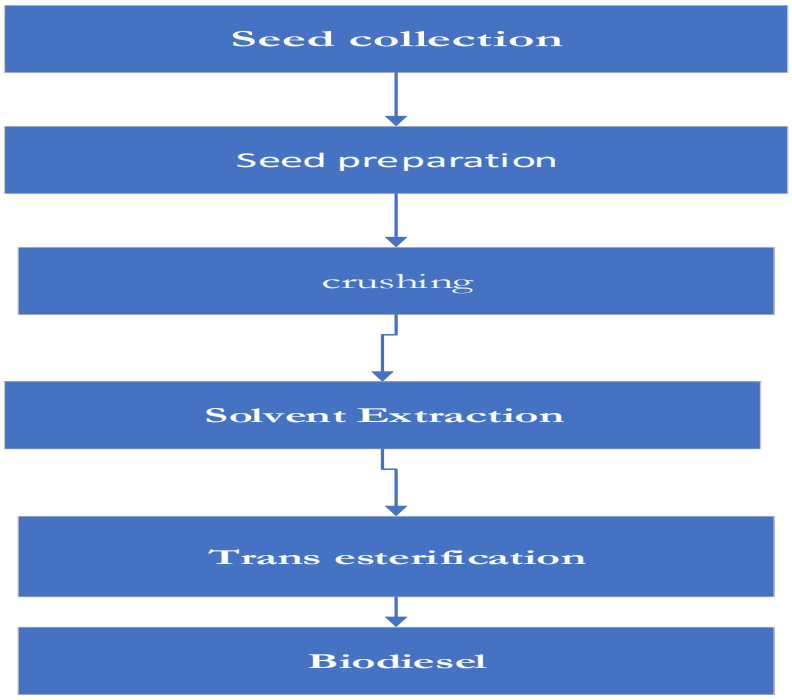


Figure 3-1:Flow chart of biodiesel production

3.4 MarulaSeed collection and preparation

The collected seed was prepared by removing the outer coverage of the kernel, then dehulling the kernel and finally the endocarp of the seed was prepared.

Figure 3-2:Seedcollection, removing the outer cover

Figure 3-3: Driedmarula and its internal parts which contain oil

3.4.1 Proximate analysis and Characterization of Raw material (marula Seeds)

Physio-characteristics of marula oil were examined according to the usual procedure recommended by AOAC (1980). The oil properties including moisture content, crude fiber, fat, fixed carbon content, volatile matter and ash contents were determined.

3.4.2 Moisture Content Determination of Marula seed

Content of moisture of the seed was indicated by the procedure set as of (AOAC, 930.15, 2016). Marula seed should be added to the dish and the dish without marula weighed and recorded, then the dish with marula seed inserted in to the oven dry by fixing the temperature at 105 degree Celsius for consecutive seven hours and the weight of the seed measured after two hours until fixed weight obtained.

$$\textbf{Moisture content, \%} = \frac{w2-w3}{w2} * 100 \text{----------(3.1)}$$

Where, w2=weight prior dried w3= seeds weight when dried

3.4.3 Ash content of the seed

The standard procedure used in examining the ash content of marula seed wasas per the method of AOAC, 923.03; 2016.Itindicates the impurities that will not burn. The presence of high ash

content affects the combustion efficiency of fuels and cause slagging and clinkering. Typical ranges of ash content should be 3% to 10% (A.K.Shaha, 2011) and the variation range is extended due to the origin of solid biofuels, species, climatic condition and specific part of the selected plant. the following formula was used in determining ash content of marula seed.

$$\text{Ash } \% = \frac{(W4 - W5)}{W4} * 100 \quad \text{(3.2)}$$

Where W_4 is prior heating weight and W_5seeds weight of after combustion

3.4.4 Determination of Volatile matter

The amount volatile matter is one important factor to determine easy ignitability of biofuels extracted from plant oils and determined by using the high-temperature furnace and the temperature was set up to 925°C for determining volatile matter, the container and its cover heated simultaneously for eight minutes (8min).

$$Volatile matter, \% = \frac{C - D}{C} * 100 \quad \text{(3.3)}$$

Where; C is weight of the seed prior drying and D is weight of seed after dried

3.5 Extraction of Sclerocaryabirrea oil

After the endocarps were sun dried to remove the moisture, oil was extracted from marula endocarp by solvent method (n-hexane as solvent). The oil obtained was utilized for biodiesel and the remaining waste was removed for animal's consumption.

3.5.1 Soxhlet extraction with hexane

The seed samples placed in a thimble, which was positioned in the center of the Soxhlet apparatus and connected to the round bottom flask containing 600 mL of n-hexane and condenser was used to prevent it from violent boiling. The set up was placed on a heating mantle for 8 hours at 93 °C as indicated in the figure 3-4. After the extraction process was accomplished the extract was quantitatively conveyed to a Heidolph rotary evaporator (model number 517-61000-00-0) at 45 °C to remove the solvent was carried out (Adejumo et al., 2013). The extraction process was carried out in triplicate each time on fresh samples (Gandure et al., 2011).

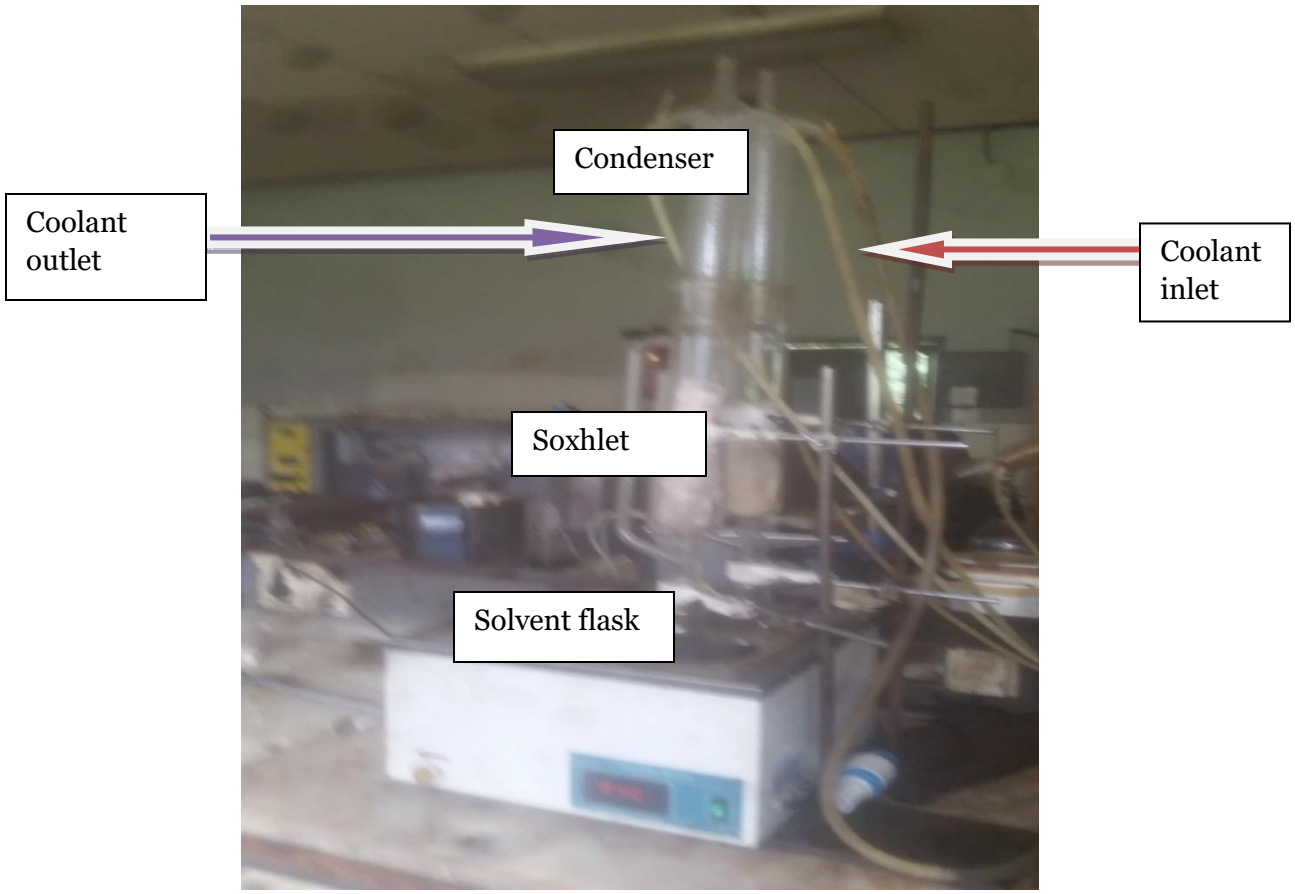


Figure 3-4: Diagram of a Soxhlet extraction setup

3.6 Crude Oil Purification and characterization of physiochemical properties of the oil

3.6.1 Oil degumming

The extracted oil from marula seed initially heated to the temperature of seventy degree Celsius and rousing up to thousand revolutions per minute (1000 rpm) in a jacketed glass vessel linked to centrifugal machine. it was stirred for about half hour(0.5hr)following the formation of black residue inside the vessel. Positive gum of the oil was removed by water and the negative gum removed by phosphoric acid.

3.6.2 Washing of the oil and neutralization

Washing of the purified oil to remove free fatty acid present in the oil, boiled water was added on to the oil that exists in the separatory funnel and the addition of water continued until the

removal of FFA was completed. At the end the oil was taken into the oven dry for drying setting its temperature at 100°C to remove the water present as indicated in the figure 3-5

Figure 3-5: crude oil washing and neutralization

3.6.3 Determination of percentage of oil yield

The amount of oil can be determined after extraction of oil from the seed of marula. The oil extraction was carried out using Soxhlet apparatus and the solvent present in the oil after extraction was recovered by simple distillation using vacuum rotary evaporator and the water bath temperature was set at 65 °C, the fooling formula was used in determination of oil yield.

$$\textbf{Oil yield} = \frac{mo}{ms}\textbf{x100}\% \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \textbf{(3.4)}$$

Where *mo*= weight of oil recovered after extraction

ms= weight of seed samples

3.6.4 Determination of acid value

Acid value is an essential parameter used to determine the quality of seed oil (Gharby et al., 2012) and it reports the extent of hydrolytic degradation that has occurred in the seed. Hydrolytic degradation is due to the water content that comes out with the oil during extraction thereby

reacting with triglycerides to form free fatty acids and by-product (Soetaredjo et al., 2008). Further degradation could be accelerated by the presence of high moisture content in the seed.

