MEASUREMENTS AND CALCULATIONS OF BIODIESEL BLEND PROPERTIES AT A CONSTANT STORAGE TEMPERATURE.

A THESIS SUBMITTED TO THE GRADUATE SCHOOL OF APPLIED SCIENCES OF NEAR EAST UNIVERSITY

By OLUWOLE ADESHINA COLE

In Partial Fulfillment of the Requirements for the Degree of Master of Science in Mechanical Engineering

NICOSIA, 2017

MEASUREMENTS AND CALCULATIONS OF BIODIESEL BLEND PROPERTIES AT A CONSTANT STORAGE TEMPERATURE.

A THESIS SUBMITTED TO THE GRADUATE SCHOOL OF APPLIED SCIENCES OF NEAR EAST UNIVERSITY

By OLUWOLE ADESHINA COLE

In Partial Fulfillment of the Requirements for the Degree of Master of Science in Mechanical Engineering

NICOSIA, 2017

Oluwole Adeshina Cole: MEASUREMENTS AND CALCULATIONS OF BIODIESEL BLEND PROPERTIES AT A CONSTANT STORAGE TEMPERATURE

Approval of Director of Graduate School of Applied Sciences

Prof. Dr. Nadire ÇAVUŞ

We certify this thesis is satisfactory for the award of the degree of Masters of Sciences in Mechanical Engineering

Examining Committee in Charge:

Assist. Prof. Kamil DİMİLLER

Committee Chairman, Automotive Engineering Department, NEU

Dr. Ali ŞEFİK

Mechanical Engineering Department NEU

Prof. Dr. Ing. Hüseyin, CAMUR

Supervisor, Mechanical Engineering Department, I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, last name: Oluwole Adeshina Cole

Signature:

Date:

ACKNOWLEDGEMENTS

Primarily, my honest appreciation is given to God for His immense wisdom, knowledge and understanding and this thesis would not have been possible without the help, support and patience of my principal supervisor in person of Assist. Prof. Dr. Ing. Hüseyin, CAMUR; for his constant encouragement and guidance. He actually walked me all through the stages of writhing my thesis.

Also. I would like to thank Prof. Dr. Mahmut Ahsen, SAVAŞ, Assist. Prof. Dr. Ali, EVCİL and Dr. Youssef KASSEM who taught me and helped with every vital information all through my course of study.

Above all, my sincere gratitude also goes to my family, my pastor in person of Dr. Anyi OBI and all my friends and well-wishers for their prayers and strong confidence in me.

Every of my research and experiment was supported by the Department of Mechanical Engineering of the Near East University and I am indebted to you all.

To my parents

ABSTRACT

Bio-diesel could have been a good alternative for euro-diesel if not for certain limiting factors. The bio-diesel used in this work is FAME based and this is directly limited by climatic condition because it is usually gotten from vegetable oil and fats. The major limiting factor to this is also the presence of enormous unsaturated fatty acidic compound. Additionally, bio-diesel inhibits the ability to be utilized at low temperatures. The euro- diesel summer used in this work is known to be the ultra-low sulphur diesel (ULSD) which is hygroscopic in nature, which makes it a case study to determine what could be the cloud point, and pour point properties achieved when 5% bio-diesel is blend with 95% euro-diesel. The kinematic viscosity, density-temperature relationship are determined ranging from -11°C to 90°C thus also considered over the storage. Due to the nature and characteristics of the both bio-diesel and euro-diesel, it is observed that kinematic viscosity and density both increased along the storage time but they both decreased at increasing temperature and increased at decreasing temperature. The total acidic number also increased over the storage time thus reducing the oxidation stability.

Keywords: Bio-diesel; cloud point; density; euro-diesel; kinematic viscosity; pour point

ÖZET

Biyodizel, belirli kısıtlayıcı faktörler için değilse bile, euro dizel için iyi bir alternatif olmuş olabilir. Bu çalışmada kullanılan biyodizel FAME tabanlı ve genellikle bitkisel yağ ve yağlardan alındığından iklimsel koşullarla sınırlıdır. Bunun en büyük sınırlayıcı faktörü, muazzam doymamış yağlı asit bileşiğinin varlığıdır. Buna ek olarak, biyodizel düşük sıcaklıklarda kullanılma kabiliyetini de engeller. Bu çalışmada kullanılan euro dizel yazının doğasında higroskopik olan ultra düşük kükürtlü dizel (ULSD) olduğu bilinir; bu da bulut noktası ne olabileceğini belirlemek için bir örnek olay incelemesi yapar ve 5 % biyodizel,% 95 euro dizel ile karışıyor. kinematik viskozite, yoğunluk-sıcaklık ilişkisi -11 °C ila 90 °C arasında değişen bir sıcaklık aralığında belirlenir ve böylece depolama süresi de göz önüne alınırsa. Buna ek olarak, toplam asit sayısı ve oksidasyon kararlılığı da depo üzerinde değerlendirilmektedir. Hem biyodizel hem de euro dizelin doğası ve özellikleri nedeniyle, kinematik viskozite ve yoğunluğun depolama süresi boyunca arttığı fakat her ikisi de artan sıcaklıkta azaldı ve azalan sıcaklıkta artmaktadır. Toplam asidik sayı da depolama süresi boyunca artmıştır, böylece oksidasyon kararlılığı azaltılır.

Anahtar Kelimeler: Akma noktası; bulut noktası; euro dizel; kinematik viskozite; soğuk akış özellikleri; yoğunluk

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	i
ABSTRACT	iii
ÖZET	iv
LIST OF FIGURES	viii
LIST OF TABLES	ix
LIST OF QUANTITIES USED	X
LIST OF ABBREVIATIONS AND SYMBOLS	xi

CHAPTER 1: INTRODUCTION

1.1 General View	1
1.2 Thesis Aim	2
1.3 Novelty	2
1.4 Literature Review	2
1.5 Thesis Overview	4

CHAPTER 2: THEORY

2.1 Cold Flow Properties	. 5
2.1.1 Cloud point	. 5
2.1.2 Pour-point	6
2.1.3 Cold filter plugging point	.7
2.2 Flash-Point	.7
2.3 Acid Value	8
2.4 Iodine Value	8
2.5 Oxidation Stability	9

2.6 Cetane Number	10
2.7 Heat of Combustion	11
2.8 Lubricity	12
2.9 Density	13
2.10 Viscosity	13
2.10.1 Viscosity units and conversion	15
2.10.2 Fluid flow and viscosity	16
2.11 Viscometers	17
2.11.1 Capillary viscometers	17
2.12 Total Acidic Number	18

CHAPTER 3: MATERIALS, METHODS AND EXPERIMENTAL SET-UP

3.1 Bio-Diesel and Euro-Diesel	. 19
3.2 Measurement of Kinematic Viscosity	. 23
3.2.1 Ubbelohde viscometer	. 23
3.3 Cooling Bath System	. 29
3.3.1 Alcohol	. 31
3.3.2 Temperature regulation	. 31
3.3.3 Accessories	. 33
3.3.4 Flow chart on kinematic viscosity	. 34
3.4 Measurement of Density using Pycnometer	. 35
3.4.1 Standards using the pycnometer	. 35
3.5 Electromagnetic Hot plates	. 36
3.6 Methodology	.36
3.6.1 Procedure i (kinematic viscosity)	. 36
3.6.2 Procedure ii (density)	. 37
3.6.3 Flow chart on density	.40
3.6.4 Procedure iii (pour point and cloud point, cfpp)	.41

3.6.5 Flow chart for measuring cloud point and pour point	45
3.6.6 Procedure iv (blend temperature stability and storage)	46

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Kinematic Viscosity over a Storage Period of 90 days at Temperature 40°C	47
4.2 Kinematic Viscosity over Testing Temperatures	48
4.3 Density over a Storage Period of 90 days at Temperature 15°C	50
4.4 Density over Testing Temperatures	51
4.5 Total Acidic Number and Oxidation Stability	53
4.6 Cloud point, Pour point, Cfpp, Calibration Curves and Cooling Curve	54
4.6.1 Calibration curve	54
4.6.2 Cooling curve	57

CHAPTER 5: CONCLUSION, POSSIBLE ERRORS AND RECOMMENDATION

5.1 Conclusion	
5.2 Possible Errors	
5.3 Recommendation	59

REFERENCES

APPENDICES
Appendix 1: ASTM D2500-09 Standard Test Method for Cloud Points of Petroleum Products
Appendix 2: ASTM D97-05 Standard Test Method for Pour Points of Petroleum Products67
Appendix 3: ASTM 6371-05 Standard Test Method for Cfpp of Petroleum Products76
Appendix 4: ASTM D664-04 Standard Test Method for Acid Value of Petroleum Products83
Appendix 5: ASTM D941-88 Standard Test Method for Density of Petroleum Products90
Appendix 6: ASTM D445-06 Standard Test Method for Viscosity of Petroleum Products95

