

ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO ENGINEERING

OPTIMIZATION AND PRODUCTION OF BIODIESEL FROM SPENT COFFEE GROUND OIL USING ACID -BASE CATALYZED METHOD

BY

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A Thesis Submitted to Addis Ababa Institute of Technology, School of Chemical and Bio Engineering in Partial Fulfillments of the Requirement for the Degree of Master of Science in Process Engineering

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June 2019

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Declaration

I declare that, this thesis entitled "**Optimization and Production of biodiesel from spent coffee ground oil using acid base catalyzed method***"* has not been submitted in any form for another degree, diploma or an award at any university or other institution of the tertiary education. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due reference to the literature and discussions. Information taken from published and unpublished work of others has been acknowledged in the text and a list of references is given. The work was under the guidance of Professor Belay Woldeyes, instructor in Addis Ababa University, School of Chemical and Bio Engineering.

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Acknowledgments

First of all, I would like to thank to God for giving me health and patience to accomplish this thesis work. Moreover, I would like to thank and express my greatest appreciation to my Advisor professor Belay Woldeyes for his instruction, encouragement, valuable advice, continuous guidance and support throughout my research study. I really appreciate his encouragement, trust and inspiration that greatly motivated me to work hard, act efficiently and accomplish more.

I would also like to thank the Chemical and Bio Engineering Laboratory staff members especially Mr. Hintsasilasie Seifu for his successive support whatever I needed throughout my study. I am also thank my friends Yeshidagna Nigussie, Alelign Aliyu and Nahom Kahsay and others, who supported me directly or indirectly to accomplish this thesis work successfully.

Finally, I wish to express my deepest gratitude to my beloved families whose guidance, encouragement, wisdom, motivation, and expectations are indispensable to my achievements and will serve as a continuous inspiration for my future career. You are all the sources of my happiness and existence.

Abstract

In Ethiopia large amount of spent coffee ground are generated from various coffee houses, restaurants and households a result of the high consumption of coffee. Until now, there are no current profitable uses, and their adequate disposal constitutes a major environmental problem. The aim of this study was optimization of reaction variables and production of biodiesel from spent coffee ground oil using acid base catalyzed method. For this study, spent coffee grounds were collected from different coffee houses, Addis Ababa. The collected spent coffee grounds were dried in an oven at 105° C for 8 hours. The oil was extracted by applying a soxhlet extraction using n-hexane and then extracted oil was converted to biodiesel using acid catalyzed esterification followed by alkali-catalyzed transesterification. The physicochemical properties of the extracted spent coffee ground oil were found to be oil yield (13.09%), density (898kg/m^3), kinematic viscosity at 40℃ (45.91 mm^2/s), saponification value (192.5mgKOH/g oil), acid value (12.2mg KOH/g),free fatty acid (FFA) (6.1%) ,iodine value (81.9 g I_2/100g) and calorific value(37.74MJ/kg). The FFA in the spent coffee ground oil was reduced from 6.1 to 0.69% with 6:1 molar ratio of methanol to oil in the presence of 3.5wt% sulfuric acid at 90min. For the second step, an optimum biodiesel yield of 91.5% was obtained with 9:1 methanol to oil molar ratio, 1.5% KOH catalyst and 90 min reaction time. The fatty acid methyl ester composition of the biodiesel produced from SCG oil was done with using GC-MS and 17.65% of saturated and 82.5% unsaturated fatty acid methyl esters were identified. The physicochemical properties the produced biodiesel were found to be density (870.3kg/m^3), kinematic viscosity at 40℃ (4.13 mm^2/s), flash point (162℃) ,calorific value(40.39KJ/kg), cetane number(57.4), acid value (0.65 mg KOH/g and iodine value (178.5 g iodine/g). The results indicated that the properties of biodiesel produced agree with the limit ASTM D6751and EN 14214 standard. Therefore, the studied physicochemical properties of the waste coffee biodiesel suggest that this fuel can be used as a fuel in diesel engines.

Keywords: *Spent coffee ground; Biodiesel; Optimization, Esterification, Transesterification*

Table of Contents Page

Acknowledgments I

Abstract II

List of Tables VII

List of Figures VIII

Acronyms IX

Chapter One 1

1. Introduction 1

1.1. Background of the study 1

1.2. Statement of the Problem 3

1.3. Objectives of the thesis 4

1.3.1. General objective 4

1.3.2. Specific objective 4

1.4. Significance of the study 5

1.5. Scope of the study 5

Chapter Two 6

2. Literature Review 6

2.1. Recent research development 6

2.2. General overview of renewable energy 8

2.3. General overview of biodiesel 9

2.4. Advantages and limitations of biodiesel 9

2.5. Raw Materials for Biodiesel Production 10

2.6. General overview of coffee 12

2.7. Coffee production in Ethiopia 13

2.8. Spent coffee grounds as source of biodiesel 13

2.9. Oil Extraction 14

2.10. Biodiesel Production methods 16
2.10.1. Dilution 16
2.10.2. Micro-emulsions 17
2.10.3. Pyrolysis 17
2.10.4. Transesterification of oils 17
2.11. Catalysis for biodiesel production reactions 19
2.11.1. Homogeneous base-catalyzed transesterification 20
2.11.2. Homogenous acid catalyzed esterification 21
2.11.3. Combination of homogeneous acid base catalyzed method 22
2.11.4. Heterogeneous base catalyzed transesterification 23
2.11.5. Heterogeneous acid catalyzed esterification 23
2.11.6. Enzyme catalyzed transesterification 23
2.12. Factors Affecting Biodiesel Production process 24
2.12.1. Effects of moisture and free fatty acids 24
2.12.2. Effect of molar ratio of alcohol to oil 24
2.12.3. Effect of reaction temperature 25
2.12.4. Effect of reaction time 26
2.12.5. Effect of catalyst type and concentration 26
2.12.6. Effect of agitation speed 27
2.13. Biodiesel quality parameters and specification standards 27
Chapter Three 30
3. Materials and Methods 30
3.1. Sample collection and preparation 31
3.1.1. Materials 31
3.1.2. Methods 31

3.2. Extraction and purification of spent coffee ground oil 32
3.2.1. Materials 32
3.2.2. Methods..... 32
3.2. Characterization of spent coffee ground oil and biodiesel..... 33
3.2.1. Materials 33
3.2.2. Methods..... 33
3.2.3. GC-MS analysis of biodiesel 36
3.3. Design of experiment for acid base catalyzed reaction..... 36
3.4. Acid base catalyzed biodiesel production process 37
3.4.1. Materials 37
3.4.2. Methods..... 38
Chapter Four..... 40
4. Result and Discussion..... 40
4.1. Moisture content of spent coffee ground..... 40
4.2. Particle size of spent coffee ground 40
4.3. Spent coffee ground oil yield 41
4.4. Characterization of spent coffee ground oil 42
4.5. Statistical analysis of acid catalyzed esterification process 44
4.5.1. Development of the regression model equation..... 46
4.5.2. Analysis and adequacy of acid esterification model by ANOVA 47
2.5.3. Effects of Individual Process Variables..... 49
4.5.4. Effects of interaction between process variables..... 51
4.5.3. Numerical optimization and validation of the result..... 53
4.6. Statistical analysis of base catalyzed transesterification process 54
4.6.1. Effects of Individual Process Variables..... 58

4.6.2. Effect of interaction parameter on biodiesel yield 59
4.6.3. Numerical optimization and validation of the result 61
4.7. Physicochemical Properties of Biodiesel 62
4.7.1. GC-MS analysis of biodiesel 65
Chapter Five 66
5. Conclusions and Recommendations 66
5.1. Conclusions 66
5.2. Recommendations 67
References 68
Appendices 74
Appendix A: Composition of spent coffee ground oil 74
Appendix B: Experimental result of spent coffee ground oil 74
Appendix C: Amount of the reactant required 75
Appendix D: Standard specification of biodiesel 77
Appendix E: Calorific value of spent coffee ground oil 78
Appendix F: Laboratory result of GC-MS 79
Appendix G: Photos during laboratory activity 80

List of Tables Page

Table 2.1: Fatty acid profile of oils and fats used for biodiesel production 12
Table 2.2: Summery of Ethiopian's coffee production..... 13
Table 2.3: Soxhlet extraction oil yields reported in other studies..... 15
Table 2.4: Comparison of main biodiesel production technologies 19
Table 3.1: Variables for optimization of FFA reduction in esterification process 37
Table 3.2: Variables for optimization of biodiesel yield in transesterification process..... 37
Table 4.1 : Moisture content of spent coffee ground..... 40
Table 4.2: Particle size determination..... 41
Table 4.3: Summery of Physicochemical properties of spent coffee ground oil 44
Table 4.4: The experimental and predicted % FFA value after esterification process 45
Table 4.5: Model summary statistics for acid catalyzed esterification..... 46
Table 4.6: ANOVA result for acid catalyzed esterification reaction..... 47
Table 4.7: Desirability specifications for esterification variables and response..... 53
Table 4.8: Model validation of the acid esterification process 54
Table 4.9: The experimental and predicted biodiesel yield values after transesterification..... 55
Table 4.10: ANOVA result for transesterification reaction..... 56
Table 4.11: Model summary statistics for base catalyzed transesterification..... 56
Table 4.12: Desirability specifications for transesterification variables and response 61
Table 4.13: Optimized conditions and validation for transesterification process..... 62
Table 4.14: Summary of physicochemical properties of produced biodiesel..... 64
Table 4.15: Fatty acid profile of spent coffee ground biodiesel 65

List of Figures Page

Figure 2.1: Classification of catalyst used for biodiesel production 20
Figure 3.1: Experimental procedures 30
Figure 4.1: Effect of particle size on oil yield (%) 42
Figure 4.2 : Diagnostic plots for adequacy of proposed model 49
Figure 4.3: Effect of (a) methanol to oil ratio (b) catalyst (c) time on % FFA reduction 51
Figure 4.4: Effect of molar ratio of methanol to oil and catalyst to %FFA reduction 52
Figure 4.5: Effect of reaction time and catalyst concentration to %FFA reduction 52
Figure 4.6: Predicted vs. actual yield for transesterification 57
Figure 4.7: Effect of individual parameters on the yield of biodiesel 59
Figure 4.8: Interaction effect of methanol to oil molar ratio and catalyst on yield 60
Figure 4.9: Interaction effect of methanol to oil molar ratio and reaction time on yield 61

Acronyms

ANOVA	Analysis of Variance
ASTM	American Society for Testing and Materials
AV	Acid Value
CCD	Central Composite Design
C.V	Coefficient of Variances
CN	Cetane number
DOE	Design of Experiment
EN	European Standard
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
FTIR	Fourier-transform infrared spectroscopy
HHV	Higher heating value
IV	Iodine value
GC-MS	Gas Chromatography and Mass Spectrometry
RSM	Response Surface Methodology
SCG	Spent coffee ground
SCGO	Spent coffee ground oil
SV	Saponification Values

Chapter One

1. Introduction

1.1. Background of the study

Energy is a basic requirement for the economic development of every country. Every sector of the economy, including the agriculture, industries, transport, commercial and domestic sectors require energy. Among different kinds of energy source, fossil fuel is the main energy source behind the rapid industrial growth of the world (A. Demirbas 2008). However, it is also known as the main source of environmental problems that are faced today and its non-renewability and emission of hazardous greenhouse gases (Gerpen et al. 2011). Due to the development of transportation vehicles and agricultural machinery, the production and consumption of petroleum oil increases persistently and it has been reported that about 75 million barrels of crude oil is consumed worldwide daily (Birhanu and Ayalew 2017).

The demand for fuel is increasing because of expansion of infrastructures and also the growing economy and as a result, the money spent to import the fuel is also rising (Gashaw and Getachew 2015) Ethiopia spends a large amount of money for importing modern energy sources. During the year 2017/18, about 3.8 million metric tons of petroleum products worth Birr 58.6 billion were imported by the Ethiopian Petroleum Enterprise (Ethiopian 2017). Due to the rising oil prices, environmental concerns and interests in energy security, different countries of the world have taken biofuel production as a potential solution (Dan and Hall 2015).

Ethiopia has a huge biomass energy potential with estimates putting the national woody biomass stock at 1,149 million tonnes with annual yields of 50 million tonnes in the year 2000. Biomass distribution across the country is uneven, with the northern highlands and eastern lowlands having low biomass cover (MWE 2012). Agro-processing industries, such as processing sugar-cane bagasse, cotton stalk, coffee hull and oil- seed shells, present an opportunity for biomass energy. But currently, there are no grid-connected biomass power plants(REEEP 2014). Biodiesel fuel, derived from biomass is believed to be an attractive substitute for petroleum-based diesel fuel, as it is renewable, readily biodegradable, non-toxic and has a low sulphur and aromatic content(A. Demirbas 2008) .

In most developed countries, biodiesel is produced from rapeseed, sunflower, soybeans, and peanuts, which are essentially edible. The use of edible oil is not suitable for a resource poor developing countries like Ethiopia ,owing to its effect on food security (Keneni 2017) . Therefore, in order to overcome this problem, the feedstock for the biodiesel production must be replaced by nonedible oil and oil extracted from waste substances have become more attractive as an alternative feedstock. Therefore, for this study oil extracted from the spent coffee ground is used for the production of biodiesel. Coffee is one of the most consumed beverages in the world and spent coffee ground is the solid residue obtained after brewing coffee grounds (Kondamudi 2008).

Coffee is the second largest traded commodity worldwide, and the world's coffee production in 2017/2018 is estimated at 9.34 million tons. An estimated 3.5 billion cups of coffee are consumed worldwide every day (Patra et al. 2016). It is grown in over 70 countries and amounts to over 16 billion pounds of beans every year(Yordanov et al. 2016). Ethiopia is the birthplace of coffee Arabica. It is grown by over 4 million smallholder farmers and employs 15 million people. Ethiopia is the world's sixth largest coffee producer, accounting for 4 percent of production (Asfaw 2014). Ethiopia's coffee production during the year 2017/18 is estimated at 7.05 million 60-kilo bags and its consumption is estimated at 3.07 million 60-kilo bags (Coffee annual report 2018).

Due to the great consumption of this product, large amounts of residues are generated in various coffee houses and restaurants and they represent a massive waste stream that poses a significant disposal challenge due to the presence of toxic compounds like caffeine, polyphenols and tannins that may result in environmental pollution (Hiwot 2014). However, spent coffee ground contain lipids, approximately 11 -20 % w/w on a dry weight basis, that can be potentially used as a feedstock for production of sustainable and cost-effective biodiesel without the need for cultivating energy crops and/or converting food to fuel (Kondamudi 2008).

Biodiesel production remains a profitable aspect of renewable energy after the adventure of Rudolf Diesel's test of vegetable oil as fuel for the engine (Goyal, Sharma, and Jain 2013). Biodiesel consists of alkyl esters derived from either the transesterification of triglycerides in oils and fats, or the esterification of free fatty acids with short-chained alcohols (Knothe 2010).

The production of biodiesel by transesterification has a drawback because the utilization of high FFA feedstock in biodiesel production processes leads to depletion of the catalysts, as well as increased purification costs, because the homogeneous alkaline catalyst saponifies the FFA, producing excess soap (Bojan and Durairaj 2012) . Esterification of oil to alkyl esters in the presence of an acidic catalyst is a route to improve the use of high FFA oils in biodiesel production (El-mashad 2008). To mitigate the problem of saponification during base catalyzed transesterification, two-step method is most commonly used (Ajala et al. 2017).

Esterification is normally carried out in a homogeneous phase in the presence of acid catalysts such as H_2SO_4, H_3PO_4 and HCl. The most common catalysts for the transesterification reaction are the alkali catalysts such as sodium hydroxide(NaOH) and potassium hydroxide(KOH) which are being used commercially in biodiesel production (Ma and Hanna 1999). Biodiesel can be used either a pure fuel (B_{100}) or can be blended with petroleum diesel to any concentration (Walz et al. 2014).

1.2. Statement of the Problem

Ethiopia is not a fossil fuel producing country yet. Most people living in Ethiopia have, until now unable to satisfy their energy requirements with fossil fuel. Due to the expansion of infrastructures and the growing economy, the demand of fossil fuel is increasing and as a result, the money spent to import the fuel is rising. Biodiesel is a potential alternative energy source that could replace fossil fuel. This thesis is intends to address the problem of spent coffee ground wastes, cost of biodiesel feedstock and dependency of fossil fuel. In Ethiopia large amount of spent coffee grounds are generated from various coffee houses and restaurants. This spent coffee grounds are not utilized till now ,they are simply rejected as waste, this leads to problems related to the waste management and disposal ,so that effective utilization at this spent coffee ground are necessary. The use of edible oil for biodiesel production may cause inflation of cost of oil leading to food insecurity because it is high cost and 75-80% of biodiesel production cost is raw material (Keneni 2017) .

Ethiopia’s coffee production during the year 2017/18 is estimated at 7.05 million 60-kilo bags and its consumption is estimated at 3.27 million 60-kilo bags (192.5metric tonnes). An availability of over 178.5 metric tonnes per year of spent coffee ground, wastes are generated

(Tefera 2018). Since, reutilizations of these residuals are a relevant subject. According to a recent research result from (Kondamudi 2008) 11 %-20 % by weight of oil was found within the spent coffee ground and about 0.91g of the spent coffee grounds are produced per 1g of ground coffee. This oil also has similar properties to current feedstock used to produce biodiesel. However ,Spent coffee ground oil contains high free fatty acid greater than 1% and direct transesterification of oil having free fatty acid content using a base catalyst promotes saponification as a side reaction which lowers the biodiesel yield by deactivating the catalyst (Patra et al. 2016). Since, pretreatment with the aid of acid catalyzed esterification reaction process should use to overcome the challenges encountered by the one-step transesterification process. The aim of this thesis is to study the spent coffee ground that can used as potential raw material for biodiesel production. The special attention is optimizing the experimental conditions such as the molar ratio of methanol to oil, catalyst concentration and reaction time on using acid base catalyzed process, and comparing the fuel properties of biodiesel with international standards.

1.3. Objectives of the thesis

1.3.1. General objective

The General objective of this thesis is optimization of reaction parameters and production of biodiesel from spent coffee ground oil using acid - base catalyzed method.

1.3.2. Specific objective

The specific objectives of this thesis are:

- To extract and determine the physicochemical properties of the spent coffee ground oil.
- To study the effect of process variables on the acid base catalyzed reaction.
- To characterize the physicochemical properties of biodiesel.

1.4. Significance of the study

- The biodiesel of the spent coffee grounds can help to reduce the fossil fuel consumption as alternative and reduces environmental pollution.
- The result of this study can be used as a reference for coffee house owners who are interested to producing their fuel requirements by establishing small-scale biodiesel production plant from their own spent coffee grounds generated daily and for the academic and research community conduct further studies.

1.5. Scope of the study

The study generally covers:

Preparation of spent coffee ground; oil extraction ; physicochemical analysis of extracted oil; optimization of acid-base catalyzed process conditions such as (methanol to oil molar ratio; catalyst concentration and reaction time) and characterization of the produced biodiesel.

Chapter Two

2. Literature Review

2.1. Recent research development

(Deligiannis 2011) has tried to carry out the study of oil extraction from spent coffee grounds for biodiesel production. He collected the coffee grounds and dried it in an oven at around 105^{o}C; the moisture content can be reduced in it (around 18-45%). The extraction was done applying a Soxhelet process and the Soxhelet device temperature is maintained at (60-75^{o}C). An organic solvent such as n-hexane was used. The oil content from spent coffee grounds has (10-15%) on dry weight basis. The oil was converted to biodiesel via transesterification reaction. All the reactions were carried out at 65 ℃ for 2 h with anhydrous methanol in methanol-to-oil molar ratio, 9:1using sodium hydroxide (NaOH) as catalyst in amount (1%). The conversion of coffee oil was found to be about 92 %.

(Hiwot 2014) has tried to carry out waste coffee residue oil of yirgalem as potential raw from indigenous species for biodiesel production. Oil was extracted using n-hexane as a solvent from waste coffee residue of yirgalem. The oil contents was 19.7 % w/w. Transesterification were carried out oil using methanol in the presence of basic catalysts to produce biodiesel. Three experiments were carried out by varying methanol to oil molar ratio, temperature % and %w/w of NaOH to oil for 3 hours. GC-MS analysis of methyl ester chemical compositions were 35.90 wt.% methyl palmitate (C16:0), 38.28 wt. % methyl linoleate (C18:2), 16.42 wt. % methyl oleate (C18:1) and 9.40 wt.% methyl stearate (C18:0) . An optimum of 95.84 fatty acid methyl ester conversion were obtained at a methanol to oil molar ratio of 6:1, 1.0 % mass NaOH, 65°C reaction temperature and 3 hour reaction time . The energy content of the oil and biodiesel were 37 MJ/Kg and 38 MJ/ Kg, which is determined by bomb calorimeter.

(Al-hamamre 2012) studied effect of type of solvents with different extraction periods for yield of oil extraction. The dried SCG (60 g) and 250 mL solvents (isopropanol, ethanol, and acetone as polar solvents and toluene, chloroform, hexane and n-pentane as nonpolar solvent) were used in this work for Soxhlet extraction. The yield of SCG oil ranges from 8.60% to 15.28% on a dry weight basis depends on type of solvent and time extraction. The highest yield is 15.28% (in a 30 min extraction time) when hexane is used as solvent. The amount of oil extracted by the polar

solvents ranges from 11.43% (in 70 min extraction time with isopropanol extraction solvent) to 12.92% (in 30 min extraction time with acetone). The results indicate that AV of SCG oil extracted with hexane is (7.3 mgKOH/g) and FFA is 3.65%. This value is lower than the values for spent coffee oil extracted with the other solvents (ethanol 3.85%, isopropanol 6.4%, chloroform 4.55%, and toluene 4.15%). The extracted oil are converted into fatty acid methyl ester by base catalyzed esterification. With one step alkali-catalyzed transesterification, oil conversion to methyl ester can be enhanced from 55–85% by increasing the reaction time, the reaction temperature and the catalyst concentration and methanol to oil molar ratio.