To standardize an approximately 0.1 M potassium hydroxide and 5gm of oil was used into a 25 mL of diethyl ether and addition of phenol of three drops. Then the mixture was titrated with potassium hydroxide solution until there was a color change from colorless to light pink.

$$\text{AV} = \frac{\mathbf{56.1}\boldsymbol{XVXM}}{\boldsymbol{m}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \textbf{(3.5)}$$

Where56.1 is the equivalent weight of KOH

V = volume, in mL, of KOH

M = molarity of KOH

m = the mass, in gramsoil

3.6.5 Saponification Value (SV)determination of the marula oil

Saponification Value (SV) is very important parameter that can be defined in milligrams and to carry out this, Two gram of oil measured and poured into the flask to which contains fifty(50ml) of half(0.5 M) of potassium hydroxide mixed. Thecombination was refluxed for 30 min, consecutively addingthree (3) drops of phenol, and it was titrated tohalf (0.5 M HCl) till coloration gone. The process was reused without oil for determining the titre value.

$$\textbf{Saponification value}(\textbf{SV}) = \frac{(\boldsymbol{t2}-\boldsymbol{t1})\boldsymbol{x}\mathbf{28.1}}{\mathbf{W}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3\text{-}6)$$

Where, t1 = titre value, without oil. t2=Oil titred value and W is Oil weight.

3.6.6 Determination of Free Fatty Acid of the Oil (DFFAO)

Five gram of the oil was filled to the flask and boiled (warmed); twenty five (25 ml) of Ethanol poured to the flask and stirred by adding two (2 drops) of phenol and a drop of 0.1 N KOH concentration for titration against it

$$\textbf{Free Fatty Acid}(\textbf{FFA}) = \frac{(\boldsymbol{titrevaluexNx}\mathbf{28.2})}{\boldsymbol{weightofsample}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.7)$$

N =normality of the solution

3.6.7 Determination of Density and Specific Gravity

The specific gravity and density were measured by density meter samples were injected to the density meter equipment to display the result.

3.6.8 Determination of Kinematic Viscosity (KV)

To get kinematic viscosity thee oil poured into the 35ml of oil container which is fitted on to the Vibroviscometer and the tip of Vibroviscometer inserted and the reading was taken as dynamic viscosity. The dynamic viscosity that was taken from thevibro viscometer was 92.8mpas and the Vibroviscometer reading indicated in the figure 3-6.

$$\mu = \frac{v}{p} \quad \text{... ... ...} \textbf{(3.8)}$$

Figure3-6: Vibroviscometer

3.7 Experimental Design for biodiesel production and optimization processes

Design expert software (DES) was utilized for the optimization of the oil and biodiesel produced experimentally at laboratory level. The purpose of manipulation of the software was to validate

the Engineering processes in the production of Biodiesel from Sclerocarya birrea seed that was conducted throughthe experiment.It is also very useful to identify which parameter of the process was optimized and validated at normal condition set for the production of oil and biodiesel. In this work, the majorpurpose was to classify the optimum combination of the selected parameter at which the maximum yield of biodiesel achieved by using design expert software. Thus, different reaction parameter wasengaged in order to observe the consequence of these parameters on the response variable and select the best combination. The biodiesel production was conducted by using a purified marula oil, methanol, and analytical grade potassium hydroxide. Transesterification reaction process commonly in use for non-edible oil are homogeneous base catalyzed or acid catalyzed, but for this specific study based catalyzed transesterification was selected because the maximum amount of free fatty acid of marula oil is greater than 2.5% which indicates transesterification employed after the oil is neutralized to remove free fatty acid (FFA)in attendance in the oil. The range and levels of the variables used for optimization were demonstrated in Table3.2, which indicates in put parameters utilizable for Design Expert Software.

Table 3.2: Design Expert Software inputs for optimization of biodiesel

	Factor 1	Factor 2	Factor 3	Response 1
Run	A: methanol to oil ratio (MoR)	B: Temperature(T)	C: catalystconcentration(CC)	Biodiesel
		^{o}C		%
1	3	67.5	1.75	
2	3	67.5	1.75	
3	6	67.5	1.75	
4	6	60.0	1.00	
5	9	60.0	1.75	
6	6	67.5	2.50	
7	9	60.0	1.75	
8	9	75.0	1.75	
9	3	67.5	1.00	
10	3	67.5	1.75	
11	3	75.0	1.75	
12	6	60.0	1.75	
13	3	67.5	2.5	
14	6	67.5	1.75	
15	9	67.5	1.75	
16	9	75.0	1.00	
17	6	67.5	1.75	

3.7.1 Feed Material Requirement for Biodiesel Production

Twenty-fivemilliliters of purified marulaoil can be utilized for consecutive steps. The volume of methanol required was calculated by using the listed equations, when the molar ratio of oil to methanol changes.

$$\frac{noil}{nmethanol} = (Y) \quad \text{..... (3.9)}$$

Where: - Y is the ratio of methanol to oil (amount) used in the runs

Substitute mass for mole;

$$\frac{\frac{poil*voil}{Moil}}{\frac{pmethanol*Vmethanol}{Mmethanol}} = Y \text{ ..... (3-10)}$$

$$\frac{mass\ of\ catalyst}{mass\ of\ oil} = x$$

X % catalyst used in each run.

3.8 Physicochemical Properties Analysis of Biodiesel (characterization)

3.8.1 Determination of Flash Point (FP) for Biodiesel

Biodiesel can be characterized by its flash point and it was examined by open cup method. First biodiesel poured on to the cup up to seventy five milliliters (75ml)mark and it was fired by Bunsen burner and mean while the spark of temperature rises up to maximum limits it catches the flame and the point is recorded as flash point of the biodiesel.

3.8.2 Determination of High Heating Values (DHHV)

Calorific value (CV)of a Biodiesel was determined Adiabatic Calorie Metter at Geological Survey of Ethiopia through hydrocarbon laboratory analysis.

3.8.3 Determination of density and specific gravity

Density and specific gravity of fuel oil or biodiesel was determined by injecting into automatic density meter of model DMA4100M

Figure 3-7: Dense meter reading of density and specific gravity

3.8.4 Determination of viscosity

The biodiesel was poured into the rectangular container of 35ml capacity and the tip of vibro viscometer inserted into the container, then the reading was taken as viscosity at 17.4^0c.

3.9 Biodiesel production procedures

The transesterification process was performed in this study and initially, about 25 ml of purifiedmarulaseed oil was poured into a 100 ml glass reactor and a steady state temperature of 60 ^{O}C at atmospheric pressure was achieved before mixing with the amount of methanol and heterogeneous catalyst. The transesterification reaction was carried out by fixing the speed of the mechanical stirrer (agitation speed) constant and temperature for the whole experiment the main parameter, which is molar ratio of oil to methanol at 1:3, 1:6 and 1:9 mass ratio of catalyst to oil, 1%,1.75% 2.5% and time of 1hr. Finally, the resulting mixture was poured in to separatory funnel and allowed to stand overnight to separate into two layers, a separate phase of glycerol and biodiesel based liquid phases. Then the bottom layer was decanted since its glycerol and then biodiesel was obtained and remained in the separatory funnel. The product was washed repeatedly with hot water until a clear layer of biodiesel was obtained.

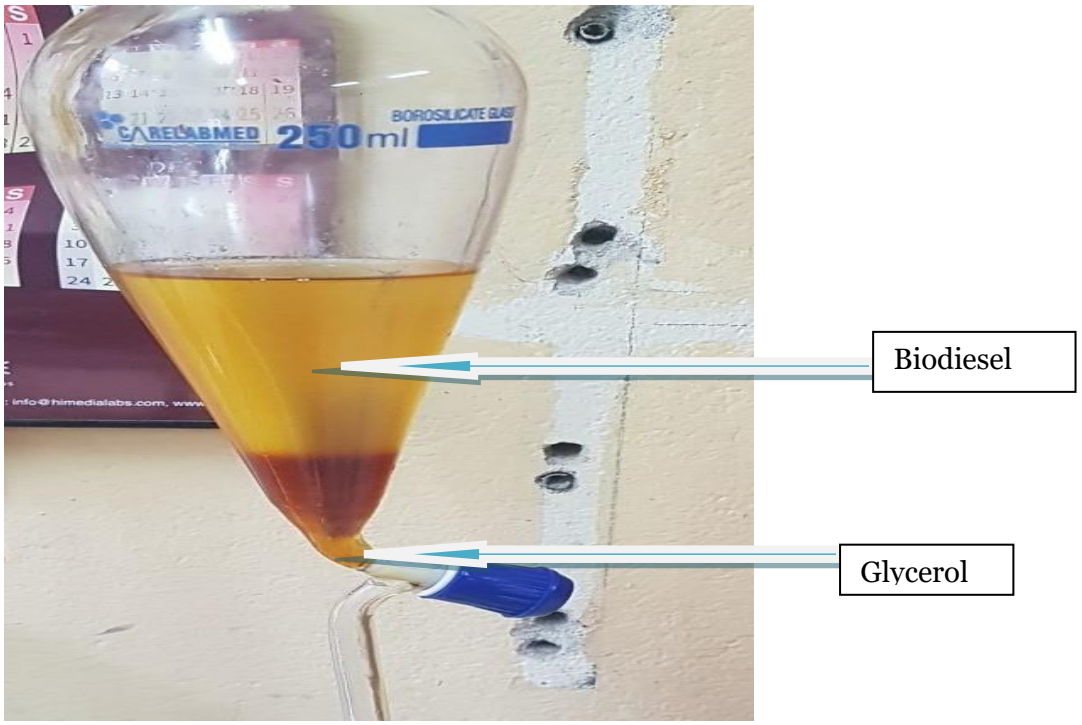


Figure 3-8: Biodiesel production time

4 Results and Discussions

4.1.1 Proximate analysis marula seed, extraction and characterization of the marula oil

Proximate analysis of the raw material of Sclerocarya birrea seed was determined and tabulated as indicated in the Table4:1

Table 4.1: Summary of Proximate analysis of marula seeds

Proximate analysis	Percentage	Test methods used
Moisture content	5.90%w/w	AOAC 930.15,2016
Crude fiber content	11.84%w/w	AOAC 962.09,2016
Fat content	47.66%w/w	AOAC 2003.06,2016
Ash content	4.27%w/w	AOAC 923.03,2016

Table 4.1: demonstrates moisture content of 5.90%w/w which is very desirable and doesn't affect the yield of the oil production but since fat content of the seed is very high which is 47.66%w/w it has great effect during production of biodiesel, this indicates it needs removal of

fat from oil before production of biodiesel by neutralizing the oil. The ash content of the seed which forms impurities is tolerable which fails in the standard 4.27%w/w.