LIST OF FIGURES

Figure 2.1:	Cloud point	6
Figure 2.2:	Pour point	7
Figure 2.3:	Brace specific fuel consumption and ignition delays versus cetane number.	11
Figure 2.4:	Simple shear of a liquid film	15
Figure 3.1:	Ubbelohde viscometer	24
Figure 3.2:	Cooling bath system	30
Figure 3.3:	Thermometer used in glass beaker for measurements at high temperature	32
Figure 3.4:	Thermostat attached to the cooling bath for measurements at low temperatures	32
Figure 3.5:	Heiddoph mr hei-tec	36
Figure 3.6:	Diagrammatic representation of measuring density using pycnometer	39
Figure 3.7:	Cloud point and pour point measurement apparatus	41
Figure 3.8:	Data logger and thermocouples	42
Figure 3.9:	Glass jar and thermocouples	44
Figure 3.10:	Bio-diesel and euro-diesel blend in an oven	46
Figure 4.1:	Kinematic viscosity (mm^2/s) for storage period of 90 days at 40°C	48
Figure 4.2:	Kinematic viscosity (mm^2/s) for 12 weeks over testing temperatures °C	50
Figure 4.3:	Density (kg/m^3) for storage period 90 days at 15°C	51
Figure 4.4:	Density (kg/m^3) for 12 weeks over testing temperature	53
Figure 4.5:	Calibration curves	55
Figure 4.6:	Cooling curves	57

LIST OF TABLES

Table 3.1:	Standards for Fame Bio-diesel	20
Table 3.2:	Standards for Euro-diesel	22
Table 3.3:	Types of Ubbelohde Viscometer for Transparent Fluids	26
Table 3.4:	Kinematic Energy Correction of the Ubbelohde Viscometer	27
Table 3.5:	Ubbelohde Technical Specification	29
Table 4.1:	Kinematic Viscosity (mm^2/s) for storage period 90 days at 40°C	48
Table 4.2:	Kinematic Viscosity (mm^2/s) for 12 weeks over Testing Temperatures	49
	°C	
Table 4.3:	Density (kg/m^3) for storage period of 90 days at 15 °C	51
Table 4.4:	Density (kg/m^3) for 12 weeks over Testing Temperatures °C	52
	Total Acidic Number (mgKOH, gr) and Oxidation Stability (hours)	
Table4.6:	Experimental Results of Cp, Pp and Cfpp	54

LIST OF QUANTITIES USED

FLUID DEFORMATION

σ	Shear stress of fluid element	pascal
τ	Alternative form of shear stress	pascal
ε	Strain rate	mm/mm
t	Shear time	S

FLOW QUANTITY

vz	Velocity in flow direction	m³/s
vr	Velocity in radial direction	rad/s
νθ	Velocity in angular direction	rad/s
v	Kinematic viscosity	mm²/s
μ	Dynamic viscosity	mm²/s
р	Flow density	kg/m³
g	Acceleration due to gravity	m/s^2
Q	Volumetric flow rate	m³/s

GEOMETRY QUANTITY

x	Elemental length	m
r	Radian length	m
æ	Length in flow direction	m
Н	Capillary height	m
R	Capillary radius	m
V	Volume	m³
L	Length of viscometer	m

DEFINED QUANTITY

K	Viscometer constant

y Correlation factor

LIST OF ABBREVIATIONS

ASTM	American Society for Test Materials
AV	Acid Value
AVE	Average
BD	Bio-Diesel
CFPP	Cold Filter Plugging Point
CGS	Centimeter-Gram-Second
CIE	Compression Ignition Engine
CN	Cetane Number
СР	Centipoise
СР	Cloud-Point
CST	Centistokes
СО	Carbon-Monoxide
CO ₂	Carbon-Dioxide
ED	Euro-Diesel
EN	European- Standard
FAME	Fatty Acid Methyl Ester
FP	Flash – Point
FIE	Fuel Injection Equipment
FTIR	Fourier Transform Infrared Spectroscopy
G	Grams
HEFRR	High Frequency Reciprocating Rig
HMN	Heptamethylnonane
IP	International Publishing Standard Methods

ISO	International Standard Organization
IV	Iodine Value
KG	Kilogram
KJ	Kilojoule
КРА	Kilopascal
LTFT	Low Temperature Flow Test
MG	Milligrams
NC	Number of Carbon Atoms
ND	Number of Double bonds
РСТ	Patent Cooperation Treaty
PP	Pour Point
РОМ	Polyoxymethylene
QG	High Heating Value
QN	Low Heating Value
SI	System Institute
SSU	Saybolt Second Universal
ST	Stokes
VS	Versus
WKS	Weeks

CHAPTER 1 INTRODUCTION

1.1 General View

Industrialization and economic development leads to higher energy consumption. Transportation is largely responsible for the increasing demand for energy (Geacai et al., 2015). Fuels derived from petroleum are the major source of energy currently. Concerns about the impact of fossil fuels on climate change and the resulting devastating consequences have made it imperative to seek for alternative clean and renewable energy sources (Geacai et al., 2015).

Biofuels are renewable energy sources, which can serve as clean alternatives to fossil fuels. For example, biodiesel is made from vegetable oils and animal fat and is increasingly gaining ground as a replacement for petroleum diesel fuel in diesel engines (Atabani et al., 2012). Biodiesel can be defined as a mixture of fatty acid alkyl esters, derived of vegetable oils, animal fats, or waste frying oils that are produced by transesterification with a monohydric alcohol such as methanol or ethanol under the presence of an alkali catalyst. This process creates a mixture of fatty acid methyl esters (FAME). Biodiesel can be used in a diesel engine either in pure form or as an additive to diesel fuel (Joshi and Pegg, 2007; Knothe, 2010).

Currently, over 95% of the world's biodiesel is being produced from edible oils such as soybean, rapeseed, peanut oils, cottonseed, palm, and sunflower oils. These oils can replace only a few percent of the petro diesel market because the biodiesel from this feedstock is more expensive than petro-diesel (Geacai et al., 2015).

Some of the advantages of biodiesel over petroleum diesel fuel include reducing global warming gas emissions, hydrocarbons (HC), carbon monoxide (CO), carbon dioxide (CO2) and other toxics emissions. Biodiesel enhances lubricity and reduces premature wearing of fuel pumps (Joshi, 2007). Biodiesel is environmental-friendly because it is biodegradable, renewable and burns cleaner. It is also easier to store because it has a higher flash point (Mejía et al., 2013). On the other hand, the disadvantages of biodiesel include high cost and poor cold flow properties (Joshi, 2007). Biodiesel starts to become a gel at low temperatures, which makes the filters to be clogged or even become so thick that it cannot be pumped from the fuel tank to the engine due to an increase in viscosity with decreasing temperature. The viscosity of biodiesel is slightly greater than that of petroleum diesel.

The increasing global production and usage of biodiesel has made it imperative to determine the effect of temperature on its physicochemical properties (Blangino, 2008). The properties of biodiesel and biodiesel fuel blends that are usually analysed include acid value, oxidation stability, flash point, iodine value, pour point and cloud point, kinematic viscosity and density.

1.2 Thesis Aim

Due to the fact that viscosity values shows significant variation between different regional feedstock and biodiesel fuel, there is a need to experimentally measure the kinematic viscosity and density which are both temperature dependant and check if it meets the standard acceptable range of values. The goal of this work is to determine experimentally the properties of 5% biodiesel and 95% euro-diesel blend from North-Cyprus kept at a steady temperature of 40°C over a long period to observe the kinematic viscosity and density, cold flow properties, total acidic number and oxidation stability.

1.3 Novelty

This thesis is unique as it specifically investigates the properties of 5% biodiesel and 95% eurodiesel from Cyprus with the binary fuel blend kept at a steady temperature of 40°C over a long period to observe its properties. The binary fuel blend sample is then subjected to varying temperature from -11°C to 90°C. The effect of the temperature change on density and kinematic viscosity of the fuel blend at different times is recorded. Additionally, the experiment will also include measuring and recording the cloud point and pour point of the fuel blend.

1.4 Literature Review

Some researchers have studied the properties of varying biodiesel blends using different methods. As result of the ever growing demand on liquid fuels and then more qualitative criteria to guarantee a high quality of the fuels during long-term storage is a priority. Over a long period, various internal and external factors affects liquid fuels which affects the physical and chemical properties which affects products performance characteristics.

There are various factors which alters the stability of the liquid fuels and several scientists already carried out different experimental and theoretical analysis as to why fuels are expected to be of high quality and to remain stable even after prolonged storage. Plenty of literature exists on research and findings relating to changes in performance characteristics of conventional fuels concerning the oxidation (ageing) process.

