PREPARATION AND CHARACTERIZATION OF BIOFUEL FROM U SED COOKING OIL

By: Debela Janko

A Thesis

Submitted to School of Applied Natural Sciences Department of Chemistry in Partial Fulfillment of the Requirements for the Degree of Master in Chemistry

Office of Graduate Studies

ADAMA SCIENCE AND TECHNOLOGY UNIVERSITY

September, 2018

Adama, Ethiopi

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By: Debela Janko

Advisor: Dr. Tegene Desalegn

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Advisor's approval sheet

To: Chemistry department

Subject: Thesis Submission

This is to certify that the thesis entitled Preparation and Characterization of Biofuel From Used Cooking Oil submitted in partial fulfillment of the requirement for degree of Masters in Chemistry, the Graduate program of the department of Chemistry and has been carried out by Debela Janko Id. No.GSU/0491/06 , under my supervision. Therefore, I recommend that the student has fulfilled the requirements and hence hereby he can submit the thesis to the department.

Dr.Tegene Desalegn	_____	_____
Name of advisor	signature	Date

APPROVAL OF BOARD OF EXAMINERS

We, the undersigned, members of the Board of Examiners of the final open defense by **Debela Janko** have been read and evaluated his/her thesis entitled "**Preparation and Characterization of Biofuel from Used Cooking Oil**" and examined the candidate. This is, therefore, to certify that the thesis has been accepted in partial fulfillment of the requirement of the Degree of Masters of Science in Chemistry

Supervisor /Advisor	Signature	Date
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DECLARATION

I hereby declare that this M.Sc Thesis is my original work and has not been presented for a degree in any other university, and all sources of material used for this thesis have been duly acknowledged.

Name: Debela Janko

Signature: _____

This M.Sc Thesis has been submitted for examination with my approval as thesis advisor.

Advisor Name: Dr. Tegene Desalegn

Signature: _____

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ACRONYMS

ASTM…….....American Society for Testing and Materials

B100……..Pure biodiesel

CP…….....Cloud point

EN……..European standard for biodiesel

DG……..Diglyceride

FAEE…….Fatty Acid Ethyl Esters

FAME…….Fatty Acid Methyl Esters

FFA…….Free Fatty Acid

FP……Flash point

psi…….....pounds per square inch

WCO…….....Waste Cooking Oil

ABSTRACT

Alternative fuel is currently an important issue all over the world. This is due to the efforts made on reducing global warming which is contributed by the combustion of petro diesel. Biodiesel is nontoxic, biodegradable, produced from renewable sources. It contributes a minimal amount of net greenhouse gases such as CO_2, SO_2 and NO_x emissions to the atmosphere. The present study is focused on the production of biodiesel from waste cooking oil thereby to reduce the cost of bio diesel, waste and pollution. Important variables such as oil to methanol ratio, types of reactants, the method of production and catalytic activities were selected to obtain a high quality biodiesel fuel within the specifications of American standards for biodiesel (ASTM). The highest biodiesel

yield (96%) was obtained using 1:6, oil to methanol ratio and 1.2%KOH catalyst by shaking the

reaction vessel. The method used was easy, fast; and the biodiesel produced under this condition exhibits characteristics almost nearest to that of biodiesel standards. The biodiesel characteristic s; including calorific value (42.71MJ/Kg), Kinematic viscosity (4.9 mm^2/s at 40 ^0C), copper strip corrosion (No.1a), acid value (0.5537mg KOH/g), density (at 15 ^0C, 0.8782g/mL), water and se diment (<0.05V %), flash point (>156), ash content (0.02) and cloud point (16) were obtained an d compared with biodiesel standards. But, the cloud point showed the result that is not valid in cold weather condition and this can be improved by blending the biodiesel with diesel fuel or preparing biodiesel by mixing waste palm oil with those having short chain fatty acid feedstock. Generally, biodiesel obtained under optimum conditions from mixtures of palm and sunflower waste cook-ing oil could be used more effectively as a fuel by blending with diesel fuel.

1. INTRODUCTION

1.1Background

Biodiesel has become more attractive nowadays, because of its environmental benefits; and the f act that the crude oil prices are increasing day by day, due to the limited resources of fossil fuels, new researches are being done to find an alternate of crude oils, through which environmental issues can be focused, mainly focusing on the edible and nonedible oils to produce biodiesel [1]. The diesel engine is widely used to provide power source and emits various forms of pollutants in gaseous, liquid and solid phases to the environment. These pollutants have a potential effect on the environment and can endanger human health [2]. The concern is increasing worldwide for environmental protection and for the conservation of nonrenewable natural resources. There are several reasons for biofuels to be considered as relevant technologies by both the developing and industrialized countries. They include energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to all countries in the world [3].

Although the volumetric heating values are a little low, biodiesel is a strong candidate to replace petroleum diesel, as their characteristics are generally similar in addition to the many attractive advantages of biodiesel over petro diesel including its low toxicity, renewability, biodegradable nature, high cetane number and flash point; and relative to conventional diesel, it emits reduced levels of pollutants. Fatty acid methyl esters are formed by transesterification, also called alcohol ysis, of vegetable oils. This process has been widely used to reduce the viscosity of triglycerides, thereby enhancing the physical properties of renewable fuels to improve engine performance [4].

Currently, more of the world biodiesel is produced from edible oil. However, a continuous and large scale production of biodiesel from edible oil has recently been a great concern because they compete with food materials the food versus fuel dispute. There are concerns that biodiesel feed stock may compete with food supply in the long-term. Non edible plant oil has been found to be promising crude oil for the production of biodiesel [5].

The use of non-edible oil for biodiesel production compared with edible oil is very significant in developing countries because of the tremendous demand of edible oil as food and they are far too expensive to be used as fuel at present [5]. The high cost of biodiesel is mainly due to the cost of virgin vegetable oil. Therefore, it is not surprising that the biodiesel produced from vegetable oil costs much more than petroleum based diesel. Therefore, it is necessary to explore ways to reduce production costs of biodiesel. In this sense, methods that permit minimizing the costs of the raw material are of special interest. The use of waste frying oil, instead of virgin oil, to produce biodiesel is an effective way to reduce the raw material cost because waste frying oil is estimated to be about half the price of virgin oil [6].

Biodiesel was prepared from waste cooking oil by a base-catalyzed transesterification reaction; but the reaction yield was too low then two-step method was conducted to increase the reaction yield [7]. In all these cases, the synthesis requires the use of either a hot plate or other heating source; which is uneconomic, slow and with a low yield.

In this study, biodiesel was prepared from mixture of palm and sunflower originated WCO by shaking method with base-catalyzed transesterification, using silica gel adsorbent and characterization of the fuel was carried out according to ASTM standard methods.

1.2 Problem Statement

The depletion of world petroleum reserves, the increase of petroleum price and environmental concerns has stimulated governments and researchers to look for alternative renewable energy sources that are technically feasible, economically competitive and environmentally acceptable [8]. Biodiesel is a clean burning fuel derived from vegetable oil or animal fat and is an advantageous alternative to fossil diesel fuel because of its biodegradability, very low sulfur content and toxicity [4]. Biofuels derived from biomass, have been gaining increasing attention recently as replacement forfossil fuels [9]. Biodiesel is the most common biofuels used in transport sector [10].

Currently, compared to petroleum based diesel, the high cost of biodiesel is a major barrier to its commercialization. A convenient way to lower the costs of biodiesel is to use the byproduct as a potential source of energy, rather than treat them as waste. A cheaper feedstock, such as waste cooking oil can be used to improve the economics of biodiesel which is competitive in price with petroleum diesel [11].

Beside to this , waste oil has many disposal problems like water and soil pollution, human health concern and disturbance to the aquatic ecosystem [12], so rather than disposing it and harming the environment, it can be used as effective and cost efficient feedstock for biodiesel production as it is readily available [13].

Therefore, due to the limited availability of agricultural area leading to competition with the food industries as well as the relatively high price for vegetable oils at the moment; making biodiesel from used cooking oil would help to reduce the costs of biodiesel production, the environment and health effect of used cooking oil and conserve resource by converting problematic waste into fuel.

1.3 Objectives of the Study

1.3.1 General Objective

- To prepare and characterize biodiesel from used cooking oil of palm and sunflower.

1.3.2 Specific Objectives

- To determine the free fatty acid of WCO that affect the yield and characteristics of the biodiesel produced.
- To produce biodiesel from the sample of used cooking oil on laboratory scale.
- To determine the biodiesel physical and chemical characteristics.
- To examine whether or not the fuel related properties of this biodiesel meet the standard and specifications of the prescribed ASTM.

1.4 Significance of the Study

This study will help to transfer knowledge/ technology to the local concerning bodies on making of biodiesel by shaking method which is expected to be fast and simple using only locally available raw materials. This research could be used as base line for other studies in the area.

2. LITERATURE REVIEW

2.1 Waste Cooking Oil as Feedstock of Biodiesel

The term “waste cooking oil” refers to vegetable oil which has been used in food production and which is no longer viable for its intended use. WCO arises from many different sources, such as domestics, commercials and industrials. WCO is a potentially problematic waste stream which requires being properly managed [14].

The disposal of WCO can be problematic when disposed, incorrectly, down kitchen sinks; where it can quickly cause blockages of sewer pipes when the oil solidifies. The properties of degraded used frying oil after it gets into sewage system are conducive to corrosion of metal and concrete elements. It also affects installations in waste water treatment plants. Thus, it adds to the cost of treating effluent of water-ways [14].