(Kondamudi 2008) has tried to study the extraction of biodiesel from spent coffee grounds and the kinetics of transesterification and purification by High Performance Liquid Chromatography (HPLC) was also discussed. He collected the coffee grounds and dried it overnight in an oven at 50℃ to remove moisture and then refluxed for 1h with n-hexane to extract the oil from the coffee particles. 300ml of solvent was used for 100g of dried spent coffee grounds for the extraction of oil. The solution was separated by filtration from coffee grounds and oil was separated from solvent using rotary evaporator. The crude oil was quantified using HPLC and the free fatty acids were converted into soap by mixing caustic water with the oil extracted. Soap was removed by centrifuging the crude oil for 30min at 5000 rpm and the purified oil was used for biodiesel production through transesterification. The transesterification was done by adding methanol and KOH to the Triglycerides. The reaction mixture was refluxed for 2 h each time. The presence of linolic acid (40.4%), palmitic acid (51.4%) and stearic acid (8.3%) was also determined.

(Ciesielczuk, Karwaczynska, and Sporek 2015) has aim to study the use of spent coffee grounds (SCG) in energy recycling using a combustion process. The SCG which is a left over from coffee made is neutralized and dried in room temperature. This SCG was then mixed with grinding dust, from beech wood processing with SCG additive waste of 10 and 25% (m/m). Using SCG as an additive has some difficulties such as high humidity of waste prevented from briquetting. A product with 10 and 25% addition of SCG was characterized by lower density, lower hardness, and uneven surface to a product made without any addition. Beech wood calorific value is high and SCG addition is making it even higher. The calorific value with 10% and 25% SCG additive is 19.12 (MJ/Kg) and 20.32 (MJ/Kg) respectively. The additive is worth considering due to a

number of factors. It has high calorific value compared to other briquettes made from pure wood and hence it contributes to an increase of profit to use as an energy source.

2.2. General overview of renewable energy

Renewable energy can replace conventional fuels in four distinct areas: electricity generation, hot water/space heating, motor fuels, and rural energy services. About 16% of global final energy consumption comes from renewable resources, with 10% of all the energy from traditional biomass, mainly used for heating, and 3.4% from hydroelectricity. New renewable (small hydro, modern biomass, wind, solar, geothermal, and biofuels) account for another 3% and are growing rapidly (Resources 2011). At the international level, at least 30 nations around the world already have renewable energy contributing more than 20% of energy supply. Wind power, for example, is growing at the rate of 30% annually, with a worldwide installed capacity of 282.5 (GW) at the end of 2015 (Ara et al. 2017).

Biomass is the fourth largest source of renewable energy in the world (Drożyner et al. 2013). The two main sources of biomass are the purpose-grown energy crops and wastes materials. Waste cooking oils, animal fats and other biomass residues are an examples for utilizing waste sources for biofuel (Raley and Austin 2018). Biofuels can be any liquid or gaseous fuels, which can be produced from biomass, including biodiesel, ethanol and biogas. The most common biofuels used in transport sector is biodiesel. They can complement and/or replace fossil fuels and reduce carbon emissions in the transport sector with/without modest changes to vehicle technology (i.e. engines) and to the existing infrastructure for fuel distribution (Version 2005) .

Ethiopia is producing various kinds of renewable energy to fulfill its energy demand. Hydropower is a major source in addition to efforts on solar, wind and geothermal energy productions. The generation heavily relies on hydropower with 3,800 MW equal to 89% of total generation capacity. Wind is the second electricity source with 324 MW equal to 8% of total generation capacity, while biomass, geothermal and liquid fossil fuels provide only 2% of total generation capacity(FDRE 2012). However, there is a huge energy demand and supply gap, which is currently covered by importing fossil fuel.

Ethiopia is currently using 75% of foreign currency earnings from export sector to buy and import oil; the majority of the fossil fuel is used by the transport sector and this is a huge burden

for the economy of the country (Birhanu and Ayalew 2017). Bio-fuel production, which can be a substitute for fossil fuel that Ethiopia is currently importing, is given a little emphasis. There is a little effort in the country to produce biofuel energy. This little effort should be organized and converted to a large scale bio-fuel production level in order to minimize the huge energy gap in the country (Consumption and Resources 2016). Ethiopia's biomass energy resource potential is considerable. Agro-processing industries, such as processing sugar-cane bagasse, cotton stalk, coffee wastes and oil- seed shells, present an opportunity for biomass energy(REEEP 2014).

2.3. General overview of biodiesel

Biodiesel refers to the kinds of alternative fuels derived from vegetable oils or animal fats. The prefix bio refers to renewable and biological nature, in contrast to the traditional diesel derived from petroleum; while the diesel fuel refers to its use on diesel engines(Venter 2013). The concept of biofuel is not new. Rudolph Diesel was the first to use a vegetable oil (peanut oil) in a diesel engine in 1911(Ma and Hanna 1999) . Biodiesel is the most commonly used liquid biofuels in the transport sector .Technically, the term biodiesel refers to mixtures of fatty acid alkyl esters produced by transesterification of vegetable oils and animal fats with alcohols or via esterification of free fatty acids with alcohols (Knothe and Gerpen 2005).

Biodiesel has good properties like renewability, biodegradability, lower emission profile and excellent lubricity amongst others. One of the biggest advantages of biodiesel compared to many other alternative fuels is that it can be used in existing diesel engines without modification, and can be blended in at any ratio with petroleum diesel. Due to the great molecular similarities between biodiesel and petroleum based diesel, this alternative fuel has a chance of fulfilling the technical requirements of diesel fuel (A. Demirbas 2008) reported that biodiesel results in a 45% reduction in total hydrocarbon emissions, 47% reduction in CO emissions and 66% reduction in particulate matter (PM) emissions. (Ma and Hanna 1999).

2.4. Advantages and limitations of biodiesel

Advantages:

- Biodiesel is renewable, non-toxic, non-flammable, portable, readily available, biodegradable, sustainable, eco-friendly, sulphur free and aromatic content, this makes it an ideal fuel for heavily polluted cities. Biodiesel also reduces particular matter content in the ambient air and

hence reduces air toxicity. It provides a 90% reduction in cancer risks and neonatal defects due to less polluting combustion (Atabani et al. 2012).

- Biodiesel has higher cetane number (about 55 to 65 depending on the vegetable oil) than petroleum diesel (47 to 53) which reduces the ignition delay (Sivaramakrishnan and Ravikumar 2006)
- Biodiesel has superior lubricity properties. This improves lubrication in fuel pumps and injector units, which decreases engine wear, tear and increases engine efficiency.
- Biodiesel is safe for transportation, handling, distribution, utilization and storage due to its higher flash point (above 100-170°C) than petroleum diesel (60-80°C)(Wakil et al. 2015).

Limitations:

- Biodiesel has 12% lower energy content than diesel, this leads to an increase in fuel consumption of about 2-10%. Moreover, biodiesel has higher cloud point and pour point, higher nitrogen oxide emissions than diesel. It has lower volatilities that cause the formation of deposits in engines due to incomplete combustion characteristics (Knothe and Gerpen 2005)
- Biodiesel causes excessive carbon deposition and gum formation (polymerization) in engines and the oil gets contaminated and suffers from flow problem. It has relatively higher viscosity (11-18 times diesel) and lower volatility than diesel and thus needs higher injector pressure (Knothe and Gerpen 2005)
- Oxidation stability of biodiesel is lower than that of diesel. It can be oxidized into fatty acids in the presence of air and causes corrosion of fuel tank, pipe and injector.

2.5. Raw Materials for Biodiesel Production

The raw materials used for production of biodiesel can be classified as plant derived, animal derived, microbial or waste materials (Walpita 2012). The most popular plant derived oils used for biodiesel production are canola, coconut, cottonseed, groundnut, jatropha, karanj, olive, palm, peanut, rapeseed, safflower, soybean and sunflower oils. Waste oils and fats (beef tallow, lard and yellow grease), waste cooking oil, the greasy by-product and microalgae oil are also considered as potential alternative feedstock for biodiesel production (Joshi 2008) .

The choice of biodiesel feedstock is determined by cost and characteristic. The cost of feedstock accounts for about 75% of the total cost of biodiesel production. Therefore, alternative feedstock's which produce high quality oil at a low cost need to be investigated in order for biodiesel to become economically viable (Boro et al. 2014). The cost of producing biodiesel is much higher than convection fuel, particularly when refined oil is used due to the high cost of the raw material (Andrew 2017). Another important factor in biodiesel production is the fatty acid composition of the source of oil or fat (Table 2.1) (Gerpen et al. 2011). Biodiesel, which contains high levels of unsaturated fatty acids, are less viscous and show higher pour and cloud points properties, which make biodiesel suitable for warm and cold weather conditions (Ahmia et al. 2014).

Higher saturated fatty acid content corresponds to higher viscosity, density, and fusion temperature. Therefore, it is desirable that raw materials for biodiesel production are rich in monounsaturated fatty acids such as oleic acid (Knothe and Gerpen 2005). Many researchers have initiated work on the use of low cost non-edible oils as alternative feedstock for biodiesel production. Among non-edible oil feedstock, seeds of castor and jatropha, and microalgae oil are proved to be a one of the highly promising reliable source having high seed oil content (Ahmia et al. 2014). For instance, the one solution to help mitigate the current economic and environmental issues associated with biodiesel production is to use waste oils and fats as the feedstock. One of these waste alternatives is the oil extracted from spent coffee grounds. Spent coffee ground just to mention as promising sources of waste oil for biodiesel production to avert food shortage (Kondamudi 2008).

Table 2.1: Fatty acid profile of oils and fats used for biodiesel production

Oils/fats	Palmitic (C16:0)	Palmitoleic (C16:1)	Stearic (C18:0)	Oleic (C18:1)	Linoleic (C18:2)	Linolenic (C18:3)	Others
Canola	3.5	-	0.9	64.4	22.3	8.2	0.7
Cottonseed	28.33	-	0.89	13.27	57.51	-	-
palm oil	43.70	0.3	4.50	40.20	9.80	0.50	1.9
Jatropha	14.20	1.0	6.90	43.10	34.40	-	3.0
Microalgae	15.5	17.3	0.3	1.3	2.2	0.9	62.5
Rapeseed	3.49	-	0.85	64.40	22.30	8.23	0.7
Soybean	11.75	-	3.15	23.26	55.53	6.31	-
Sunflower	6.08	0.1	3.26	16.93	73.73	-	0.2
Tallow	29.0	-	24.5	44.5	-	-	2.0

2.6. General overview of coffee

Coffee is one of the most important agricultural commodities in international trade ranking second after fossil fuel and representing an important source of income for millions of people in coffee growing countries (such as Asia, Africa and Latin America) (Slater A. & Mishra K. 2012). Coffee is produced in more than 70 countries. There are approximately 80 species that have been identified to belong in the genus Coffea. However, only two types of beans are economically significant and are cultivated for commercial use: Arabica *(coffea Arabica)* and Robusta *(coffea canehora),* each a magnitude of verities adapted to a board range of ecological and cultural conditions (Asfaw 2014).

Coffee is a tropical plant, which grows between the latitudes of 25degree North and 25-degree south. Ideal average temperatures range between 15 – 24℃ for Arabica and 24 - 30 ℃ for Robusta (Ga, Homann, and Hm 2016). Arabica is considered to be a coffee of superior quality due to the milder and more flavorful taste developed during roasting of the beans and represents 70-75 % of the total worldwide production while Robusta represents about 25-30% (Blinová et

al. 2017). The mainly producers of coffee in the world are Brazil, Colombia, Vietnam and Ethiopia(Bank, Global, and Discussion 2010).

Total worldwide production of Arabica coffee in 2016/17 accounted for 5.3 million tonnes, while Robusta coffee accounted for 3.8 million tonnes. The production of Arabica coffee is estimated to increase in 2017/18 by 10.2 % relative to 2016/17, whereas Robusta coffee output is expected to decrease by 10.6 %. World coffee production for 2018/19 is estimated at a record 174.5 million bags, up 15.6 million from the previous year (USDA Foreign Agricultural Service 2018)

2.7. Coffee production in Ethiopia

Ethiopia is the birthplace of coffee Arabica. Ethiopia has been into coffee production for more than 1100 years now (Kodama 2009). It is grown by over 4 million smallholder farmers and employs 15 million people, or roughly 15 percent of the country's population at different points along the value chain. Ethiopia is the world's sixth largest coffee producer. It is also the largest producer in Africa, accounting for about 40 percent of continental production (Coffee annual report 2018).The major coffee producing administrative regions are Kefa, Sidamo, Ilubabor, Welega and Harerge followed by Shewa, Gamu Gofa, Arsi, Gojam, Bale and Welo producing substantial amounts, mainly for local consumption (Asfaw 2014) . Ethiopia's coffee production during the year 2017/18 is estimated at 7.05 million 60-kilo bags and its consumption is estimated at 3.27 million 60-kilo bags (table2.2) (Tefera 2018) .

Table 2.2: Summery of Ethiopian's coffee production

Year	2013/14	2014/15	2015/16	2016/17	2017/18
Production (1,000MT 60-kg bags)	6.345	6,475	6,510	6,943	7,055
Area(1,000 HA)	519	525	528	529	532

2.8. Spent coffee grounds as source of biodiesel

In the process of converting the raw fruit of the coffee plant into the finished coffee, there are many solid wastes and wastewater are generating. The main solid by-products from cultivation and preparation of coffee are coffee cherry husk, coffee pulp, coffee silver skin and spent coffee

grounds. Spent coffee grounds are the solid residues obtained from the treatment of coffee powder with hot water to prepare coffee (Patra et al. 2016).

Hence, there is interest in evaluating the potential of this waste material as an alternative feedstock for biodiesel production. When coffee is extracted in water, most of the hydrophobic compounds, including oils, triglycerides, and fatty acids remain in the grounds, as do insoluble carbohydrates like cellulose, indigestible sugars and other polysaccharides, there is a lot of opportunity to exploit them as a feedstock for biofuel(Ga, Homann, and Hm 2016).

Spent coffee ground also contains medium oil content about 11 – 20 wt% on a dry weight basis and the dominant fatty acids of extracted oil from SCG were linoleic (C18:2), palmitic (C16:0) and oleic (C18:1) whose carbon length suits the production of diesel fuel (Ga, Homann, and Hm 2016). Spent coffee ground are less expensive, higher stability in a sense that the oil does not decompose quickly (due to its high antioxidant content), has a pleasant smell and the relatively low levels of saponifible matter makes the oil remain viscous and not congeal easily thus making it very well suited to use in biodiesel production (Patra et al. 2016).

Oil extracted from spent coffee ground have relatively high level of free fatty acids (>3.65%), which is above the satisfactory limit of 0.5–1% for one-step alkaline transesterification and favours side reactions such as soap formation during transesterification reaction using base catalysts (Ballesteros, Teixeira, and Mussatto 2014).

2.9. Oil Extraction

Generally, large-scale seed oil extraction is achieved either by mechanically pressing the seeds against a solid surface or by using chemical solvents (as in hot water extraction, Soxhlet extraction and ultrasonic techniques). Alternatives to these well-established industrial processes include supercritical fluid extraction (SFE), ultrasonic-assisted extraction (UAE) and enzymatic oil extraction which are currently under investigation by many researchers over the world (Atabani et al. 2012).

The most common and efficient solid-liquid extraction method used in producing oil for biodiesel production is the solvent extraction method; where a solute fraction (oil) is transferred

from a solid material (seed) to a liquid solvent. Solvents such as *n*-hexane, used in this method are relatively cheap and can be recycled (Li et al. 2015) .

The SFE and UAE techniques, despite their high oil recovery yields, have drawbacks of being highly energy intensive and difficult to scale-up for commercial biodiesel production (Rajalingam et al. 2016). The mechanical extraction method, on the other hand, requires large quantities of seeds for very slow oil recovery rates. It is known to damage both the oil and the meal as pressing generates high temperatures during operation. Moreover, mechanical presses used are seed-type specific; making the mechanical press incapable of being used to extract oil from different type of seed. In the case of the enzymatic oil extraction method, long oil processing times are a major drawback (Atabani et al. 2012).

The solvent extraction of oils from spent coffee grounds are a process of separating a soluble component from the insoluble solid matrix in which it is dispersed with the use of an organic solvent . There are a number of studies that have investigated the recovery of oils from SCG through solvent extraction, with the majority of them using a Soxhlet method with dry SCG (Deligiannis 2011);(Caetano, Silva, and Mata 2012) and (Al-hamamre 2012).

Soxhlet solvent extraction involves the solubilisation of the oil present in SCG by a liquid organic solvent and its separation from the solvent-wetted grounds through numerous cycles of evaporation and condensation of the solvent. Hexane is regarded as the most effective solvent in studies which have considered a range of solvents. Table 2.3 shows the oil yields obtained from SCG by Soxhlet solvent extraction with hexane in previous studies, along with information about the oil content, SCG-to-solvent ratio and process duration.

Table 2.3: Soxhlet extraction oil yields reported in other studies

Study	Oil yield on dry weight basis (%) w/w	Duration of extraction (h)	Coffee to solvent ratio (w/v)
(Deligiannis 2011)	15	-	-
(Caetano, Silva, and Mata 2012)	16	9.5	1:20
(Kondamudi 2008)	13.4	1	1:3
(Al-hamamre 2012)	15.3	0.5	1:20

2.10. Biodiesel Production methods

The alternative diesel fuels must be technically and environmentally acceptable and economically competitive. From the viewpoint of these requirements, triglycerides (vegetable oils/animal fats) and their derivatives may be considered as viable alternatives for diesel fuels. The problems with substituting triglycerides for diesel fuels are mostly associated with their high viscosities, low volatilities and polyunsaturated character. The problems have been mitigated by developing vegetable oil derivatives that approximate the properties and performance and make them compatible with the hydrocarbon-based diesel fuels through:

- Dilution
- Micro-emulsions
- Pyrolysis
- Transesterification

2.10.1. Dilution

The straight use of vegetable oils to replace the conventional fuels encounters the operational problems due to its high viscosity 11-to-17 times higher than diesel fuel. Hence, crude vegetable oils are mixed diluted with diesel fuel to improve the viscosity and to be used for diesel engines (Suwannakarn 2008). Dilution of vegetable oils can be accomplished with such materials as diesel fuels, solvent or ethanol, and the diluted product used to run the engine. Nevertheless, the long term use of this blending in a modern diesel engine becomes impractical because of the decrease in power output and thermal efficiency by carbon deposits (Gebremariam and Marchetti 2017).

Polymerization, as a result of reactivity of C-C double bonds that may be present, lower its volatility which causes the formation of carbon deposits in engines due to incomplete combustion, and oil ring sticking, thickening and gelling of the lubricating oils as a result of contamination (Ma and Hanna 1999). Studies by (Singh, S.P and Singh 2010) used pre-combustion chamber engines with a mixture of 10 % vegetable oil and 90 % petroleum diesel to maintain total power without any alteration or adjustment to the engine. Since it was not technically feasible to substitute 100 % vegetable oil for diesel fuel, more dilutions were tried

and a blend of 20 % vegetable oil and 80 % diesel fuel was found to be successful(Ma and Hanna 1999).

2.10.2. Micro-emulsions

A micro emulsion is technically defined as a stable dispersion of one liquid phase into another, which has the droplet diameter approximately 100 nm or less. Micro emulsion process has been studied for biodiesel production as a means to improve the viscosity of vegetable oils by blending with a simple alcohol i.e., methanol or ethanol (Suwannakarn 2008) . However, the significant injector needle sticking, the carbon deposits, the incomplete combustion, and the increase in the viscosity of lubricating oils are reported for utilizing the fuel produced from this process in long term run(Ma and Hanna 1999).