Corrosion or destruction of materials in consequences of chemicals or electrochemical interactions between the materials and its environment. Corrosion attacks a variety of materials with corresponding environment. Corrosion attacks a variety of materials and not just metals alone which is why corrosion is a common problem whenever petroleum products are in contact with metal parts and alloys whether during production, distribution, operation or storage. Corrosion changes are caused by certain constituents of the fuel ranging from sulphur compounds, organic compounds, water soluble inorganic acids and bases.

Hydrocarbons, the essential components of petroleum-based fuels are likely during storage to react with atmospheric oxygen and with one another. The theory is based on chain reactions which will off cause contaminate storage tanks, promote corrosion of transfer pipelines, cause filter plugging and similar problems in the fuel distribution system.

Geacai et al. (2015) used experimental data to evaluate the accuracy of viscosity calculations with various models, for mixtures of biodiesel with pure constituents as well as for biodiesel with diesel fuel. Also, the refractive index of the blends or empirical correlative equations was used to calculate the viscosity of the blends.

Saltas et al. (2017) examined the impact of biodiesel aging on the deposits produced inside regular rail Fuel Injection Equipment (FIE). They analyzed the FAME constituents, the major fuel properties and their rates of degradation. A reference test to assess the predisposition of diesel engine fuels to produce deposits was proposed.

Zhou et al. (2017) used Fourier transform infrared spectroscopy (FTIR) and other instrumental systems to investigate the oxidative degradation of biodiesel mixtures. They found that the TD-DES method displayed outstanding forecasting operation for FTIR and TGA in the evaluation of oxidative degradation.

Banga and Varshney (2010) studied the impact of impurities produced during transesterification process of biodiesel and how to remove the impurities. It also underscored the impact of elongated storage on the performance of biodiesel.

Syam et al. (2013) produced biodiesel from waste frying oil and analyzed the properties. They got a biodiesel yield of up to 99%. The biodiesel properties were in the range of standard specifications and they conform to diesel engine operating conditions.

Lima et al. (2010) investigated the use of a pycnometer in measuring biodiesel density. The results revealed substantial deviation from values gotten from national metrology institute. But they are still within the Brazilian standards for commercial applications.

Ullah (2013) examined the impact of aging biodiesel and diesel gasoline blend in the presence of polymer. Polymer was used to provide a car-like environment. The fuel blends were aged at

850C for 100 hours within a polymer material. The polymer was monitored to observe its influence on the fuel blend and to observe the compatibility of the polymer with the fuel.

The polymer used was POM (Polyoxymethylene) which is likewise used in vehicles. Four various schemes (open and nitrogen scheme, with and without antioxidants) were created. No change was detected in the fuel whilst aged inside the presence of polymer. The polymer was later aged for 1600 hours with the fuel being replaced weekly (after 100 hours) and collecting the sample after 400 hours. The alteration in chemical composition with the use of IR spectroscope and scanning electron microscope, fuel penetration in the polymer, residue on the surface of the polymer and material swelling were investigated at each aging interval. In the inert system, no substantial change was observed during the aging period. The higher quantity of residue was detected in the open system. The residue was further polymerized on the surface of the polymer after 1200 and 1600 hours. The polymer swelled more in 1.6-hour stable fuel than in nine-hour fuel. The strength of the polymer was substantially reduced by the presence of cracks on its surface (almost 35 % increase in fragility), which was confirmed by the use of charpy impact test.

1.5 Thesis Overview

The rest of this thesis is divided into 5 chapters, which are structured as follows.

Chapter 1 is an introduction about the thesis. In this chapter, a definition of the thesis is presented, the aims are outlined and a literature overview of the thesis is discussed.

Chapter 2 discusses the theory and general review of bio-diesel and euro-diesel in several aspects. The properties of biodiesel and the theory of the capillary viscometer are also discussed. The definitions of standards are also mentioned briefly in this section.

Chapter 3 is a detailed and general explanation on the biodiesel and euro-diesel samples used. It also presents the measurement procedure and experimental setup.

Chapter 4 is a detailed explanation of the results obtains from the blends of biodiesel and eurodiesel.

Chapter 5 gives the conclusion and recommendation on the behaviour of the biodiesel and euro-diesel fuel blend.

CHAPTER 2 THEORY

The study of the properties of biodiesel and euro diesel as well as the effect of temperature on those properties is important in determining their suitability as alternatives to conventional diesel fuel. The properties of biodiesel and biodiesel fuel blends that are usually analysed include acid value, oxidation stability, flash point, iodine value, pour point and cloud point, kinematic viscosity and density.

2.1 Cold Flow Properties

Normally, all fuels for compression ignition engines (CIE) could lead to starting problems at low temperatures, because of the fuel's deteriorating properties at low temperatures. The cause of these issues is the formation of small crystals suspended within the liquid form, which could clog gas filters in part or completely. Due to the sedimentation of these crystals at the inner walls of the tubes of the fuel system, the drift segment through the pipes is reduced, causing poor engine fuelling. In extreme conditions, when low temperatures persist longer (e.g. overnight), the piping system may be completely blocked through the solidified gasoline. The cloud drift performances of the fuels can be qualified through the cloud point (CP), the pour point (PP), the cold filter plugging point (CFPP) and viscosity (v). A substitute for CFPP is the low-temperature flow test (LTFT). Lately, the US introduced a brand-new technique for assessing the cold flow attributes of biodiesel, referred to as cold soak filtration test (CSFT). The cloud point, pour point, cold filter plugging point are the various cold flow properties, which will be examined in this work.

2.1.1 Cloud point

The cloud point (CP) is the temperature at which crystals inside the fuel begin to form. The cloud point is reached while the temperature of the biodiesel is low sufficiently to make wax crystals to precipitate. First, cooling temperatures lead to the formation of the solidified wax crystal nuclei that are submicron in size and invisible to the naked eye. More decrease of temperature makes the crystals to develop. The temperature at which the crystals turn out to be visible (the crystal's diameter 0.5μ m) is referred to as the cloud point because the crystals develop a cloudy suspension. Beneath the CP, those crystals might plug filters or drop to the bottom of a reservoir. The CP is the most typically used determinant of low-temperature

operability of the fuel. The cloud point of biodiesel is generally higher than the cloud point of petroleum diesel. The cloud point of biodiesel depends on the character of the feedstock that was used to produce it (Barabás & Todoruţ, 2010; Barabás & Todoruţ, 2011). It is usually between -5°C and 17°C. Figure 2.1 is a pictorial representation of the cloud point. Appendix 1, which is ASTM D 2500-09, is the American standard test method for cloud point of petroleum products.



Figure 2.1: Cloud point

2.1.2 Pour-point

The pour point is the temperature at which the fuel consists of many agglomerated crystals that it is a gel and will stop flowing. This occurs if the temperature of the biodiesel drops below CP, while the microcrystals merge and shape into large clusters, which may additionally disrupt the flow of the biodiesel via the pipes of the engine's fuel system. Like the cloud point, the pour point values also rely on the feedstock used to create the biodiesel. Pour point values are varies from -15°C to 16°C. Despite the fact that CP and PP are easily measured, they give only indicative values for the minimum temperature at which the fuel may be used. As at cloud point, the fuel can nevertheless be used in suitable situations, at pour point that is no longer possible. In other words, cloud point overestimates minimal working temperature and pour point underestimates it (Barabás & Todoruţ, 2011). Figure 2.2 is a pictorial representation of the pour point. Appendix 2, which is ASTM D 97-05, is the American standard test method for pour point of petroleum products.



Figure 2.2: Pour point

2.1.3 Cold filter plugging point

This can be defined as the minimum point at which every blends of fuel will still flow through any filter. It is noted that clogging of fuel blends begins after this temperature. Appendix 3, which is ASTM D 6371-05, is the American standard test method for cold filter plugging point of diesel and heating fuels.

2.2 Flash-Point

The flash point is the minimum temperature computed to a barometric pressure of 101.3 kPa at which the gas will ignite on utilization of an ignition supply within defined conditions. It is used to categorize fuels for storage, delivery and distribution with respect to the degree of hazard. The flash point does not have a direct impact on the combustion; greater values make fuels safer in connection with storage, fuel dealing with and delivery. FP varies inversely with the volatility of the fuel. For biodiesel, in the US, the minimum flash point is 93°C, 120°C in

Europe and 100°C in Brazil. Biodiesel's flash point decreases swiftly as the quantity of residual alcohol increases (The flash point of methanol is 11–12°C, and that of ethanol is 13°C–14°C). For this reason, measuring the biodiesel flash point assists to depict the presence of methanol or ethanol. As an instance, the presence of 0.5% methanol in biodiesel brings down biodiesel flash point from 170°C to 50°C. If flash point is used to ascertain the methanol content, the ASTM standard enforces a minimum value of 130°C for it. This restriction may be considered too excessive, because at the maximum allowable concentration of methanol of 0.2% w/w biodiesel, flash point reduces below 130°C. (Anastopoulos et al., 2009; Barabás & Todoruţ, 2010; Barabás et al., 2011). ASTM D 93-10 is the American standard test method for flash point of petroleum products.