Any fatty acid source may be used to prepare biodiesel. Thus, any animal or plant lipid should be a ready substrate for the production of biodiesel. The use of edible vegetable oils and animal fats for biodiesel production has recently been of great concern because they compete with food materials-the food versus fuel dispute [15, 16].

There are concerns that biodiesel feedstocks may compete with food supply in the long-term [17, 18]. From an economic point of view; the production of biodiesel is a very feedstock sensitive. Many previous reports estimated the cost of biodiesel production based on assumptions, made by their authors, regarding production volume, feedstock and chemical technology [19, 20].

In all these reports, feedstock cost comprises a very substantial portion of overall biodiesel cost. A computer model was developed to estimate the capital and operating costs of a moderately size d industrial biodiesel production facility. Calculated production costs included the cost of the feedstock and of its conversion to biodiesel [21].

The model is flexible in that it can be modified to calculate the effects on capital and production costs of changes in feedstock, changes in the type of feedstock employed, changes in the value of the glycerol coproduct and changes in process chemistry and technology. It wasreported that for biodiesel produced from soybean oil, the cost of the oil feedstock accounted for 88 % of total estimated production costs [21].

A conceptual design of alternative production plants was used with a techno economic analysis in order to compare these alternatives. In all these cases, more than 80% of the production cost was associated with the feedstock itself; and consequently efforts should be focused on how to d eveloping technologies of capable of using lower cost feedstock, such as recycled cooking oils [22]. Reusing of these waste greases not only reduce the burden of the government in disposing the waste, maintaining public sewers and treating the oily waste water, but also lower the produc -tion cost of biodiesel significantly [23].

2.2 Biodiesel

Biodiesel is an alternative fuel derived from vegetable oil or animal fat. The main components of vegetable oils and animal fats are triglycerides or also known as esters of fatty acid attached to glycerol. Normally, triglycerides of vegetable oil and animal fat consist of several different fatty acids [24].

Different fatty acids have different physical and chemical properties and the composition of the fatty acids will be the most important parameters influencing the corresponding properties of the vegetable oils and animal fats. The reaction associated with biodiesel production is a transesterifi -cation reaction. This is a reaction that converts one form of ester to another. Vegetable oils are triglyceride ester (esters of 3molecules of fatty acids with one molecule of glycerol). They react with monohydroxy alcohols like methanol and ethanol, producing corresponding esters. Glycerol is the byproduct [24].

2.2.1 Benefits of Biodiesel

One of the main driving forces for biodiesel widespread use is the limitation of greenhouse gas emissions (CO_2 being the major one) by the Kyoto Protocol. Along with ethanol and other biomass derived fuels, biodiesel is an important bio-energy. When plants photosynthesize, they use the sun's energy to pull CO_2 out of the atmosphere and incorporate it into biomass. Part of the solar energy is locked into the chemical structure within the biomass. There are a number of thermal, chemical or microbial processes that can be used to release this energy or convert it into a more convenient form for human use. As a form of bio-energy, biodiesel is nearly carbon-neutral, i.e., the CO_2 it produces on burning will be absorbed naturally from CO_2 in the air and recycled without an overall net increase in the atmospheric CO_2 inventory, thus making an almost zero contribution to global warming [25].

There are many distinct benefits of using biodiesel compared to diesel fuel [26]:

a) Considered to be environmentally friendly, biodiesel is one of the most renewable fuels compared to diesel fuel.
b) It is biodegradable.
c) It is derived from a renewable domestic resource, thus reducing dependence on and preserv -ing petroleum. It can be domestically produced, offering the possibility of reducing petroleum imports,
d) Reductions of most exhaust emissions relative to conventional diesel fuel, generating lower emissions of hydrocarbons, particulates and carbon monoxide;
e) Biodiesel has a relatively higher flash point, >150 °C, indicating that it presents a very low fire hazard; leading to safer handling and storage,

f) Biodiesel provides greater lubricity than petroleum diesel, thus reducing engine wear. Infa ct, biodiesel can be used as a lubricity enhancer for low-sulphur petroleum diesel formulations,
g) Biodiesel can be used directly in most diesel engines without requiring extensive engine modifications.
h) Toxicity tests show that biodiesel is considerably less toxic than diesel fuel [27].

2.3 Chemical composition of biodiesel

Unlike fuels of petroleum origin, which are composed of hundreds of hydrocarbons (pure substances), biodiesel is composed solely of some fatty acid ethyl and methyl esters; their number depends on the feedstock used to manufacture biodiesel and is between 6 and 17 [28]. The fatty acid methyl and ethyl esters in the composition of biodiesel are made up of carbon, hydrogen and oxygen atoms that form linear chain molecules with single and double carbon-carbon bonds. The molecules with double bonds are unsaturated; (e.g., 18:1 indicates 18 carbon atoms and one double bond). The ester composition of biodiesel (methyl and ethyl esters) is shown in Table 2.1 [29]. The highest concentrations are C18:1, C18:2, C18:3, followed by C18:0. A significant exception is biodiesel from coconut oil, in the case of which the highest concentration is C12:0, C14:0 and C16:0, hence this biodiesel is more volatile than the others.

The physicochemical properties of biodiesel produced from a given feedstock are determined by the properties of the esters contained.

Table2.1: Fatty acid composition of different biodiesels (methyl and ethyl esters), (% m/m) [29].

Ester	C8:0	C10:0	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1
ALME	–	–	–	0.6	6.9	3	75.2	12.4	1.2	0.4	–
RME	–	–	–	–	3.8	1.9	63.9	19	9.7	0.6	–
REE	–	–	–	–	4.9	1.6	33.0	20.4	7.9	–	–
CME	–	–	–	–	4.2	2	57.4	21.3	11.2	1.2	2.1
SME	–	–	–	–	9.4	4.1	22	55.3	8.9	–	–
SEE	–	–	–	–	10.8	3	26.5	47.3	9	–	–
SFME	–	–	–	–	4.2	3.3	63.6	27.6	0.2	–	–
PME	–	–	0.2	0.5	43.4	4.6	41.9	8.6	0.3	0.3	–
COME	–	–	–	–	12.1	1.8	27.2	56.2	1.3	0.4	–
AME	–	–	–	–	11.6	4.4	49.6	33.7	0.7	–	–
OEE	–	–	–	–	11.6	3.1	74.9	7.8	0.6	–	–
TME	–	–	0.2	2.9	24.3	22.8	40.2	3.3	0.7	0.2	0.6
FOME	–	–	0.2	7.7	18.8	3.9	15	4.6	0.3	0.2	1.4
JME	–	–	–	–	12.7	5.5	39.1	41.6	0.2	0.2	–
JME	–	–	–	–	12.5	30.9	34.4	20.4	–	–	–
WCOME	–	–	0.1	0.1	11.8	4.4	25.3	49.5	7.1	0.3	–
WCOEE	–	–	2.0	–	15.7	3.1	29.6	41.5	1.0	–	–
SAFME	–	–	–	–	7.3	1.9	13.6	77.2	–	–	–
CCME	6.3	6	49.2	18.5	9.1	2.7	6.5	1.7	–	–	–
CCEE	7.5	6	53.3	17.1	7.3	1.9	5.5	1.4	–	–	–
YMME	–	–	–	–	2.6	1.2	20.6	20.6	13.3	0.9	10.7
YGME	–	–	0.1	0.5	14.3	8	35.6	35	4	0.3	–

- C8:0 – caprylate, C10:0 – caprate, C12:0 – laurate, C14:0 –myristate, C16:0 –palmitate, C18:0 – stearate, C18:1 – oleate, C18:2–linoleate, C18:3–linolenate, C20:0 –arachidate.

ALME – algae methyl ester, CCEE – coconut oil ethyl ester; CCME – coconut oil methyl ester; CME – canola oil methyl ester; COME – corn oil methyl ester; FOEE – fish oil ethyl ester; FOME – fish oil methyl ester; JME – jatropha oil methyl ester; OEE – olive oil ethyl ester; PME – palm oil methyl ester; REE – rapeseed oil ethyl ester; RME – rapeseed oil methyl ester; SAFME – safflower oil methyl ester; SEE - soybean oil ethyl ester; SFME – sunflower oil methyl ester; SME – soybean oil methyl ester; TME – tallow methyl ester; WCOEE – waste cooking oil ethyl ester; WCOME – waste cooking oil methyl ester; YGME – yellow grease methyl ester; YMME –yellow mustard oil methyl ester

2.4 Biodiesel Fuel Properties

The determination of biodiesel fuel quality is an issue of great importance to the successful commercialization of this fuel. It is important to control the quality of biodiesel to meet the ASTM standard before using it in a diesel engine. Problems will occur in diesel engine when using biodiesel that does not meet the international standard. For example, triglycerides and diglycerides, if present, would increase the overall viscosity of biodiesel ester and cause the formation of sediments when used in a diesel engine [30].

Hydroperoxides are very susceptible to an oxidation reaction yielding aldehydes and acids. In addition, hydroperoxides, if present, can induce polymerization and form insoluble gums and sediments [31].These compounds do not combust properly and result in carbon deposits. Free fatty acids in a biodiesel may increase the likelihood of corrosion [1].

The unsaturated free fatty acids are susceptible to an oxidation reaction, which leads to the formation of hydroperoxides and ultimately increases deposits in fueling system [1]. In order to test the quality of biodiesel as a diesel fuel substitute, ASTM has set a standard for biodiesel as a fuel for use in diesel engines.