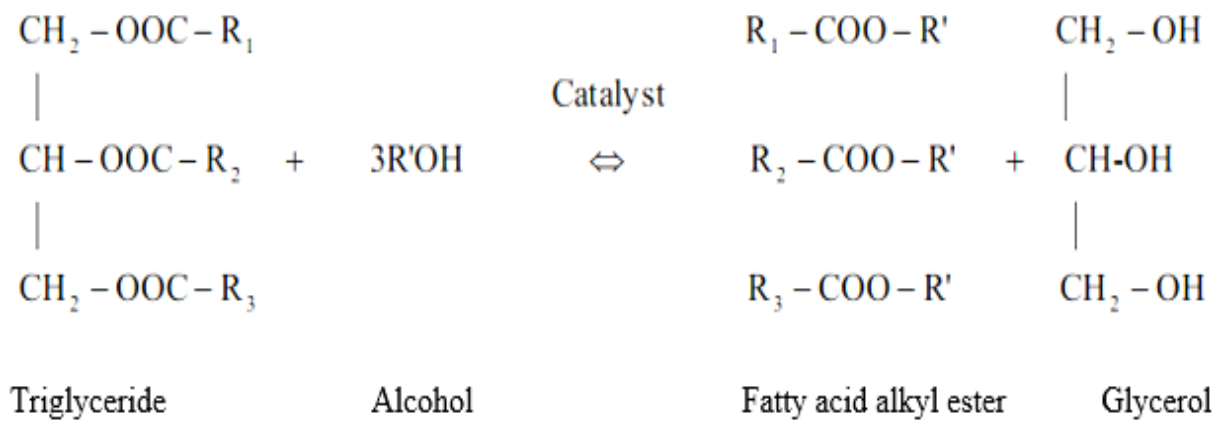
2.10.3. Pyrolysis

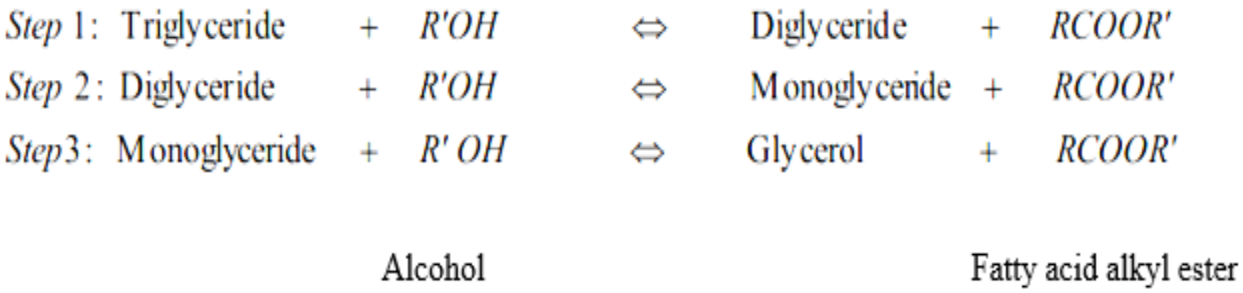
Pyrolysis is defined as the conversion of one substance into another by means of heat in the absence of air or oxygen at temperatures range from 450 °C to 850 °C or by heat with the aid of a Lewis acid catalyst. The Lewis acid catalysts used in this process include zeolites, clay montmorrilite, aluminum choride, aluminum bromide, ferrous choride, and ferrous bromide. However, the removal of oxygen during thermal processing also eliminates the environmental benefits associated with using an oxygenated fuel. The points to be considered are the expensive equipment for the process. In addition, these fuels are produced more like gasoline rather than diesel (Suwannakarn 2008). The equipment for 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 (Gashaw and Getachew 2015)

2.10.4. Transesterification of oils

Among the present methods, transesterification has been widely accepted as the most viable method to produce biodiesel. Transesterification is the chemical reaction of vegetable oils, waste oils, animal fats, or microalgae oils with excess primary alcohol in the presence of a suitable catalyst, thereby restructuring its chemical structure. This conversion reduces the high viscosity of the oils and fats(A. Demirbas 2008).

The transesterification reaction consists of a sequence of three consecutive reversible reactions as shown in below equations. The triglyceride (TG) is converted step wisely into di-glycerides, mono-glyceride and finally glycerol, releasing each time a molecule of ester per molecule of alcohol consumed. One mole of glycerol and three moles of alkyl esters are produced (for each mole of TG converted) at the completion of the net reaction. These separate into three layers, with glycerol at the bottom, a middle layer of soapy substance, and biodiesel on top (Ma and Hanna 1999).





Where: Transesterification reaction (R_x represents the hydrocarbon chains of the fatty acid triglyceride and R′ the hydrocarbon chain of the alcohol)

Table 2.4: Comparison of main biodiesel production technologies

Technologies	Advantage	Disadvantage
Dilution (direst blending or micro-emulsion	• Simple process	• High viscosity • Poor volatility • Poor stability
Pyrolysis	• Simple process • No-polluting	• High temperature is required • Equipment is expensive • Low purity
Transesterification	• Fuel properties are closer to diesel • High conversion Efficiency • Low cost • It is suitable for industrialized production	• Low free fatty acid and water content are required (for base catalyst) • Waste water is produced because products must be neutralized and washed • Accompanied by side reactions • Difficult reaction products separation

2.11. Catalysis for biodiesel production reactions

The choice of catalyst and biodiesel production route depends on the physicochemical properties of the selected oil. In most case the appropriate biodiesel production process is selected depends on the amount of undesired compounds such as free fatty acids (FFAs) and water in the oil or fat (Islam et al. 2015). The catalysts used are classified as homogeneous (acid and base), heterogeneous (acid and base), and enzymes (fig 2.1). Biodiesel can also be produced by vegetable oil transesterification using a supercritical fluid process without catalysts. Transesterification of vegetable oils via supercritical alcohol process and enzyme catalysis have not been used for commercial production of biodiesel due to the high operating costs.

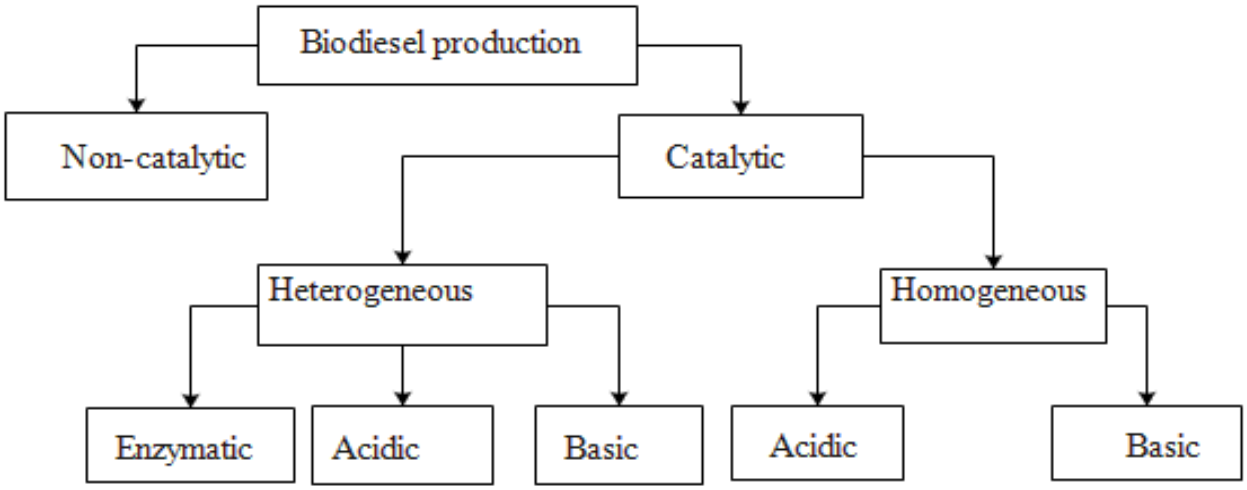


Figure 2.1: Classification of catalyst used for biodiesel production

2.11.1. Homogeneous base-catalyzed transesterification

The homogenous base catalyzed transesterification process is the reaction of a triglyceride with an alcohol in the presence of alkaline catalysts to form esters (biodiesel) and glycerol. Homogeneous alkali catalysts commonly used in the transesterification of triglycerides are sodium hydroxide (NaOH),sodium methoxide($NaOCH_3$), potassium hydroxide(KOH),and potassium methoxide($KOCH_3$) (Vyas, Shukla, and Subrahmanyam 2011).

Sodium and potassium hydroxide are preferred over the others mainly because they are able to achieve high conversion and high yield (≥97%) under mild conditions (25-70°C) in a short reaction time (20min to 2h) (A. F. Lee et al. 2007). Besides, they are widely available and economical. The standard conditions for the alkaline transesterification are 6:1 molar ratio of methanol to oil, concentration of catalyst in the range of 0.5–1.5% (depending on the FFA content of the feedstocks) and temperature of 60°C (Verhé et al. 2011).

Alkali catalysts are very sensitive to the presence of water and FFAs. In the presence of FFAs (≥ 1%) or water (≥ 0.3%), the alkali catalysts become ineffective due to soap formation and catalyst deactivation (M. F. Demirbas 2006) . Base catalysts react with FFA to form soap, causing difficulty in separation of biodiesel and glycerol. This soap formation seriously hinders the production of fuel grade biodiesel and gives rise to formation of gels, increase viscosity and greatly increase product separation cost. It is also found that the water produced during soap formation promotes formation of FFAs when esters are present. Water had more effect on alkali

catalyzed transesterification due to increased soap formation and emulsification (Talha and Sulaiman 2016).

The application of an alkaline catalyst in transesterification of waste oil and non-edible are somewhat limited because of the high FFA and water contents. These limitations, low-cost feed stocks such as waste vegetable oils are not appropriate candidates for alkali-catalyzed transesterification unless an extra pre-treatment step is performed(S. J. Lee 2010). When an alkali catalyst is added to these feedstocks, the FFAs rapidly react with the catalyst to form soap and water as shown in the reaction bellow:

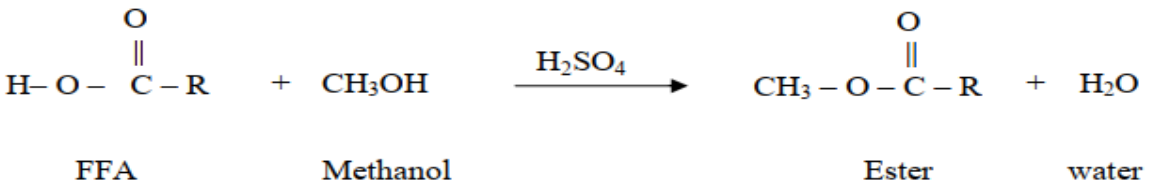
$$\underset{\text{FFA}}{R-COOH} + \underset{\text{Base}}{NaOH} \rightarrow \underset{\text{Soap}}{R-COONa} + \underset{\text{water}}{H_2O.}$$

2.11.2. Homogenous acid catalyzed esterification

Homogeneous acid-catalyzed transesterification has not attracted much attention for industrial-scale production of biodiesel compared to the base-catalysis (Ma and Hanna 1999). However, due to an increase in the use of 2nd generation feedstock containing high levels of FFAs, the acid-catalyzed transesterification holds an important advantage over base catalyzed transesterification. The presence of FFAs in the feedstock should not significantly affect the performance of the acid catalyst. The acid catalyst has the ability to simultaneously catalyze both esterification and transesterification (Parameter and Minyak 2010).

Homogenous acid-catalyzed transesterification is recommended for feedstocks containing high levels of FFAs (≥ 1%). The most commonly used acids for homogeneous biodiesel reactions are sulfuric, phosphoric, hydrochloric and organic sulfonic acids. Among these, the most frequently used catalyst is sulfuric acid because of its higher activity, cheap price and availability (Meher, Sagar, and Naik 2004). Furthermore, acid-catalyzed transesterification requires more severe reaction conditions such as high reaction temperature, high alcohol to oil ratio and long reaction time. This is illustrated by (Yimer and Sahu 2014) study in which 90% conversion was achieved for the acid-catalyzed transesterification of waste cooking oil (≈38% FFA) after 10h by using a methanol to oil ratio of 16:1 and 4 wt. % H_2SO_4 at a reaction temperature of 95°C.

The rate of acid-catalyzed transesterification is about 4000 times slower than that of a alkali-catalyzed process. Another disadvantage of the acid-catalyzed homogeneous biodiesel process is that all the equipment has to withstand the corrosive effect of the acids. The cost of corrosion resistant vessels contributes to the cost of acid-catalyzed process (Verma et al. 2016). When oils and fats with high free fatty acids are to be used for biodiesel production, an acid catalyst such as sulfuric acid can be used to esterify the free fatty acids to methyl esters as shown in the following reaction.



2.11.3. Combination of homogeneous acid base catalyzed method

In order to overcome some of the limitations associated with acid and base homogeneous catalysts while benefitting from their advantages, some studies have explored the use of a combination of both catalysts to produce biodiesel from low quality feedstock. This involves acid catalysis followed by alkali catalysis (Bouaid et al. 2012).

This approach solves the reaction rate problem by using each technique to convert high free fatty acid feedstocks quickly and effectively. Since acid catalysis is relatively fast for converting the FFAs to methyl esters, it is used as a pretreatment for the high FFA feedstocks. Then, when the FFA level has been reduced to 1%, or lower, an alkali catalyst is added to convert the triglycerides to methyl esters. Water formation due to the presence of free fatty acids is still a problem during the pretreatment phase (Bojan and Durairaj 2012).

One approach is to simply add so much excess methanol during the pretreatment that the water produced is diluted to the level where it does not limit the reaction. Molar ratio of alcohol to free fatty acid as high as 30:1 may be needed to reduce the free fatty acid to 1% using hydrochloric acid catalyst. The disadvantage of this approach is that more energy will be required to recover the excess methanol (Sukjit and Punsuvon 2013)

2.11.4. Heterogeneous base catalyzed transesterification

Homogeneous catalysts showed greater performance toward transesterification to obtain biodiesel. The problems associated with the homogeneous catalysts are the high consumption of energy, form unwanted soap byproduct by reaction of the FFA, expensive separation of the homogeneous catalyst from the reaction mixture and generation of large amount of wastewater during separation and cleaning of the catalyst and the products. (Ma and Hanna 1999). The use of heterogeneous catalysts could be an attractive solution. Heterogeneous catalysts can be separated more easily from reaction products. Undesired saponification reactions can be avoided by using heterogeneous catalysts. They enable the transesterification of vegetable oils or animal fats with high contents of FFAs, such as deep-frying oils from restaurants and food processing (Feng and Fang, 2011).

2.11.5. Heterogeneous acid catalyzed esterification

Heterogeneous acid catalysts are the most promising catalysts for biodiesel production and are expected to dominate commercial industries in the coming years(Lam, Lee, and Mohamed 2010). This is due to the simplicity in biodiesel purification step that eliminates waste water, reusability that make continuous process possible, and their ability to handle low quality feedstock with high FFA content via simultaneous esterification and transesterification. Heterogeneous acid catalysis, however, usually requires extreme reaction temperature, higher reaction time, and high pressure is necessary to the reaction mixture especially when the operating temperature is above the boiling point of the corresponding alcohol in order to maintain the reacting alcohol in liquid state (Oloruntoba 2016) .

The common drawbacks of convectional esterification catalysis mentioned above (homogeneous and heterogeneous catalysis) are the high temperature and pressure requirement that are involved during the esterification. Therefore, there is an urgent need to explore a technology that can efficiently reduce the FFA content of the oil as a pretreatment step for biodiesel production under ambient conditions (Anais and Mbadinga 2015).

2.11.6. Enzyme catalyzed transesterification

Enzymatic transesterification has drawn researcher’s attention due to the downstream processing problem posed by chemical transesterification. Huge amount of wastewater generation and

difficulty in glycerol recovery are some of the problems that eventually increase the overall production cost of biodiesel and being not environmental benign(Ma and Hanna 1999).

In contrast, enzyme catalysis occurs without the generation of by-products, easy recovery product, mild reaction condition, insensitive to high FFA oil and catalyst can be reuse. Thus, enzyme catalyzed biodiesel production has proven to have high potential to be an eco-friendly process and a promising alternative to the chemical process. However, enzyme catalyzed biodiesel production has some limitations especially when implemented in industrial scale because of high cost of enzyme, slow reaction rate and enzyme deactivation (Lam, Lee, and Mohamed 2010).

2.12. Factors Affecting Biodiesel Production process

Transesterification reaction is strongly affected by several factors, including free fatty acid content and moisture , the type and concentration of catalyst (alkaline or acid), alcohol to oil molar ratio, reaction temperature, reaction time and agitation speed .

2.12.1. Effects of moisture and free fatty acids

The water and FFA contents are critical factors for transesterification. Water can cause soap formation and frothing. The resulting soaps can induce an increase in viscosity, formation of gels and foams, and make the separation of glycerol difficult. Water has a more negative effect than the presence of FFA, and hence the feedstock should be water-free. Base-catalyzed transesterification requires water free and low acid value (< 1) raw materials (A. Demirbas 2008) for biodiesel production.

If the oil samples have high FFA content (more than 1%) then the reaction requires more alkali catalyst to neutralize the FFA (Mathiyazhagan and Ganapathi 2011). The problem with processing low cost oils and fats is that they often contain large amounts of FFAs that cannot be converted to biodiesel using alkaline catalyst (Taghizade 2016)

2.12.2. Effect of molar ratio of alcohol to oil

According to (Yakubu 2015) molar ratio of alcohol to triglyceride plays a vital role in biodiesel yield. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of glyceride to yield three moles of fatty acid methyl ester and one mole of glycerol.

Excess amount of alcohol increases conversion of fats into esters within a short time. Therefore, the yield of biodiesel increases with increase in the concentration of alcohol up to certain concentration. However further increase of alcohol content does not increase the yield of biodiesel but it rather increases the cost of alcohol recovery (Ma and Hanna 1999) . A molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester yields higher than 98% by weight. Higher molar ratio of alcohol to vegetable oil interferes in the separation of glycol (Gashaw and Getachew 2015).

(Akhihiero, Oghenejoboh, and Umukoro 2016) Studied the effect of molar ratio variation on the yield of biodiesel from the transesterification of Jatropha seed oil with methanol using various concentrations of sodium hydroxide catalysts. The result showed that a methanol/oil molar ratio of 8:1 with NaOH concentration of 1% w/w gave the optimum yield of biodiesel. Biodiesel yield was found to reduce with increasing NaOH concentration and higher methanol/oil ratio. This is because at higher methanol/oil ratio, the excess methanol reacted with the NaOH to form soap instead of speeding up the production of biodiesel.

2.12.3. Effect of reaction temperature

Rate of reaction and yield of the biodiesel product are clearly influenced by temperature. A higher reaction temperature can decrease the viscosities of oils and result in an increased reaction rate, and a shortened reaction time. However, when the reaction temperature increases beyond the optimal level, the yield of the biodiesel product decreases because a higher reaction temperature accelerates the saponification reaction of triglycerides (Mathiyazhagan and Ganapathi 2011).

The reaction temperature must be less than the boiling point of alcohol in order to ensure that the alcohol will not leak out through vaporization. In the alkali transesterification reaction, the temperature maintained by researchers during different steps ranges between 45 and 65℃. Therefore, the reaction temperature near the boiling point of the alcohol is recommended for faster conversion (Polytechnic et al. 2010).

2.12.4. Effect of reaction time

Conversion rate of fatty acid esters increases with reaction time (Ma and Hanna 1999). At the beginning, the reaction is slow due to the mixing and dispersion of alcohol into the oil. After a while, the reaction proceeds very fast. Normally, the yield reaches a maximum at a reaction time of <90 min, and then remains relatively constant with a further increase in the reaction time (Ma 1998). Moreover, excess reaction time will lead to a reduction in the product yield due to the backward reaction of transesterification, resulting in a loss of esters as well as causing more fatty acids to form soaps (Caetano, Silva, and Mata 2012).

2.12.5. Effect of catalyst type and concentration

The type of catalyst and concentration to be used in biodiesel production is the most important factor that influences the performance of the transesterification reaction, since its purpose is to improve the yield and the reaction rate. The selection of the catalyst is greatly dependent on the type and quality of feedstock (Scully, Jaiswal, and Abu-ghannam 2016).

Different types of catalyst are employed in biodiesel production. For virgin oil or feedstock oil having FFA and moisture content as low as 0.5-1 wt. % and 0.06 wt. % respectively, alkali catalyzed reaction provide a high conversion in relatively short reaction time (Ma and Hanna 1999). For higher FFA containing oils (≥ 1 wt. %), acid catalysts can be used to catalyze esterification and transesterification simultaneously(Fruit 2016).

The alkaline catalysts such as sodium hydroxide and potassium hydroxide are most widely used. These catalysts increase the reaction rate several times faster than acid catalysts. As the catalyst concentration increases the conversion of triglyceride and the yield of biodiesel increase. This is because an insufficient amount of catalysts result in an incomplete conversion of the triglycerides into the fatty acid esters(A. F. Lee et al. 2007).

Usually, the yield reaches an optimal value when the catalyst (NaOH) concentration reaches 1.5 wt.% and then decreases a little with a further increase in catalyst concentration. The reduction of the yield of the biodiesel is due to the addition of excessive alkali catalyst causing more triglycerides to react with the alkali catalyst and form more soap (Boro et al. 2014).

2.12.6. Effect of agitation speed

Oils and alcohols are not totally miscible, thus reaction can only occur in the interfacial region between the liquids and transesterification is a moderately slow process. So, adequate mixing is very important in the transesterification process, to promote contact between these two feedstocks. Mechanical mixing is commonly used in the transesterification process. The intensity of the mixing could be varied depending on its necessity in the transesterification process (Gashaw and Getachew 2015). When vegetable oils with high kinematic viscosity are used as the feedstock, intensive mechanical mixing is required to overcome the negative effect of viscosity to the mass transfer between oil, alcohol and catalyst. In transesterification reaction, agitation speed plays an important role in the formation of the end product (biodiesel). Due to the reverse behavior of transesterification reaction, lower agitation speed slows down the product formation; however, higher stirring speed favors formation of soap(Vyas, Shukla, and Subrahmanyam 2011).

2.13. Biodiesel quality parameters and specification standards

Accordingly, biodiesel standards established in various countries and regions around the world, including the United States (ASTM D 6751), Europe (EN 14214), Brazil, South Africa, Australia and elsewhere. The European EN 14214 and the American Society for Testing and Materials (ASTM) D-6751 standards are the most commonly used (Amit Sarin 2012).

Kinematic Viscosity: Viscosity is defined as the resistance of liquid to flow. It therefore affects the operation of fuel injection equipment, particularly at low temperatures when an increase in viscosity affects the fluidity of the fuel. (Knothe 2010) . A low viscosity can result in an excessive wear in injection pumps and power loss due to pump leakage (Ashqer and Musameh 2015). Kinematic Viscosity is measured according to EN-ISO 3104 where it is limited to 3.5–5.0 mm^2/ s and according to ASTM D-445 where it is limited to 1.9– 6.0 mm^2 /s (Amit Sarin 2012) .

Flash Point(FP): The flash point temperature of diesel fuel is the minimum temperature at which the fuel will flash upon application of an ignition source (Gerpen et al. 2011). The flash point of biodiesel is higher than the prescribed limit of diesel fossil fuel, which is safe for transport, handling and storage purpose. Higher values indicate materials that are less likely to

ignite accidentally (Amit Sarin 2012). Flash point is measured according to EN-ISO 3679 where it is limited to 120℃, and according to ASTM D-93 where it is limited to 93℃

Density: Density is important because it gives an indication of the delay between the injection (ignition quality) and combustion (specific energy) of the fuel in a diesel engine. This can influence the efficiency of the fuel atomization for airless combustion systems. 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 (Pratas et al. 2011). Density is measured according to EN-ISO 3675/12185 where it is limited to 860–900 kg/ m^3.