2.3 Acid Value

The acid value (AV), also known as neutralization number or acid number is the mass of potassium hydroxide (KOH) in milligrams this is needed to neutralize the acidic constituents in one gram of sample. The acid value is used to ascertain the presence of acid molecules in a biodiesel sample. In a normal procedure, a particular amount of sample dissolved in organic solvent is titrated with a solution of potassium hydroxide with known concentration and with phenolphthalein as a colour indicator. The acidic compounds that could possibly be observed in biodiesel are residual mineral acids from the production process, residual free fatty acid from the hydrolysis procedure or the post-hydrolysis process of the esters and oxidation byproducts within the shape of different natural acids (Berthiaume & Tremblay, 2006). This factor is a direct measure of free fatty acids constituents, hence the corrosiveness of the fuel, blockage of filter and the presence of water within the biodiesel. A too excessive quantity of free glycerine can lead to functioning issues at reduced temperatures and blockage of fuel filter. This factor can be used to determine how fresh the biodiesel is as well. Fuel that has oxidized after being stored in an extended period will likely have a higher acid price (Barabás & Todorut, 2011). Appendix 4, which is ASTM D 664-04, is the American standard test method for acidic value of petroleum products.

2.4 Iodine Value

The iodine value (IV) or iodine number was introduced in quality standards of biodiesel to assess their oxidation stability. The IV is a measurement of overall unsaturation of fatty acids measured in g iodine/100 g of biodiesel sample, when adding iodine to the double bonds. Biodiesel with excessive IV is freely oxidized in contact with air. The iodine value greatly

relies upon on the nature and ester composition of the feedstock is used in biodiesel production. Consequently, the IV is confined in diverse areas of the world depending on the particular situations: It is 120 in Europe and Japan, 130 in Europe for biodiesel as heating oil, 140 in South Africa, in Brazil it isn't constrained and in the U.S, Australia and India it isn't part of the quality standard (it would omit feedstock's like sunflower and soybean oil). Biodiesel with high IV has a tendency to polymerize and produce deposits on fuel injector nozzles, piston rings and their ring grooves. The likelihood of polymerization increases with the extent of unsaturation of the fatty acids (Barabás & Todoruţ, 2011). ASTM D 5554-15 is the American standard test method for determining the iodine value of petroleum products while BS EN 14111:2003, is the European standard test method for acidic value of petroleum products.

2.5 Oxidation Stability

The quality of biodiesel can be influenced by oxidation in the course of storage (in contact with air) and hydrolytic degradation (in contact with water). Both operations may be qualified by the oxidative balance and hydrolytic balance of the biodiesel. Biodiesel oxidation can arise during storage in the course of waiting for transportation or in the fuel system the vehicle itself. Biodiesel stability can mean either of two issues: long-time storage stability or aging stability at increased temperatures or pressures as the fuel is circulated repeatedly through the fuel system of an engine (NREL, 2009).

Storage stability is especially significant for biodiesel; it can be defined as the capability of the fuel to resist chemical modifications throughout long-term storage. Those changes typically consist of oxidation because of contact with oxygen from the air (Gerpen, 2005).

Biodiesel composition greatly influences its stability in contact with air. Unsaturated fatty acids, especially the polyunsaturated ones (e.g. C18:2 and C18:3) have an excessive propensity to oxidation. After oxidation, hydro peroxides (one hydrogen atom and a couple of oxygen atoms) are attached to the fatty acid chain. Oxidation reactions maybe catalysed via a number of the materials present in the storage container, which are light materials. After the chemical oxidation reactions hydro peroxides are produced, this could eventually create quick chain fatty acids, aldehydes, and ketones. Hydro peroxides can polymerize forming massive molecules. Therefore, oxidation increases the viscosity of biodiesel. Furthermore, oxidation increases acid value, the coloration changes from yellow to brown, the engine fuel system can produce solid deposits (pipes and filters), the lubricity and heating value of the biodiesel is decreased. The esters can hydrolyse to long chain free fatty acids in the presence of water,

which additionally makes the acid value to rise (Gerpen, 2005). These acids can catalyse different degradation reactions which include reverse trans-esterification and oxidation. The water needed for hydrolysis may be present as a pollutant (Engelen, 2009). Appendix 5, which is EN 15751: 2014, is the European standard test method for oxidation stability of petroleum products.

2.6 Cetane Number

Cetane number (CN) is a dimensionless index that is a property of the quality of ignition fuels For compression ignition engines (CIE). Considering the fact that in the CIE burning of the fuel-air aggregate is initialized with the aid of compression ignition of the fuel, the cetane number is a key indicator of the quality of fuel since it explains the ease of its self-ignition. Theoretically, the cetane number is described within the range of 15-100; the bounds are given through the two reference fuels used in the experimental computation of the cetane number: a linear-chain hydrocarbon, hexadecane (C16H34, also known as n-cetane), highly sensitive to ignition, having a cetane number of 100, and a strongly branched-chain hydrocarbon, 2,2,4,4,6,8,8-heptamethylnonane (HMN, also referred to as isocetane), having the identical chemical formula C16H34, with excessive resistance to ignition, having a cetane number of 15. The cetane number is defined as the percentage by volume of normal cetane in a mixture of normal cetane and HMN, which has identical ignition properties as the test fuel.

Hence, the cetane number is given by the formula:

CN = n - cetane(%, v/v) + 0.15 * HMN(%, v/v) (2.1)

The cetane number shows ignition delay, i.e. the time lag between the injections of fuel Into the combustion chamber and self-ignition of the fuel-air aggregate. As a consequence, ignition time lag indicates a low cetane number and vice versa. The lower and upper boundaries of the cetane number make certain the right functioning of the engine. If the cetane number is too low, it will be hard to start the engine, particularly at low temperatures and the engine will operate raggedly and loudly, with cycles devoid of combustion, it will warm more slowly, combustion could be incomplete and engine pollution will growth, in particular hydrocarbon emissions. For a fuel with a high cetane number, ignition will be completed before a right mix with air, leading to incomplete combustion and the rise of the quantity of exhaust smoke. In addition, if the cetane number is extremely high the fuel will ignite near the injector making it to overheat, and unburned fuel particles can block the injector nozzles. The desirable range of the CN (Fig. 1) is between 41 and 56, but should not exceed 65 (Băţaga et al., 2003). Figure 2.3 is a graphical representation of brake specific consumption and ignition delay vs fuel cetane number.

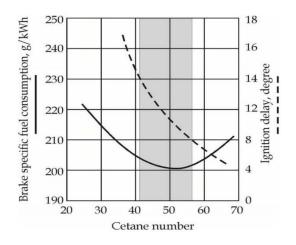


Figure 2.3: Brake specific fuel consumption and ignition delay vs fuel cetane number

The minimum cetane number for biodiesel is 51 in the European Union, 47 within the US and 45 in Brazil. The minimum CN for diesel oil is 40 in the US (ASTM D 975) and 51 in Europe (EN 590). (Bamgboye & Hansen, 2008; Barabás & Todorut, 2010).

2.7 Heat of Combustion

The heat of combustion (heating value) at constant volume of a fuel consisting of only the elements carbon, hydrogen, oxygen, nitrogen, and sulphur is defined as the quantity of heat liberated when a unit quantity of the fuel is burned in oxygen in an enclosure of constant volume, the products of combustion being gaseous carbon dioxide, nitrogen, sulphur dioxide, and water, with the initial and final temperature of the fuel and the oxygen and the products at 25°C. The unit quantity can be mol, kilogram or square meter. Therefore, the units of measurement of the heating value are kJ/kmol, kJ/kg. The volumetric heat of combustion, i.e. the heat of combustion by the density of fuel, can be calculated by means of multiplying the mass heat of combustion by the density of the fuel (mass/volume). The volumetric heat of combustion, rather than the mass heat of combustion is vital to volume-dosed fuelling systems, such as diesel engines. The gross (or high/upper) heating value (Qg) is gotten whilst all

products of the combustion are cooled to the initial temperature at the beginning of the combustion and the water vapour produced in the course of combustion is condensed. The net or lower heating value (Qn) is acquired by subtracting the latent heat of vaporization of the water vapour produced by the combustion from the gross or higher heating value.

The net heat of combustion is associated with the gross heat of combustion:

$$Qn = Qg - 0.2122. H$$
 (2.2)

Where H is the mass percentage of hydrogen in the gas.