2.4.1 Density at 15 °C

This property is important mainly in airless combustion systems because it influences the efficiency of atomization of the fuel [32]. Density, relative density or specific gravity is a factor governing the quality and pricing of biodiesel. However, this is uncertain indication of its quality unless correlated with other properties. The density of biodiesel is need to make mass to volume conversions, calculate flow and viscosity properties, and is used to judge the homogeneity of bio diesel in tanks [33]

2.4.2 Kinematic Viscosity

Viscosity is a measure of the resistance of a liquid to flow due to internal friction of one part of fluid moving over another. It affects the atomization of a fuel upon injection into the combustion chamber and thereby, ultimately, the formation of engine deposits; the higher the viscosity, the greater the tendency of the fuel to cause such problems. Viscosity is important for establishment of optimum storage, handling and operational conditions. High viscosity is a major fuel property explaining why neat vegetable oils have largely been abandoned as an alternative diesel fuel [34].

The viscosity of petro diesel fuel is lower than that of biodiesel, which is also reflected in the kinematic viscosity limits at 40 ^{0}C of petro diesel standards, which are 1.9-4.1 mm^2/s for diesel fuel in the ASTM petro diesel standard [33]. The difference in viscosity between the parent oil and the alkyl ester derivatives can be used to monitor biodiesel production [35]. The effect on viscosity of blending biodiesel and conventional petroleum derived diesel fuel was also investigated, and an equation was derived that allows calculation of the viscosity of such blends [25].

2.4.3 Cloud point (CP)

The cloud point (CP) is the temperature at which crystals first start to form in the fuel. The cloud point is reached when the temperature of the biodiesel is low enough to cause wax crystals to precipitate. Initially, cooling temperatures cause the formation of the solid wax crystal nuclei that are submicron in scale and invisible to the human eye. Further decrease of temperature causes these crystals to grow [36].

The temperature at which crystals become visible (the crystal's diameter 0.5 m), is defined as the cloud point; because the crystals form a cloudy suspension. Below the CP these crystals might plug filters or drop to the bottom of a storage tank. The CP is the most commonly used measure of low temperature operability of the fuel. The biodiesel cloud point is typically higher than the cloud point of conventional diesel. The cloud point of biodiesel depends on the nature of the feed stock, and is -5°C for algae methyl ester; 17 °C, 13 ^{0}C respectively for tallow and palm oil methy l ester due to their high content of saturated fatty acids [36, 4].

2.4.4 Flash point (FP)

The flash point is the minimum temperature calculated to a barometric pressure of 101.3 kPa at which the fuel will ignite (flash) on application of an ignition source under specified condition. It is used to classify fuels for transport, storage and distribution according to hazard level. The flash point does not affect the combustion directly; higher values make fuels safer with regard to storage, fuel handling and transportation. FP varies inversely with the fuel volatility. Biodiesel's flash point decreases rapidly as the amount of residual (unreacted) alcohol increases (methanol flash point is 11-12^{0}C, and ethanol's is 13-14^{0}C). Thus, measuring the biodiesel flash point helps indicate the presence of methanol or ethanol. For example, the presence of 0.5% methanol in biodiesel reduces biodiesel flash point from 170 ^{0}C to 50 ^{0}C. If flash point is used to determine the methanol content, the ASTM standard imposes for it a minimum value of 130 °C. This limit may be considered too severe, because at the maximum permissible concentration of methanol of 0.2% w/w biodiesel flash point drops below 130 °C [36, 37].

2.4.5 Acid number

The acid number is the quantity of base, expressed as milligrams of KOH per gram of sample, required to titrate a sample to a specified end point [38]. Acid number determination is an important test to assess the quality of a particular biodiesel. It can indicate the degree of hydrolysis of the methyl ester, a particularly important aspect when considering storage and transportation as large quantities of free fatty acids can cause corrosion in tanks [39]. Usually, for a base catalyzed process, the acid value after production will be low since the base catalyst will strip the available free fatty acids. This test should be performed regularly as a part of the producer Quality Control program [38].

2.4.6 Water and sediment

Appreciable amounts of water and sediment in biodiesel tend to cause fouling of the fuel handling facilities and to give trouble in the fuel system of a burner or engine. An accumulation of sediment in a storage tanks and on a filter screens can obstruct the flow of fuel from the tank to the combustor. Water can cause corrosion of tanks and equipments, and if detergent is present, water can cause emulsions or a hazy appearance. Water supports microbial growth at the fuel- w ater inter faces in fuel systems and cause clogging of the filter and damage fuel system [40].

While biodiesel is generally considered to be insoluble in water, it actually absorbs considerably more water than diesel fuel does. Biodiesel can contain as much as 1500 parts per million of dissolved water. At the most, biodiesel should contain 0.050% by volume of water [41].

2.4.7 Ash Content

This test monitors the mineral ash residual when fuel is carbonized and the residue subsequently heated to a constant weight in a muffle furnace at a temperature of 775 ± 25^{o}C, cooled and weighed [42]. Ash can result from abrasive solids, water or oil soluble metallic compounds like soaps or from extraneous solids such as dirt and rust, and unremoved catalysts. For biodiesel , this test is an important indicator of the quantity of residual metals in the fuel that came from the catalyst used in the esterification process. Producers that use a base catalyzed process may wish to run this test regularly. Many of these spent sodium or potassium salts have low melt ing temperatures and may cause engine damage in combustion chambers [43].

2.4.8 Calorific Value

The heat of combustion is a measure of the energy available from a fuel. Knowledge of this value is essential when considering the thermal efficiency of equipment for producing either power or heat. The heat of combustion is designated as one of the chemical and physical requirements of both commercial and military turbine fuels and aviation gasoline. The mass heat of combustion, the heat of combustion per unit mass of fuel, is a critical property of fuel intended for use in the weight-limited craft such as airplanes, surface effect vehicles, and hydrofoils. The range of such craft between refueling is a direct function of the heat of combustion and density of the fuel [44].

2.4.9 Copper strip corrosion

The copper strip corrosion is used for the detection of the corrosiveness of copper to fuels and solvents due to the presence of acids in the fuel [43]. For B100, the most likely source of a test failure would be excessive free fatty acids, which are determined in accordance with an additional specification. The producer may choose to run this test periodically, but the acid number determination is the more important acid content Quality Control (QC) measurement [45].

Table 2.2: Comparison of biodiesel and petro diesel characteristics [43]

Properties	**ASTM Standard**	**Biodiesel**	**Diesel**
Specific gravity, at 15 ^{0} C	D 1298	0.88	0.85
Kinematic viscosity (mm2/s), at 40°C	D445	1.9–6.0	1.3 – 4.1
Water and Sediment (V/V%)	D 2709	0.05 max	0.05 max
Flash point (°C)	D 93	130 to 170	60 to 80
Cloud point (°C)	D 2500	Report	Report
Cetane number	D 613	47 to 60	40 to 55
Pour point	D 97	Report	Report
Copper corrosion	D 130	No.3	No.3 max.
Biodegradability		Biodegrades readily	Poor biodegradability
Calorific value (MJ/Kg)	D 24O		
Acid value (mgKOH/g)	ASTM D 974	0.8	0.5
Ash content (%)	D 482		0.01

2.5 The Biodiesel Process

2.5.1 Esterification Process

Esterification, as it applies to biodiesel production, is the chemical reaction by which a fatty acid, typically a free fatty acid in degraded or second-use oil, reacts with an alcohol to produce an alkyl ester and water (see equation i). The process differs from the transesterification reaction in that the reaction is occurring directly between the alcohol and the fatty acid molecule. The intermediate steps of cleaving the fatty acid chains from the glycerin backbone are not present. For this reason, no glycerin is produced during the esterification reaction [46].

$$\underset{\text{FFA}}{\text{R-COOH}} + \underset{\text{Alcohol}}{\text{R}'\text{-OH}} \xrightleftharpoons{\text{Catalyst}} \underset{\text{Ester (Biodiesel)}}{\text{R-COO-R}'} + \text{H}_2\text{O} \quad \text{.....(i)}$$

Conventionally, virgin vegetable oils and high-grade animal fats are the feedstock of choice for biodiesel production due to low levels of impurities, such as free fatty acids and sulfated proteins, which can cause problems with processing and final product quality. Rapeseed alone comprises of roughly 84% of the lipid stocks used for biodiesel production. By comparison, sunflower and palm oil each represent 13% of the feedstock with soybean trailing with a 1% share. All other feedstock such as waste cooking oils, animal fats, jatropha, peanut, mustard, etc. make up the remaining 2% [47].

Second use oils such as yellow or brown grease are thermally or chemically degraded waste oils that primarily contain grease collected from restaurant or industrial grease traps. Most of this oil is spent cooking oil from restaurants that has been thermally degraded by sustained high temperatures. It further degrades when in contact with water in the grease trap through a process known as hydrolysis. This degradation produces molecules known as free fatty acids. Fatty acids will chemically react with the typical alkaline catalysts used in base catalyzed biodiesel reactions to form soap. Free fatty acids are always present in oils, however mass concentrations above 4% will generate more soap than can be dealt with reasonably in a conventional base-catalyzed reaction and will prevent the reaction from going to completion in almost all cases [48].

2.5.2Trans-esterification Reaction

The chemical reaction by which a lower alcohol reacts with a triglyceride to yield a fatty acid alkyl ester is known as transesterification. It occurs easily with the lower alcohols such as methanol or ethanol. The process is slow under normal conditions without the presence of a catalyst. Traditionally, an alkaline catalyst such as sodium or potassium hydroxide is used to catalyze and accelerate the reaction at standard temperatures and pressures [49].