4.2 Oil extraction of marula

The desired amount of marula oil was extracted from the collected seeds using Soxhlet apparatus. The extraction step was prepared for 92.22 g of the sample and the experiment was repeated in triplicate. The oil content (oil yield) of the dried marula seeds was determined by equation 3.5.

Table 4.2: Oil yield of s.birrea

Run	Sample (g)	V (cm3)	M=s*v	Yield (%)	Average
1	92.22	38.26	35.31	38.29	41.57
2	92.22	40.35	37.24	40.38	
3	92.22	45.99	42.45	46.03	

The average oil content of the seed was calculated and obtained an average of 41.57%. This indicated that the marula seed has elevated oil content which can be good potential for biodiesel production with non-edible plant that could not compete with human food consumption

4.3 Characterization of physiochemical properties of marula oil

The physicochemical properties of the oil were studied to determine its potential for use as a biodiesel feedstock. The physicochemical parameters (Table 4.3) suggest the suitability of the oil for conversion into biodiesel. The content of Free Fatty Acid (FFA) of the oil was slightly high; as a result earlier reports suggested that higher FFA content lowers the biodiesel yield which may be due to formation of soap which makes the separation of biodiesel difficult. However, in the present study, the yield was reportedly increased by employing a heterogeneous catalyst. Similarly, reported the use of a heterogeneous catalyst in the preparation of biodiesel production the comparison of physiochemical properties of marula seed conducted before and in this study indicated in table 4.3.

Table 4.3: Physiochemical properties of marula oil

Physiochemical properties of the oil	units	Bikila	Gadisa
Average oil content	%	41.57	61.36
Time of extraction	hr	3-5	3
Volatile matter	%	84.62	-
Fixed carbon content	%	5.22	-
Acid value	mgKOH/g	7.52	3.6
Free Fatty Acid	%	3.8	1.81
Saponification value	mgKOH/g	229.015	190
Ester value	mgKOH/g	221.49	--
Kinematic viscosity	mm^2s^{-1}	0.1024	-
Density	$gcm-^{3}$	0.906	-
Specific gravity at 15ºC	-	0.923	0.899
Refractive index	-	-	1.467

4.3.1 Determination of acid value

Acid value is an essential parameter used to determine the quality of seed oil (Gharby et al., 2012) and it reports the extent of hydrolytic degradation that has occurred in the seed. Hydrolytic degradation is due to the water content that comes out with the oil during extraction thereby reacting with triglycerides to form free fatty acids and glycerol (Soetaredjo et al., 2008). Further degradation could be accelerated by the presence of high moisture content in the seed. and the acid value recorded was 7.52.

4.3.2 Determination of Saponification value of the marula oil(DSV)

Saponification value (SV) is very important property in characterizing oil from marula seed and it was recorded as 229.

4.3.3 Determination of ester value of the oil

Ester Value determined was 221.49milligrams of potassium hydroxide which is very valuable property for characterization of the oil.

4.3.4 Determination of Density and Specific Gravity

The specific gravity and density were measured by density meter samples were injected to the density mater equipment to display the result. The results were 0.923 and 0.906g/cm^3 respectively.

4.3.5 Determination of Kinematic Viscosity (KV)

The dynamic viscosity that was taken from the vibro viscometer was 92.8mpas.

$$\mu = \frac{v}{p} \quad \text{... ... ...} \quad \textbf{(4.1)}$$

$$\mu = \frac{92.8\ mpas}{0.906 g/cm3}$$

μ= 0.1024mm^2/s

Where;-

μ =kinematic viscosity (kv), mm^2/s

ν=dynamic viscosity, mPa.sec and ρ=density, kg/m^3

4.4 Oil optimization using design expert

During the optimization of the oil two parameters were employed, these are time in hour and temperature in degree celisius.as indicated in the Table 4.4 the model and the two parameters were significant.

4.4.1 ANOVA analysis of oil yield

Table 4.4Anova Analysis in puts

Source	Sum of Sq	df	Mean Sq	Value of F	Value of P	
Models	789.11	3	263.04	230.21	< 0.0001	significant
A-Temperature	130.32	1	130.32	114.06	< 0.0001	
B-Time	61.03	1	61.03	53.41	< 0.0001	
AB	453.21	1	453.21	396.66	< 0.0001	
Residual	10.28	9	1.14			
Lackof Fit	10.28	1	10.28			
Pure Error	0.0000	8	0.0000			
Cor Total	799.39	12				

The mean square value and the value of F illustrates the model is important and indicates significance of the model, the value of P, which is below 0.0500 demonstrates the model terms accuracy.

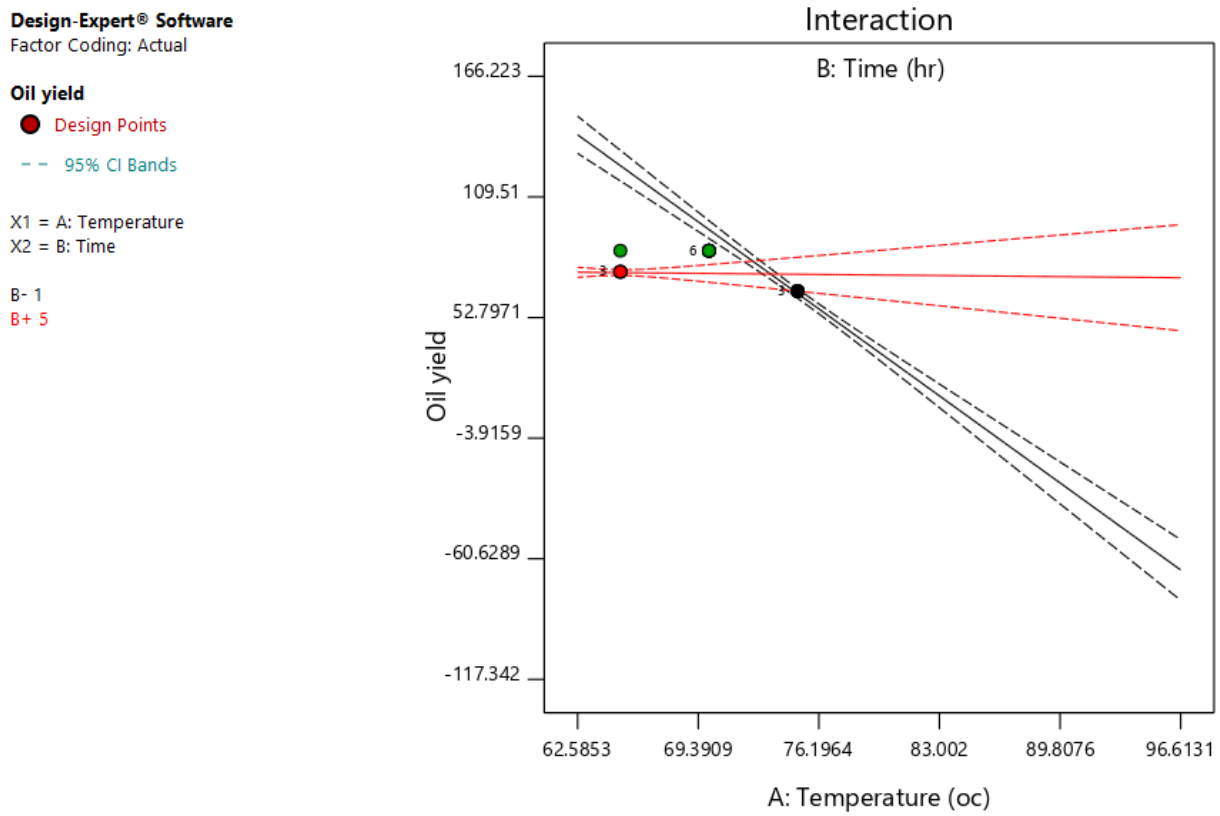
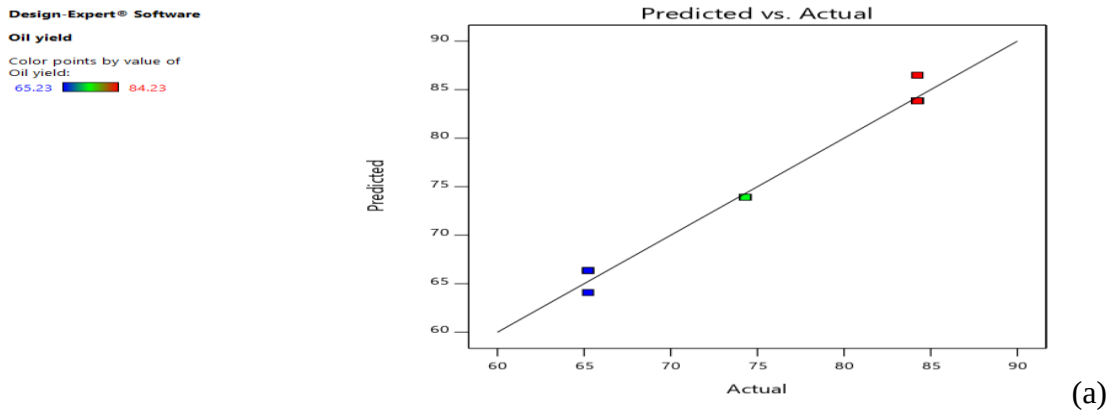


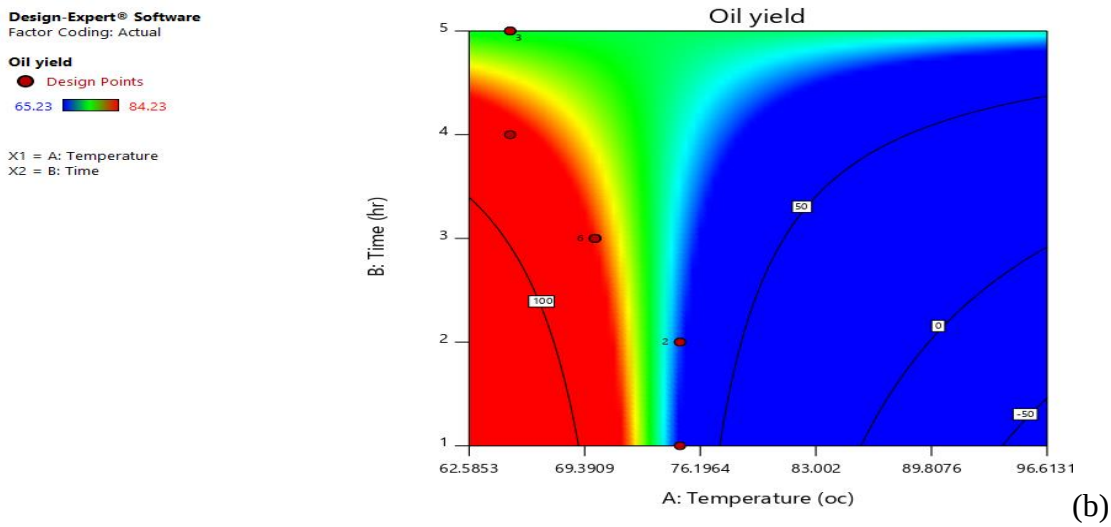
Figure 4-1: Interaction graph

The graph indicates the relationship between temperature, time and oil yield. The figure illustrates that as temperature increases the product or oil yield decrease but at medium temperature with effective time the product can be increased.