In internal combustion engines, the temperature of exhaust gases is greater than the boiling temperature of water (water vapour is discharged), for assessing the heating value of the fuel, the lesser heating value of the biodiesel is of greater relevance. The heating value of fatty acid esters will increase with molecular chain length with the quantity of carbon atoms (NC) and decreases with their degree of unsaturation the variety of double bonds (ND). The mass heating value of unsaturated esters is lower than that of saturated esters, but because of their greater density, the volume heating value of unsaturated esters is greater than that of saturated esters (Barabás & Todoruţ, 2011). ASTM D240-02 is the American standard test method for heat of combustion of petroleum products.

2.8 Lubricity

Lubricity describes the ability of the fuel to lessen the friction between surfaces that are under load. This ability lessens the harm that can be result from friction in fuel pumps and injectors (Schumacher, 2005). Lubricity is an essential factor in the use of low and ultra-low sulphur fuels (ULSD). The lubricity of the fuel may be measured with High Frequency Reciprocating Rig (HFRR) test methods as described at ISO 12156-1. The maximum corrected wear scar diameter (WS 1.4) for diesel fuels is 460 µm (EN 590). Reformulated diesel fuel has a lesser lubricity and needs lubricity boosting additives (which need to be compatible with the fuel and other additives already used in the fuel) to avoid excessive engine wear. The lubricity of biodiesel is great. Biodiesel can be used as a lubricity improver (Barabás & Todoruţ, 2011). ISO 12156-1, EN 590 are respectively the International standard and European standard for lubricity of petroleum products.

2.9 Density

Fuel density (ρ) is the mass of unit volume, computed in a vacuum. Considering the fact, that density is highly impacted by temperature, the quality standards states that density be determined at 15°C. Fuel performance is directly influenced by fuel density, since a number of the engine parameters, including cetane number, heating value and viscosity are strongly related to density. The density of the fuel also influences the quality of atomization and combustion. As diesel engine fuel systems (the pump and the injectors) meter the fuel by means of volume, change of the density influences the fuel mass that reaches the combustion chamber, hence the energy content of the fuel dose, thereby changing the fuel/air ratio and the engine's power. Understanding that density is likewise necessary in the manufacturing, storage, delivery and distribution process of biodiesel since it is a vital factor to be taken into consideration in the planning of those processes. Density over storage time and temperature is generally altered thereby increasing atomization and inhibits lubrication of injection system components. The density of esters relies upon on the molar mass, the free fatty acid content, the water content and the temperature.

The density of biodiesel is generally greater than that of diesel fuel and is determined by fatty acid composition and purity (Barabás & Todoruţ, 2011). Appendix 6, which is ASTM D941-88, is the American standard test method for determining density of petroleum products.

2.10 Viscosity

The viscosity of liquid fuels is their ability to restrict the relative movement tendency of their composing layers because of intermolecular attraction forces (viscosity is the opposite of fluidity). Viscosity is one of the most vital properties of biodiesel. Viscosity affects the ease of starting an engine, the spray quality, the volume of the particles (drops), the penetration of the injected jet and the quality of the fuel-air mixture combustion (Alptekin and Canakci, 2009). Fuel viscosity has both a higher and a lower limit. The fuel with a too low viscosity gives a very free spray, the drops having a low mass and speed. This results in inadequate penetration and the production of black smoke owing to combustion without the presence of oxygen (near the injector) (Bățaga et al., 2003). A too viscous biodiesel results in the production of too huge drops that can infiltrate the opposite wall of the injector. The surface of the cylinder being cold, it will disrupt the combustion reaction and blue smoke will be produced (intermediate combustion product including aldehydes and acids with offensive smell) (Bățaga et al., 2003). Incomplete combustion leads to decreased engine strength.

Excessive viscosity results in the increased formation of deposits in the combustion chamber deposits and the rise of the required fuel pumping energy, as well as the increase in wear and tear of the pump and the injector parts because of higher mechanical effort. Excessive viscosity also leads to functional troubles at low temperatures due to the fact the viscosity increases with reducing temperature .Viscosity over storage time and tear of the fuel system. Viscosity additionally influences the lubricity of the fuel as some parts of the fuel system can simplest be lubricated with the aid of the gasoline (pumps and injectors). Due to the presence of the electronegative oxygen, biodiesel is extra polar than diesel gasoline; as a result, the viscosity of biodiesel is better than that of diesel fuel. The viscosity of pure ethyl esters is higher than viscosity of methyl esters (Dabir et al., 2007). Appendix 7, which is ASTM D445-06, is the American standard test method for determining viscosity of petroleum products.

There are two different forms of viscosity:

a. Absolute or dynamic viscosity

b. Kinematic viscosity

Dynamic viscosity is the tangential force per unit area needed to slide one layer (A) against another other layer (B) as shown in figure 1.1 below whilst the two layers are maintained at a unit distance. In figure 1.1, force F makes layers A and B to slide at velocities v^1 and v^2 , respectively.

Since the viscosity of a fluid is defined as the degree of how resistive the fluid is to flow, it can be described in mathematical form as:

Shear stress = σ (Strain or shear rate)

Where μ is the dynamic viscosity.

Figure 2.4 is a representation of the simple shear of a liquid film.

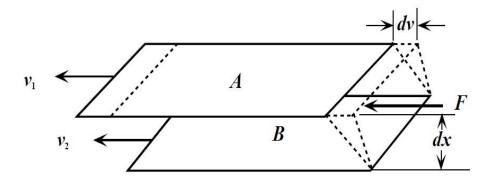


Figure 2.4: Simple shear of a liquid film

If τ is shear stress and *e* is strain rate, then the expression becomes:

$$\tau = \mu e \tag{2.3}$$

The strain rate is generally expressed as

$$e = \frac{1}{x} \frac{dx}{dt} = \frac{V}{x} \tag{2.4}$$

Where *x* is the length, *t* is the time, and dx/dt is the velocity *v*. Therefore, the dynamic viscosity can be written as:

$$\mu = \tau \, \frac{x}{\nu} \tag{2.5}$$

Kinematic viscosity requires knowledge of density of the liquid (ρ) at that temperature and pressure and is defined as:

$$v = \frac{\mu}{\rho} \tag{2.6}$$

2.10.1 Viscosity units and conversion

Common units for viscosity are poise (P), Stokes (St), Saybolt Universal Seconds (SSU) and degree Engler. Centipoise (CP) is the most convenient unit to report absolute viscosity of liquids. It is 1/100 of a Poise. (The viscosity unit Poiseuille, in short Poise was named after French physician, Jean Louis Poiseuille (1799 - 1869).

In the SI System (*Système International d'Unités*) the dynamic viscosity units are $N \cdot s/m^2$, $Pa \cdot s$ or kg/m·s where N is Newton and Pa is Pascal, and, $1 Pa \cdot s = 1 N \cdot s/m^2 = 1 \text{ kg/m} \cdot s$. The dynamic viscosity is often expressed in the metric system of units called CGS (centimeter-gram-second) system as g/cm·s, dyne·s/cm² or poise (P).

Where,

1 poise = dyne \cdot s/cm² = g/cm \cdot s = 1/10 Pa \cdot s

In British system of units, the dynamic viscosity is expressed in lb/ft·s or lbf·s/ft². For the SI system, kinematic viscosity is reported using Stokes (St) or Saybolt Second Universal (SSU) units. The kinematic viscosity is expressed as m2/s or Stokes (St), where 1 St = 10^{-4} m²/s. Stokes is a large unit, and it is usually divided by 100 to give the unit called Centistokes (cSt). 1 St = 100 cSt.

$$1 \text{ cSt} = 10-6 \text{ m}^2/\text{s}$$

The specific gravity of water at 20.2°C (68.4°F) is one, and therefore the kinematic viscosity of water at 20.2°C is 1.0 cSt. Saybolt Universal Seconds (SUS) is defined as the efflux time in Saybolt Universal Seconds (SUS) required for 60 millilitres of a petroleum product to flow through the calibrated orifice of a Saybolt Universal viscometer, under a fixed temperature, as prescribed by test method ASTM D 881. This is also called the SSU number (Seconds Saybolt Universal) or SSF number (Saybolt Seconds Furol). Degree Engler is used in Great Britain for measuring kinematic viscosity. The Engler scale is based on comparing a flow of a fluid being tested to the flow of another fluid, mainly water. Viscosity in Engler degrees is the ratio of the time of flow of 200cm³ of the fluid whose viscosity is being measured to the time of flow of 200cm³ of water at the same temperature (usually 20°C but sometimes 50°C or 100°C) in a standardized Engler viscosity meter (Dabir et al., 2007).

2.10.2 Fluid flow and viscosity

Liquid viscosity values are required by process engineers for quality control, while design engineers use the parameter for setting the optimum conditions for the chemical reactions and operations. Liquid viscosity is also critical in determining of the power needed for the unit operations including mixing, pipeline design, pump characteristics, atomization (liquid droplets), storage, injection, and delivery.