The catalytic reaction is complicated; however the necessity for a catalyst arises from the relative insolubility of alcohol in oils. Catalysts provide a phase-transfer as well as an ion exchange effect which reduces reaction times by many orders of magnitude [49].

Transesterification consists of a number of consecutive, reversible reactions. The triglyceride is converted stepwise to diglyceride, monoglyceride and glycerol. A mole of ester is liberated at each step. The reactions are reversible, although the equilibrium lies towards the production of fatty acid esters and glycerol [50, 24].

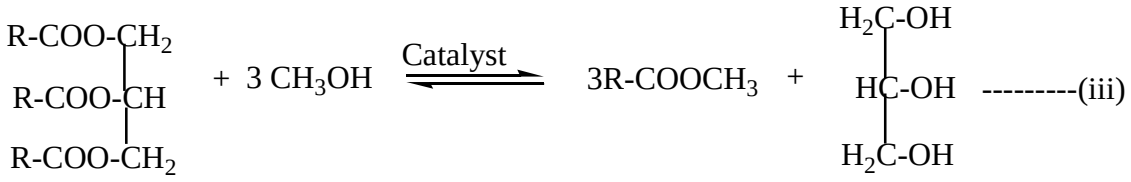
Triglyceride (TG) + R'OH $\rightleftharpoons$ Diglyceride (DG) + $R'COOR_1$

Diglyceride (DG) + R'OH $\rightleftharpoons$ Monoglyceride (MG) + $R'COOR_2$……..…. (ii)

Monoglyceride (MG) + R'OH $\rightleftharpoons$ Glycerol (GL) + $R'COOR_3$

The reaction mechanism for alkali-catalyzed transesterification was formulated as three steps. The first step is an attack on the carbonyl carbon atom of the triglyceride molecule by the anion of the alcohol (methoxide ion) to form a tetrahedral intermediate. In the second step, the tetrahedral intermediate reacts with an alcohol (methanol) to regenerate the anion of the alcohol (methoxide ion). In the last step, the rearrangement of the tetrahedral intermediate results in the formation of fatty acid ester and a diglyceride [51]. Homogeneous base catalyst commonly used for transesterification includes: Alkaline metal alkoxides such as Sodium methoxide ($NaOCH_3$) or potassium methoxide ($KOCH_3$) and alkaline metal hydroxides (e.g. KOH and NaOH) [52].

The basic reaction for conventional biodiesel process is [41]:



---------(iii)

Vegetable oil (Triglyceride) + alcohol ⇌ Ester (biodiesel) + glycerol

It was reported that alkaline metal alkoxide catalyst relatively are the most conventional active catalyst for biodiesel synthesis as they give yields greater than 98% in a short reaction time of th ree minutes. However, their requirement for the absence of water makes them inappropriate for typical industrial processes in which water cannot be completely avoided [53].

Producing alkoxide ions (methoxide ion or ethoxide ion) using (homogeneous) base catalysts, like NaOH or KOH is a key to the transesterification reaction. The mechanism of base catalyzed transesterification of vegetable oils occurs in five steps as given by equations iv, v, vi and viii.

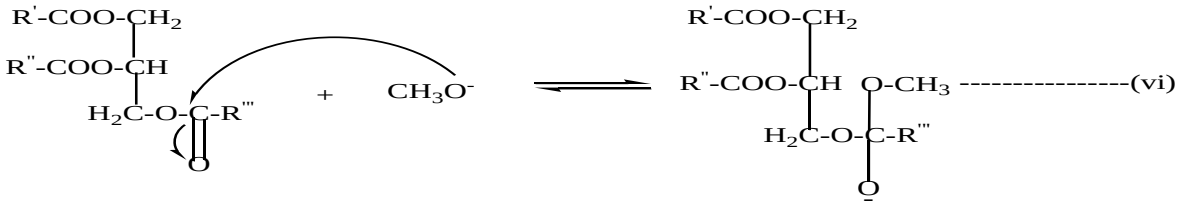
1. KOH catalyst dissolves in methanol, with potassium ion disassociating itself to become more of a spectator as given in equation iv.

   $KOH \rightarrow K^+ + OH^-$…… (iv)

2. The hydroxyl ion (OH^-) deprotonates methanol forming a Nucleophilic methoxide catalyst and water.

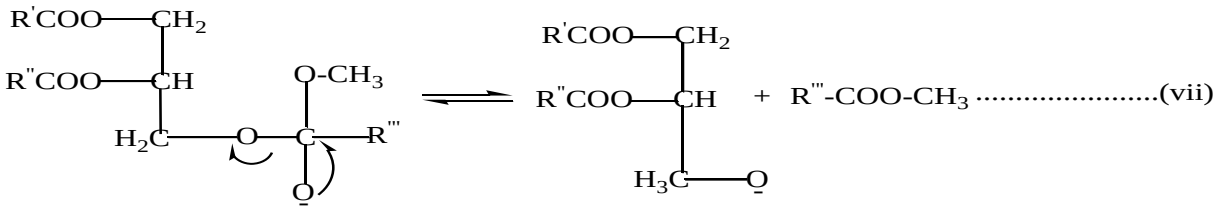
   $OH^- + CH_3OH \rightleftharpoons CH_3O^- + H_2O$…….... (v)

3. The nucleophile catalyst then attacks the carbon of the carbonyl group of the triglyceride to form an unstable tetrahedral intermediate as given in equation vi.

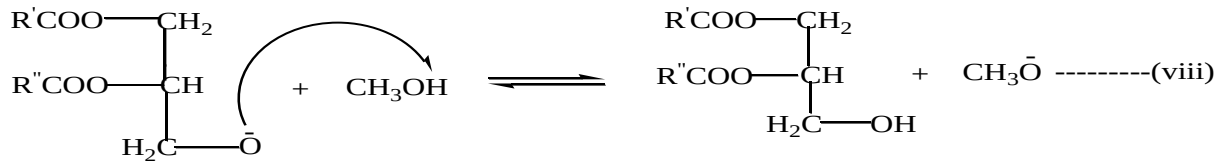


----------(vi)

4. The intermediate dissociates into FAME and diglyceride anion as shown in equation vii.



The diglyceride ion deprotonates methanol to form a stable diglyceride and at the same time regenerates the active catalytic methoxide as shown in equation viii.



5. Once methoxide catalyst is regenerated, the cycle starts again at another tri-, di-, or mono-glyceride to finally form glycerol and 3 equivalents of FAME. For alkaline metal hydroxides, it is important to mention that they are cheaper than metal alkoxides but less active.

However, they are good alternatives since they can give the same high vegetable oil conversion just with an increased catalyst concentration of about 1or 2mole%. The presence of water is not required in this process as it will give rise to hydrolysis of some of the produced ester leading to soap formation [53] as shown in equations ix and x.

Hydrolysis of ester to give FFA as shown by equation ix,

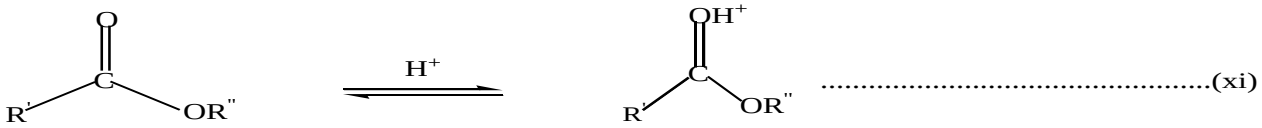
FFA then reacts with the base to form soap as shown in equation x,

It has been shown that base homogeneous catalysis is preferred for the commercially synthesis of biodiesel because it proceeds far more rapidly than acid-catalyzed transesterification. After the transesterification reaction an acid neutralization process is used to neutralize the base, a process that contaminates the produced glycerol [53].

Purity of glycerol produced is about 80 to 90% depending on the process used for synthesis [53]. To use a vegetable oil of low quality with high free fatty acids (FFAs) for biodiesel production, homogeneous acid catalyst is employed as the feedstock catalyst. They have the disadvantage of being corrosive to equipment. The use of acid catalysts not only avoids soap formation, but allow sfor the simultaneous esterification of FFA and transesterification of triglycerides to biodiesel [54].

It is therefore, being reported that the higher the FFA in the feedstock, the more sodium or potassium methylate you need. More sodium methylate means more soap formation. It was suggested that acid-catalyzed production of biodiesel can economically compete with base-catalyzed proces s using virgin oils, especially when the former uses low-cost feedstock [54]. The typical mechanism of the acid-catalyzed transesterification of vegetable oils occurs in three steps as explained in the given equations xi, xii and xiii.

(i) Protonation of the carbonyl group by the acid catalyst leading to carbocation as in equation xi.

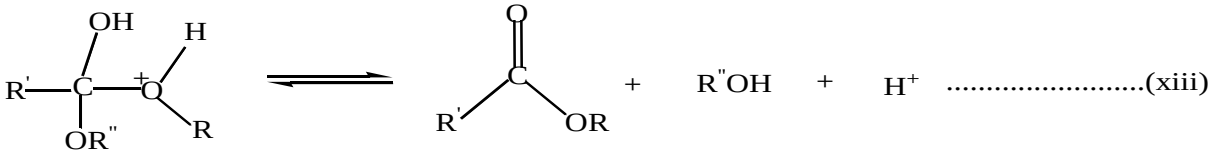


.....(xi)

(ii) Nucleophilic attack of the alcohol by the carbocated to produce a tetrahedral intermediate as shown in equation xii.