Acid value (AV): The acid value measures the amount of unreacted acids remaining in the finished fuel, and is also an indicator of oxidized fuel. A high acid value will damage fuel pumps and fuel filters (Islam et al. 2015). For biodiesels, the acid number is an indicator of the quality of the product. Specifically, it detects the presence of any unreacted fatty acids still in the fuel, or of any acids that were used in processing. This is also an indication of the condition of the stability of the fuel, because the acid number increases as the fuel ages. Higher acid content causes severe corrosion in fuel supply system of an engine(A. F. Lee et al. 2007). Acid number is measured according to EN 14104 and ASTM D-664 where it is limited to 0.5 mg KOH per g.

Cetane Number (CN): The cetane number is a measure of ignition quality of diesel fuels. It is the indication of ignition characteristics or ability of fuel to auto-ignite quickly after being injected. Cetane number provides information on ignition delay time when injected into the combustion chamber. Better ignition quality of the fuel is always associated with higher CN value (Sivaramakrishnan and Ravikumar 2006). CN is measured according to EN-ISO 5165 where it is limited to 51 min, and according to ASTM D-613 where it is limited to 47 min (Amit Sarin 2012).

Iodine Value (IV): The iodine number is an index of the number of double bonds in biodiesel which determines the unsaturation degree of the biodiesel. This property influences the oxidation stability and polymerization of glycerides, leading to the formation of deposits in diesel engines

injectors (Knothe and Gerpen 2005) . IV number is measured according to EN-ISO 14111 where it is limited to 120 g per 100 g.

Heat of Combustion: Heat of Combustion is the amount of heat energy released by the combustion of a unit volume of fuel. A measure of energy available in a fuel. The greater the heat of combustion, the lower is the fuel consumption (Knothe and Gerpen 2005). This is an important property of the bio-diesel that determines the suitability of the material as alternative to diesel fuels (Sivaramakrishnan and Ravikumar 2006). The heat of combustion of methyl esters is measured in a bomb calorimeter according to ASTM D2015 where it limited to 37 – 42.5MJ/kg.

Water content: Water content is the amount of water content in the biodiesel determines the caloric value and the shelf life of the fuel. Biodiesel with higher water content has lower oxidation stability and the greater probability of oxidation products will be formed during long storage period. Water content and sediment is measured according to ASTM D-2709 and is limited to 0.050% by volume(Amit Sarin 2012)

Low -temperature flow properties: Low-temperature performance is one of the most important properties for users of biodiesel and it is mainly indicated by the cloud point (CP) and pour point (PP). The CP is the temperature at which a sample of the fuel starts to appear cloudy, indicating that wax crystals have begun to form which can clog the fuel lines and filters in a vehicle's fuel system. The PP is defined as the temperature at which the fuel ceases to flow. The cessation of flow results from an increase in viscosity or from the crystallization of wax from oil (Amit Sarin 2012).

Chapter Three

3. Materials and Methods

The experiments of production of biodiesel from spent coffee ground oil has been done in the laboratory of Chemical Engineering department at the Institute of Technology, Addis Ababa University. The experiments were classified into two parts, the preliminary and main experiments. The preliminary experiments consist of the preparation of spent coffee ground up to the characterization of extracted oil while the main experiment involves acid - base catalyzed transesterification process including optimization of reaction variables and characterization of produced biodiesel. The experimental procedures followed in this work is shown in Fig. 3.1.

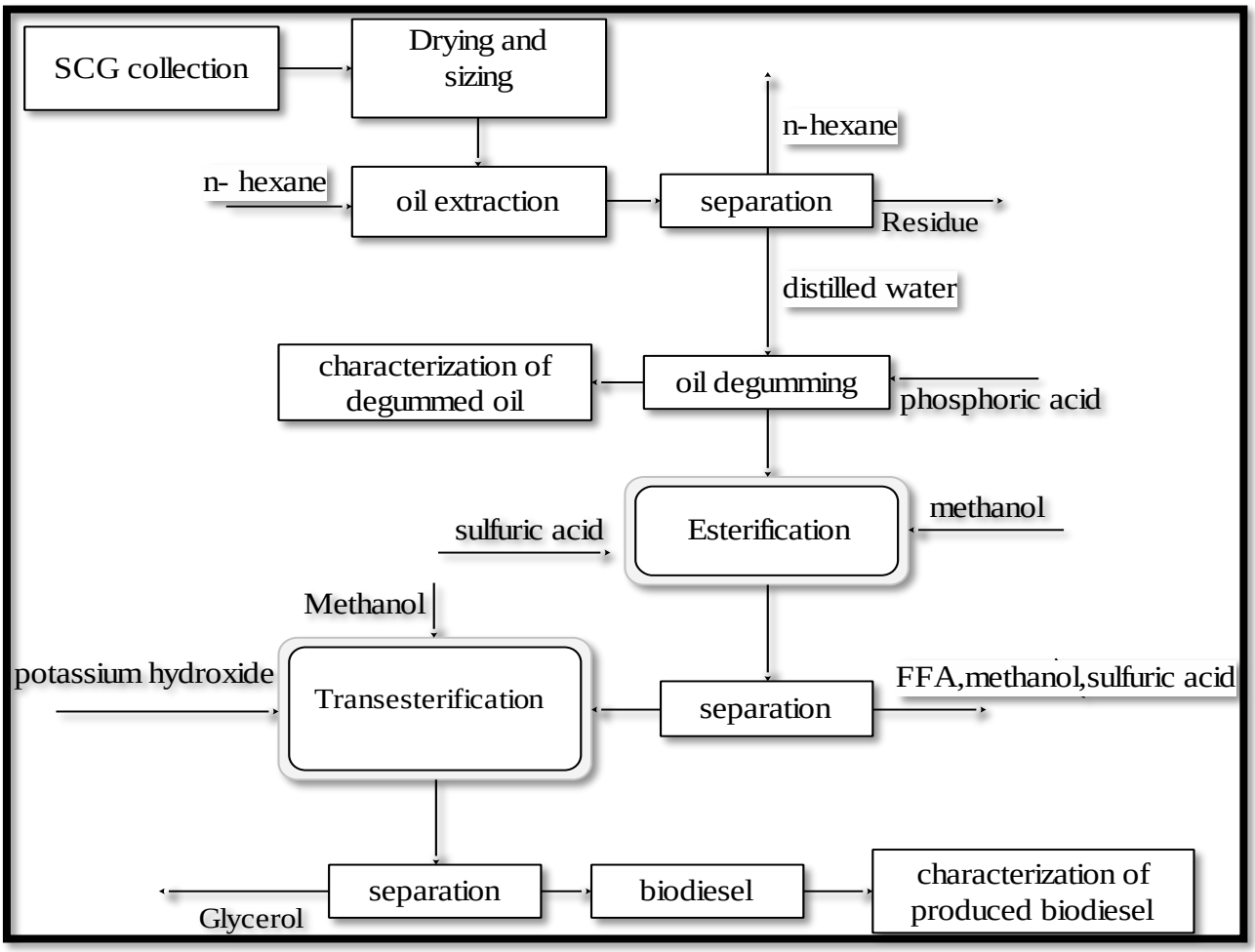


Figure 3.1: Experimental procedures

3.1. Sample collection and preparation

3.1.1. Materials

In this study spent coffee ground was used as sample and the main equipments used for sample preparation were analytical balance, crucible, desiccator, drying oven and sieve shaker

3.1.2. Methods

For this study, the spent coffee grounds were collected from different local coffee house in Addis Ababa particularly which are obtained around Addis Ababa institute of Technology (AAiT) in December, 2019. 15 kg of wet spent coffee ground were collected for the sample preparation. Sample preparation process was included: drying and particle sizing of dry spent coffee ground. The collected spent coffee ground must be dried to eliminate the moisture content before introduced into the extraction process. The moisture from the sample was removed by oven drying at 105°C. The total moisture content and the drying time of the SCG samples was determined by using 20 grams of wet samples in oven drying at 105℃ followed by cooling in a desiccator and reweighted at intervals of 1 hours, until no change in the measured weight between subsequent measurement. The moisture content of spent coffee ground was calculated using eqn.3.1.

$$\text{Moisture content (M)\%} = \frac{W_1 - W_2}{W_1} \times 100 \quad (3.1)$$

Where: W_1 = weight of initial of SCG

W_2 = Final mass of the SCG

After drying, the necessary particle size of the dried SCG were conducted using laboratory test sieves with different pore sizes ranging from 0.18 and 1.4 mm. The vibratory sieve shaker was operated at a speed of 40 rpm for 10 minutes. All of the sieves were weighed before and after the shaking process in order to calculate the mass of particles that was retained in each. The average particle size of the SCG was determined using eqn. 3.2.

$$\text{Average particle size} = \frac{1}{\sum \frac{x_i}{D_P}} \quad (3.2)$$

where: D_p = average sieve pore size

X_i = mass fraction of particles that remain in a specific sieve

3.2. Extraction and purification of spent coffee ground oil

3.2.1. Materials

Hexane was used as a solvent for oil extraction and phosphoric acid and water distilled was used for degumming process and the main equipments used were round bottom flask, filter papers, measuring cylinder, reflux condenser, soxhlet apparatus, water bath, chiller, vacuum rotary evaporator, analytical balance, thermometer and overhead agitator.

3.2.2. Methods

The extraction process was carried out using 120 grams of spent coffee ground and 600 ml of non-polar solvent, n-hexane with the purity (99%) using different particle size (0.18-1.4 mm for 4 hours at 70^{o}C in the Soxhlet apparatus. Condenser, extractor and the flask were arranged in a vertical position on a water bath. The condenser was filled in with water and continuous water supply was maintained throughout the process. As the solvent boils, the vapor rises through the vertical tube to the condenser, the condensate then drips on the sample and seeps through the pores of filter paper into the powder. After the oil had been drained out from the sample completely, the extracted oil was removed and the fresh weighed sample was filled in to the extractor chamber. This was continued until significant amount of oil was extracted. After the end of the process, the vacuum rotary evaporator was used at 50 ℃ to remove the solvent from the solutions of hexane-to-SCG oil, and then the samples were transferred into flask. The solvent was recovered using condenser for reusing in extraction of oil. The percentage of oil extracted was determined using eqn. 3.3.

$$\text{SCG oil content} = \frac{W_o}{W_s} \times 100 \qquad (3.3)$$

Where: W_O= weight of oil extracted, grams

W_s = weight of the sample, grams

Degumming converts the phosphatides in the extracted SCG oil to hydrated gums, which are insoluble in oil and readily separated as sludge. In this process, the extracted oil was heated up to 60^{0}C for about 2 hours and then 3% (v/v) distilled water (which first was heated to approximately 60 ºC) and 1.5% phosphoric acid (v/v) were mixed with the extracted oil. The solution was heated up to 70^{0}C and stirred at a speed of 500 rpm for 30 minutes.

The impurities were separated using a centrifuge at a speed of 3000 rpm for 30 minutes. The degummed oil was dried at105ºC for30 minutes and then stored for further characterization.

3.2. Characterization of spent coffee ground oil and biodiesel

3.2.1. Materials

The main materials used for characterization were spent coffee ground oil, biodiesel, ethanol (97%), diethy1 ether, phenolphthalein indicator, 0.1 M KOH solution, 0.5 M ethanolic KOH solution, 0.5M HCl solution, hydrochloric acid. The main apparatus and equipments used were pycnometer, analytical balance .vibrio viscometer, water bath and thermometer, conical flask, beaker, burette, Erlenmeyer flasks, pipet, measuring cylinder, bomb calorimeter, water bath, reflux condenser, Bunsen burner and GC-MS.

3.2.2. Methods

- **Determination of density**

Density was determined using empty pycnometer bottle that was weighed, then filled up with water and reweighed. The water was poured out and dried the bottle. The bottle was filled up with the oil or biodiesel and the weight was recorded. The experiment was conducted at 25°c. The specific gravity and density of oil or biodiesel was calculated using eqn.3.5 and 3.6 respectively.

$$\text{Specific gravity} = \frac{W_2 - W_1}{W_3 - W_1} \quad (3.5)$$

Where: W_1 = weight of empty pycnometer

W_2 = weight of bottle with oil sample

W_3 = weight of bottle with water

$$\text{Density} = SG \times \rho_{water} \quad (3.6)$$

- **Determination of viscosity**

The viscosity of (oil or biodiesel) was determined by using vibrio viscometer. Initially, the sample was kept in the water bath heated by water bath until it reaches the equilibrium temperature (40ºC). After maintaining the equilibrium temperature**,** the viscometer tip was

inserted in the sample and the reading was taken from the controller. This was done in duplicate and the average dynamic viscosity was recorded. The kinematic viscosity of the (oil or biodiesel) was calculated using eqn. 3.7.

$$\text{Kinematic viscosity} = \frac{\mu}{\rho} \quad (3.7)$$

Where: μ = dynamic viscosity, mpa.sec

ρ = density of oil or biodiesel, g/cm^3

- **Determination of acid value and FFA**

The acid number is used to quantify the amount of acid present, in (oil or biodiesel). It is the quantity of base, expressed in milligrams of potassium hydroxide that is required to neutralize the acidic constituents in 1 gram of sample. Acid value was determined by titrimetric method. In a 250mL conical flask, 1g of (oil or biodiesel) was mixed along with 25mL of mixture of solvent (equal volume of diethy1 ether and ethanol). The resultant (oil or biodiesel) solution was titrated with 0.1 M potassium hydroxide (KOH) solution, using phenolphthalein indicator. The titration continued, until a pink color solution was obtained, indicating the equivalence or end. The equivalence point is reached when the number of acid moles in the oil is equal with the number of base moles that have been added and the reactants have stopped reacting. The total acidity (acid number) in the (oil or biodiesel) was calculated using eqn. 3.8.

$$\text{Acid value (mg KOH/g oil)} = \frac{56.1 \times M \times V}{W} \quad (3.8)$$

Where: M = the morality of standard KOH (0.l M)

V = the volume of KOH used

56.1 = the molar mass of potassium hydroxide

W = the weight in gram of the (oil or biodiesel) sample

$$\text{FFA}\ (\%) = \frac{AV}{2} \times 100 \quad (3.9)$$

- **Determination of saponification value**

The saponification value of (oil or biodiesel) is defined as the number of mg of KOH required to neutralize the free fatty acid and to saponify the esterified organic matter in 1gram of fat. Saponification value was estimated by refluxing a weighed quantity of (oil or biodiesel) with excess of standard alcoholic KOH solution and then it was titrated with the alkali against a standard acid. About 2 g of (oil or biodiesel) was added into a conical flask containing in 25 ml of 0.5 M ethanolic potassium hydroxide solution. The flask was heated at 78 °C with stirring under reflux for 30 min frequently to ensure that the sample was fully dissolved. Then, the excess KOH solution was titrated hot solution with 0.5M HCl solution using 5 drops of phenolphthalein indicator until a pink endpoint was reached. A blank was carried out at the same time (without (oil or biodiesel)). The saponification value was determined using Eqn. 3.10.

$$\text{Saponification value mg KOH/g oil} = \frac{56.1 \times M \times (V_B - V_T)}{W} \quad (3.10)$$

Where: M = molar concentration of HCl solution used

V_B = the volume of 0.5M HCl in ml used in the blank titration

V_T= the volume of 0.5M HCl in ml used for (oil or biodiesel) titration,

W = the weight in gram of the (oil or biodiesel)

- **Determination of Calorific value**

The calorific value of fuel is the thermal energy released per unit quantity of the fuel when the fuel burned completely. Calorific value of oil and biodiesel was measured at Geological Survey of Ethiopia using adiabatic bomb calorimeter.

- **Determination of Iodine value**

Iodine value is an important measure that allows determination of the degree of unsaturation in fuels. The iodine value of the oil and biodiesel was determined using the empirical formula suggested by (A. Demirbas 2008) for determination of calorific value. After rearrangement, the iodine value (IV) was calculated using eqn. 3.12

Calorific value = 49.43 - [0.041(SV) + 0.015(IV)] (3.11)

Iodine value = $\frac{49.43-CV-0.041SV}{0.015}$ (3.12)

Where: CV = Calorific Value and SV =Saponification number

- **Determination of cetane number**

The cetane number is a measure of ignition quality or ignition delay and is related to the time required for a liquid fuel to ignite after injection into a compression ignition engine. Cetane number was calculated from the model reported by (A. Demirbas 2008) by iodine value (IV) and saponification value (SV) using eqn.3.13.

$$\mathrm{CN} = 46.3 + \frac{5448}{\mathrm{SV}} - 0.225\mathrm{IV} \quad (3.13)$$

Where: CN= cetane number

SV=saponification value

IV= iodine value

- **Flash point**

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

3.2.3. GC-MS analysis of biodiesel

Gas chromatography and mass spectrometry was carried out to determine the percentage of fatty acid methyl esters components present in the biodiesel obtained from the spent coffee ground oil. GC-MS analysis was carried out in JIJE Analytical Testing Service Laboratory.

3.3. Design of experiment for acid base catalyzed reaction

The design of experiment (DOE) and statistical analysis were carried out through the Design Expert 7.0.0 software application. Experiments were carried out according to response surface

methodology a central composite design approach. The response of the output measured were %FFA reduction and biodiesel yield gained from esterification and transesterification reaction respectively. Process variables were molar ratio of methanol to oil, catalyst concentration (wt%) and reaction time. Reaction temperature and rotation speed was set at 60℃ and 500 rpm respectively. The CCD consisted of 17 experimental runs ($2^k + 2k + m$). Where: k is the number of factors and m is the number of replicated center points), 8 factorial points (2^k), 6 axial points ($2\times k$), and 3 replicated center points (m=3). Here: k is the number of independent variables, and k=3-.The axial point would have α (rotatable) $= (2^k)^{1/4} = 1.6818$. The factors, ranges and levels used in this study are shown in following tables.

Table 3.1: Variables for optimization of FFA reduction in esterification process

Process parameter	Range of variables				
	-1.68(-α)	-1	0	+1	1.68 (+α)
Molar ratio of methanol to oil	0.95	3	6	9	11.05
Acid catalyst concentration H_2SO_4 (%wt)	0.98	2	3.5	5	6
Reaction Time(min)	40	60	90	120	140

Table 3.2: Variables for optimization of biodiesel yield in transesterification process

Process parameter	Range of variables				
	-1.68(-α)	-1	0	+1	1.68(+α)
Molar ratio of methanol to oil	3.95	6	9	12	14.05
Base catalyst concentration KOH (%wt)	0.24	0.75	1.5	2.25	2.76
Reaction Time(min)	40	60	90	120	140

3.4. Acid base catalyzed biodiesel production process

3.4.1. Materials

The main materials and equipments used were spent coffee ground oil, methanol (CH_3OH ,99%), sulfuric acid (H_2SO_4 ,98%),potassium hydroxide (KOH), three neck round bottom flask,

measuring cylinder, separating funnel, beakers, reflux condenser , water bath, chiller, agitator, analytical balance and thermometer.

3.4.2. Methods

In order to process the transesterification reaction to convert the SCG oil into biodiesel, first the FFA within the SCG oil should be less than 1.0 %. To decrease the FFA content of the SCG oil and increase the biodiesel yield, acid catalyst esterification and alkali catalyst transesterification were employed. In this study, sulfuric acid was chosen as acid catalyst and potassium hydroxide as alkaline catalyst. Both acid catalyzed esterification and base catalyzed transesterification were conducted in a 500 mL three neck bottom flask reactor. An oil quantity of 10 ml was used for the acid catalyzed esterification experiments, and 20 ml of esterified oil was used for each base catalyzed transesterification reaction.

3.4.2.1. Acid catalyzed esterification process

The free fatty acid reduction of the SCG oil was conducted using acid esterification of the oil with methanol in the presence of sulfuric acid as catalyst. The SCG oil was first heated to 100^0C while stirred mechanically at 500 rpm for 30 min to homogenous the oil. The reaction was conducted in a 500 ml three necked round-bottomed flask attached with a reflux condenser and placed in a water bath with a temperature controller. The different molar ratio of oil to methanol, acid catalyst concentration and reaction time through acid esterification process were examined to obtain the optimum condition that gives a product with a minimum amount of FFA. Therefore, for this study different process variables amount as mentioned in the design matrix of concentrated sulfuric acid (0.98-6.02% based on oil weight) and (0.95:1 - 11.05:1) molar ratio of methanol to oil was added to the reaction flask containing pre-heated oil. The reactor was conducted for (40-140 min) and stirred 500rpm at a temperature of 60^oc throughout the reaction. Finally, the reaction product mixture was then poured into a separating funnel and allowed to settle for 5hours. After a period of 5 hours the mixture get settled in two layer with the top layer contains fatty acid methyl ester and untreated glycerides which were subjected to second step in a transesterification process. The bottom layer contains the water and free fatty acids were separated from the upper layer. The optimum condition having the lowest FFA was used for the transesterification reaction.