The flow properties of liquids are usually determined by the viscosity and are generally divided into three classes:

- a) Newtonian
- b) Time independent Non-Newtonian
- c) Time dependent Non-Newtonian

When the viscosity of a liquid stays consistent and is unaffected by the applied shear stress, this sort of liquid is called a Newtonian liquid. In the case of the non-Newtonian liquids, viscosity is determined by the applied shear force and time. For time independent nonNewtonian fluid, when the shear rate is altered, the shear stress does not change proportionally (Dabir et al., 2007).

2.10.3 Viscometers

Measuring of viscosity is very crucial in so many aspects of life. A good knowledge of viscosity is vital for several industrial systems. Diverse theories which are developed for prediction or computation of viscosity need to be proved by the use of experimental data. There are several extensive classifications for instruments used in the measurement of viscosity: There are some viscometers that combine characteristics of two or three types of viscometers stated above, for example, Friction tube, Norcross, Brookfield, Viscosity sensitive rotameter, and continuous consistency viscometers. Some devices also are automated for process control and for uninterrupted measurement of viscosity. Several instruments named after pioneers within the field as well manufactured with the aid of popular instrument producers are available for each of the categories (Dabir et al., 2007).

2.10.4 Capillary viscometers

Capillary viscometers amongst other types of viscometers are most extensively used for measuring viscosity of Newtonian liquids. They are easy to operate; require a little quantity of sample liquid, control of temperature is simple, and inexpensive. In capillary viscometers, the volumetric rate of flow of the liquid flowing through a fine bore (capillary) is measured, commonly by way of noting the time needed for a specific volume of liquid to flow through two graduation marks. The liquid may pass through the capillary tube either via the impact of gravity (Gravity type Viscometer) or an external force. Inside the equipment where an extraneous force is applied, the liquid is driven through the capillary at a predetermined rate and the drop in pressure across the capillary is measured. Capillary viscometers can give direct computation of viscosity from the flow rate, pressure and various dimensions of the devices. Nevertheless, maximum of the capillary viscometers ought to be first calibrated with one or extra liquids of recognized viscosity to reap "constants" for that specific viscometer (Dabir et al., 2007).

The vital components of a capillary viscometer are

1. A liquid reservoir,

- 2. A capillary of acknowledged dimensions,
- 3. A provision for measuring and controlling the implemented stress,
- 4. A means of measuring the glide charge, and

5. A thermostat to hold the desired temperature.

Several styles of capillary viscometers have been made through version of above elements (Dabir et al., 2007). Commercially produced capillary viscometers may be categorized into three groups depending on their design:

- 1. Modified Ostwald viscometers,
- 2. Suspended-level viscometers
- 3. Reverse-flow viscometers.

2.11 Total Acidic Number

The total acidic number or the total acidic value is that quantity which is used to determine how acidic a substance could be. The substance can be bio-diesel or euro-diesel or blends of both as the case may be. Acidic number can be further explained as the amount of potassium hydroxide measured in milligrams needed to neutralize the acidic concentration in 1 gram of a sample.

CHAPTER 3 MATERIALS, METHODS AND EXPERIMENTAL SET-UP

3.1 Bio-Diesel and Euro-Diesel

The euro-diesel used as samples in this report is that which already certified every quality control and issued certificate of quality from oil refineries limited dated July 6 2017. The sample was taken from stock tank No 453/510 before loaded at the Haifa oil docks (Table 3.2). Furthermore, the euro-diesel used in this report as sample is referred to as the euro-diesel summer between the period from 1st April to 30th September and lastly no FAME is added. The bio-diesel used as sample in this report is FAME based and the most common way that thus is produced is the transesterification process. Transesterification process in general overview is a chemical reaction between triglyceride (vegetables and animal fats) and alcohol (methanol or ethanol) in the presence of alkaline catalyst (NaOH, KOH) to produce fatty acid methyl esters. Table 3.1 and 3.2 respectively includes the standards for FAME biodiesel and euro diesel.

NAME	METHOD	UNIT	SPE	CS	RESULT	
			Min	Max		
FAME content	EN 14103	mass %	96.5		>99.5	
Density at 15°C	ISO 12185	kg/m³	860.0	900.0	876.4	
Kinematic	EN ISO 3104	mm²/s	3.500	5.000	4.483	
Viscosity at						
40°C						
Flash point	ISO 3679	°C	101		>140	
(rapid						
equilibrium)						
Cetane Number	EN 15195		51.0		59.7	
Copper	EN ISO 2160			Class 1	1A	
Corrosion						
(3hrs/ 50°C)						
Oxidation	EN 14112	hours	8.0		>11	
stability						
(110°C)						
Acid number	EN 14104	mg KOH/g		0.50	0.31	
Iodine value	EN14111	gl2/100g		120	74	
Linolenic acid	EN 14103	mass%		12.0	2.6	
methyl ester						
Polyunsaturated	EN 15779	mass%		1.0	< 0.10	
methyl esters						
(>=4 double						
bounds)						
Methanol	EN 14110	mass%		0.20	0.02	
Glyceride	EN 14105					
content						
Mono-glyceride		mass%		0.70	0.21	
Di-glyceride		mass%		0.20	0.02	
Tri-glyceride		mass%		0.20	< 0.03	
Free glycerol		mass%		0.02	< 0.010	
Total glycerol		mass%		0.25	0.065	
Water Karl	EN ISO	mg/kg		300	160	
Fischer	12937					
Contamination	EN 12662 98	mg/kg		24	<6	
Sulphated ash	ISO 3987	mass%		0.02	< 0.005	
Sulphur (S)	EN ISO	mg/kg		10.0	9.8	
	20846					
Group i metals	EN 14538	mg/kg		5.0	<2.0	
(Na+K)						
Group ii metals	EN 14538	mg/kg		5.0	<2.0	
(Ca+Mg)						
Phosphorus	EN 14107	mg/kg		4.0	<4	
content						

 Table 3.1: Standards for FAME Biodiesel

Table 3.1: Continued

Cold filter plugging point	EN116	°C	+5	+5
Melting point of organic chemicals	ISO 6321	°C		+10
Kinematic viscosity at 20°C	ASTM D445	mm²/s		7.2

PROPERTIES	UNITS	LIMITS		RESULTS	METHOD
		LOW	HIGH		
DENSITY 15°C	KG/M ³	820.0	845.0	827.8	ASTM D 4052
CETANE NUMBER		51.5		55.0	ASTM D 613
CETANE INDEX		47.0		54.8	ASTM D 4737
KINEMATIC VISCOSITY 40°C	CST	2.0	4.5	2.8	ASTM D 445
COLD FILTER PLUGGING PONT, CFPP	DEG C		5	-6	IP 309
SULPHUR CONTENT	MG/KG		10.0	5.3	ASTM D 5453
COPPER STRIP CORROSION, 3 HRS 50°C	NO.		1	1	ASTM D 130
OXIDATION STABILITY	MG/L		25	3	ASTM D 2274
CARBON RESIDUE (ON 10 PCT RESIDUE)	WT PCT		0.30	0.01	ASTM D 4530
WATER CONTENT	MG/KG		200	39	ASTM D 6304
TOTAL CONTAMINATION	MG/KG		24	2	IP 440
ASH CONTENT	WT PCT		0.010	0.000	ASTM D 482
STRONG ACID NO.		NIL		NIL	ASTM D 974
TOTAL ACID NO.	MG KOH/GR		0.2	0.1	ASTM D 664
FLASH POINT	DEG C	55		67	ASTM D 93
RECOVERED 250°C	VOL PCT		65	40	ASTM D 86
RECOVERED AT 350 DEG C	VOL PCT	85		92	ASTM D 86
95%RECOVERED	°C		360	360	ASTM D 86
LUBRICITY, WSD 1.4, 60°C	UM		440	385	ISO 12156/1
POLYCYCLIC AROMATIC HYDROCARBONS	WT PCT		11	2	IP 391
DENSITY IN AIR	KG/M ³			826.7	CALC
COLOUR (ASTM)	SCALE		1.0	0.5	ASTM D 1500
APPEARANCE		& Bright		Clear & Bright	ASTM D 4176

Table 3.2: Standards for Euro Diesel

3.2 Measurement of Kinematic Viscosity

Measurement of viscosity is a very crucial part of this work because it allows to actually help with understanding how this blend will react over a long period. It is to be known that kinematic viscosity directly relates with temperature, which is dependents on storage time. The measurement of viscosity is with an equipment known as viscometer and they are of various types. In cases where the fluid cannot be well defined, then rheometers are used for measurement of viscosity.