(a)

Figure 4-2: Predicted versus actual graph including contour line indication



(b)

Fig 4-2 (b) contours line indication of time and temperature relation in relation with the oil yield.

The Fig 4-2 (a) indicates the points of actual value and predicted value scattered on the line concisely which demonstrates the actual value and the predicted value are nearly close to each other. From the graph the actual value is around 85% and that of predicted value is around 86% that illustrates the values are close to each other for which the model is perfectly fit.

4.5 Physicochemical Properties Analysis of Biodiesel (characterization) of marula

Initially checking physicochemical properties of marula oil is very important, because parameter such as free fatty acid, moisture content is highly affected next transesterification reaction and yields of biodiesel. This was the major properties of oil that help in decision making for next

process to select which types of transesterification appropriate, types of catalyst and to estimate oil quality as well as oil content of given feedstock. Physicochemical properties of the samples of biodiesel were analyzed for its density, specific, calorific value gravity; viscosity, iodine value, and flash point were tabulated in Table 4.5. All determinations were done three times and the average values were taken.

Table 4.5Physiochemical properties of biodiesel

Physicochemical properties	units	value
Iodine value	mgI_2/gm	115.0
Specific gravity	-	19.96
Density	g/cm^3	0.915
Flash point	^oC	235.0
viscosity	mpa.s.	11.30
Heating value(calorific value)	MJ/Kg	42.55

4.5.1 Biodiesel characterization

4.5.1.1 Determination of Iodine Value

Iodine value is the important property measured out of hundred (100gm) of the biodiesel sample. It was illustrated in the table 4.5, which was $115gmI_2/100gm$. Iodine value is used to measure the chemical stability property of substance against oxidation and the higher the iodine value the higher the number of double bond and hence lesser stability, The result was in the suitable range as the ASTM requirement is a maximum of 115.

4.5.1.2 Determination of Flash Point (FP)

The value of flash point was found to 235^0C which were similar with other researcher's value at 240^0C

Flash point is the lowest temperature by which a fuel vapors will ignite in air. A non-flammable FAME should have flash point high enough to within the standard limit for safe storage purpose. High content of methanol will lower the flash point and viscosity of the FAME and thus lead to dangerous storage instabilities. The higher the flash point the safer the fuel and vice versa. As result shown in Table 4.5the flash point were found to be 235^oC.

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

4.5.1.3 Determination of Calorific value

Calorific value (CV)of a biodiesel was determined by Adiabatic Calorie Metter at Geological Survey of Ethiopia through hydrocarbon laboratory analysis, the result found was 10178.77 Cal/gm which is 42.55MJ/Kg is attached at the appendix E of this paper. The Heat of combustion refers to the measure of energy content in the fuel. Heating value of fuels is an important measure of its releasing energy for producing work. As results presented in Table 4.5 the result calorific value was 42.55 MJ/kg which is in agreement with standard specification limit EN 14214 (>35 MJ/kg).

4.5.1.4 Determination of density and specific gravity

Density and specific gravity of fuel oil or biodiesel was determined by injecting into automatic density meter of model DMA4100M and the density was 0.915g/cm^3 and specific gravity was as 19.96 as indicated in the Figure 4-3.

Figure4-3: Dense meter measurement value

4.6 Feed Material Requirement for Biodiesel Production

Twenty five milliliters of purified marula oil was used for each run. The volume of methanol required was calculated by using the listed equations, when the molar ratio of oil to methanol changes.

$$\frac{noil}{nmethanol} = (Y) \quad \ldots\ldots\ldots\ldots \quad \ldots\ldots\ldots\ldots \quad (4.1)$$

Where: - Y is the ratio of methanol to oil (amount) used in the runs

Substitute mass for mole;

$$\frac{\frac{poil*voil}{\text{Moil}}}{\frac{\text{pmethanol}*\text{Vmethanol}}{\text{Mmethanol}}} = \boldsymbol{Y} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.2)$$

$$\frac{\frac{0.906g/ml*25ml}{277.8\text{g/mol}}}{\frac{\mathbf{0.79gm/ml}*\text{Vmethanol}}{\mathbf{32.04gm/mol}}} = \mathbf{1/6}$$

Therefore,**Vmethanol** required is **20.147ml**.

The amount of catalyst required was calculated by using the equation and

$$moil = poil * voil \qquad (4.3)$$

$$moil = \frac{0.906gm}{ml} * 25ml$$

moil =22.65gm

$$\frac{massofcatalyst}{massofoil} = X \quad (4.4)$$

Where: - X is the amount of catalyst need for each steps(%)

The amount of catalyst required for the reaction when the ratio of catalyst weight to oil is 1.75%;

$$\frac{massofcatalyst}{22.65gm} = 1.75\%$$

Mass catalyst used was 0.396gm

All the experimental results for each run calculations attached on the appendix Table 1 and Table2

4.7 Biodiesel optimization and graphical analysis using design Expert software

4.7.1 Process of Transesterification

The biodiesel yield was investigated mainly for the three major effect parameters namely methanol to oil ratio (MOR), Temperature (T) and Catalyst Concentration (CC). In this investigation, the reaction time and mixing intensity kept constant for all experimental runs (1hr and 500rpm) respectively (Mathiyazhagan, M, 2011). Since Soxhlet extraction oil produces high-quality oils, degumming was enough to reduce the acid values or no need for esterification process in order to reduce the acid values. Twenty five milliliters of degummed marula oil was

used for each run under given constraint. The statistical analysis of the biodiesel yields and the effect of selected parameters were discussed in the next session

4.7.2 Graphical analysis using design expert for statistical analysis

Design expert software of version11.0.0 was utilized for statistical analysis of for the experiment carried out in the laboratory using Box Behnken Design (BBD) for each parameters and the reply of measurement of the yields of biodiesel as discussed in section 3.7. For analysis of the experiment the inputs were feed in to the software and graphical analysis were shown properly for each experimental runs as recorded in Table4.6 below

Table4.6inputs of the software for result analysis

	Factor 1	Factor 2	Factor 3	Response 1
Run	A:methanol to oil ratio	B:Temperature	C:catalyst concentration	Biodiesel
		oc		%
1	3	67.5	1.75	75
2	3	67.5	1.75	75.22
3	6	67.5	1.75	75.32
4	6	60	1	85
5	9	60	1.75	84.56
6	6	67.5	2.5	71.32
7	9	60	1.75	94.32
8	9	75	1.75	83.5
9	3	67.5	1	69.35
10	3	67.5	1.75	73.32
11	3	75	1.75	60
12	6	60	1.75	93.45
13	3	67.5	2.5	70.88
14	6	67.5	1.75	83.5
15	9	67.5	1.75	85
16	9	75	1	84.32
17	6	67.5	1.75	83.5

the result of ester exchange processes for each run from marula oil was tabulated in table 4.6.Biodiesel yield values were different for different parameters during the preparation of biodiesel at laboratory level. It was observed that the actual yield well confirmed with the predicted value generated by the Design Expert software (BBD). The maximum biodiesel yield of marula oil was 94.32% at optimal combination of the process variable. From the actual investigation of each run verified that the optimum conditions at which maximum yield was

found at 9:1 methanol to oil ratio, at 60oC temperature, and at 1.75% KOH concentration of the oil in transesterification. Therefore, at this best possible mixture mass production of marula biodiesel were made to obtain the required amount of biodiesel for this study. Using Design expert, the value of biodiesel yields was predicted as well as possible combination process variable was selected.

4.7.3 ANOVA Analysis

Anova analysis is the very important parameter which indicates the factors that are significant and none significant for determination of the validity of the model showing experimental results accuracy.

Table 4.7: Anova analysis result

Source	Squares sum	df	Square mean	Value of F	Value of P	
Model	970.14	3	323	13	0.0003	significant
A-methanol to oil ratio	543	1	543	22	0.0004	
B-Temperature	259	1	259.32	10	0.0063	
C-catalyst loading	19.66	1	19.66	0.8005	0.3872	
Residual	319	13	24.56			
Lack of Fit	224	8	28.11	1.49	0.3434	not significant
Error	94	5	18.88			
Cor Total	1289	16				

The significance of model is adequate as the value of P less than0.05% that indicates model accuracy and model terms significance. The higher the P values the less significance and accuracy of model terms. When lack of fit is none significant and high it demonstrates the model is fit.