3.4.2.2. Base catalyzed transesterification process

The acid pretreated oil under optimum conditions was used in the second step to produce biodiesel and to investigate the optimum conditions of methanol to oil molar ratio, catalyst to oil ratio and reaction time. Firstly, the pretreated oil was heated up to 60℃ and taken in the three-neck reaction flask. The catalyst and alcohol mixture was added and the mixture was again heated to 60℃ and stirred at 500-rpm speed in agitator. The reactions were conducted at different methanol to oil molar ratios (3.95:1, 6:1, 9:1, 12:1,and 14.05:1),catalyst to oil ratios (0.24,0.75,1.5,2.25 and 2.76%wt) and reaction time(40,60,90,120 and 140min) to find the optimum conditions to get the maximum biodiesel yield. After the reaction was complete, the mixture was poured into the separating funnel and allowed to settle overnight. The mixture was separated into two liquid layers, methyl ester layer on top and glycerol layer at the bottom. Glycerol was flowed out from the separating funnel, and the remaining ester layer was washed three times with warm (50℃) distilled water (30% v/v) to remove soap, residual alcohol, catalyst, and unreacted tri, di-, and mono-glycerides. Finally, the remained moisture in the methyl ester was removed using rotary evaporator at 100°C, for 1 hour. Based on the initial amount of pretreated SCG oil, the biodiesel yield was calculated using Eqn. 3.14.

$$\text{Biodiesel yield (\%)} = \frac{\text{weight of biodiesel}}{\text{weight of oil}} \times 100 \qquad (3.14)$$

Chapter Four

4. Result and Discussion

4.1. Moisture content of spent coffee ground

The moisture content of spent coffee grounds was determined by applying an oven drying method, which is described in Sections 3.1. During solvent extraction process, the moisture content within the SCG may form a barrier between the solvent and the SCG oil which leads to a low extraction efficiency (Al-hamamre 2012). For this study, the percentage moisture in the spent coffee ground samples is given in table 4.1. As the result shown in table 4.1 the measured spent coffee ground moisture contains was 58% and this values are in the range of the previous research reported by (Kondamudi 2008) (50-60% w/w). This result indicated that moisture content of spent coffee ground is high. Oven drying at temperatures of 105 °C for durations of 8 hours was needed to remove the moisture content with in the SCG prior to oil extraction.

Moisture content (M) % = $\frac{W_1 - W_2}{W_1} \times 100 = \frac{20 - 8.41}{20} \times 100 = 58\%$

Table 4.1 : Moisture content of spent coffee ground

Drying time (hrs.)	0	1	2	3	4	5	6	7	8	M (%)
Sample weight(g)	20	16.23	13.9	11.13	10.34	9.45	8.92	8.42	8.41	58

4.2. Particle size of spent coffee ground

The particle size of the spent coffee ground was carried out using vibratory sieve shaker with different range pore size sieves. The particle size determination of spent coffee grounds are shown in table 4.2. As the result shown in table, 4.2 the measured average particle size of the spent coffee ground mixed sample were 0.523 mm with the values calculated in eqn. 3.2.

Table 4.2: Particle size determination

Sieve Size(mm)	Mass of Retained (g)	Average sieve size(D_{pi})	Mass fraction(x_i)	$\frac{X_i}{D_{pi}}$
0.18	2.04	-	0.0204	-
0.5	31.75	0.34	0.3175	0.9338
0.71	30.52	0.605	0.3052	0.5045
0.85	15.19	0.78	0.1519	0.1947
1	13.73	0.925	0.1373	0.1484
1.4	5.16	1.2	0.0516	0.043
Pan	1.61	0.7	0.061	0.087
	$\sum = 100$		$\sum X_i = 1$	$\sum = 1.912$

Average particle size $= \frac{1}{\sum \frac{x_i}{dp_i}} = \frac{1}{1.917}$ =0.523mm

4.3. Spent coffee ground oil yield

The spent coffee ground oil was extracted using soxhlet extraction method, which is described in Sections 3.2.2. From the 120 grams of spent coffee ground, 17.5 ml of oil was extracted using soxhlet by using hexane as a solvent. Then, the density of the spent coffee ground oil was measured using vibrio viscometer and the result was found to be 0.898g/cm^3. The mass of the oil extracted was calculated using eqn.3.3. The oil content was found to be 13.09%.

Mass of oil extracted = $\rho_{oil} \times V_{oil}$ = 0.898$\frac{g}{cm^3}$ ×17.5cm^3 =15.715g

The oil content of the SCG was calculated using eqn. 3.4.

Oil yield (%) = $\frac{W_o}{W_s} \times 100 = \frac{15.715}{120} \times 100$ =13.09%

This result indicates that there is quite significant as compared to other major biodiesel feedstock such as soybean oil (20%) (Ahmia et al. 2014). While, this raw material is cultivated specifically to produce biodiesel but spent coffee ground are waste .Therefore, rather that dispose it is better to use, as raw material for biodiesel production.

Effect of particle size on oil yield: The effect of particle size of spent coffee ground on extraction yield was carried out at constant extraction time of 4 hour and temperature of 70℃ . Figure 4.1 shows that the highest percentage of oil yield was obtained from the intermediate size particle between 0.5and 0.71 mm, which is 13.09%. Therefore, for oil extraction, the particles passed and retained from 0.5 and 0.71 are used.

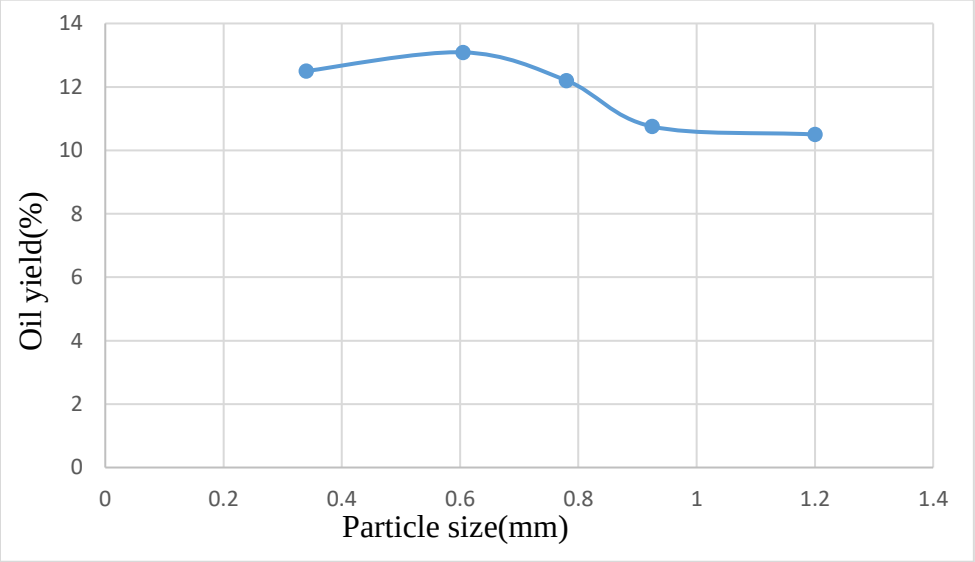


Figure 4.1: Effect of particle size on oil yield (%)

4.4. Characterization of spent coffee ground oil

The physical and chemical properties of the extracted oil such as density, kinematic viscosity ,acid value, percentage FFA content, saponification value ,and iodine value were determined in the preliminarily step of the experimental work by methods described previously in chapter 3 (section 3.3) .

Density: The density of spent coffee ground oil was measured using picnometer at 25℃ . The density of the SCG oil was calculated using eqn. 3.6. The measured specific gravity was 0.898.Therefore, density of SCG oil was found to be 898kg/m^3. The standard for diesel engine fuel states that the fuel should have a density between 0.86 and 0.90 g/cm^3, thus the measured density of spent coffee ground oil is unsuitable for direct usage as a substitute for diesel fuel.

Kinematic Viscosity: The kinematic viscosity of SCG oil was measured using Vibrio viscometer. The system detects the dynamic viscosity. The kinematic viscosity of the spent

coffee ground was calculated using eqn. 3.7. The average observed dynamic viscosity at 40℃ was 41.227mpa.s. Therefore, the average kinematic viscosity of SCG oil was calculated to be 45.91 mm^2/s. Fuels with greater viscosity increases the problems in atomization and damages the fuel injector, thus ultimately results in incomplete combustion and poor engine performance leads to damaging of the engine and also the deposition of solid unburned particles (Knothe and Gerpen 2005). This result shows that the SCG oil obtained is highly viscous and direct usage of spent coffee ground oil in diesel engines can cause problems in injection pump and combustion chamber, hence, the transesterification reaction should be used to minimize this viscosity.

Acid value: The acid value of the spent coffee ground oil was done by titration method. The acid value of the oil and %FFA were calculated using eqn. 3.8 and 3.9 respectively. The result of acid value and %FFA were obtained to be 12.2KOH/g oil and 6.1% respectively which is higher than the recommended value reported by (Ma and Hanna 1999) . When an alkali catalyst is added to these higher FFA feed stocks, the FFAs rapidly react with the catalyst to form soap and water. Therefore, acid pretreatment process (esterification) should be used to reduce the FFA with in SCG oil prior to conduct the transesterification reaction.

Saponification value: The saponification value of oil is a measure of the tendency of the oil to form soap during the transesterification reaction. The saponification of the spent coffee ground oil was calculated using eqn. 3.10. The saponification value for spent coffee ground oil was 192.5 mg KOH/g. This indicates that the SCG oil has a higher tendency of forming soap during transesterification reaction.

Calorific value: Calorific value is the thermal energy released per unit quantity of fuel when the fuel is burned completely. It measures the energy content in a fuel. The calorific value of the spent coffee ground oil was carried out at geological survey of Ethiopia using adiabatic bomb calorimeter. The calorific value of the spent coffee ground oil was found to be 37.74MJ/kg. The result shows that SCG oil have a slightly lower calorific than that of petroleum crude oils (41-48MJ/kg), but similar to that of other vegetable oils, and therefore can be considered an attractive feedstock for biodiesel production.

Iodine value: Iodine value measures the degree of unsaturation in a fat or vegetable oil and determines its oxidative stability. The more unsaturation is present in the oil, the higher the

iodine value. The iodine value of the spent coffee ground oil was calculated using eqn.3.11. The iodine value for spent coffee ground oil was found to be 81.9 g I_2 per100 g of oil. This result shows the level of unsaturation of the oil. According to EN 14214, 2004 biodiesel used as diesel fuel must have an iodine value of less than 115 g I_2 per 100 g of sample. The result dictates it is preferable for biodiesel production.

Molecular weight = $\frac{168300}{S_v - A_v} = \frac{168300}{192.5-12.2}$ = 933.4 g/mol

Table 4.3: Summery of Physicochemical properties of spent coffee ground oil

Properties	Units	Experimental Result
Oil yield	%	13.09
Density at 25ºC	g/ml	898
Kinematic viscosity at 40ºC	mm^2/sec	45.91
Acid Value	mg KOH/g Oil	12.2
FFA	%	6.1
Saponification value	mg KOH/ g Oil	192.5
Calorific value	MJ/kg	37.74
Iodine value	g I_2/100goil	81.9
Molecular weight	g/mol	933.4

4.5. Statistical analysis of acid catalyzed esterification process

The initial FFA for spent coffee ground oil was 6.1%, which means we could not directly use this oil toward transesterification. Because high FFA can cause soap formation. The resulting soaps can induce an increase in viscosity, formation of gels and foams, and make the separation of glycerol difficult (A. Demirbas 2008). Therefore, in order to reduce this FFA content of oil to less than 1%, a pre-treatment step (esterification) was required. As discussed in the previous chapter methanol to oil molar ratio (A), concentration of catalyst (B) and reaction time (C) were considered as the factors and the % FFA reduction as the response in the esterification step.

The observed reduction FFA value obtained from the experiment are presented in table 4.4. This result indicated that the reduction of the FFA content in oil was highly successful, as reduced from the FFA range of 4.25 to 0.69%. The maximum reduction was observed when the reaction took place at 6:1 methanol to oil molar ratio for 90min in the presence of 3.5%wt H_2SO_4 and the minimum reduction was found when the reaction took place at 3:1 methanol to oil molar ratio for 60 min and 2%wt H_2SO_4.

Table 4.4: The experimental and predicted % FFA value after esterification process

Run	Methanol to oil molar ratio	H_2SO_4 Concentration%(wt)	Reaction time (min)	%FFA reduction	
				Actual value	Predicted value
1	3.00	2.00	60.00	4.25	4.17
2	9.00	2.00	60.00	2.79	2.70
3	3.00	5.00	60.00	3.09	2.95
4	9.00	5.00	60.00	1.87	1.96
5	3.00	2.00	120.00	3.41	3.23
6	9.00	2.00	120.00	1.82	1.87
7	3.00	5.00	120.00	2.63	2.64
8	9.00	5.00	120.00	1.77	1.76
9	0.95	3.50	90.00	2.98	3.16
10	11.05	3.50	90.00	1.25	1.18
11	6.00	0.98	90.00	3.13	3.26
12	6.00	6.02	90.00	2.16	2.15
13	6.00	3.50	39.55	3.17	3.25
14	6.00	3.50	140.45	2.26	2.29
15	6.00	3.50	90.00	0.79	0.73
16	6.00	3.50	90.00	0.69	0.73
17	6.00	3.50	90.00	0.72	0.73

4.5.1. Development of the regression model equation

Model summary statistics for reduction of FFA is presented in table 4.5. From table 4.5 it can be seen that the difference between adjusted and predicted R^2 values is less than 0.2 in the case of the quadratic model. Therefore, the quadratic model was selected for the determination of optimized conditions during esterification process.

Table 4.5: Model summary statistics for acid catalyzed esterification

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	Predicted residual sum of square of the model (PRESS)	
Linear	0.87	0.4303	0.2988	0.2416	12.97	
2-level factorial (2FI)	0.97	0.4490	0.1183	-0.2807	21.90	
Quadratic	**0.14**	**0.9915**	**0.9806**	**0.9345**	**1.12**	**suggested**
Cubic	0.12	0.9976	0.9873	0.5417	7.84	Aliased

The statistical significance and the goodness of fit of the developed quadratic model, as well as the effect of individual variables and their interactions were analyzed by analysis of variance (ANOVA). The results of analysis of variance are shown in table 4.6.

The final equation in terms of coded factors is given as eqn. (4.1).

$$\%\,\text{FFA Reduction} = 0.73 - 0.59 \times A - 0.33 \times B - 0.29 \times C + 0.12 \times A \times B + 0.029 \times A \times C + 0.16 \times B \times C + 0.51 \times A^2 + 0.70 \times B^2 + 0.72 \times C^2 \quad (4.1)$$

Where: A, B, and C are the molar ratio of methanol to oil, and catalyst concentration and reaction time, respectively.

Final equation in terms of actual factors is given as eqn. (4.2)

%FFA Reduction =17.739-[1.002× Methanol to oil molar ratio] –[2.871 × H_2SO_4 concentration]-[0.168× Reaction time]+[0.027 × Methanol to oil molar ratio × H_2SO_4 concentration] +[3.194^-4 × Methanol to oil molar ratio × Reaction time] +[3.472^-3× H_2SO_4 concentration × Reaction time]+[0.057 ×Methanol to oil molar ratio^2]+[0.311 × H_2SO_4 concentration ^{2}]+[8.045^-4 × Reaction time ^{2}] (4.2

Table 4.6: ANOVA result for acid catalyzed esterification reaction

Source	Sum of Squares	Df	Mean Square	F-Value	p-value	Remark
Model	16.95	9	1.88	90.88	< 0.0001	Significant
A	4.73	1	4.73	228.33	< 0.0001	>>
B	1.51	1	1.51	72.86	< 0.0001	>>
C	1.11	1	1.11	53.74	0.0002	>>
AB	0.12	1	0.12	5.67	0.0487	>>
AC	6.612^-3	1	6.612^-3	0.32	0.5898	Not significant
BC	0.20	1	0.20	9.42	0.0181	Significant
A^2	2.95	1	2.95	142.52	< 0.0001	>>
B^2	5.51	1	5.51	265.95	< 0.0001	>>
C^2	5.91	1	5.91	285.11	< 0.0001	>>
Residual	0.15	7	0.021			
Lack of Fit	0.14	5	0.028	10.62	0.0883	Not significant
Pure Error	5.267^-3	2	2.633^-3			
Cor Total	17.10	16				

C.V. (%) = 6.31, R^2 = 0.9915, Pred. R^2 = 0.9345, Adj. R^2 = 0.9806, Adeq. Precision = 31.228

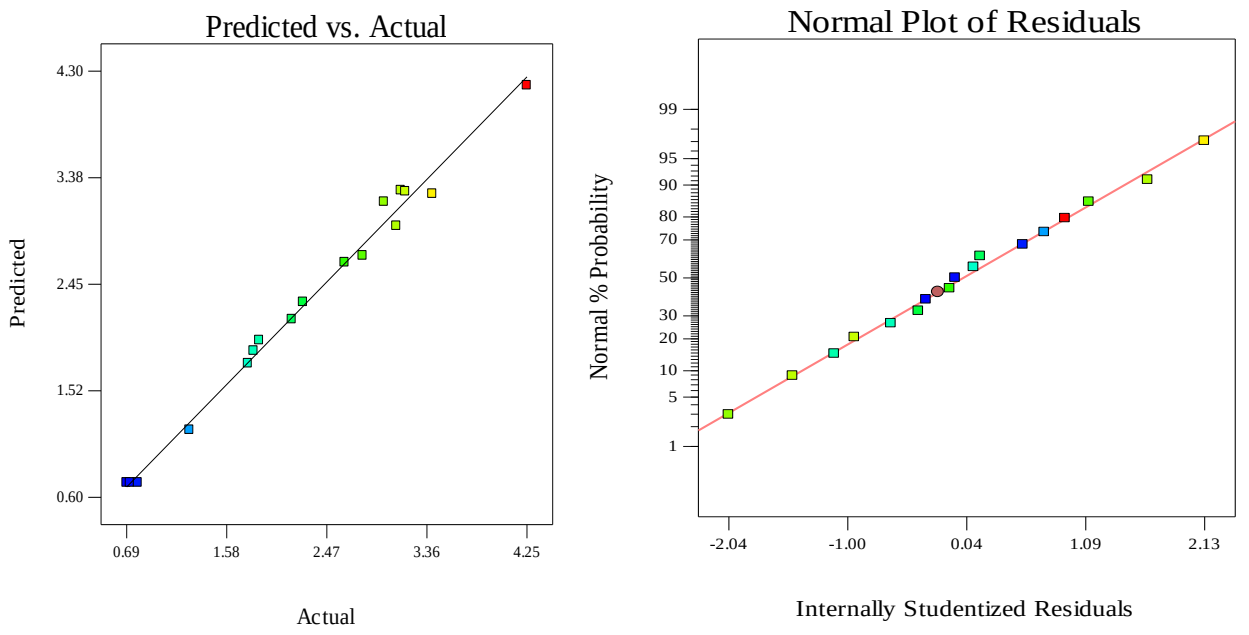
4.5.2. Analysis and adequacy of acid esterification model by ANOVA

The quality of the model fit for acid catalyzed esterification process were evaluated by the Fisher's test (F-value), the probability value (p-value), the lack of fit, the coefficient of determination (R^2), adjusted R^2 (R^2adj), and predicted R^2 (R^2pred). The F-value and P-value of the obtained quadratic model presented in table 4.6 were found to be 90.88 and (<0.0001) respectively. These imply that the quadratic model is significant. As a result of that, the model can sufficiently predict the % FFA reduction based on the investigated factors affecting acid catalyzed esterification process. From the table 4.6 the p-value of the main three effects i.e. A, B and C were significant based on their estimated p-values (<0.05) which indicated that the model was suitable for use in this experiment and suggesting that all parameters influenced to %FFA

reduction. The quadratic (A^2, $B^2$and C^2) and the interactive effects of AB and BC were significant ($p<0.05$). The lack of fit low F-value of 10.62 and high p-value of 0.0883 implied that the model was not significant relative to the pure error. The p-value of the lack of fit parameter was greater than 0.05, indicating that there is good fit between the quadratic model and the experimental % FFA reduction obtained.

The coefficient of determination reflects the variability of the dependent response variable, which is explained by its relationship with the independent process variables. In this study, the R^2 value was 0.9915, which indicates that 99.15% of the variability in the %FFA reduction was attributed to the independent factors considered, and only 0.85% of the total variations was not explained by the developed regression model. The R^2 value was close to unity, which indicated that the experimental data obtained is linearly fits in the chosen model equation. The adjusted and predicted R^2 for this study was obtained as 0.9806 and 0.9345 respectively. The difference between the adjusted R^2 and predicted R^2 values was 0.0461, which is below the maximum allowable difference of 0.20. This shows a good fit between the actual and predicted% FFA reduction. The developed model had a high degree of precision, as the adequate precision found was high enough at 31.228. The coefficient of variance (C.V.) obtained for this study was found to be low (4.38%), which indicates that the experimental data are accurate and reliable to suggest that the quadratic model was capable of optimizing the process.

The predicted values versus actual values is shown in Fig.4.2a. The Figure implies an appreciable agreement between the predicted and actual results; because of the data have linear behavior and are distributed close to diagonal line. The normal % probability and studentized residual plot was used to show the distribution pattern of the data. As shown in Fig 4.2b the residuals quite closed to a straight line indicating that they were normally distributed in the model response. Therefore, the obtained second-order polynomial model is quite satisfactory for predictions of %FFA residue from esterification reaction.