.....(xii)

(iii) Intermediate breaks down to form a new ester, eliminates glycerol and regenerates the catalyst as in equation xiii. The sequence is repeated twice.



.....(xiii)

Where;

R = alkyl group of the alcohol, R' = Carbon chain of the fatty acid, R'' = Glyceride

The acid-catalyzed transesterification mechanism shown in equations x, xi and xii is for a monoglyceride and can be extended to di- and triglycerides. According to this mechanism, carboxylic acids can be formed by reaction of the carbocation with water present in the reaction mixture. This suggests that an acid-catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduce the yields of alkyl esters [54].

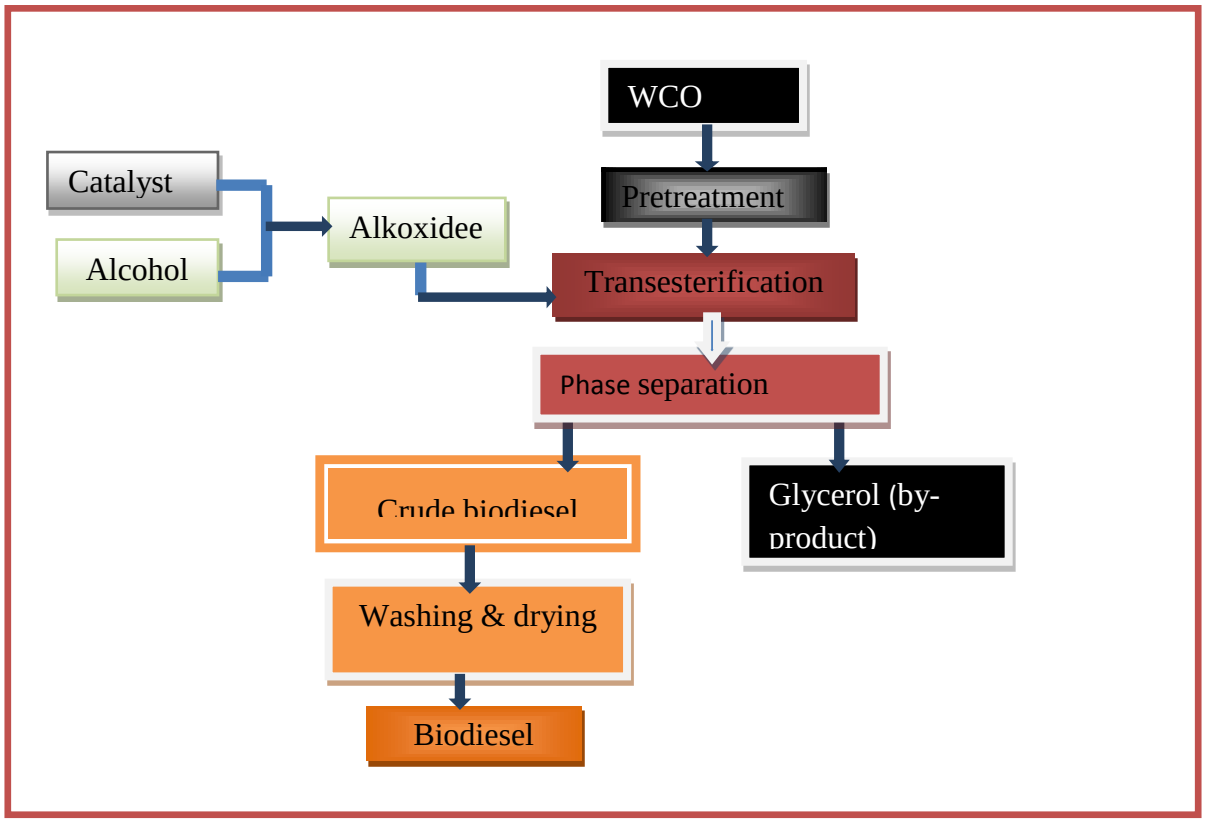


Figure 2.1 Biodiesel Production Pathways (Source: prepared flow chart)

2.6 Variables Influencing the Transesterification Reaction

2.6.1Molar Ratio of Vegetable Oil to Methanol

Because of its low price and highly reactive nature, methanol is a commonly used alcohol for transesterification [55]. The stoichiometric ratio required for transesterification reaction is 1:3 moles of vegetable oil to alcohol. However, it has been found that the molar ratio of vegetable oil to alcohol depends on the type of catalyst used for the reaction [24].

For example, the molar ratio of 1:6 of oil to ethanol has been found to be the most suitable in the case of alkali-catalyzed transesterification, because an excess of alcohol is required to drive the reaction [24]. For acid catalyzed transesterification reaction, a 1:30 vegetable oil to alcohol ratio is generally used [56].

2.6.2 Moisture Contents

Water content promotes the formation of soap during the reaction and reduces catalyst efficiency . The presence of water in acid catalyzed transesterification reduces the percentage of biodiesel produced to a greater extent compared to an alkaline catalyst. For example, in a reaction mixture of soybean oil, methanol and sulfuric acid, 0.5% water content reduces the resultant biodiesel conversion from 95% to 90% [57].

2.6.3 Free Fatty Acid

For an alkali catalyzed transesterification reaction, vegetable oil should not contain any free fatty acid. If any free fatty acid is present in vegetable oil, alkaline catalyst is utilized in neutralizing this free fatty acid which only consumes the catalyst and slows down the reaction. The acid value of glycerides should be less than1for a NaOH catalyzed transesterification reaction. Acid value is the milligrams of potassium hydroxide required for neutralizing the free fatty acids present in 1g of vegetable oil [54].

2.6.4 Catalyst

Transesterification reaction can occur in the absence of catalysts. However, it may require high temperature, pressure and long reaction times. If all these requirements are met, the process cost is relatively high. This method produces relatively high purity esters and soap free glycerol, but since it is uneconomical; it is typically not considered for the industrial production of biodiesel. Three types of catalysts are generally used for biodiesel production. These are alkaline catalysts, acidic catalysts, and enzymes [58].

a) Alkaline catalysts

Alkaline catalysis is the most commonly used process for the production of biodiesel. Its main advantage is that, a high ester yield is obtained in a short reaction time under a mild condition. However, alkaline catalysts are highly sensitive to FFA in vegetable oils. Therefore, only the oilswith low FFA produce high ester yields after transesterification. However, deacidification of thevegetable oil prior to transesterification reduces this issue. Examples of alkaline catalysts are: NaOH, KOH, alkali metal carbonates (such as sodium carbonate, and potassium carbonate) [57].

Some advantages for using base catalyzed reaction are [53]:

- Due to the general availability of the products, the price is fairly competitive and there are little issues with product supply.
- Since the operations occur in the same phase as the reactants, the handling becomes much easier. Handling all liquids is easier than handling one liquid and one solid or a combination of them.
- Conversion to methyl ester is direct with no intermediate steps.
- It achieves high conversion (98%) with minimal side reactions and low reaction time.
- It uses low temperature ($65^{o}C$) and pressure (20psi) processing.

Some of the problem arising in using base catalyst includes [53]:

- High energy demand
- Post-reaction treatment to remove the catalyst from the product-biodiesel.
- Reusability–Non reusability of the catalyst involved
- Interferences occasioned by the presence of free fatty acid and water during the reaction
- Difficulty in the recovery of glycerol after the reaction and
- Post-reaction treatment of the alkaline waste-water to obviate the environmental effects of its disposal.
- More soap formation.

b) Acidic catalysts

Acid–catalyzed transesterification requires a relatively high temperature (~100 °C), pressure (~5 bars) and large amounts of alcohol. It is also slower in comparison to alkaline catalysis. The only advantage of this type of catalytic conversion is that it can efficiently esterifies free fatty acids in vegetable oils and is therefore used to transesterify high free acid containing feedstock, such as waste edible oil [49].

The disadvantages of using acid catalyst include the following [54]:

- Water formation during acid esterification hinders the process. Care should be taken to get rid of water via drying, and this adds to the cost.
- Reusability—Non reusability of the catalyst involved.
- Catalyst involved is corrosive. The H_2SO_4 and other acid catalysts currently used in the biodiesel synthesis are fairly corrosive and need to be handled with extreme carefully.
- More methanol is used.
- More soap is formed

c) Enzymes

Enzymes or lipases extracted from microorganisms can also be used as catalysts for the trans-esterification reaction [49].

The advantages of these biocatalysts are [49]:

(a) Biodiesel conversion under mild temperature, pressure, and pH conditions.
(b) No catalyst residues or soap in the final product. High quality glycerol is produced.
(c) These catalysts efficiently esterify FFA and thus can be used for transesterification of oils or fats containing high free fatty acid contents.

The disadvantages of these catalysts include:

(a) Long reaction times and higher catalyst concentrations are required.
(b) These catalysts are expensive and not economical for commercial use.
(c) Enzymes are typically difficult to remove from the final products (i.e., biodiesel and glycerol) after the reaction is completed.

2.6.5 Reaction Temperature

Temperature has no detectable effect on the ultimate conversion to ester in the transesterification reaction. However, a higher temperature decreases the time required to reach a maximum conversion. Transesterification reaction can be conducted at various temperatures ranging from room temperature to the boiling point of the alcohol employed (68 ^{0}C in case of methanol) so that the reactor does not need to be pressurized. Thus, the usual temperature used for transesterification in most literature is 60 -65^{0}C. When the reaction temperature closes or exceeds the boiling point of methanol (68^{0}C), the methanol will vaporize and form a large number of bubbles which may inhibit the reaction [59].