4.7.4 Diagnostic analysis using graphs

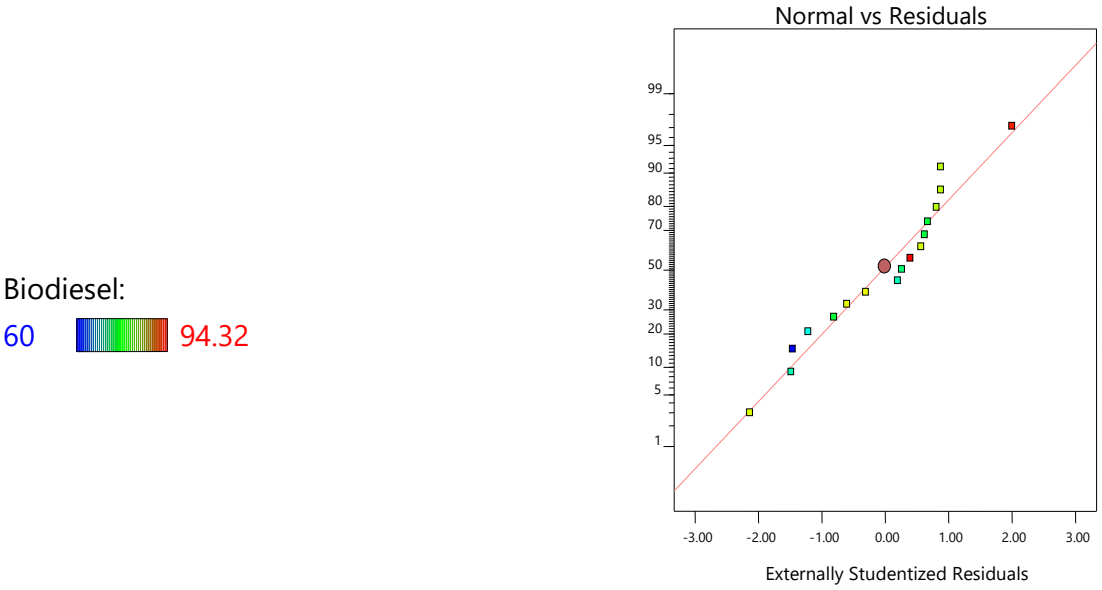


Figure 4-4: Graph of normal versus residual

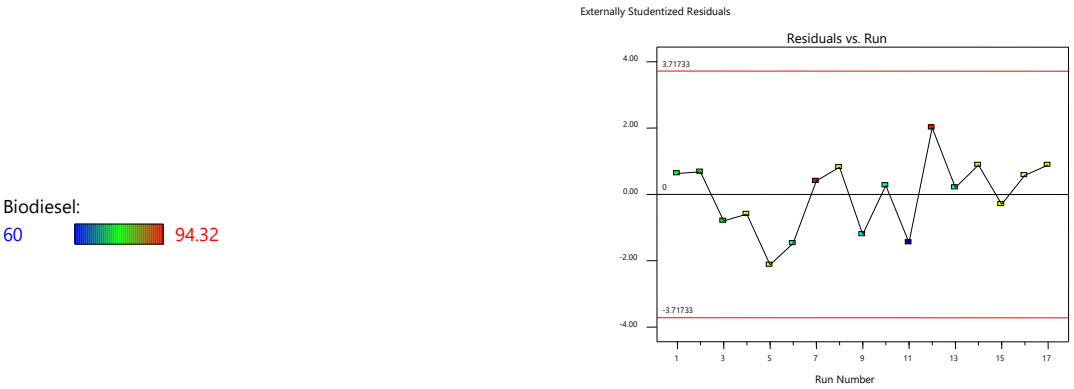


Figure 4.5: Graph of residuals versus run number

From the above Fig 4-4 the points, which indicates values of normal plot of residuals were closely scattered along the line of externally standardized residuals and maximum product is around 94.32%, from the fig 4-5 the points made sinusoidal graph on the externally standardized residual line to indicate the residual versus run numbers.

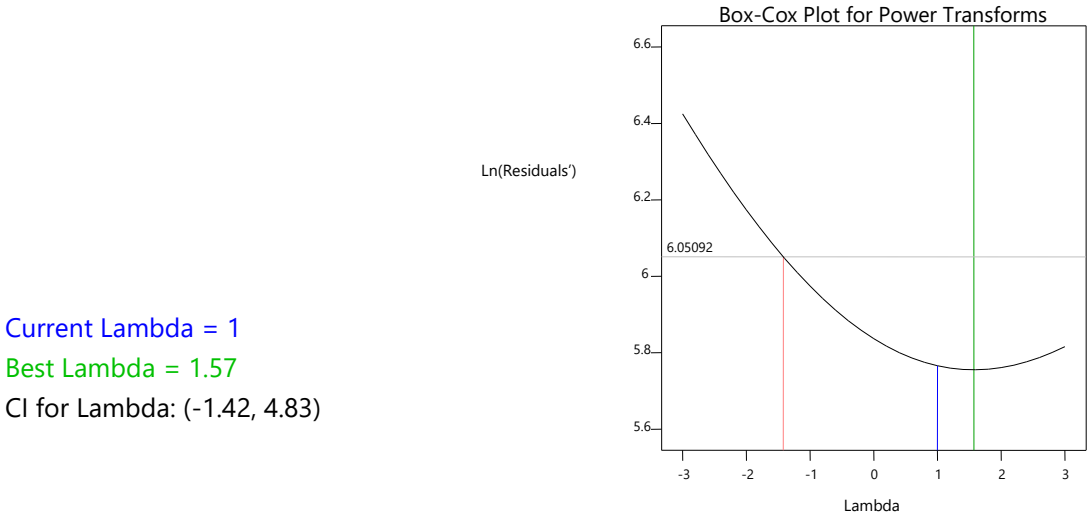


Figure 4-6: Graph of Box-cox for power transform

From the Fig 4-6.the box –cox for power transmission versus unit residuals CI Lambda is in the range of (-1.42, 4.83), thus the design the lambda was unit or 1 which is in the range while the best lambda is 1.57.

4.7.5 Comparison of actual and predicted biodiesel

The result from the experimental runs were analyzed based on actual value, predicted value, leverage and cook's distance ,the values from the software were tabulated in table 4.8below.

Table 4.8 Comparison of the result

Run Order	Actual Value	Predicted Value	Residual	Leverage	Cook's Distance
1	75.00	72.03	2.97	0.140	0.017
2	75.22	72.03	3.19	0.140	0.020
3	75.32	79.21	-3.89	0.061	0.011
4	85.00	87.39	-2.39	0.377	0.056
5	84.56	92.55	-7.99	0.268	0.326
6	71.32	77.19	-5.87	0.295	0.208
7	94.32	92.55	1.77	0.268	0.016
8	83.50	80.23	3.27	0.366	0.099
9	69.35	74.05	-4.70	0.361	0.198
10	73.32	72.03	1.29	0.140	0.003
11	60.00	65.87	-5.87	0.277	0.186

12	93.45	85.37	8.08	0.187	0.189
13	70.88	70.01	0.8653	0.333	0.006
14	83.50	79.21	4.29	0.061	0.013
15	85.00	86.39	-1.39	0.171	0.005
16	84.32	82.24	2.08	0.495[1]	0.085
17	83.50	79.21	4.29	0.061	0.013

4.7.6 Coefficients in Terms of Coded Factors

Table4.9 Coefficients in coded factors

Factor	Coefficient Estimate	df	Standard Error	VIF
Intercept	78.54	1	1.51	
A-methanol to oil ratio	7.18	1	1.53	1.04
B-Temperature	-6.16	1	1.90	1.02
C-catalyst concentration	-2.69	1	3.00	1.02

The coefficient approximation represents the predictable alter in reaction per unit vary in issue charge when all outstanding factors are held unvarying. The interrupt in an orthogonal design is the in general normal response of all the runs. The differential factor (df) value which is unity indicates orthogonality of factors to each other and the value of VIF close to 1 shows the multi-collinearity of factors and the value less than ten (10) are also acceptable.

4.7.7 Final Equation in Terms of Actual Factors

Table 4.10final equations in actual factors

Biodiesel	=
+125.00023	
+2.39281	methanol to oil ratio
-0.821372	Temperature
-2.68855	catalyst concentration

The equation in terms of real factors can be used to generate estimations about the response for given levels experimental runs. This equation should not be used to resolve the comparative

impact of each factor because the coefficients are scaled to put up the units of each factor and the cut off is not at the center of the plan gap.