(a) (b)

Figure 4.2 : Diagnostic plots for adequacy of proposed model

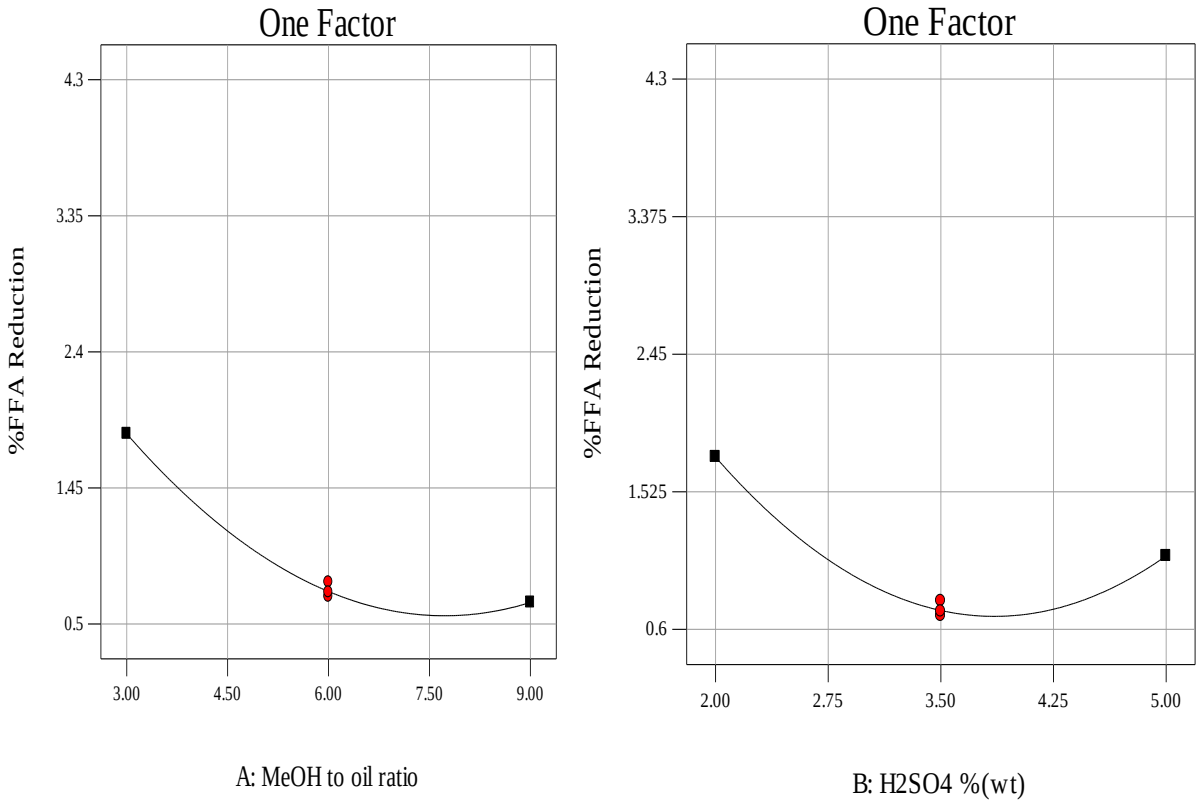
2.5.3. Effects of Individual Process Variables

Effect of Molar ratio of methanol to oil: The molar ratio of methanol to oil is one of the most influential factors on esterification. Excess methanol is required to drive the equilibrium towards forward reaction and increase the rate of formation of esters as esterification is a reversible process . The effect of methanol to oil molar ratio on % FFA is shown in Fig. 4.3a. The catalyst concentration and the reaction time were set at the optimum value of 3.5 wt % and 90 min, respectively. It can be seen that the %FFA was decreased from 1.823 to 0.56% as methanol to oil molar ratio increased from 3:1 to 7.5:1. The % FFA was reduced sharply to 0.69% at methanol to oil molar ratio of 6:1 and then decreased gradually to 0.56% at 7.5:1. Further increase of the methanol to oil molar ratio beyond to 7.5:1 the FFA content of oil was slightly increased, which is due to resulting in the formation of large amounts of water as by products which tends to reverse the reaction, reduce the rate of the forward reaction and increase the separation time.

Effect of catalyst concentration: Effect of sulfuric acid (H_2SO_4) concentration on the %FFA reduction of the SCG oil was carried out with its concentration varying from 2 to 5 wt.% and other reaction variables were kept constant as 6:1 molar ratio of methanol to oil and 90 min of

reaction time. From Fig. 4.3b, it can be seen that when the acid catalyst concentration is increased from 2 to 3.5 wt. % the percentage FFA content in the oil was reduced from 1.76 to 0.69%. Further increase in the catalyst concentration from 3.5 to 5 wt.%, the percentage of FFA reduction was slightly increased from 0.69 to 1.1% , which is due to the amount of excessive catalysts result in hydrolysis reactions of oil that are present.

Effect of Reaction time: Effect of reaction time on acid catalyzed esterification reaction is shown in Fig.4.3c. The constant molar ratio of methanol to oil of 6:1 and constant sulfuric acid concentration of 3.5% were maintained with reaction time variations. It can be seen, the FFA reduced linearly to 0.69% at 90 minutes of reaction time. When adding more reaction time resulting in % FFA reduction was slightly increased this is due to owing to the inhibitive effect on the reduction of FFA with progress of reaction time caused by water formation during esterification, which prevents the reaction proceeding in a forward direction.



(a) (b)

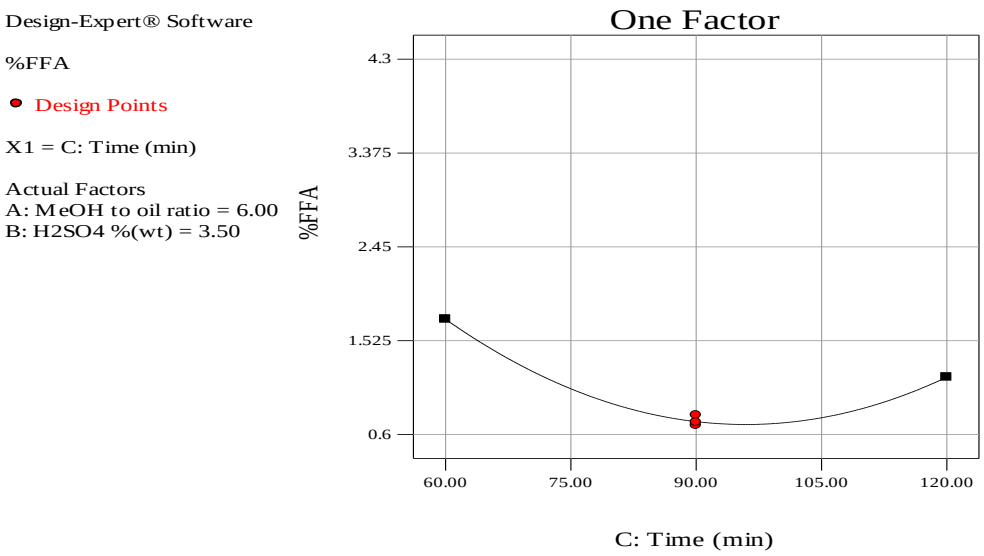


Figure 4.3: Effect of (a) methanol to oil ratio (b) catalyst (c) time on % FFA reduction

4.5.4. Effects of interaction between process variables

The interaction effect of two independent factors on the FFA reduction are discussed in fig.4.4 and 4.5. The two-dimensional and three-dimensional response surface plots was used to identify the interaction effect. Each plot presents the effect of two variables on the FFA reduction, holding the third variable at constant level.

Fig.4.4a and fig 4.4b shows the 2D and 3D response surface interactions between the molar ratio of methanol to oil and catalyst concentration on the FFA value of oil after esterification reaction. It can be seen that the % FFA was decreased with both molar ratio of methanol to oil and catalyst concentration increased and at low catalyst concentration FFA reduce with increasing methanol to oil ration. However, at higher catalyst concentration, there seemed to be less effect of increase methanol to oil molar ratio.

Fig.4.5a and 4.5b shows 2D and 3D response surface relationships between catalyst amount and reaction time on the final value of FFA in the oil. The figure shows that both catalyst concentration and reaction time affects FFA. FFA is reduces from 2.6 to 0.69 % when both variables increase up to the medium , but as the catalyst concentration and time of reaction exceeds the FFA value continues rising .At low reaction time, there was slight decrease in FFA with increase catalyst concentration.

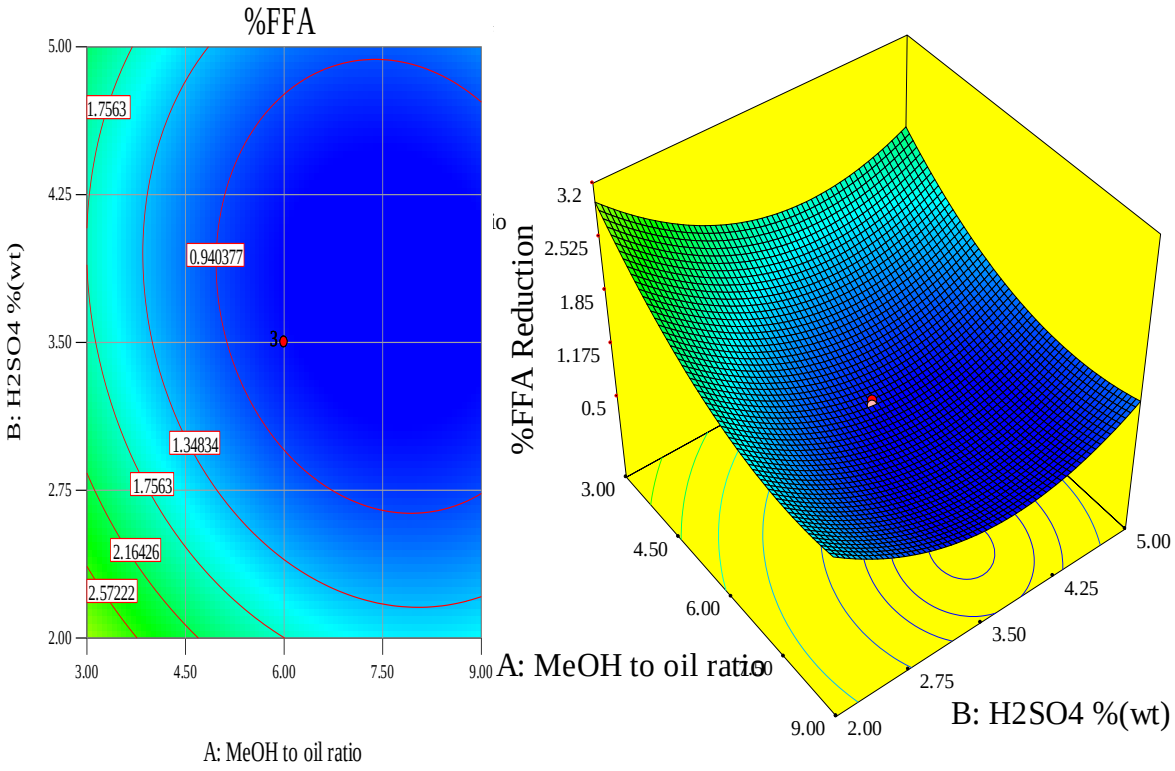


Figure 4.4: Effect of molar ratio of methanol to oil and catalyst to %FFA reduction

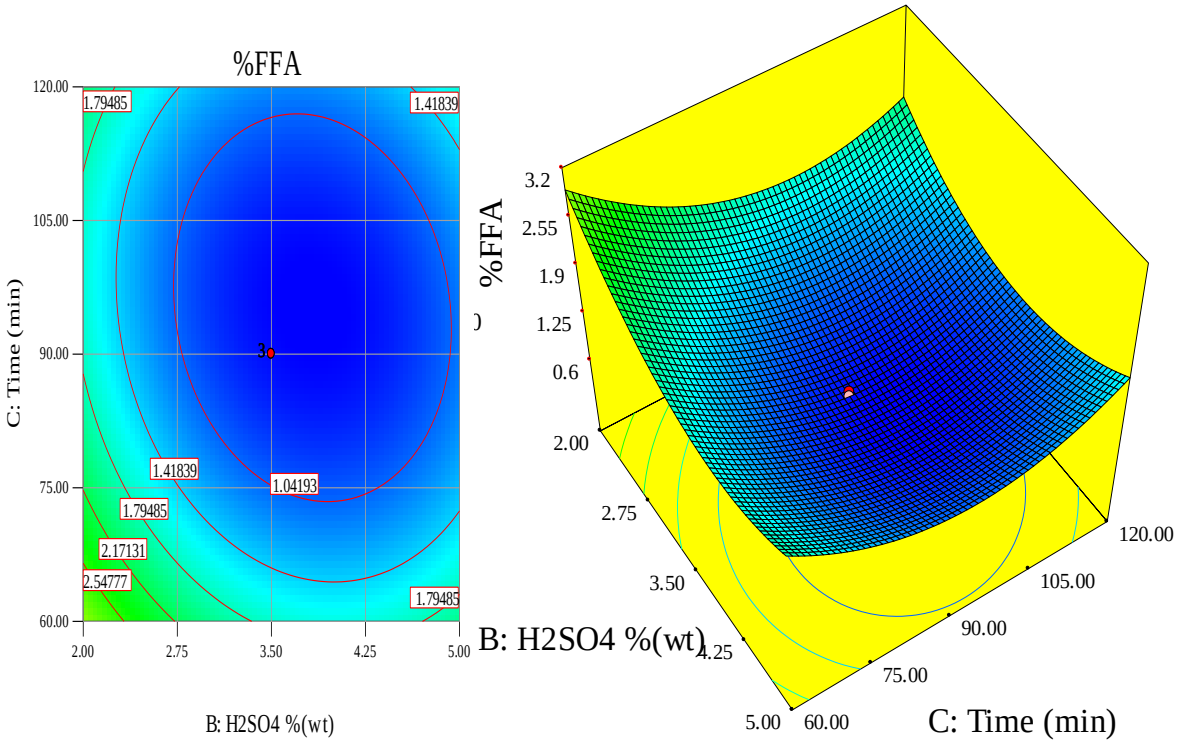


Figure 4.5: Effect of reaction time and catalyst concentration to %FFA reduction

4.5.3. Numerical optimization and validation of the result

Numerical optimization technique based on desirability function was carried out to determine the optimum conditions for the reduction of % FFA content of the SCG oil prior to conduct transesterification reaction. The numerical optimization as provided in the Design Expert 7.0.0 software was employed on the model. In the esterification reaction, the goal for methanol to oil molar ratio, catalyst concentration and reaction time were set in range based upon the requirements of the % FFA was set on minimize.

Table 4.7: Desirability specifications for esterification variables and response

Independent factors	Optimazation Goal	Lower Limit	Upper Limit
Methanol to oil molar ratio	is in range	3	9
H_2SO_4 concentration %(wt)	is in range	2	5
Reaction time (min)	is in range	60	120
%FFA Reduction	minimize	0.69	4.25

The selected solution was based on its closeness to the set optimization goals and maximum combined desirability function value. For this study, the selected optimum FFA (0.6054 %) from the experiments corresponding to the parameters methanol to oil molar ratio (6.4:1), catalyst concentration is 3.7 (% wt), and reaction time is 94 minutes was found while the desirability was 1. In addition to this, once the optimal value of the design parameters has been selected, the final step was to predict and verify the improvement of the quality characteristic using the optimum level of the design parameters. Therefore, to verify the validation of the study, triplicate experiments was carried out based on predicted value of each variables. The model validation of the acid esterification process is shown in table 4.8. As it shown in the table average actual value of %FFA was found to be 0.61% .This result indicated that the errors between the predicted and the actual value were less than 1%, hence , the regression model was satisfactory.

Table 4.8: Model validation of the acid esterification process

Variables	Optimum value
Methanol to oil molar ratio	6.4
Catalyst concentration %(wt)	3.7
Reaction time(min)	94
%FFA predicted	0.6054
%FFA actual	0.61
Error (%)	0.75

Finally, the density of the esterified oil for this optimal condition was measured prior to calculate the yield of transesterification process. The measured density of esterified spent coffee ground oil was 0.885g/ml.

4.6. Statistical analysis of base catalyzed transesterification process

Similar to the esterification discussed earlier, transesterification process was carried out with varying methanol to oil molar ratio (A),catalyst concentration (B) and reaction time (C), at constant stirring speed at 500 rpm and reaction temperature of 60 ℃ to determine corresponding optimum conditions using RSM. The experimental and predicted result of biodiesel yield (%) of the central composite design and the statistical analysis of the ANOVA are given in Table 4.9 and 4.10 respectively.

The final equation in terms of coded factors is given as eqn. (4.3).

$$\text{Biodiesel yield } (\%) = 91.29 + 1.94 \times A + 2.49 \times B + 2.05 \times C - 2.19 \times A \times B - 3.19 \times A \times C - 1.31 \times B \times C - 5.27 \times A^2 - 4.48 \times B^2 - 4.13 \times C^2 \quad (4.3)$$

Final equation in terms of actual factors is given as eqn. (4.4)

Biodiesel yield(%) = -77.833+[15.840× Methanol to oil molar ratio] +[41.203 × KOH concentration %(wt)]+[1.299× Reaction time]-[0.972 × Methanol to oil molar ratio × KOH concentration %(wt] -[0.035 × Methanol to oil molar ratio × Reaction time] -[0.058× KOH concentration %(wt)× Reaction time]-[0.58606 ×Methanol to oil molar ratio^2]-[7.963× KOH concentration %(wt) ^{2}]-[4.584^-3 × Reaction time ^{2}] (4.4

Table 4.9: The experimental and predicted biodiesel yield values after transesterification

Run	Methanol to oil molar ratio	KOH concentration %(wt)	Reaction time (min)	Density (g/ml)	Volume (ml)	Biodiesel Yield (%)	
						Actual value	predicted value
1	6.00	0.75	60.00	872.5	12.95	63.50	64.26
2	12.00	0.75	60.00	871.4	15.95	78.00	78.88
3	6.00	2.25	60.00	871.7	15.41	75.50	76.23
4	12.00	2.25	60.00	870.7	16.65	81.50	82.10
5	6.00	0.75	120.00	870.4	15.53	76.00	77.35
6	12.00	0.75	120.00	872.9	15.9	78.00	79.22
7	6.00	2.25	120.00	870.1	16.97	83.00	84.07
8	12.00	2.25	120.00	872.9	15.49	76.00	77.19
9	3.95	1.50	90.00	871.6	15.21	74.50	73.12
10	14.05	1.50	90.00	871.2	16.54	81.00	79.63
11	9.00	0.24	90.00	872.5	15.5	76.00	74.44
12	9.00	2.76	90.00	871.5	17.15	84.00	82.80
13	9.00	1.50	39.55	871.9	15.71	77.00	76.18
14	9.00	1.50	140.45	871.5	17.35	85.00	83.06
15	9.00	1.50	90.00	870.2	18.5	90.50	91.29
16	9.00	1.50	90.00	870.5	18.68	91.40	91.29
17	9.00	1.50	90.00	870.3	18.7	91.50	91.29

Table 4.10: ANOVA result for transesterification reaction

Source	Sum of Squares	Df	Mean Square	F-Value	p-value	Remark
Model	792.25	9	88.03	29.53	< 0.0001	Significant
A-Methanol to oil molar ratio	51.16	1	51.16	17.16	0.0043	>>
B-KOH concentration %(wt)	84.42	1	84.42	28.32	0.0011	>>
C-Reaction time (min)	57.22	1	57.22	19.19	0.0032	>>
AB	38.28	1	38.28	12.84	0.0089	>>
AC	81.28	1	81.28	27.26	0.0012	>>
BC	13.78	1	13.78	4.62	0.0686	Not significant
A^2	313.64	1	313.64	105.2	< 0.0001	>>
B^2	226.17	1	226.17	75.86	< 0.0001	>>
C^2	191.87	1	191.87	64.36	< 0.0001	>>
Residual	20.87	7	2.98			
Lack of Fit	20.26	5	4.05	13.36	0.0711	Not significant
Pure Error	0.61	2	0.30			
Cor Total	813.12	16				
C.V. = 2.15, R^2 = 0.9743, Pred. R^2 =0.8102, Adj. R^2 =0.9413, Adeq. Precision = 20.415						

Table 4.11: Model summary statistics for base catalyzed transesterification

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	6.91	0.2371	0.0611	-0.1107	903.15	
2FI	6.98	0.4011	0.0418	-0.6646	1353.48	
Quadratic	**1.73**	**0.9743**	**0.9413**	**0.8102**	**154.34**	**Suggested**
Cubic	2.56	0.9758	0.8710	-4.1785	4210.77	Aliased

The model F-value of 29.53 implied the model is significant for the transesterification. There is only 0.01% chance that an F-value this large could occur due to noise. Values of "Prob> F" less than 0.05 indicated model terms are significant. In this case A, B, C, AB, AC, A^2, B^2 and C^2 are significant model terms as shown Table 4.10. The "Lack of Fit p-value" of 0.0711 implied the Lack of Fit was not significant relative to the pure error. There is 7.11% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit was required to validate the model. The "Predicted R^2 = 0.8102 was in agreement with the "Adj R^2=0.9413. Moreover, the Adeq Precision" measured the signal to noise ratio. The ratio of 20.415indicated an adequate signal. The coefficient of determination (R^2 = 0.9743) found, implied that the accuracy of the predictive model was adequate.

The predicted values versus actual values is shown in Fig. 4.6. The data have linear behavior and are distributed close to diagonal line. Therefore, the obtained second-order polynomial model is quite satisfactory for predictions of biodiesel yield from transesterification reaction.