3.2.1 Ubbelohde viscometer

The ubbelohde viscometer is a device, which was invented by a German chemist Leo ubbelohde. It is a measuring instrument, which uses a capillary-based method of measuring viscosity. The main advantage of this device is that the values obtained are independent of the total volume and it is highly recommended for higher viscosity cellulose polymer solution. It possesses the same viscometer constant for all temperatures; it exhibits great speed and proper accuracy. Low quantity of sample is needed during experiment and low susceptibility to errors and cost effectiveness. Figure 3.1 below shows same details about the ubbelohde.

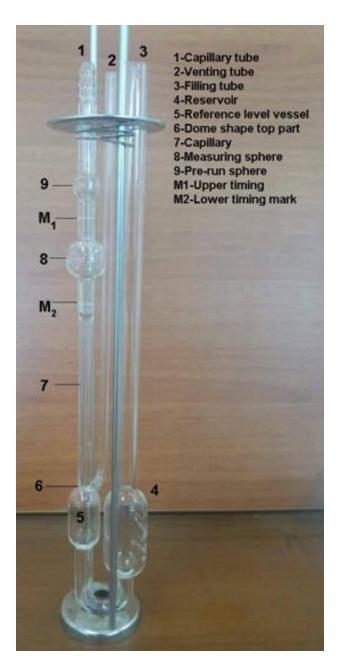


Figure 3.1: Ubbelohde viscometer

The viscosity basically consist of the capillary tube(1) venting tube (2) filling tube (3) reservoir (4) reference level vessel (5) dome-shaped top part (6) capillary (7) measuring sphere(8) prerun sphere (9) M_1 upper timing mark and M_2 timing mark.

Samples are been introduced into reservoir (4) through the filling tube (3) the viscometer at the bare must be filled completely and free to bubbles and forms of particulate. Most importantly, the desired temperature must be obtained before the measurement is carried out, and after this,

a finger is placed over venting tube (2) the sucked through the capillary tube (1). Afterwards, the suction is disconnected from capillary tube (1) and the finger removed from venting tube (2). The liquid is allowed to travel back through the measuring bulb and the time it takes to travel between M_1 (upper timing mark) and M_2 (lower timing mark) is recorded which is the measurement of viscosity. The produce just explained above is also the same way to determine the measurement of the flow time of the ubbelohde viscometer not forgetting the use of stopwatch as an important accessory. The stopwatch must be timed properly to improve the accuracy not minding cloudy situations. In addition, there must be proper and correct detection of the meniscus passage.

The ubbelohde viscometer is been recommended for use than other forms of viscometer because of the series of advantages such as speed, acceptable level accuracy, ability to possess the same constant temperature all through the experimental exercise by been effective to determine translucent Newtonian liquids in the ranges 0.3 to about 100,000cSt (mm^2/s) . Lastly, this equipment is not very expensive and required just little amount of sample. The little disadvantages of ubbelohde viscometer are the prospect of clogging and that little changes in the temperature of cooling bath or the glass beaker will make the result of the ubbelohde viscometer not accurate. Table 3.3, 3.4 and 3.5 respectively includes the types of ubbelohde viscometer and the ubbelohde technical specification. The choice of using the ubbelohde viscometer is because of how versatile it is in its applications and it enables transparent and high temperature measurement. For the purpose of this work and the measurement, range involved enables us to be able use three kinds of viscometer, which are Ic, Oc and I. The subsequent tables below shows the kinematic energy correction for ubbelohde viscometer and the technical specification for ubbelohde viscometer and the technical specification for ubbelohde viscometer and the technical specification for ubbelohde viscometer.

Size no:	Approximate	Kinematic	Inside	Volume,	Inside Diameter
	Constant,	Viscosity	Diameter of	Bulb	of Tube P,ml
	(mm²/s)/s	Range (mm ² /s)	Tube, R, mm	C,ml	(± 5%)
			(±2%)	(±5%)	
0	0.001	0.3 ^A to 1	0.24	1.0	6.0
Oc	0.003	0.6 to 3	0.36	2.0	6.0
Ob	0.005	1 to 5	0.46	3.0	6.0
Ι	0.01	2 to 10	0.58	4.0	6.0
Ic	0.03	6 to 30	0.78	4.0	6.0
Ib	0.05	10 to 50	0.88	4.0	6.0
2	0.1	20 to 100	1.03	4.0	60
2c	0.3	60 to 300	1.36	4.0	6.0
2b	0.5	100 to 500	1.55	4.0	6.0
3	1.0	200 to 1000	1.83	4.0	6.0
3c	3.0	600 to 3000	2.43	4.0	6.0
3b	5.0	1000 to 5000	2.75	4.0	6.5
4	10	2000 to 10,000	3.27	4.0	7.0
4c	30	6000 to 30,000	4.32	4.0	8.0
4b	50	10,000to50,000	5.20	5.0	8.5
5	100	20,000to100,000	6.25	5.0	10.0

Table 3.3: Types of Ubbelohde Viscometers for Transparent Fluids

^A300-s least flow time; 200-s least flow time for all other units

Flow	Capillary no								
time	0	0c	0a	I	Ic	Ia	1		
40	_B	B	B	1.03	0.45	0.15			
50	B	B	B	3.96	0.66	0.29	0.10		
60	_B	B	B	2.75	0.46	0.20	0.07		
70	_ ^B	B	B	2.02	0.34	0.15	0.05		
80	_ ^B	B	4.78 ^B	1.55	0.26	0.11	0.04		
90	_B	_B	3.78 ^B	1.22	0.20	0.09	0.03		
100	_B	7.07 ^B	3.06 ^B	0.99	0.17	0.07	0.02		
110	_B	5.84 ^B	2.53	0.82	0.14	0.06	0.02		
120	_B	4.91 ^B	2.13	0.69	0.12	0.05	0.02		
130	_B	4.18 ^B	1.81	0.59	0.10	0.04	0.01		
140	_B	3.61 ^B	1.56	0.51	0.08	0.04	0.01		
150	_B	3.14 ^B	1.36	0.44	0.07	0.03	0.01		
160	_B	2.76	1.20	0.39	0.06	0.03	0.01		
170	_B	2.45	1.06	0.34	0.06	0.02	0.01		
180	_B	2.18	0.94	0.30	0.05	0.02	0.01		
190	_B	1.96	0.85	0.28	0.05	0.02	0.01		
200	10.33 ^B	1.77	0.77	0.25	0.04	0.02	0.01		
225	8.20	1.40	0.60	0.20	0.03	0.01	0.01		
250	6.64	1.13	0.49	0.16	0.03	0.01	< 0.01		
275	5.47	0.93	0.40	0.13	0.02	0.01	< 0.01		
300	4.61	0.79	0.34	0.11	0.02	0.01	< 0.01		

Table 3.4: Kinematic Energy Correction Ubbelohde Viscometer ISO 3105/DIN51562/Part1/BS188/NFT 60-100 Ref.No.501...530...532. Correction seconds A

325	3.90	0.66	0.29	0.09	0.02	0.01
350	3.39	0.58	0.25	0.08	0.01	0.01
375	2.95	0.50	0.22	0.07	0.01	0.01
400	2.59	0.44	0.19	0.06	0.01	< 0.01
425	2.30	0.66	0.29	0.09	0.01	< 0.01
450	2.05	0.58	0.25	0.08	0.01	< 0.01
475	1.84	0.50	0.22	0.07	0.01	
500	1.66	0.44	0.19	0.06	0.01	
550	1.37	0.23	0.1	0.03	0.01	
600	1.15	0.20	0.09	0.03	0.01	
650	0.98	0.17	0.07	0.03	< 0.01	
700	0.85	0.14	0.06	0.02	< 0.01	
750	0.74	0.13	0.05	0.02	< 0.01	
800	0.65	0.11	0.05	0.01		
850	0.57	0.10	0.04	0.01		
900	0.51	0.09	0.04	0.01		
950	0.46	0.08	0.03	0.01		
1000	0.42	0.07	0.03	0.01		

 Table 3.4: Continued

^A from the above the correction stated are related to the respective theoretical constant.

^B for a more accurate measurement, the flow time should not be applied. The selection of a smaller sized viscometer of capillary diameter.

Type No	Capillary No	Capillary	Constant K	Measuring
		Dia I±	(mm²/s)s	Range (mm ² /s)
		0.01(mm)		
52503	Oc	0.36	0.002856	0.6-3
52510	Ι	0.58	0.009820	2-10
52513	Ic	0.36	0.02944	6-30
52520	II	0.58	0.08947	20-100
52523	IIc		0.2821	60-300

Table 3.5: Ubbelohde Technical Specification

For example

Determining the kinematic viscosity of (5% BD+ 95%ED) at 40°C

Capillary I constant (K) = $0.009820 \text{ (mm^2/s) s}$

Flow time (average time) (t) = 312.3333s

Kinetic energy correction (HC) y for 312.3333 = 0.09

$$V = k (t-y) \tag{3.1}$$

V= 0.009820 (312.3333-0.09) = 3.0662mm²/s

3.3 Cooling Bath System

Figure 3.2 shows the set up used in determining the kinematic viscosity and density 20°C to a lower temperature of -11°C.