4.7.8 Diagnostic Analysis of Model graph by one factor

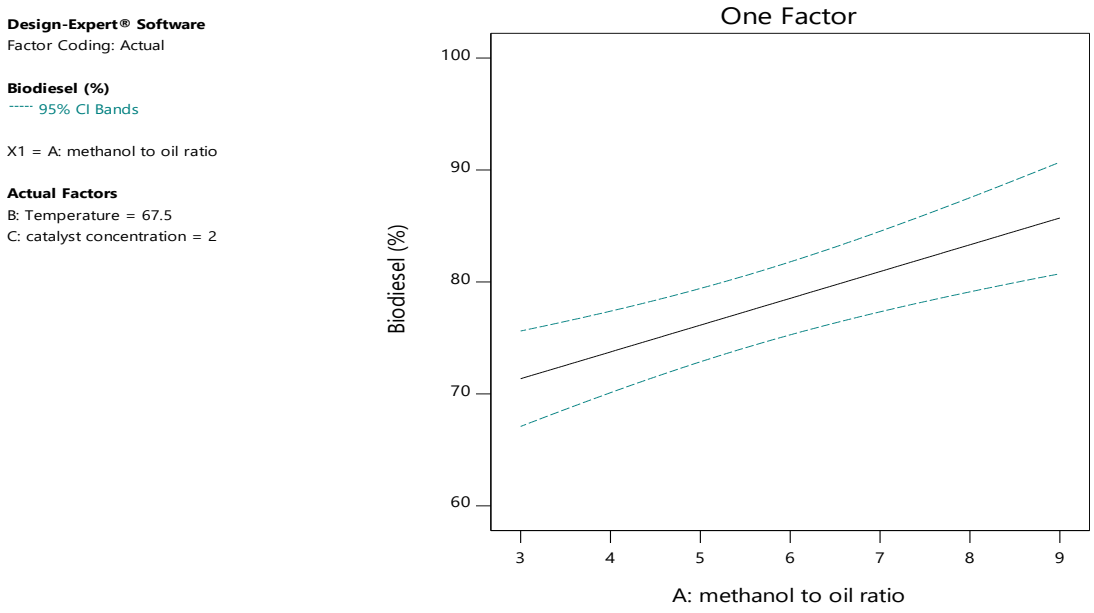


Figure 4-7:.one factor graph

4.7.9 Diagnostic Analysis of Model graphs of all factors

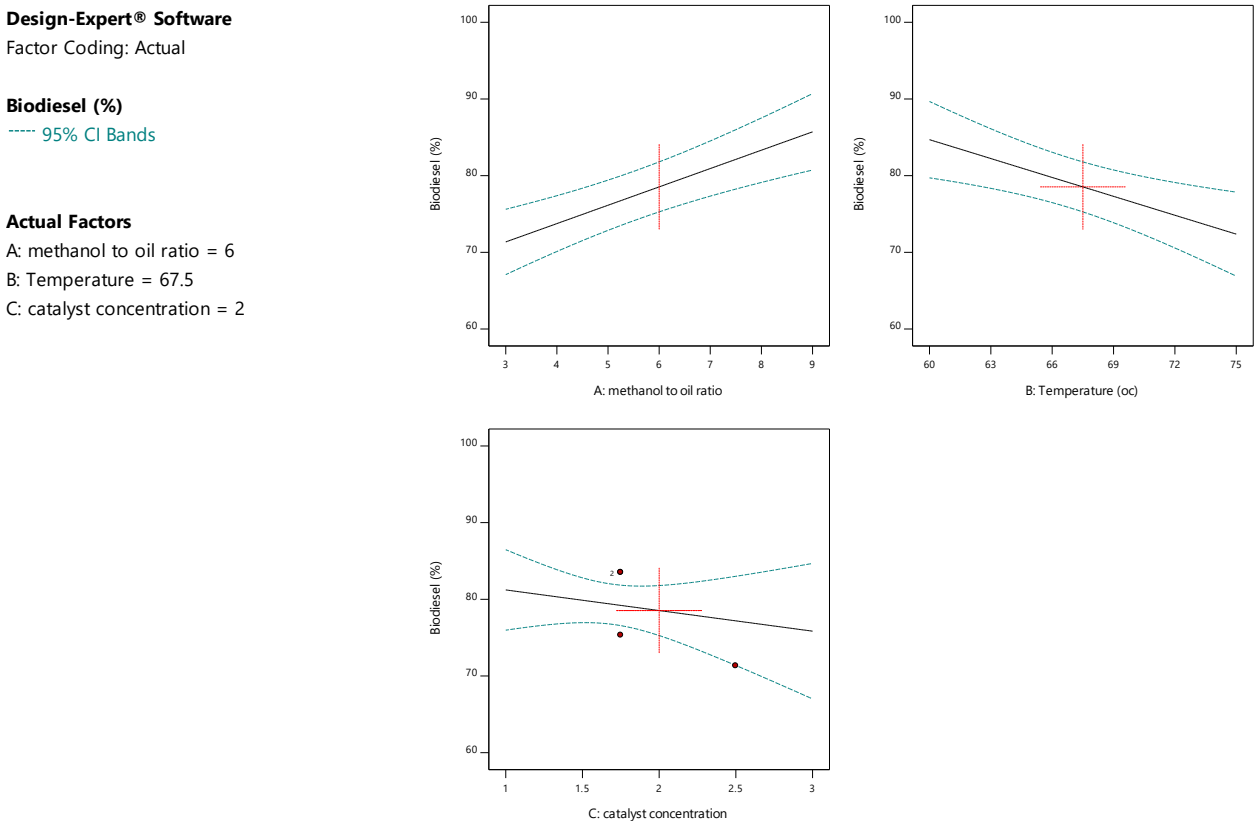


Figure 4-8: all factor graphs

Fig 4-7 demonstrates that as the biodiesel yield increases as methanol to oil ratio increases and Fig 4-8 illustrates the correlation between the three factors related to the biodiesel yield, as methanol to oil ratio increase biodiesel yield increases, as temperature increases biodiesel decrease and as catalyst saturated biodiesel nearly minimized.

4.7.10 Diagnostic Analysis of Interactions graph

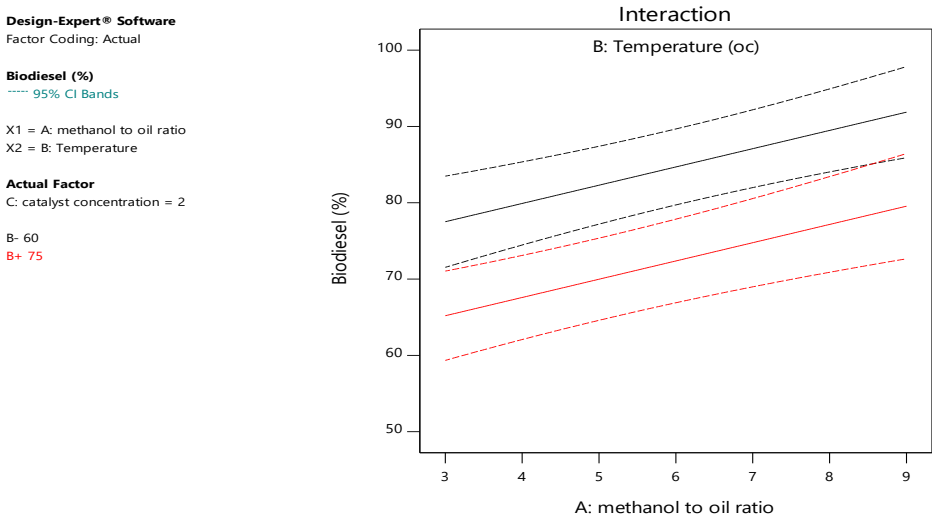


Figure 4-9:.Interaction graphs

The Fig 4-9.Illustrates the interaction graph between biodiesel yield, temperature and methanol oil ratio, thus as methanol oil ratio increases with medium temperature the biodiesel yield increases

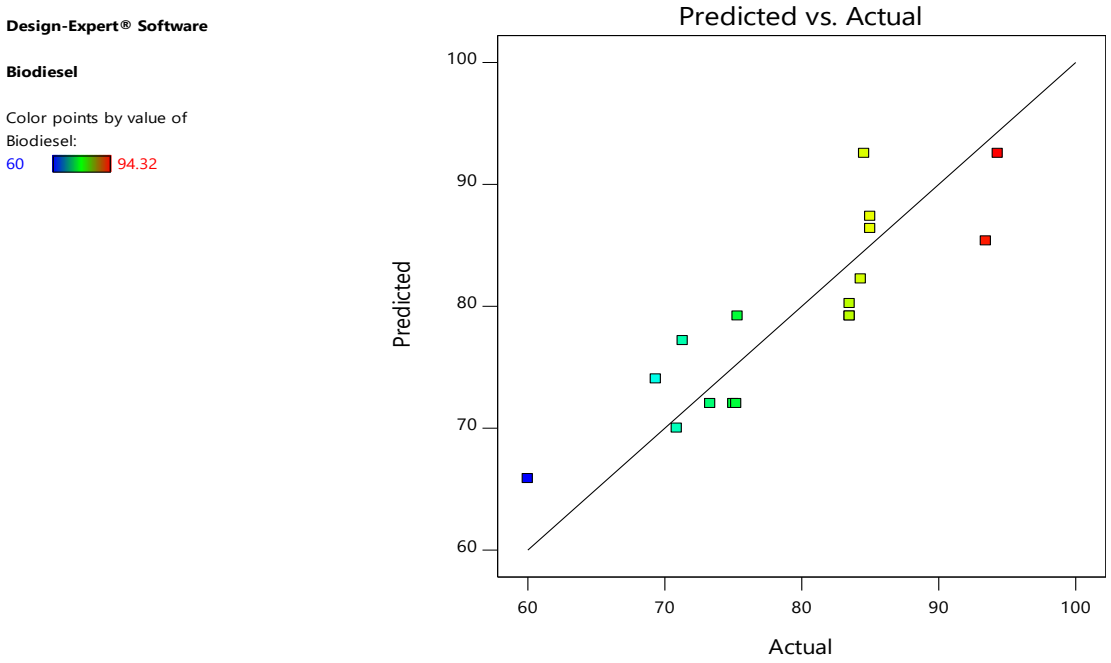


Figure 4-10: Predicted versus actual graph

4.7.11 Predicted versus actual graph Diagnosis model adequacy Test

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

The graph of the estimated results obtained using the developed correlation versus actual values forms a line of unit sloped correlation versus actual values forms a line of a unit slope, i.e. the line of a perfect fit with points corresponding to zero error between predicted values and actual values as shown in Figure 4-10.

Table 4.11: Model adequacy validation using Standard deviation, Mean and CV

Std. Dev.	**4.96**		R^2	**0.7524**
Mean	79.27		**Adjusted R^2**	0.6953
C.V. %	6.25		**Predicted R^2**	0.5637
			Adeq Precision	11.0981

The low value of the coefficient of variation (CV=6.25%) indicates that the result of the integral model is reliable. The quality of the model fit was evaluated by the coefficient of determination (R^2), this value is calculated to be 0.7524 for the response. The value of R-square (R2) was 0.7524 this indicates that 75.24% of the total variation in biodiesel yield was attributed to the experimental variables studied. The closer the R2 value to unity, the better the model will be as it will give predicted values which are closer to the actual optimum values for the response.

From Table 4.8 the regression model was found to be highly significant with the correlation coefficients of determination of R-squared (R^2), adjusted R-squared and predicted R-squared having values of 0.7524, 0.6953 and 0.5637 respectively. The adjusted coefficient of determination (R2adj=0.6953) is also very high, supporting the significance of the model. However, quadratic terms of temperature, quadratic terms of catalyst concentration and cross product of methanol to oil ratio and temperature (AB) are found to be insignificant ($p>0.05$). Regression analysis of the experimental data also shows that methanol to oil ratio and catalyst concentration of reaction variables has positive and negative linear effects respectively on biodiesel yield.