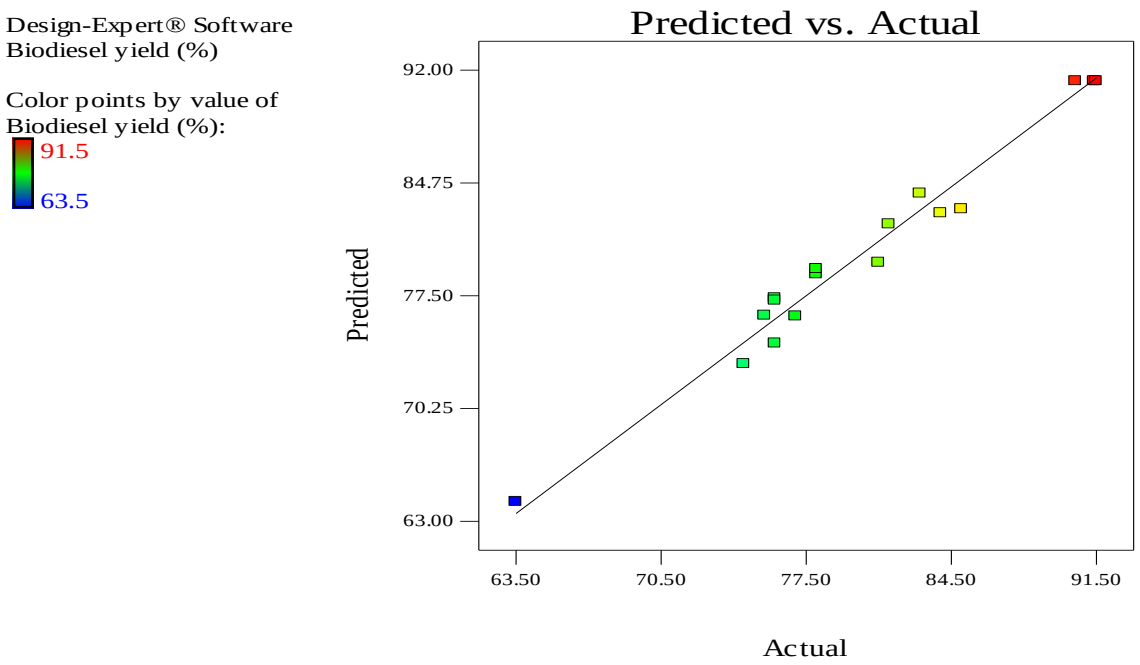


Figure 4.6: Predicted vs. actual yield for transesterification

4.6.1. Effects of Individual Process Variables

Effect of methanol to oil molar ratio: One of the most important parameters affecting the yield of the ester is the molar ratio of alcohol to vegetable oil**.** The stoichiometry of the transesterification reaction requires 3:1 molar ratio to yield 3mol of ester and 1mol of glycerol, but from literature, it is found that excess alcohol is required to drive the reaction close to completion. The presence of slight excess amount of alcohol during the transesterification reaction is essential to break the glycerin- fatty acid linkages (Guo 2006). The effect of methanol to oil molar ratio on biodiesel yield (%) is shown in fig.4.7a .The effect of methanol to oil molar ratio in the range of 6:1 to 12:1 was investigated, keeping the catalyst concentration at 1.5%wt and reaction time for 90min. As shown in Fig. 4.7a, the maximum biodiesel yield was obtained at a methanol to oil molar ratio of 9:1. Further increase in molar ratio of methanol to oil beyond 9:1 the yield of biodiesel was reduced. Because, an excess of methanol, will interfere with the separation of glycerin because there is an increase in solubility with part of the glycerin present in the biodiesel phase. In addition, the glycerin that remained in the biodiesel phase may drive the equilibrium back to the reverse reaction.

Effect of catalyst concentration: The effect of catalyst concentration affects the yield of the biodiesel production in a positive manner up to a certain concentration. As the catalyst concentration increases the conversion of the yield of biodiesel increase. This is because an insufficient amount of catalysts result in an incomplete conversion of the triglycerides into the fatty acid esters. The effect of catalyst concentration on biodiesel yield is shown in fig. 4.7b. It can be seen that, when the catalyst concentration increased from 0.75 to 1.5%wt the biodiesel yield was increased linearly from 84.2 to 91.4. As shown in the figure further increase of catalyst concentration beyond 1.5%wt the biodiesel yield decreases drastically. This is due to a higher catalyst concentration greater than 1.5% soap formation occurred and a lower yield of biodiesel was obtained and separation phase was difficult for higher catalyst concentration.

Effect of reaction time: The effect of reaction time on biodiesel yield is shown in figure 4.7c. It can be seen that the biodiesel yield is increased with increase in reaction time up to 90 min and after that yield is decreased. 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(Ma and Hanna 1999).

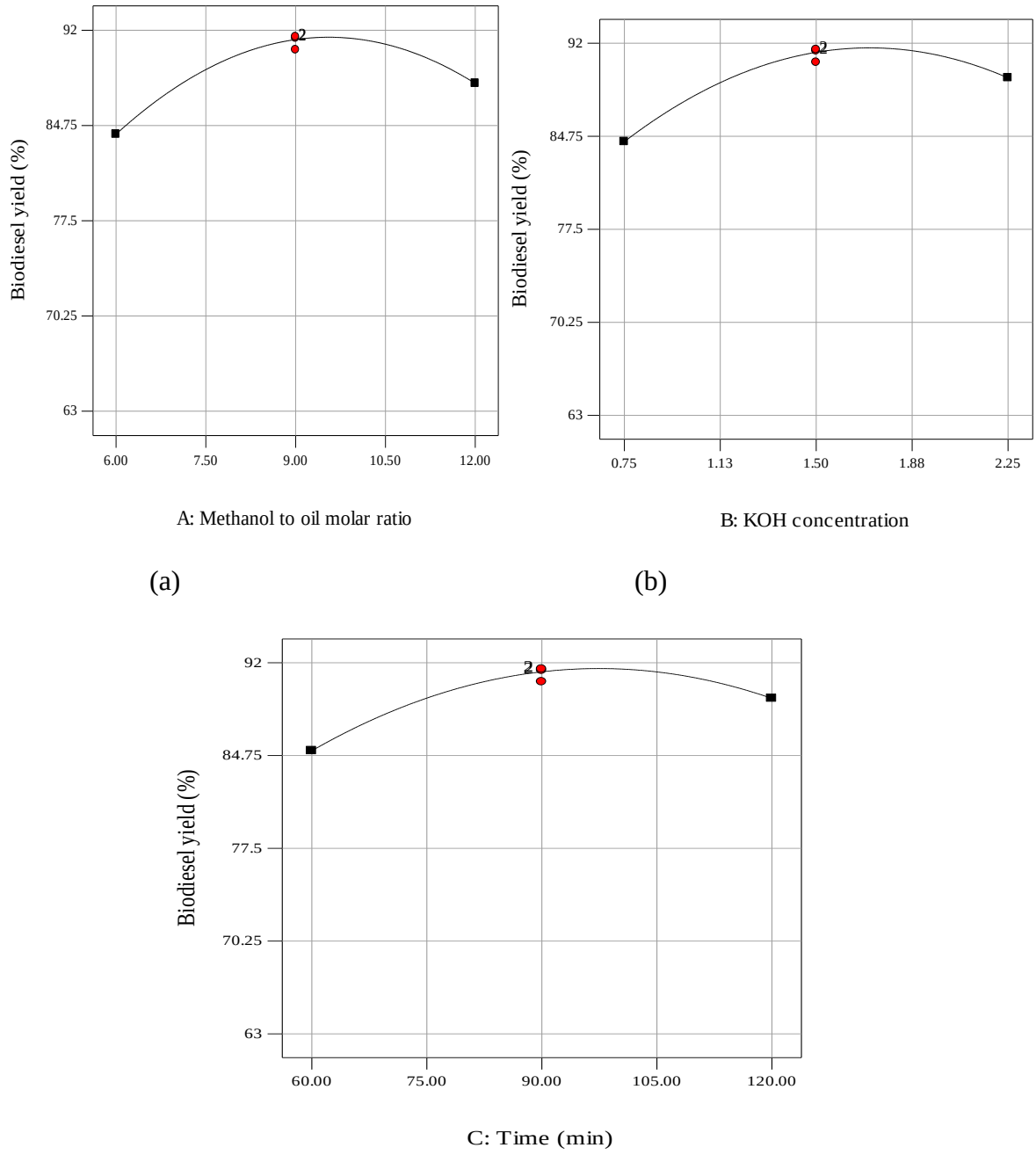


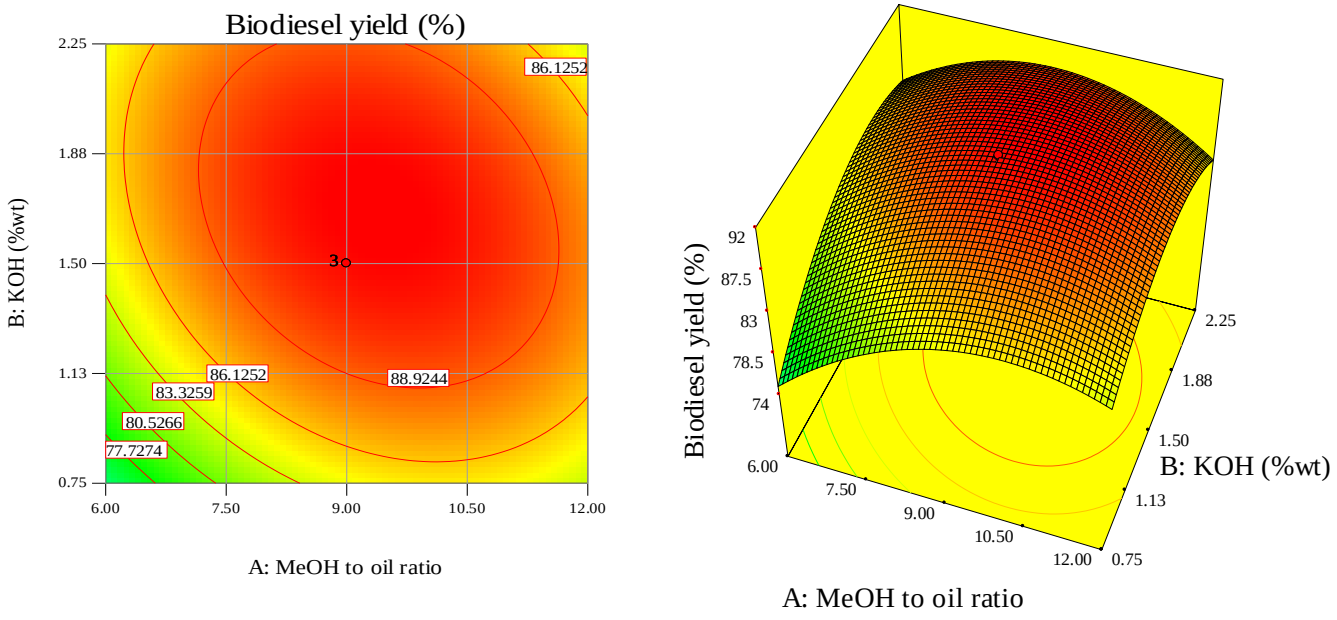
Figure 4.7: Effect of individual parameters on the yield of biodiesel

4.6.2. Effect of interaction parameter on biodiesel yield

The 2D contour and 3D response surface plots showing the effect of methanol to oil molar ratio, catalyst concentration and reaction time and their interactions on biodiesel yield are shown in Figs. 4.8 – 4.9.

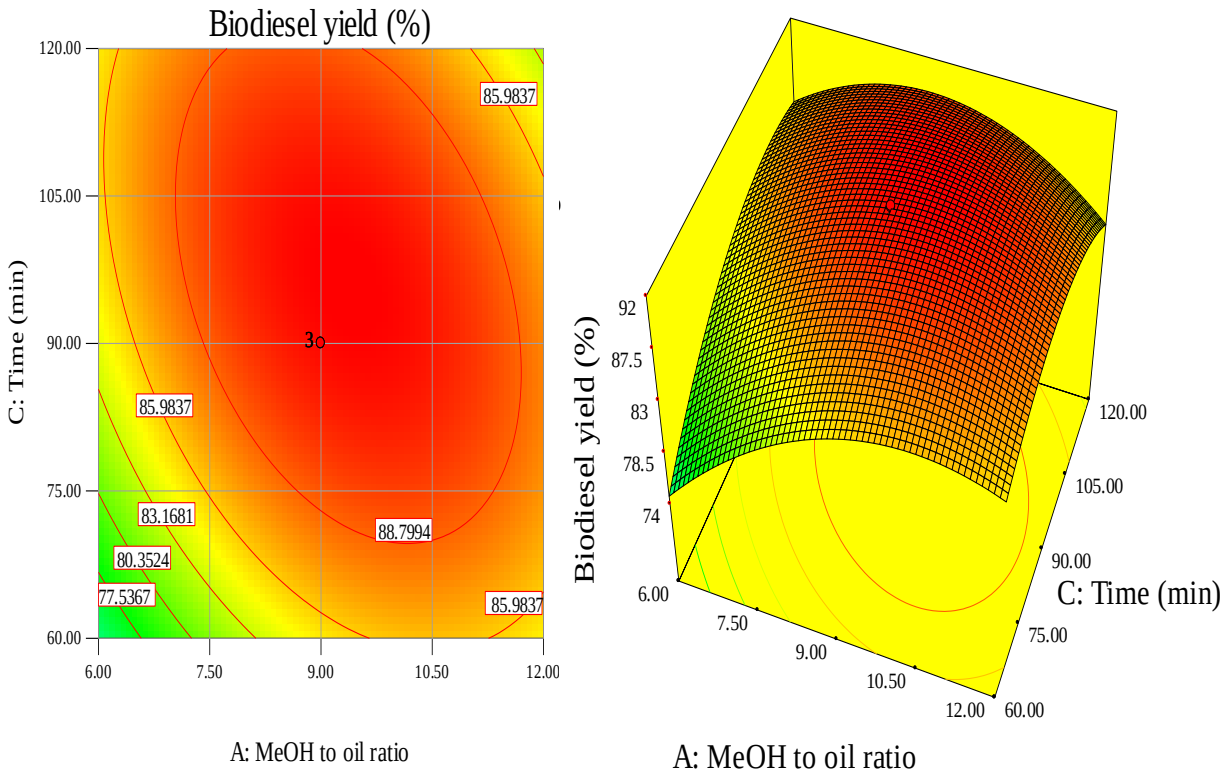
Fig. 4.8 shows 2D counter and 3D response plots between methanol to oil molar ratio and catalyst concentration for constant reaction time (90min). From Fig.4.8, it can be seen that, the biodiesel yield increases with the increasing methanol to oil molar ratio and catalyst concentration. Afterwards, the yield start to slightly decrease as the molar ratio increases. In general, a high molar ratio results in a higher rate of methyl ester formation and ensures completion of the reaction. However, overloading of methanol would inactivate the catalyst and reversed the reaction since transesterification is a reversible reaction.

Fig. 4.9 shows the 2D counter and the 3D surface plot of effect of methanol quantity and reaction time for constant catalyst concentration (1.5%wt). From Fig.4.9, it is observed that, when reaction time was less with less amount of methanol to oil ratio, the biodiesel yield was very less as there was incomplete reaction and thus for given reaction time, the yield found to be increase with increase in molar ratio of methanol to oil till maximum yield was reached for that particular parameters . It found to decrease with further increase in molar ratio of methanol to oil used. Moreover, for given molar ratio of methanol to oil, yield was found to increase with increase in reaction time.



(a) (b)

Figure 4.8: Interaction effect of methanol to oil molar ratio and catalyst on yield



(a) (b)

Figure 4.9: Interaction effect of methanol to oil molar ratio and reaction time on yield

4.6.3. Numerical optimization and validation of the result

Similar to esterification discussed earlier, the numerical optimization of transesterification process variables was employed in the Design Expert 7.0.0 software.

Table 4.12: Desirability specifications for transesterification variables and response

Independent factor	Optimization Goal	Lower Limit	Upper Limit
Methanol to oil molar ratio	is in range	6	12
KOH concentration %(wt)	is in range	0.75	2.25
Reaction time (min)	is in range	60	120
Biodiesel Yield (%)	maximize	63.5	91.5

The predicted optimum values of methanol to oil molar ratio, catalyst amount and reaction time were found to be 9.35:1, 1.58 % and 91.95 min, respectively, to achieve 91.718 % of biodiesel; while desirability was 1.00 for the experiment. Once the optimal value of the design parameters

has been selected, the final step was to predict and verify the improvement of the quality characteristic using the optimum level of the design parameters. By evaluating the yield under transesterification, the average possible predicted yield is found to be 91.718%, as illustrated in the Table 4.13

Table 4.13: Optimized conditions and validation for transesterification process

Predicted optimal conditions and yield				Validation experiments				E (%)
A	B	C	Y (%)	Y1 (%)	Y2(%)	Y3(%)	Avarage Y(%)	0.129
9.35	1.58	91.95	91.718	91.7	91.72	91.68	91.7	

Where: A: Molar ratio (methanol/oil); B: Catalyst concentration (%wt); C: Reaction time (minutes; E: error and Y: biodiesel yield

The predicted conversion value of 91.718% was approximately equal to the average observed value of 9.71%. Therefore, the experimental value showed acceptable agreement with the predicted values. The errors values between the predicted and the observed results were less than 1% biodiesel conversion, indicating that the regression model was satisfactory.

4.7. Physicochemical Properties of Biodiesel

The physical and chemical properties of the produced biodiesel was characterized by according to the procedures mentioned under section 3.3.2. The biodiesel produced from esterified spent coffee ground oil using the optimal conditions were analyzed for their fuel properties. Their properties were compared to the ASTM D 6751 and European (EN14214) biodiesel standard in order to confirm their suitability as fuel in diesel engines.

Density: The density of a fuel is an important factor for good engine performance; the higher the density, the more difficult it becomes to pump the fuel. The density of the biodiesel produced was obtained to be 870.3kg/m^3 and it met the EN 14214 regulation, which required a biodiesel density between 0.86 – 0.90 g/ml. On transesterification, the density was reduced from 898 to 870.3g/ml; this could be due to presence of free fatty acids in the oil.

Viscosity: The viscosity of the produced biodiesel measured at 40 °C was found to be 4.13 mm^2/s. After transesterification of the oils to their corresponding biodiesel, the kinematic viscosity oil was significantly reduced from 45.91to 4.13mm^2/s. The reduction in viscosity is expected in biodiesel production, since transesterification reduces viscosity and improves other fuel properties. Biodiesel having high viscosity does not burn completely and often leads to operational problems including deposit formation in the fuel injector of diesel engines .When compared to the ASTM D6751 and EN14214 the kinematic viscosities of the biodiesel obtained are within this specified range.

Acid value: Acid value is the number of milligram of KOH required to neutralize the free fatty acid in 1g of the oil. The acid value of the produced biodiesel was found to be (0.35 mg KOH/g) and it conforms to the ASTM standard. The acid number of biodiesel depends on the fatty acid content of the feedstock used. The result indicates that there was appreciable reduction in percentage free fatty acid of the biodiesels compared to their oils, as high proportion of the FFA was reduced during esterification and the transesterification cleaning and drying processes were effective. Since, this low acid values in these fuels will not pose any threat to the engine operating components, especially the fuel injection equipment.

Iodine value: Iodine value is one of the crucial property of biodiesel that greatly influences the oxidation stability, polymerization of glycerides and unsaturation degree. This can lead to the formation of deposits in diesel engines injectors. The iodine value of the produced biodiesel was calculated using the empirical formula that was discussed in eqn.3.12. The iodine value of SCG biodiesel was 78.5 mg I_2/100g. The result was in the acceptable range as the limit for EN14214 standard is 120 g I_2/100 g.

Flash point: The flash point is the lowest temperature at which an applied ignition source will cause the vapours of the fuel to ignite. The flash point was determined after the sample was dried to remove residual methanol and water according to the standard method, ASTM D93. The measured flash point of biodiesel was 162°C. This result shows that high flash point temperatures for fuels ensure safe handling and storage. The produced biodiesel from SCG oil thus meet the requirements of the ASTM D6751 biodiesel standards, which prescribe the minimum flash point of 130^oC.

Calorific value: The calorific value of the produced biodiesel was carried out at geological survey of Ethiopia. The calorific value or heat of combustion of a fuel oil is a measure of the amount of heat released during complete combustion of a unit mass of the fuel, expressed in kilojoules per kilogram. The calorific value of SCG oil based biodiesel was 9648.64 Cal/gm, which is equal to 40.39MJ/kg. This result is in the range of the requirement set by the ASTM standard for the calorific value of biodiesel 37-42.5MJ/kg. Thus, based on the SCG biodiesel calorific result, the SCG biodiesel can be used as potential alternative fuel.

Cetane number: Cetane number is another important property of fuels; this is a measure of the combustion quality of a diesel during compression ignition. The ignition quality, as a result of the cetane number affects engine performance, cold starting, warm up, and engine combustion roughness. Cetane rating is related to the volatility of the fuel where more volatile fuels have higher ratings. A high cetane fuel also may lead to incomplete combustion and smoke if the fuel ignites too soon by not allowing enough time for the fuel to mix with air for complete combustion (Joshua, 2012). The cetane number of the SCG biodiesel was calculated using eqn. 3.12. As the result shown in table 4.15 the cetane number was found to be 57.4, which is well within range; it is hence suitable to run in diesel engines.

Table 4.14: Summary of physicochemical properties of produced biodiesel

Biodiesel properties	Units	Measured values	ASTM D6751	EN14214
Density @ 25ºC	kg/m^3	870.3	880	860–900
Kinematic viscosity @40℃	mm^2/s	4.13	1.9-6.0	3.5-5.0
Flash point	℃	162	130 Minimum	110 Minimum
Acid value	mg KOH/g	0.35	0.5 maximum	0.5 maximum
Saponification value	Mg KOH/kg	189.45	-	-
Iodine value	g I_2 per 100 g	78.5	-	120
High heating value	Mj/kg	40.39	37-42.5	>35
Cetane value	-	57.4	47Minimum	51 Minimum

4.7.1. GC-MS analysis of biodiesel

The fatty acid methyl ester profile of SCG biodiesel was done by GCMS at JIJE analytical testing service laboratory. The chromatogram revealed the presence of saturated and unsaturated fatty acid with major and minor composition. From table 4.18, the results showed that Linoleic acid (18:2) was the predominant fatty acid (47.63%) in biodiesel sample. The other major component of biodiesel 9, 12-octadecanoic acid Methyl Ester (31.99%), Hexadecanoic acid, methyl ester (9.51%) and Methyl stearate (5.14%) were present in the SCG biodiesel. The other fatty acids were minor in concentrations. The percentage of saturated, mono-unsaturated and di-unsaturated fatty acids constitute are 17.65, 34.23 and 48.12% out of the total fatty acid compositions. From this result, the biodiesel containing more unsaturated fatty acid is less viscous and thus can be transferred more easily from the reservoir to the engine at low temperature. This result shows that the biodiesel can be considered as a better biodiesel at low temperatures. It emits lower HC and CO, and less smoke compared to highly saturated biodiesel fuel.