3. MATERIALS AND METHODS

3.1 Experimental materials

For this work waste cooking oils originated from palm oil and sunflower was used as feedstock. It was obtained from EYOHA Food Corner and Bakery located in Addis Ababa, Yeka sub-city.

Chemicals

Analytical grade chemicals were used throughout the research work. These are Potassium hydroxide pellet, Petroleum ether, Silica gel, Methanol, Ethanol, Isopropyl alcohol, Phenolphthalein, P-Naphtholbenzein.

Apparatus

The apparatus used for the study were: glass capillary viscometer, hot plate with magnetic stirrer, digital balance, thermometer, pipette, separating funnel, burettes, oil test centrifuge, bottles,flash point tester, adiabatic bomb calorimeter, digital density meter, cloud point tester and muffle furnace.

Figure 3.1 WCO obtained from restaurant (April, 2018)

3.2 Experimental Setup and Procedures

There are four operations for the preparation of biodiesel: Pre-treatment, transesterification, phase separation, and purification (washing and drying).

3.2.1 Pre-treatment of WCO

Preparation of Waste Cooking Oil

The WCO samples were collected and allowed to stand for about 3 to 4 weeks so that impurities were settled down and the liquid portion was decanted. The remaining dirt, suspended material, charred food, and other non oil material were removed by filtering the decanted WCO through a clean double layer of light woven cotton material. Then, the filtered cooking oil sample obtained was tested for FFA before transesterification.

Acid Value and Free Fatty Acid of WCO

In base-catalyzed transesterification, high FFA content (>1 % w/w) will lead to soap formation which reduces catalyst efficiency, causes an increase in viscosity, leads to gel formation and makes the separation of glycerol difficult [60].

Acid value was determined by the acid–base titration technique. KOH was used as a standard alkali solution. Free fatty acid of oil was calculated as percent by mass of oleic acid, which was obtained by dividing the acid value by 2.

Into 250mL Erlenmeyer flask, 2g of sample was introduced. 100 mL of titration solvent (which is mixture of 50mL ethanol and 50mL p-ether) and 1mL of indicator solution (phenolphthalein) were added to the flask. The mixture was stirred until the sample was entirely dissolved by the solvent. Without delay, the mixture was titrated with standardized 0.1N KOH solution by shaking vigorously to a pink endpoint.

Blank titration was performed on a 100 mL of the titration solvent and 1mL of the indicator solution by similar procedure.

The Acid value was calculated by the following equation:

$$\text{Acid value} = \frac{(A - B) \times N \times 56.1}{W} \quad \text{.....(3.1)}$$

A = Volume in milliliters of standard KOH used in the titration

B = Volume in milliliters of standard KOH used in titrating the blank

N = Normality of standard KOH, W = Weight of the sample

56.1= weight of KOH (Sum of mass of K=39.1, O=16, H=1)

The acid value calculated was used to estimate the amount of KOH required for neutralizing free fatty acid in addition to KOH needed for transesterification.

3.2.2 Single Step Alkaline Catalyzed Transesterification

The simplest way to produce biodiesel is called transesterification reaction. In the reaction, base catalyst (KOH) is used to convert triglycerides into three smaller separate ester molecules, which one ending in -OCH_3. A molecule of glycerol is formed as a byproduct. This is a reverse reaction , so excess methanol is needed to drive the reaction toward the product. One of the recent focuses in organic chemistry has been the attempt to make the reaction more energy efficient.

Most biodiesel syntheses require the use of either hot plate or a microwave. Instead of heating, biodiesel can be made simply by shaking the reaction vessel for 5 minute intervals of time [61]. By this study the method was followed to prepare biodiesel from waste cooking oil.

3.2.3 Amount of KOH Needed as Catalyst

The FFA contained in the waste oil can be neutralized by basic KOH to produce an undesired substance (a soap, which is an emulsifying agent). The amount of KOH needed, therefore, should allow for the amount needed in the production of the potassium methoxide catalyst as well as that is necessary for the neutralization of the free fatty acid in the oil.

In table 4.1, it is shown that the free fatty acid content of WCO is 1.0119% which is almost equal toASTM limit. Therefore, additional catalyst is required to neutralize the FFA in the feedstock; which is calculated as following [62]:

(% FFA) x (0.197)/0.86 = 1.0119x (0.197)/0.86= 0.2%, it indicates that 0.2% of the triglycerides weight of additional KOH is needed. The factor 0.197 represents the ratio of the mass KOH to the mass of free fatty acid (oleic acid), 0.86 reflects that reagent grade of KOH is only 86% pure. Therefore, a total of 1.2% of triglyceride weight of KOH is required since 1% of triglyceride weight of KOH is required for the transesterification process.

i) Heating of the Oil

390g of the WCO in a beaker was pre-heated to about 60 ^{0}C using hot plate with temperature range of 0-100 ^{0}C for 30minutes to further reduce the reaction time.

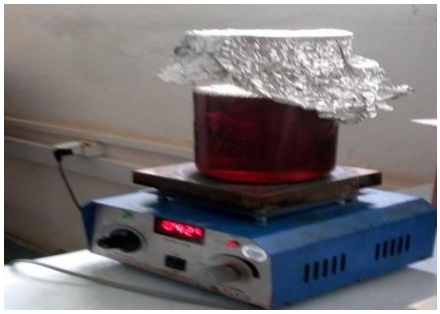


Figure 3.2 Heating of WCO before transesterification (June, 2018)

ii) Mixing of Methanol and Catalyst

A 4.7g KOH (1.2% of WCO) was added to 65g methanol and continuously agitated for 5minutes using magnetic stirrer, prior to methanolysis of the heated oil.

iii) Transesterification Reaction

The methanol was added to the pre-heated oil in a 1L container serving as a batch reactor. Then the mixture was shaken for 5 minutes and left for 5hr for phase separation to take place due to gravity in a separating funnel. Thus, the reaction products separated into two layers; the ester product formed the upper layer and the byproduct glycerin formed the lower layer.

3.2.4 Separation of Biodiesel and Glycerin

The biodiesel and glycerol separation is typically the first step of product recovery in biodiesel processes. The separation process is based on the facts that fatty acid methyl esters and glycerol are sparingly mutually soluble, and that there is a significant difference in density between the ester and glycerol phases (Fig 3.3).

The presence of methanol in one or both phases affects the solubility of ester in glycerol and glycerol in ester. The glycerol density depends on the amount of methanol, water, and catalyst in the glycerol.

This density difference is sufficient for the use of simple gravity separation techniques for the two phases. However, the rate of separation is affected by several factors. Most biodiesel processes use relatively intense mixing, at least at the beginning of the reaction, to incorporate the sparingly soluble alcohol into the oil phase. If this mixing continues for the entire reaction, the glycerol can be dispersed in very fine droplets throughout the mixture. This dispersion requires from one hour to several hours to allow the droplets to merge into a distinct glycerol phase [63]. For this reason, mixing by shaking was generally done for a 5minutes as the reaction begins to progress, to reduce the time required for phase separation.

The presence of significant quantities of mono-, di-, and triglycerides in the final mixture can lead to the formation of an emulsion layer at the ester glycerol interface [64].This layer represents a net loss of product, unless it is recovered and separated. At worst, the ester phase will not meet the biodiesel specification and will have to be re-run.

If problems with mono-, di- and triglyceride will occur, one should re-evaluate the entire reaction to see where improvement can be made to improve process yields in the preceding steps.
However during the separation process this was not significantly observed. After completion of transesterification, the reaction mixtures were allowed to settle down for 5 hours. Thus, crude biodiesel was separated from glycerin phase effectively, because the settling time was enough for phase separation.

The glycerin phase was drained out from the bottom and the top phase (crude methyl ester) was separated from the bottom phase and then poured into another flask. Fig 3.3 shows the separation of the phases. After separating the phases, the residual catalyst and alcohol were washed from the ester with hot water.

Figure 3.3 Biodiesel and Glycerin separation

3.2.5 Washing Process

The washing process is one of the crucial processes that will determine the quality of the finished product. It is the purification process that is responsible for removing contaminants, and it is therefore the functional requirement to remove the impurities that remain in the raw biodiesel. Purification processes, including washing and drying are necessary, since untreated biodiesel can contain impurities such as free glycerol, soap, free fatty acid, methanol, catalysts, metals and glycerides. The remaining methanol in the biodiesel has safety risks; and can corrode the engine components, the residual catalyst can damage engine components, and soap in the biodiesel can reduce fuel lubricity and cause injector coking and other deposits [43].

Traditional water wash has been widely used and proved to be effective to remove most impurities. It was that found only water washing has purified biodiesel, direct from glycerol separation, to the requirements of European Standard for Biodiesel [65]. However, there are many disadvantages. If the water is mixed too excessively with the oil, it will create mayonnaise like emulsion and will take quite some time to settle out [66].

Although water is generally not soluble in biodiesel, biodiesel still has some affinity to water and a small amount will remain in the fuel unless it is removed. Thus methyl esters loss happens due to retention of ester in the water phase [67].

The raw biodiesel was purified by washing with deionized water warmed to 45^0C to remove all the residual water soluble byproducts. The separating funnel was shaken gently for 2 minutes and the mixture was then allowed to settle for 10 minutes to separate biodiesel and water layers. The water was removed as waste from the bottom phase. The process was repeated a minimum of four times until the water remains clear which indicates the biodiesel is reasonably clean.