4.7.12 Diagnostic Analysis 3D model graph of adequacy Test

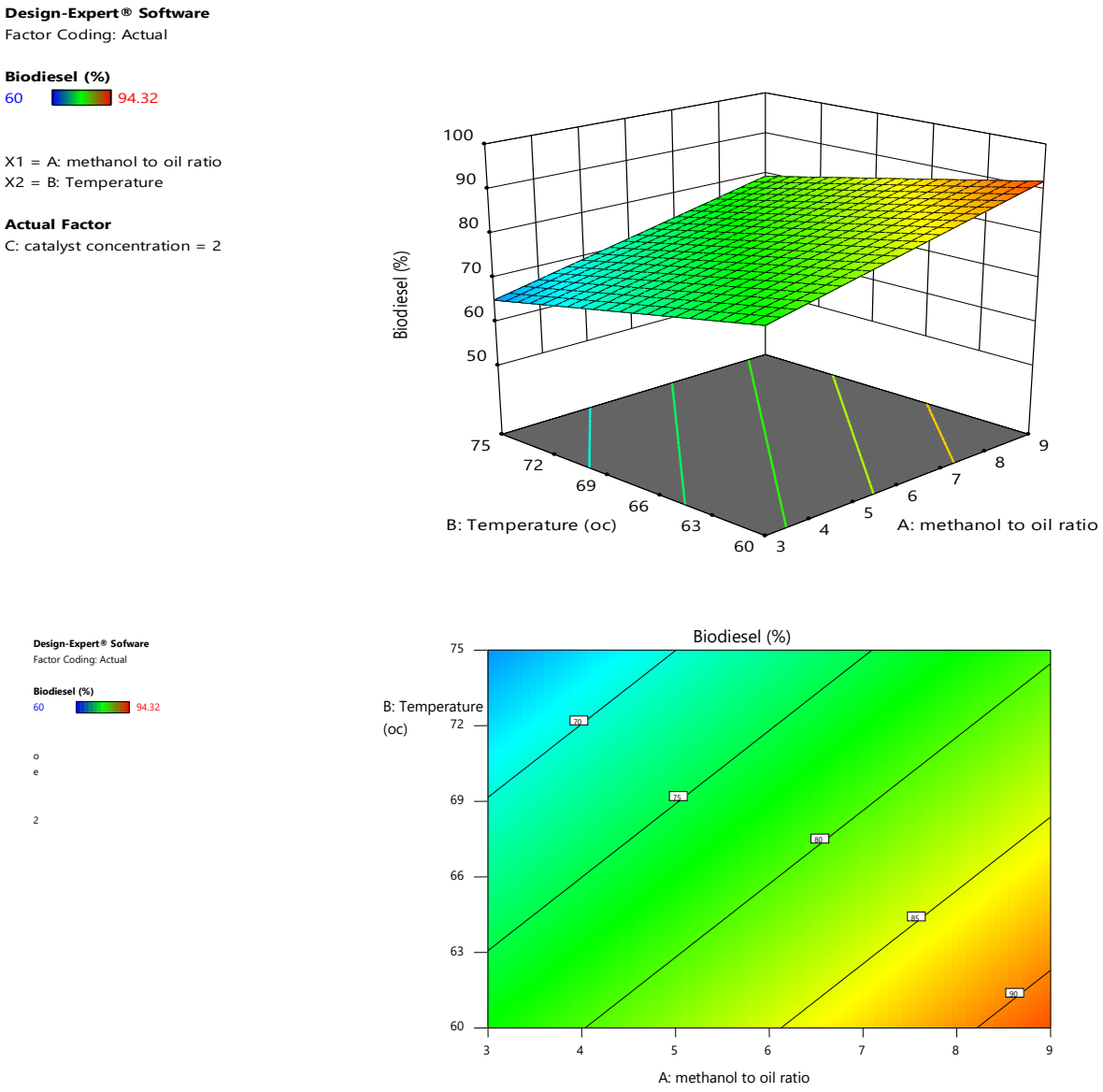


Figure 4-11:3Dmodel graph and contours line graph

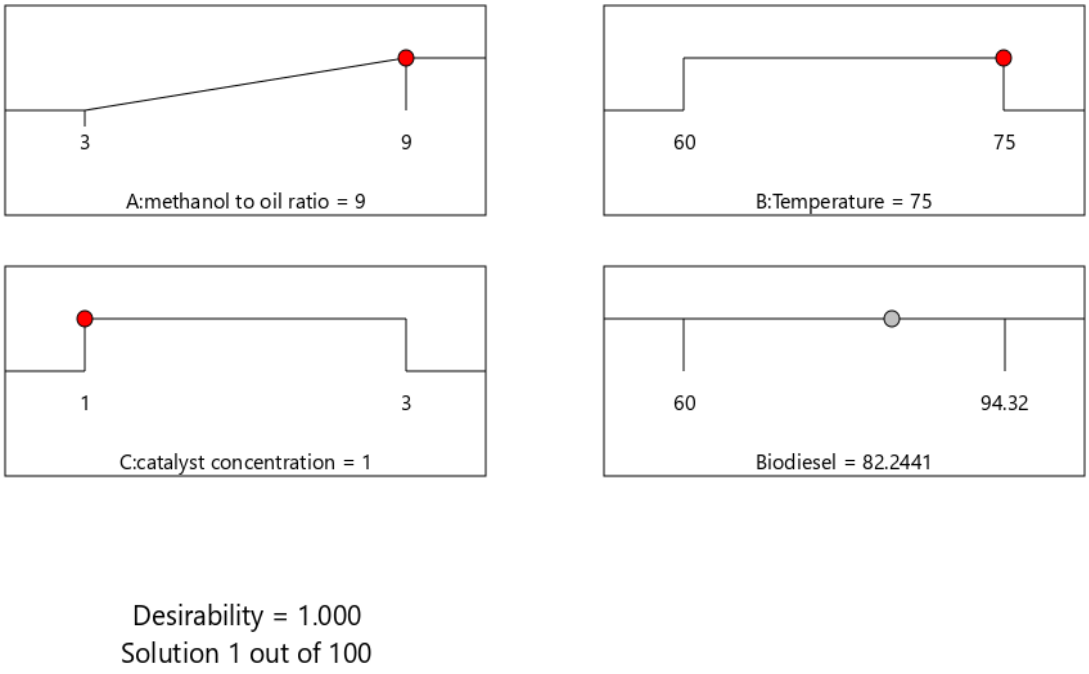


Figure 4-12: Desirability of biodiesel yield

The above indicates the numerical analysis with unit desirability which shows the model perfect fit and range of methanol to oil ratio used was between(3,9),temperature used in the range of (60,75^{o}c)and catalyst concentration was in the ratio of(1,3)

4.8 Discussion

In order to evaluate Soxhlet n-hexane as possible method for marula oil extraction, the impacts of temperature on the yield were evaluated and the oil was characterized. To determine the optimal safe operating conditions and study effects of temperature on the yield selected condition between 60 to 75^{o}c. Particle size effects on the yield were not studied. However, the material was ground prior to the extraction and after extraction the oil characteristics have been determined. The extraction period was dynamic and lasted from three hours to five hours based on temperature adjusted. Optimization of oil and Biodiesel were carried out using Design expert software and each characteristics of biodiesel were determined experimentally.

The effect of each process parameters was evaluated and physiochemical properties were determined. Catalyst loading beyond the optimum have the great effect on the production of biodiesel and it should maintain at the optimum. The biodiesel obtained in this study was 94.32% at the molar oil ratio of 9:1at the catalyst loading of 1.75%, this demonstrates that high biodiesel yield can be obtained at optimum catalyst loading.

5 Conclusion and Recommendation

5.1 Conclusion

Alternative Energy that is very essential to combat global warming particularly, the emission of Greenhouse gases is producing Biodiesel, which have less emission and have positive influence on environmental pollution. There are many resources useful for production of Biodiesel has future hope to solve dependence of fuels on fossil fuels.

From the experimental analysis carried out in this study reveals biodiesel produced from marula have acceptable quality. The marula seed oil was extracted using chemical extraction and chemically converted to biodiesel through transesterification to fatty acid methyl ether in the presence of KOH as catalyst. In this study different reaction parameter (reaction temperature, methanol to oil ratio and catalyst concentration) were analyzed to investigate biodiesel optimization. In the experimental analysis to optimize the effect of variable processes, for biodiesel production at optimum condition was evaluated using design expert software.

Generally, biodiesel is the most important alternative fuel to combat global warming manifesting itself throughout the world today and it is helpful for transportation to minimize carbon emission for vehicles.

5.2 Recommendation

Further study should be considered for the following points

- Shelf life of marula oil should be investigated in order to determine the oil stability during storage time.
- The effect of frying/cooking temperatures on the oxidative stability of the seed oils should be studied.
- A comparison of solvent extraction, aqueous extraction at higher temperatures and screw press extraction with supercritical co_2 extraction and aqueous enzymatic extraction at higher temperatures of marula
- The available varieties of the sclerocarya birrea seed in Ethiopia at different region should be studied and it may become economically competitive. The people need to be fully aware of sclerocarya birrea seeds oil uses for their specific purpose
- Ultimate analysis and gas chromatography of the biodiesel were not determined, thus Other researchers can investigate to determine the properties that were not determine by this study

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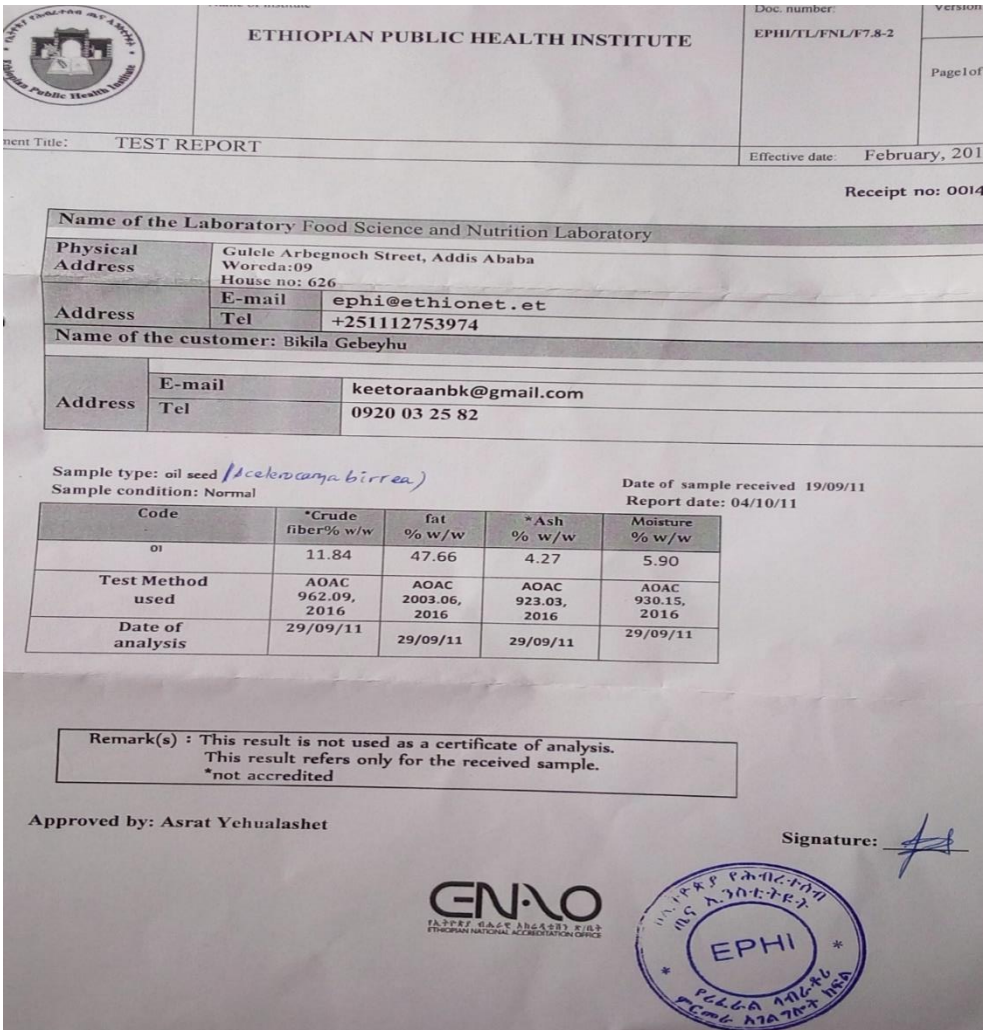
Appendixes