Table 4.15: Fatty acid profile of spent coffee ground biodiesel

Fatty acid methyl ester	Formula	Retention time	Area %
7-Hexadecenoic acid, methyl ester, (Z)-	$C_{17}H_{32}O_2$	13.92	0.13
Hexadecanoic acid, methyl ester	$C_{17}H_{34}O_2$	14.44	9.51
Heptadecanoic acid, methyl ester	$C_{18}H_{36}O_2$	17.26	0.06
9,12-Octadecadienoic acid, methyl ester	$C_{19}H_{34}O_2$	20.14	47.63
9-Octadecenoic acid, methyl ester, (E)-	$C_{19}H_{36}O_2$	20.49	31.99
9-Octadecenoic acid (Z)-, methyl ester	$C_{19}H_{36}O_2$	20.60	1.26
Methyl stearate	$C_{18}H_{32}O_2$	21.51	5.14
9,12-Octadecadienoic acid (Z,Z)-	$C_{19}H_{36}O_2$	21.70	0.33
12,15-Octadecadienoic acid, methyl ester	$C_{19}H_{34}O_2$	24.53	0.11
Eicosanoic acid, methyl ester	$C_{21}H_{42}O_2$	29.46	0.81
Docosanoic acid, methyl ester	$C_{23}H_{46}O_2$	34.24	1.93

Chapter Five

5. Conclusions and Recommendations

5.1. Conclusions

In coffee consuming countries, spent coffee ground waste constitutes a source of severe contamination and serious environmental problems. However, spent coffee ground waste is a good feedstock for biodiesel production when used in substantial quantities. The present study aimed at producing an alternative energy from spent coffee ground waste. The two-step acid base catalyzed methods are used to produce biodiesel from spent coffee ground. The process parameters affecting the FFA and yield of biodiesel has been studied and the statistical and experimental design was done by using design expert 7.0.0 software based on central composite design by response surface methodology. The effects of methanol to oil molar ratio, catalyst concentration and reaction time were investigated. Several physicochemical properties such as kinematic viscosity, density, calorific value, acid value, FFA, iodine value and flash point were used to compare the result with international standard. Gas chromatography and mass spectroscopy was also used to identify the fatty acid methyl ester components in the produced biodiesel. The results of the study showed that the FFA content with in SCG oil was reduced from 6.1 to 0.69% during the acid catalyzed esterification reaction that occurred in the presence of 3.5% acid catalyst (w/w) and 6:1 molar ratio for 90 min. The optimum reaction conditions for base catalyzed transesterification of the esterified oil were found to be 9:1 molar ratio of methanol to oil, 1.5% catalyst (w/w) at 90min reaction time. These conditions gave FAME yield of 91.5% by weight. When molar ratio of methanol to oil, catalyst concentration and reaction time were increased, the % FFA value decreased and biodiesel yield increased until the optimal amount. However, further addition of these working variables during transesterification reaction results in reduction of biodiesel yield due to formation of emulsion, which made difficulty in the separation of biodiesel from glycerol. The physiochemical results clearly indicate that the produced biodiesel was in good agreement with ASTM standard. Based on results of this study, it can be concluded that; the utilization of spent coffee ground waste as biodiesel production can reduces the environmental pollution and reduces the overdependence on petroleum in Ethiopia. It also provides alternative energy solutions for small-scale holders.

5.2. Recommendations

Based on the current study of this investigation the following recommendations are forwarded:

- The potential use of spent coffee ground emerges to be hopeful promising applications in the biodiesel production. In our country Ethiopia large amount of spent coffee grounds are disposed to land, until now SCG have no conversion to usable products and as such among the major problems. Hence, it recommended that government or other investor's to recover this very valuable product as well as to contribute to the country in reducing the highly rising quantity of wastes.
- This study found a good relation between the chemical composition of biodiesel and various important fuel quality parameters. This research can be further extended for additional fuel properties such as lubricity, copper strip corrosion, distillation temperature, fire point, cloud point, pour point etc.
- Optimizing biodiesel production using acid base catalyzed methods of spent coffee ground oil in various agitation speed and reaction temperature also suggested for further study.
- A further study of blending of biodiesel with petrol diesel is recommended since it would be able to improve the spent coffee ground biodiesel properties in a diesel engine.
- Further research should be done on the cost benefit analysis to determine the commercial viability of producing biodiesel from spent coffee ground on in large scale.

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Appendices

Appendix A: Composition of spent coffee ground oil

Table A1: Fatty Acid composition of spent coffee ground oil

Fatty acid		Chemical structure	Weight %
Palmitic	C 16	CH3(CH2)14COOH	33.99
Stearic	C 18	CH3(CH2)16COOH	10.91
Oleic	C 18:1	CH3(CH2)7CH=CH(CH2)7COOH	7.16
Linoleic	C 18:2	CH3(CH2)3(CH2CH=CH)2(CH2)7COOH	23.27
Arachidic	C 20	$CH_3 (CH_{2)18} COOH$	4.04

Source : (Deligiannis 2011)

Appendix B: Experimental result of spent coffee ground oil

Table B1: Viscosity of spent coffee ground oil

Dynamic viscosity (mpa.sec) at 40°C	Average dynamic Viscosity (mpa sec)	Density of oil (g/cm^3)	Kinematic viscosity (mm^2/sec)
41.25	41.227	0.898	45.91
42.204			

Table B2: Acid value and %FFA of spent coffee ground oil

Run	$M_{KOH,ml}$	Mass of oil (g)	Titration volume, ml	Color change	Acid value (mg KOH/g oil)	FFA (%)
1	0.1	1	2.18	Brown to pink	12.23	6.03
2	0.1	1	2.17	Brown to pink	12.173	6.17
Average value					12.2	6.1

Table B3: saponification value of spent coffee ground

Run	V_{KOH}	V_{HCl}	Mass of oil(gm)	Saponification Value (mg KOH/g oil)	Color change
1	27.5	13.7	2	192.84	Brown to pink
2	27.2	13.5	2	192.1	Brown to pink
Average = 192.5					

Appendix C: Amount of the reactant required

For esterification reaction

(Base: 10ml of SCG oil)

- Amount of methanol required in volume (methanol to SCG oil ratio (9:1))

$N_{CH_3OH} = 6 \times N_{oil}$ (C-1)

$$\frac{V_{CH_3OH} \times \rho_{CH_3OH}}{M_{CH_3OH}} = 6 \times \frac{V_{oil} \times \rho_{oil}}{M_{oil}}$$

Where: M_{oil} =933.4 g/mol, $\rho_{oil} = 0.898 g/ml$

M_{CH3OH} =32.04 g/mol $\rho_{CH3OH} = 0.7818 g/ml$

$$V_{CH3OH} = 6 \times \frac{V_{oil} \times \rho_{oil}}{M_{oil}} \times \frac{M_{CH3OH}}{\rho_{CH3OH}} = 6 \times \frac{10 \times 0.898}{933.4} \times \frac{32.04}{0.7818} = 2.37ml$$

- Amount of the Sulfuric Acid (H_2SO_4) catalyst required in volume (3.5 wt% H_2SO_4 to oil)

$V_{H2SO4} = \quad = 0.035 \times \frac{V_{oil} \times \rho_{oil}}{\rho_{H2SO4}}$, where: ρ_{H2SO4} = 1.84g/ml

$V_{H2SO4} = \quad = 0.035 \times \frac{10 \times 0.898}{1.84} = 0.17ml$

For transesterification reaction

Base: 20 ml of esterified oil

- Amount of KOH catalyst required in mass (1.5wt%KOH to oil)

  Mass of KOH =0.015×mass of oil

  Mass of KOH =0.015× $(0.898g/ml \times 20ml)$ =0.27gram

- Amount of methanol required (9:1)

$N_{CH_3OH} = 9\times N_{oil}$

$$\frac{V_{CH_3OH}\times\rho_{CH_3OH}}{M_{CH_3OH}} = 6 \times \frac{V_{oil}\times\rho_{oil}}{M_{oil}}$$

Where: Density of esterified oil =0.885g/ml

$$V_{CH3OH} = 9 \times \frac{V_{oil}\times\rho_{oil}}{M_{oil}} \times \frac{M_{CH3OH}}{\rho_{CH3OH}} = 9 \times \frac{20\times0.885}{933.4} \times \frac{32.04}{0.7818} = 7ml$$

Appendix D: Standard specification of biodiesel

Table D1: Standard specification of biodiesel

Property specification	Units	Diesel ASTM D975		Biodiesel			
		Test method	Limits	ASTM D6751		EN 14214	
				Test method	Limits	Test method	Limits
Flash point	°C	ASTM D975	60–80	ASTM D 93	130 minimum	EN ISO 3679	101 minimum
Cloud point	°C	ASTM D975	−15 to −5	ASTM D2500	−3 to −12	–	–
Pour Point	°C	ASTM D975	−35 to −15	ASTM D97	−15 to −16	–	–
Cetane number		ASTM D4737	46	ASTM D613	47 minimum	EN ISO 5165	51 minimum
Density at 15 °C	Kg/m^3	ASTM D1298	820–860	ASTM D 1298	880	EN ISO 3675/ 12185	860–900
Kinematic viscosity at 40 °C	mm^2/s	ASTM D445	2.0 to 4.5	ASTM D445	1.9–6.0	EN ISO 3104	3.5–5.0
Iodine number	g I_2/ 100 g	–	–	–	–	EN 14111	–
Acid number	mg KOH/ g	–	–	ASTM D664	0.5 maximum	EN 14104	0.5 v maximum
Cold filter plugging point	°C	EN 590	−8	ASTM D6371	Maximum +5	EN 14214	–
Oxidation stability		ASTM D2274	25 mg/L maximum	–	–	EN 14112	3 h minimum
Carbon residue	% m/m	ASTM D4530	0.2 maximum	ASTM D 4530	0.050 maximum	EN ISO 10370	0.3 maximum
Copper corrosion		ASTM D130	Class 1 maximum	ASTM D 130	No. 3 maximum	EN ISO 2160	Class 1
Distillation temperature	°C	ASTM D86	370 maximum	ASTM D 1160	360	–	–
Lubricity (HFRR)	m	IP 450	0.460 mm (max.) (all diesel containing less than 500 ppm – sulphur)	ASTM D6079	520 maximum	–	–
Sulphated ash content	%mass	–	–	ASTM	D874 0.002 maximum	EN ISO 3987	0.02 maximum
Ash content	%mass	ASTM D482	100 maximum	–	–	–	–
. Water and sediment		ASTM D2709	0.05 maximum	ASTM D 2709	0.005 vol% maximum	EN ISO 12937	500 mg/kg
Monoglycerides	% mass	–	–	–	–	EN 14105	0.8 maximum
Diglycerides	% mass	–	–	–	–	EN 14105	0.2 maximum
Triglycerides	% mass	–	–	–	–	EN 14106	0.2 maximum
Free glycerine	%mass	–	–	ASTM D 6584	0.02 maximum	EN 1405/ 14016	0.02 maximum
Total glycerine	%mass	–	–	ASTM D6548	0.24	EN 14105	0.25
Phosphorus	%mass	–	–	ASTM D4951	0.001 maximum	EN 14107	0.001 maximum
Sulphur (S 10 grade)	ppm	ASTM D5453	10 maximum	–	–	–	–
Sulphur (S 15 grade)	ppm	–	–	ASTM D5453	150 maximum	–	–
Sulphur (S 50 grade)	ppm	ASTM D5453	50 maximum	–	–	–	–
Sulphur (S 500 grade)	ppm	ASTM D5453	500 maximum	ASTM D5453	500 maximum	–	–
Carbon	wt%	ASTM D975	87	ASTM PS121	77	–	–
Hydrogen	wt%	ASTM D975	13	ASTM PS121	12	–	–
Oxygen	wt%	–	–	ASTM PS121	11	–	–
BOCLE scuff	g	ASTM D975	2000–5000	ASTM PS121	> 7000	–	–
Conductivity at ambient temperature	pS/m	ASTM D2624	50 m minimum at ambient temp. (all diesel held by a terminal or refinery for sale or distribution)	–	–	–	–
Total contamination	mg/kg	–	–	ASTM D5452	24	EN 12662	24
Boiling point	°C	–	–	ASTM-D7398	100–615	–	–
Saponification value	mg KOH/g	–	–	ASTM D5558	370 maximum − 95	–	–

Appendix E: Calorific value of spent coffee ground oil

1cal = 4.1868 Joule

Calorific value (MJ/kg) =9,015.72 $\left(\frac{cal}{gm}\right) \times \frac{1000gm}{1kg} \times \frac{4.1868J}{1cal}$ =37, 747,016.5$\frac{J}{kg}$ = 37.74$\frac{MJ}{kg}$

	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: - 03/06/2019

Customer Name: - Yohannes Alemu.

Request No: - GLD/358/19

Report No: GLD/TR/298/19

Sample type: - Liquid

Sample Preparation: - None

Date Submitted: - 27/05/2019

Number of Sample: -One (1)

Elements to be determined:- Calorie.

Method of analysis:- Adiabatic Calorie Metter.

Collector's Code	Calorific Value cal/gm
SCG oil	9,015.72

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

Analysts

Hayimanot Bayeh

Shashie Hailie

Approved By

Alemnesh Abate

Quality Control

Negash Worku

Figure E1: Calorific Value of spent coffee ground oil

Appendix F: Laboratory result of GC-MS

JIJE LABOGLASS Pvt. Limited Company	JIJE Analytical *Testing* Service Laboratory	Doc. No: JATSL/F5.10-3	Page 1 of 1	
			Ver. No: 04	Effective Date: July 08, 2017
	Analytical Test Report			
Customer Name	AAiT	Test Report No	122	
Contact Person:	Yohannes Alemu	Reported Date:	18/04/2019	
Sample Type:	Spent Coffee Ground Oil	Test Request No:	Not Specified	
Sample Source:	Not Specified	Tel:	+251 934 65 00 87	
Sample collected by:	Customer	Fax:	Not Specified	
Sample Collected Date:	27/07/2011 EC	E-mail:	johalemu65@gmail.com	
Sample Received Date:	15/04/2019	Tested By:	LE-02	
Sample Condition	Normal	Date Tested:	16-17/04/2019	

S/N	Name	Formula	RT	Area	Area %
1	Methyl tetradecanoate	C15H30O2	10.93	512771.00	0.10
2	7-Hexadecenoic acid, methyl ester, (Z)-	C17H32O2	13.92	701418.00	0.13
3	Hexadecanoic acid, methyl ester	C17H34O2	14.44	51217652.00	9.51
4	n-Hexadecanoic acid	C16H32O2	15.30	294911.00	0.05
5	Heptadecanoic acid, methyl ester	C18H36O2	17.26	342947.00	0.06
6	9,12-Octadecadienoic acid, methyl ester	C19H34O2	20.14	256591397.00	47.63
7	9-Octadecenoic acid, methyl ester, (E)-	C19H36O2	20.49	172353941.00	31.99
8	9-Octadecenoic acid (Z)-, methyl ester	C19H36O2	20.60	6795710.00	1.26
9	Methyl stearate	C19H38O2	21.51	27672379.00	5.14
10	9,12-Octadecadienoic acid (Z,Z)-	C18H32O2	21.70	1750974.00	0.33
11	cis-Vaccenic acid	C18H34O2	22.02	1716068.00	0.32
12	12,15-Octadecadienoic acid, methyl ester	C19H34O2	24.53	569985.00	0.11
13	Z,Z,Z-4,6,9-Nonadecatriene	C19H34	27.58	284725.00	0.05
14	12,15-Octadecadienoic acid, methyl ester	C19H34O2	28.40	272133.00	0.05
15	cis-Methyl 11-eicosenoate	C21H40O2	28.62	2852042.00	0.53
16	Eicosanoic acid, methyl ester	C21H42O2	29.46	4382727.00	0.81
17	Docosanoic acid, methyl ester	C23H46O2	34.24	10422007.00	1.93

S/N	Parameters	Test Methods
1	Fatty Acid Profile	GC-MS

Remark:

1. This test report is only for specific sample (s) which has been tested by JIJE Analytical *Testing* Service Laboratory.

Verified by

Name: Gemechu Sorsa — Signature: ..... — Date: 18/04/2019

Technical Signatory

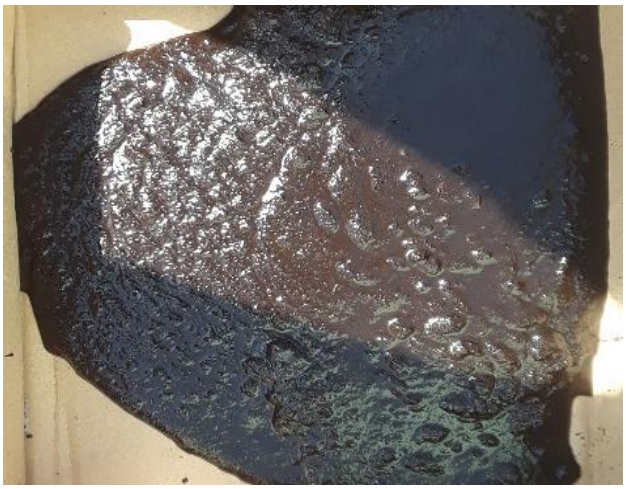
Authorized by

Name: Mulugeta Terefe — Signature: ..... — Date: 18/04/19

Laboratory Manager

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P.O. Box: 70077
E-mail: jije@ethionet.et
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Web site: www.jijelaboglassplc.com
Physical Address: Nifas Silk Lafto Sub City, Kebele 01, House Number New, Lebu, 200 m off the main road by the side of Abtam Center, Addis Ababa, Ethiopia.

Appendix G: Photos during laboratory activity



(a) Wet spent coffee ground



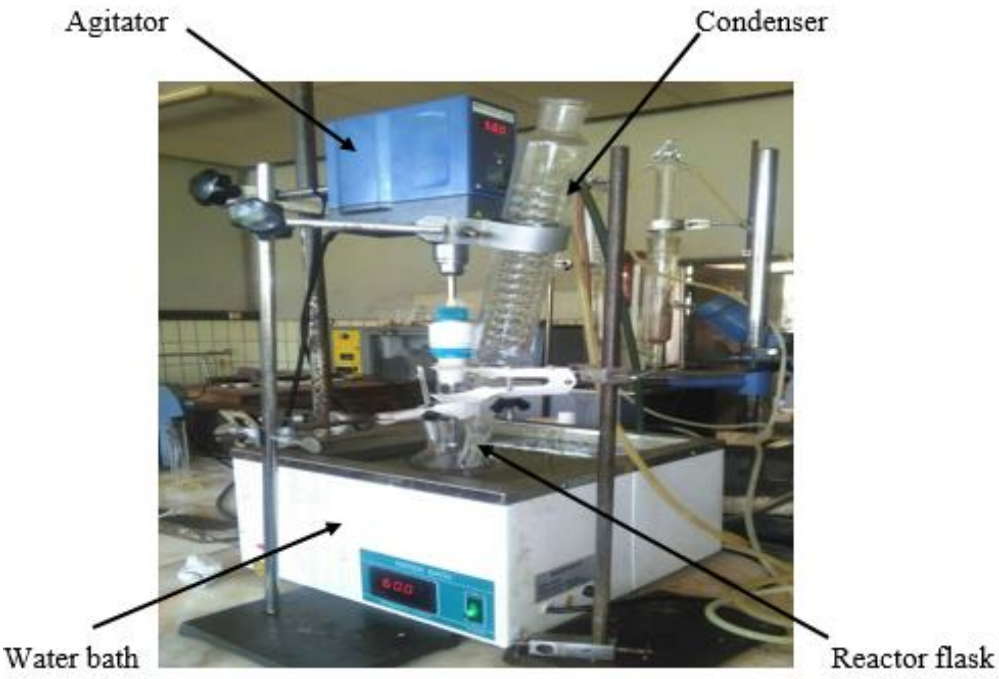
(b) Dried spent coffee ground



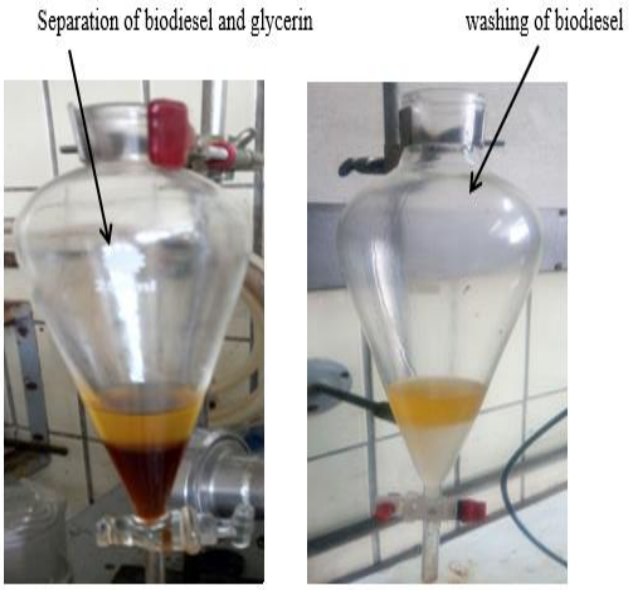
(A) Laboratory setup of soxhlet extraction unit



(B) vacuum rotary evaporator



(C) Experimental setup for the biodiesel production





(D)Separation of biodiesel (E) Washing of biodiesel (F) Produced biodiesel