Figure 3.4 Biodiesel Washing

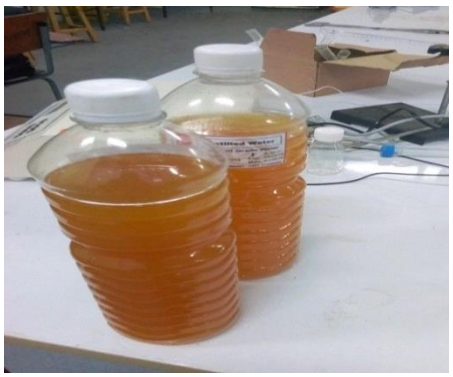


Figure 3.5 Washed biodiesel

The presence of water will give rise to hydrolysis of some of the produced ester leading to soap the formation [53]. Thus, it needs to avoid the water from the produced biodiesel. Silica gel was added to the raw biodiesel and allowed to settle for a 24 hour. After separation of the biodiesel from silica gel it was filtered using filter paper. Then, the clean biodiesel was dried on a hot plate to 110 ^{0}Cfor 45minutes (See fig 3.6). The final product was then analyzed to determine its fuel properties.

Figure 3.6 Heating biodiesel to dry

Figure 3.7 Dried and cleaned biodiesel

3.3 Biodiesel Yield

After purification process the biodiesel yield was then determined. The yield of biodiesel was ca lculated by the following equation:

$$\%Yield = \frac{W\ (biodiesel)}{W\ (Oil)} \times 100 \quad \text{.....(3.2)}$$

Where, W (biodiesel) is the weight of produced biodiesel and W (oil) is weight of WCO

3.4 Determination of Biodiesel Fuel Characteristics

The physical and chemical properties of the biodiesel prepared were determined by using ASTM standard test methods at the Ethiopian Petroleum Enterprise laboratory and Ethiopian Geological survey. The methods employed for characterizations are summarized as following:

3.4.1 Acid value

Acid value was determined by the acid base titration technique in accordance with ASTM [38]. Into 250mL Erlenmeyer flask, 20g of sample, 100mL of titration solvent (Isopropyl alcohol) and 0.5 mL of the indicator solution (P-Naphtholbenzein) were added. The mixture was stirred until the sample was entirely dissolved by the solvent. The mixture was titrated with the standardized KOH solution by shaking vigorously to green black end point. Then acid value was calculated using the equation 3.1 above.

3.4.2 Kinematic viscosity

A viscometer was inserted into a water bath at 40^0C and left for 30minutes. The sample was added to the viscometer and allowed to remain in the bath till it reaches the test temperature. Then the sample was allowed to flow freely and the time required for the meniscus to pass from the first to the second timing mark was taken using a stop watch. The procedure was repeated 3 times and the average value was taken and then multiplied with the viscometer calibration constant to give the kinematic viscosity in accordance with ASTM method [68].

$$v = c \times t \quad \text{.....(3.4)}$$

3.4.3 Density

Density was measured with a digital density meter in accordance with ASTM test method [33]. Test specimen was drawn from the sample container and automatically injected into the density meter glass cell and the result was automatically recorded in g/mL.

3.4.4 Flash point

The flash point was measured with a Pensky-Martens closed cup tester in accordance with the ASTM test method [69]. A brass test cup of specified dimensions filled into the inside mark with the test specimen and fitted with a cover of a specified dimensions, was heated and then stirred at specified rates. An ignition source was directed into the test cup at regular intervals with simultaneous interruption of stirring, until the flash was detected.

3.4.5 Ash Content

The 20g sample in a crucible was ignited and allowed to burn until only a carbonaceous residue remains. The carbonaceous residue was reduced to ash by heating in a muffle furnace at a temperature of 800^0C, cooled and weighed in accordance with ASTM test method [41]. The mass of ash as percentage of original sample was calculated using the following formula:

$$\text{Ash, mass\%} = \frac{m\,(ash)}{m(sample)} \times 100 \quad \text{.....(3.3)}$$

Where, m (ash)-mass of ash, m (sample)-mass of sample

3.4.6 Cloud point

The specimen was cooled in the cooling bath at specified rate; and then examined periodically in accordance with ASTM test method [70]. The cloud point was reported at which any cloud was observed at the bottom of the test jar which was confirmed by continued cooling.

3.4.7 Water and Sediment

Water and sediment test was done using 100mL of biodiesel in a centrifuge tube and centrifuging it at 800 rpm for 10 minutes in accordance with ASTM method [40]. The volume of water and sediment was obtained as percentage of volume using the following formula on equation 3.5.

$$\% \text{ (v/v)} = \frac{V1}{V2} \quad \text{.....(3.5)}$$

Where, V1- Volume of water and sediment, V2- Volume of the sample

3.4.8 Calorific Value

Calorific value was measured using the adiabatic bomb calorimeter by charging 1gram of sample based on the ASTM test method [44].

3.4.9 Copper Corrosion

Copper corrosion was tested using the ASTM method [43]. A polished copper strip was immersed in biodiesel in the test tube and allowed to heat in a 100 ^{0}C oil bath for 3 hours. After 3 hours, the strip was removed, examined, and compared with a set of copper strip corrosion standards furnished by ASTM.

4. RESULTS AND DISCUSSION

Currently, there is a growing concern on the situation of fossil fuel as the sole source of energy; and the environmental pollution emanated from the utilization of fossil fuel resulted in a consider able attention given to the alternative source of energy. Biodiesel is considered as a perfect altern ative source of energy that can compete with fossil fuel in terms of performance and efficiency.

However, production of biodiesel from vegetable oil and animal fat also raised a serious concern of food crisis and the critics other production of biodiesel from edible oil. This makes it difficult to justify the use of edible oil for fuel, considering the tremendously increment in the demand for the oil. Hence, the need to produce the biodiesel from WCO, which is regularly poured down the

drain and resulting in the environmental and human health problem when integrated into the food chain through animal feeding, is the focus of this study. The preparation processes and the results obtained from the characterization of the biodiesel produced from the WCO are hereby presented

4.1 Acid value of WCO

The acid value of WCO, used in this study, was determined by the acid base titration technique and the value was about 2mg KOH/g.It is almost equal to the value which is often recommended as the limit for an efficient transesterification using the base catalyzed reaction [60]. The WCO contained about 1% weight of the FFA. Thus, the feedstock was directly transesterified without significant yield loss.

Table 4.1Acid Value of WCO

Test NO.	Wt. of WCO, g	Normality of KOH,N	Volume of KOH for titration	Volume of KOH for blank titration	Acid value, mg KOH/g	%FFA, Acid value/2
1	20	0.1	7.35	0.12	2.0280	1.0140
2	20	0.1	7.30	0.12	2.0196	1.0098
Average					2.0238	1.0119

4.2 Transesterification

The potassium hydroxide used reacted with the methanol to produce the potassium methoxide catalyst. A reaction mixture contained 65g of methanol available for the production of the biodiesel sample and 4.7g of potassium hydroxide catalyst, for every 390g of the cleaned WCO. The KOH was added at 1.2% of the weight of cleaned oil.

During the transesterification process the reaction mixture changed to a turbid white-brown color (due to saponification as a result of FFA content of WCO sample) within the first few minutes, and then it changed to a dark-brown color. After stopping the agitation the color changed to red-brown and automatically formed two layers at the top transparent red-brawn, at the bottom black layer was formed.

4.3 Methyl Ester Yield

The product yield considering either crude or purified esters is defined as the mass percentage of the final product relative to the initial mass of the WCO introduced into the transesterification. According to this study, it is possible to prepare methyl ester of acceptable quality from WCO with simple method of transesterification with high yields. The maximum biodiesel yield obtained was 96% by weight. However, the variations in biodiesel yield were observed in some batches of transesterification.

This might be due to the variations in reaction conditions such as speed and duration of shaking the reaction mixture. The agitation of the reaction mixture was done manually. This could not keep the consistence of agitation throughout the batches. The reported time for the preparation of biodiesel by the same method was 10minute [71]. However, for the present study, the obtained result shows that the higher shaking speed and long time resulted in the formation of less fatty acid methyl esters; and Vigorous shaking for 5minutes was required for a better yield.

4.4 Biodiesel Fuel Characteristics

The physical and chemical properties of the methyl esters obtained by single-step alkali trans-esterification of the WCO are summarized in the following table.

Table 4.2 Fuel Properties of biodiesel from WCO

No.	Property	Test Method ASTM	Biodiesel Limit	Petro-diesel Limit	Result
1	Total acid value, mg KOH/g	D 974	0.8	0.5	0.5537
2	Kinematic viscosity at 40 ^{0}C,mm^2/s	D 445	1.9 to 6	1.3 to 4.1	4.89
3	Density at 15 ^{0}C, g/mL	D 4052	0.88	0.85	0.8782
4	Density at 20 ^{0}C, g/mL	D 4052	0.88	0.85	0.8748
5	Flash point(PMCC), ^{0}C	D 93	130 to 170	60 to 80	>156
6	Ash content, W/W%	D 482	0.02	0.01	<0.02
7	Cloud point, ^{0}C	D 2500	Report	Report	16
8	Water and Sediment, V/V%	D 2709	0.05	0.05	<0.05
9	Calorific value, MJ/Kg	D 240			41.243
10	Copper strip corrosion 3 hrs @ 100 ^{0}C	D 130	N0.3	N0.3	1a
11	Yield, %	-	-	-	96
12	Color				Nearest to golden

4.4.1 Total Acid Value

The acid value is defined as the milligrams of KOH required to neutralize the free acids in 1g of sample [38]. The acid value determination is an important test to assess the quality of a particular biodiesel. It can indicate the degree of hydrolysis of the methyl ester, a particularly important aspect when considering storage and transportation as large quantities of free fatty acids can cause corrosion in tanks [39].