Appendix A: proximate Analysis of marula seed



ETHIOPIAN PUBLIC HEALTH INSTITUTE

Doc. number: EPHI/TL/FNL/F7.8-2 | Version | Page1of

ment Title: TEST REPORT | Effective date: February, 201

Receipt no: 0014

Name of the Laboratory Food Science and Nutrition Laboratory		
Physical Address	Gulele Arbegnoch Street, Addis Ababa Woreda:09 House no: 626	
Address	E-mail	ephi@ethionet.et
	Tel	+251112753974
Name of the customer: Bikila Gebeyhu		
Address	E-mail	keetoraanbk@gmail.com
	Tel	0920 03 25 82

Sample type: oil seed (Sclerocarya birrea)
Sample condition: Normal

Date of sample received 19/09/11
Report date: 04/10/11

Code	*Crude fiber% w/w	fat % w/w	*Ash % w/w	Moisture % w/w
01	11.84	47.66	4.27	5.90
Test Method used	AOAC 962.09, 2016	AOAC 2003.06, 2016	AOAC 923.03, 2016	AOAC 930.15, 2016
Date of analysis	29/09/11	29/09/11	29/09/11	29/09/11

Remark(s) : This result is not used as a certificate of analysis.
This result refers only for the received sample.
*not accredited

Approved by: Asrat Yehualashet

Signature:

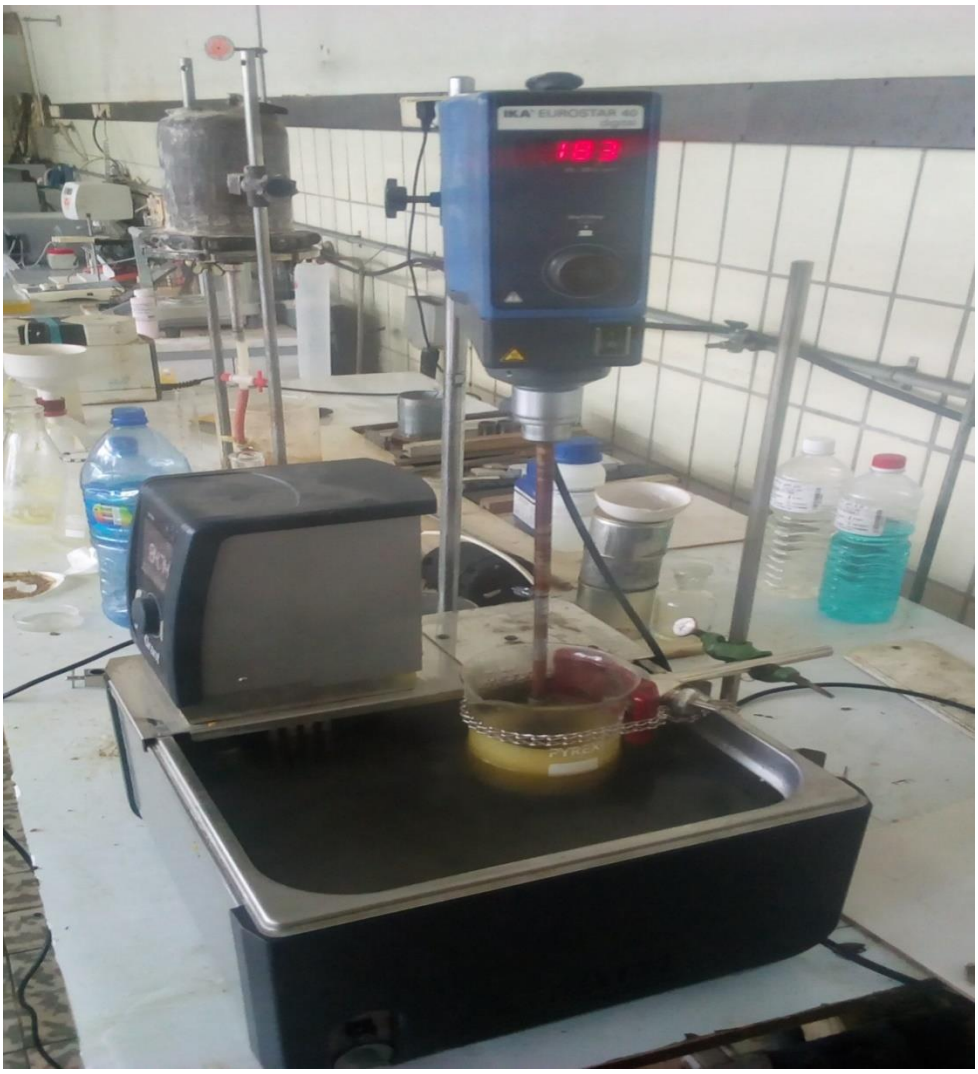
ENAO ETHIOPIAN NATIONAL ACCREDITATION OFFICE

EPHI

Appendix B: Soxhletapparatus set up duringoil extraction time

Appendix C: sample weighing figure for each run

Appendix D: oil stirring using stirrer for neutralization to remove free fatty acid



Appendix E: determined calorific value

GEOLOGICAL SURVEY OF ETHIOPIA
GEOCHEMICAL LABORATORY DIRECTORATE
Document Title: Hydrocarbon Laboratory Analysis Report

Doc.Number: GSE/F 5.10-2 | Version No: 1 | Page 1 of 1 | Effective date: May, 2017

Customer Name: - Bikila Gebeyehu

Issue Date: - 18/09/2020
Request No: - GLD/RN/173/20
Report No: - GLD/TR/578/20
Sample Preparation : - 60 Mesh
Number of Sample: -One (01)

Sample type: -Bio diesel
Date Submitted: - 03/09/2020
Elements to be determined:- Calorific Value.
Method of analysis:- Adiabatic Calorie Metter.

Collectors' Code	Calorific Value Cal/gm.
Sclerocarya Birrea	10178.77

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

Analysts
Haimanot Bayeh
Shashe Haile
Sisay Abay

Approved By
Alemnesh Abate

Quality Control
Negash Wodu

Geological Survey of Ethiopia
Central Geochemical Laboratory

Appendix F feed material requirement calculation results

$$\frac{noil}{nmethanol} = (Y)$$

Where: - Y is the ratio of methanol to oil (amount) used in the runs

Substitute mass for mole;

$$\frac{\frac{poil*voil}{\text{Moil}}}{\frac{\mathbf{pmethanol*Vmethanol}}{\mathbf{Mmethanol}}} = \boldsymbol{Y}$$

$$\frac{\frac{0.906g/ml*25ml}{277.8\text{g/mol}}}{\frac{\mathbf{0.79gm/ml*Vmethanol}}{\mathbf{32.04gm/mol}}} = \mathbf{1/6}$$

Therefore,**Vmethanol** required is **20.147ml**.

The amount of catalyst required was calculated by using the equation and

$$moil = poil * voil$$

$$moil = \frac{0.906gm}{ml} * 25ml$$

moil =22.65gm

$$\frac{massofcatalyst}{massofoil} = X$$

Where: - X is the amount of catalyst need for each runs (%)

The amount of catalyst required for the reaction when the ratio of catalyst weight to oil is 1.75%;

$$\frac{massofcatalyst}{22.65gm} = 1.75\%$$

Mass catalyst used was 0.396gm, the results for catalysts tabulated below

Table 1: The amount of catalyst and methanol

Oil to methanol ratio		Catalyst amount	
Ratio	Amount used (ml)		Amount used (gm)
1:3	9.92	1%	0.2265
1:6	20.147	1.75%	0.396
1:9	29.761	2.5%	0.56625

Table 2: Amount of catalysts and methanol used for biodiesel optimization

Reaction parameters	Run #1		Run#2		Run#3		Run#4		Run#5		Run#6	
Methanol volume(ml)	3:1	9.92	3:1	9.92	6:1	20.147	6:1	20.147	9:1	29.76	6:1	20.147
Catalyst concentration(gm)	1.75	0.396	1.75	0.396	1.75	0.396	1	0.2265	1.75	0.396	2.5	0.625
Temperature ^{o}c	67.5		67.5		67.5		60		60		67.5	

Reaction parameters	Run #7		Run#8		Run#9		Run#10		Run#11		Run#12	
Methanol volume	9:1	29.76	9:1	29.76	3:1	9.92	3:1	9.92	3:1	9.92	6:1	20.147
Catalyst concentration	1.75	0.396	1.75	0.396	1	0.2265	1.75	0.396	1.75	0.396	1.75	0.396
Temperature	60		75		67.5		67.5		75		60	

Reaction parameters	Run #13		Run#14		Run#15		Run#16		Run#17	
Methanol volume(ml)	3:1	9.92	6:1	20.147	9:1	29.76	9:1	29.76	6:1	20.147
Catalyst concentration(gm)	2.5	0.566	1.75	0.396	1.75	0.396	1	0.2265	1.75	0.396
Temperature	67.5		67.5		67.5		75		67.5	

Table 3; Standard Specifications of Biodiesel: USA and European

Property	Unit	USA	EU	Recommended Test method
		ASTM D 6751	EN 14214	
Density, 150C	Kg/m3	-	860 -900	ASTM D 445
Kinematic viscosity, 40oC	mm2/s	1.9 -6.0	3.5 -5.0	
Flash point	oC	≥ 120	≥ 130	ASTM D 93
Cloud point	oC	-	-	
Total sulphur 100%	w%	≤ 0.05	≤ 0.01	ASTM D 5453
Sulphated Ash	w%	≤ 0.02	≤ 0.02	ASTM D 874
Water content	mg/Kg	-	≤ 500	
Total contamination	mg/Kg	-	≤ 24	
Water and sediment	% vol.	≤0.05		ASTM D 2709
Corrosion (Cu) @50oC		≤ No.3	class 1	ASTM D 130
Cetane number	Mg	≥ 47	≥ 51	ASTM D 613
Acid number	KOH/g	≤ 0.8	≤ 0.5	ASTM D 664
Oxidation			≥ 6	
Stability 110oC	hours			
Methanol content	%w%		≤ 0.2	
Ester content	%w%		≥ 96.5	
Triglycerides	%w%		≤ 0.20	
Diglycerides	%w%		≤ 0.80	
Monoglycerides	%w%			
Free glycerol	%w%	≤ 0.02	≤ 0.02	ASTM D 6584
Total glycerol	%w%	≤ 0.24	≤ 0.25	ASTM D 6584
Iodine value	gI2/100g		≤ 120	
Phosphorus	mg/Kg	≤ 10	≤ 10	ASTM D 4951