The test result for the acid value for WCO methyl ester was found to be 0.5537mgKOH/g. The biodiesel is within specification as it falls under the ASTM [43] limit for acid value (0.8mg KOH/g). This shows that the transesterification, cleaning and drying processes were done in an effective way. Usually, for a base catalyzed process, the acid value after production will be low since the base catalyst will strip the available free fatty acids.

4.4.2 Kinematic Viscosity

Viscosity affects the atomization of a fuel upon injection into the combustion chamber and thereby, ultimately, the formation of engine deposits; the higher the viscosity, the greater the tendency of the fuel to cause such problems [72]. Viscosity of biodiesel methyl ester measured at 40 ^{0}C was found to be 4.89mm^2/s.

This value falls under the range recommended by ASTM. The ASTM standard for biodiesel viscosity is 1.9-6.0 mm^2/s at 40 ^{0}C. The value is surprising for waste frying oils biodiesel, as it is known that during the frying process under high temperatures in the presence of air and moisture, a variety of degradation reactions can occur, leading eventually to changes in the properties of the oil, including an increase in the viscosity of WCO and its biodiesel product [73]. Viscosity also increases with chain length and with increasing degree of saturation (i.e., with decreasing degree of unsaturation) [74]. This high viscosity property can be improved by blending the biodiesel with petro diesel or with biodiesel having low viscosity.

4.4.3 Density at 15 ^{0}C

The density of biodiesel is used to judge the homogeneity of biodiesel. This property is important mainly in airless combustion systems because it influences the efficiency of atomization of the fuel [32]. The result obtained (Table 4.2) showed that the methyl ester produced in this study has a density of 0.8782 g/mL which falls in the range (0.88 g/mL, specified according to the ASTM standard [33].

4.4.4 Flash point

The flash point of a fuel is the lowest temperature at which its vapor can be ignited. The flash point temperature is the measure of the fuel to form a flammable mixture with the air. It is only one of the numbers of the properties which must be considered in assessing flammability hazard of material [63].

For biodiesel, a flash point of below 130 ^{0}C is considered to be out of specification [43].The measured flash point of this biodiesel was 156^{0}C, indicating very low or negligible methanol levels in the biodiesel. This high flash point is probably not only due to very low methanol content but more likely due to the presence of methyl esters with C16 and C18 carbon chain lengths which pre-dominate the biodiesel [29].

4.4.5 Ash Content

Ash may come from abrasive solids, soluble metallic soaps, and remaining catalysts. It can result from oil or water soluble metallic compounds or from extraneous solids such as dirt and rust. The knowledge of the amount of ash forming materials present in a product can provide the information as to whether or not the product is suitable for use in a given application [42].The maximum ASTM limit for ash content is 0.020 % by mass and the evaluated biodiesel ash content is less than 0.020% by mass, which is nearest to the maximum ASTM limit value. This shows that effective washing was done in the purification process.

4.4.6 Cloud Point

Low temperature operability of biodiesel fuel is an important aspect for the engine performance standpoint in cold weather conditions [9]. Cloud point is the temperature at which a cloud of wax crystals first appear in the oil as it is cooled [64]. The property is related to the use of biodiesel in the cold temperature. The cloud point of methyl ester obtained in this study was 16 ^{0}C.

It was found that biodiesel derived from palm oil has a cloud point that ranges from 10 ^{0}C to 20 ^{0}C, which may cause trouble in cold seasons and confirmed that the cold flow behavior of FAME/FAEE is one of the few research problems at low temperature because of their crystallization properties [59]. The value obtained is high and matches with this result.

The biodiesel made from feed stocks containing higher concentrations of high melting point satu -rated long chain fatty acids tends to have relatively poor cold flow properties [75]. This insures that the high value of CP comes from the palm oil which has higher fatty acid alkyl esters [76].

From this result it is clear that methyl ester would be suitable candidate as diesel fuel substitute in tropical countries and not as suitable at B100 in colder climate conditions. Therefore, Cold flow properties of the biodiesel can be reduced by blending with petro diesel, treating with petro diesel fuel additives, transesterification of vegetable oils with long or a branched chain alcohols, and crystallization fractionation [43].

4.4.7 Water and Sediment

An accumulation of sediment in a storage tanks and on a filter screens can obstruct the flow of fuel from the tank to the combustor [40]. Water can cause corrosion of tanks and equipments. The biodiesel sample prepared in this study had $<$ 0.05 v% water and sediments. This value met the ASTM standard requirement (which is 0.05 vol. % Max) and shows that the purifying and drying process was almost effectively done.

4.4.8 Calorific Value

Calorific value is an important parameter in the selection of fuel. The calorific value of biodiesel is usually lower than that of diesel due to its higher oxygen content [44]. For the present study, the calorific value of the biodiesel was established to be 9866.85cal/g (41.243MJ/Kg).

The result is nearest to that of diesel fuel according to ASTM standard [77], which represents the amount of heat transferred to the chamber during combustion and available energy in the fuel. T his indicates that the produced biodiesel is applicable as fuel to generate enough energy in the engine.

4.4.9 Copper Strip Corrosion

The copper corrosion test measures corrosion forming tendencies of fuel when used with copper, brass, or bronze parts. The presence of acids can tarnish copper. The ASTM maximum limit for copper corrosion is number 3 [45].

The WCO biodiesel passed ASTM specifications as the copper strip immersed in biodiesel and was allowed to heat in a 100^0C oil bath for 3hr has a rating of 1a, when compared with a set of the copper strip corrosion standards furnished by the ASTM. This indicates that the copper strip changed to slightly tarnish in the produced biodiesel. Usually, for a base catalyzed process, the acidity will be low since the base catalyst will strip the available free fatty acids.

5. CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

This study reports the production of biodiesel from WCO as alternative to petro diesel. Based on the results of experimental analysis, it can be concluded that this feedstock is suitable for the production of biodiesel. Also, the origin of feed stock had a high effect on biodiesel quality. For instance, the use of WCO from palm oil results in high cloud point of biodiesel which can in hibits the availability of the fuel in cold conditions.

It can also be concluded that, base-catalyzed transesterification by shaking method is more suitable for biodiesel production in easy and fast way with a high yield and quality. Except for the cloud point, the other parameters met the ASTM standard. Therefore, the biodiesel produced by this study can be more effective by blending with diesel fuel.

5.2 RECOMMENDATION

For future studies, it is recommended that transesterification reaction be carried out by using shaker to maximize the yield and save the energy, which is the problem during manual shaking. It can also be recommended that one can produce biodiesel with a low cloud point by mixing palm oil feedstock with those having short chain fatty acids. Biodiesel produced from WCO originated from mixture of palm and sunflower oil should be used by blending with diesel fuel.

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APPENDEX

Table1. Biodiesel yield at different shaking time

Test No.	WCO (g)	Shaking time (min.)	Crude Biodiesel (g)	Crude Biodiesel yield (%)	Purified Biodiesel (g)	Purified Biodiesel Yield (%)
1	380	10	335	88	328	86
2	385	8	365	95	350	91
3	388	7	377	97	368	95
4	390	5	381	98	374	96
Average				94.5		92

Table 2: Total Acidity, mg KOH/gram of sample D-974

Test No.	KOH required for titration of the sample(A), mL	KOH required for titration of the blank(B), mL	Weight of sample used (W), g	Normality of KOH(N)	Acid Number, mg KOH/g = (A-B)x(Nx56.1)/W
Test 1	2.08	0.1	20.0	0.1	0.5554
Test 2	2.07	0.1	20.02	0.1	0.5520
Average					0.5537

Table 3: Kinematic Viscosity, D-445

Test No.	Viscometer number	Viscometer constant, mm^2/s^2	Flow time, s	Kinematic viscosity, c x t
1	29439	0.009194	532	4.8912
2	29439	0.009194	531	4.8920
Average				4.8866

Table 4: Density at 15^0C & 20^0C, D-4052

No. of Tests	1	2	Average
Density at 15^0C, g/mL	0.8749	0.8747	0.8748
Density at 20^0C, g/mL	0.8781	0.8783	0.8782

Table 5: Water and Sediment, D-2709

Test No.	1	2	3	Average
Volume of water and sediment per 100mL of sample in the 1^{st} test tube, mL	0.040	0.050	0.046	0.045
Volume of water and sediment per 100mL of sample in the 2^{nd} test tube, mL	0.041	0.049	0.047	0.046
Water & sediment, %V=(V1+ V2/2)				0.046

Table 6: Flash Point D-93

Properties	Test 1		Test 2		Test 3		Ave.
	Observed	Corrected	Observed	Corrected	Observed	Corrected	
Temp., ^{0}C	149	155	151	157	153	158	156.67
Barometric pressure, mmHg	575		575		580		
** Corrected flash point=C + 0.033(760-P), Where, C-Observed flash point, P-ambient barometric pressure(mmHg)							

Table 7: Ash Content D-482

Test No.	Mass of sample , (g)	Mass of Empty crucible, (g)	Mass of ash plus crucible, (g)	Mass of ash, (g)	%Ash=Mass of ash/Mass of sample x100
Test 1	20.0	21.2	21.204	0.004	0.020
Test 2	20.1	21.1	21.103	0.003	0.015
Average					0.0175