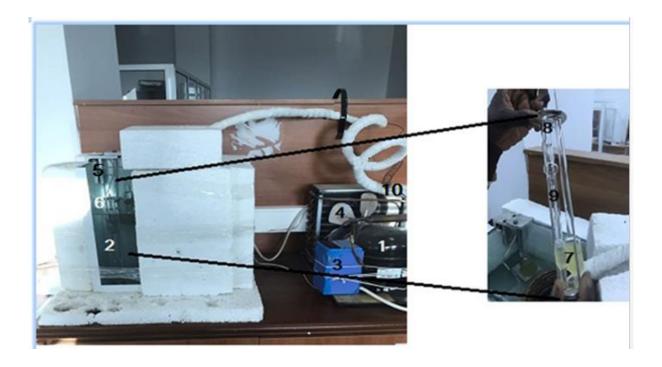


Figure 3.2: Cooling bath system

- 1. Compressor
- 2. Cooling bath glass
- 3. Thermostat
- 4. Radiator
- 5. Holder
- 6. Alcohol as a cooling bath
- 7. Samples
- 8. Capillary holder
- 9. Ubbelohde capillary viscometer
- 10. Coil

The bio-diesel samples (7) is poured into ubbelohde capillary viscometer (9) which is held by the capillary holder (8) in an upright position and immersed into the cooling bath where alcohol is used as the liquid in the cooling bath because of the ability not freeze up until -114 degree Celsius. This is a coil (10) directly connected to the compressor (1) which cools down the liquid bath and the compressor is cooled down by the radiator (4). A thermostat (3) which automatically turns on and off the compressor controls the cooling bath temperature. It is needed for the cooling bath to be thermally isolated by thick layers of foam to maintain the inside temperature of the cooling bath while there is also need to insulate the outer glass of the cooling bath with fibre materials to prevent heat gain from the environment at low temperature.

3.3.1 Alcohol

It is known fact that the freezing point of alcohol cuts across the different kinds of alcohol blends and atmospheric pressure. In general, if there are particulates of water in the alcohol, then the freezing point will be higher. Therefore, while pure alcohol will freeze at -114°C, water will freeze at 0°C and thus, alcohol is been used in the cooling bath, which is purchased from local shops here in northern Cyprus.

3.3.2 Temperature regulation

There is a greater need to have a constant or homogenous temperature all through the alcohol in the cooling bath and all through the water used in the glass beaker and that is why there is an equipment called the thermostat attached to the cooling bath to maintain a desired temperature in the cold bath. Cooling in the cold bath is achieved by sensing and removing warm air and not by adding cool air. The thermostat usually have a knob or button that allows users to adjust the temperature setting. Once a user sets the desired temperature, the thermostat maintains that temperature by controlling the flow of electricity to the compressor. If the thermostat is the brain of the cooling system then the compressor is the heart of the cooling system. In the case of the glass beaker, the water used is mixed manually to maintain a homogenous temperature all through the water used. Figure 3.3 and 3.4 respectively shows the thermometer and thermostat used to control the temperature during experiments.



Figure 3.3: Thermometer used in the glass beaker for measurements at high temperatures



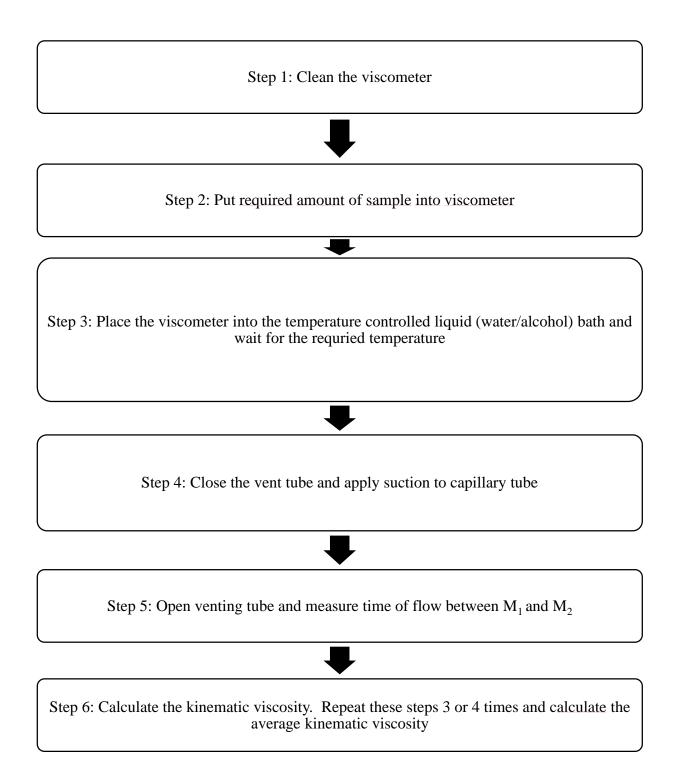
Figure 3.4: Thermostat attached to the cooling bath for measurements at low temperatures.

3.3.3 Accessories

For proper, accurate and effective readings, additional accessories are been used and this include:

- 1. Fibre insulator- This placed around the cold bath to prevent heat gain from the environment at relatively low temperature.
- 2. Beaker insulator- This is used to prevent heat loss to the environment at relatively high temperature.
- 3. Glass pipette- This is used for transporting the required amount of bio-diesel sample into the viscometer.
- 4. Syringe This is used for suction purposes.
- 5. Stop watch- This used for measurement of time
- 6. Viscometer holder- This was used in holding the ubbelohde viscometer in an upright position.

3.3.4 Flow chart on kinematic viscosity



3.4 Measurement of Density using Pycnometer

The word pycnometer or pycnometer is from a Greek word puknos, which means density. The pycnometer also known as a specific gravity bottle that is glass flask fitted with a glass stopper and a fine hole through it. It is a device, which enables the density of fluid to be measured accurately. The system with which this works is that the there is an initial measurement of the weight of the glass bulb and then the glass bulb is then weighed again after it is filled with the intended sample. The net difference between them is calculated followed by division with its specific gravity and finally, the accurate density is achieved.

3.4.1 Standards using the pycnometer

The pycnometer is a fragile equipment so must be handled with care. It is delicate and expensive; precaution should be taken such as.

- 1. Been very careful not to inter-switch either the bulb or the stopper of the pycnometer with another person because both the bulb and stopper are engraved with the same number.
- 2. Before the first weighing, the pycnometer must be clean and dry.
- 3. Always use a pipet to fill samples into the bulb until halfway up the neck and then slowly insert the capillary stopper.
- 4. When the glass bulb is full, there will off course not be any air bubbles in the bulb or capillary of the device and no space for air at the top either.
- 5. Finally, before weighing the full pycnometer, the outside should be perfectly dry.
- 6. Make sure the required temperature is maintained.
- 7. Make sure the electronic balances is set to 0.00 before placing the full pycnometer.

3.5 Electromagnetic Hot Plates

The hiedolph mr hei-tec electromagnetic heater is a device such that the top is made of aluminium, which makes heating faster, and this device is actually needed when supposed to determine the kinematic viscosity and density at elevated high temperatures 30°C to 90°C. Water is used as the liquid in the glass beaker for this temperature range but when the range increases more than this, silicon oil will be used. Figure 3.5 is a diagrammatic representation of the electromagnetic hot plate used in this work.



Figure 3.5: Heidolph mr hei-tec

3.6 Methodology

3.6.1 Procedure i (kinematic viscosity)

The following explains the procedure in determining the kinematic viscosity of the blend sample used in the work.

- Before use, first clean the IC viscometer with cleaning materials, which includes 70% of pure water, 15% of hydrogen peroxide and 15% of tuz ruhu. Afterwards, you then rinse again with acetone and it must be completely dry and free of dust or any particulate before starting the experiment.
- 2. If there are still possible particles in the viscometer, make sure you remove with suction syringe.
- 3. There is need to charge the viscometer by introducing samples of the blends into the lower reservoir and make sure it is enough up until the upper making line in the lower u-tube.
- 4. Place the viscometer into the viscometer holder and insert vertically into the cooling bath or glass beaker, which is maintained at a desired temperature.
- 5. Allow an ample-time for the sample to be at a homogenous temperature for both the cooling bath and glass beaker.
- 6. The venting tube is closed and suction is now carried out until the blends fills the bigger and smaller bulb and passes the upper timing mark and then suction is discontinued, while the venting tube is opened.

- The efflux time t which is the interval for the blend to descend from timing mark M₁, to the upper edge of the lower timing mark M₂ is the measured.
- 8. The kinematic viscosity of the sample is derived by multiplying the efflux time t by the calculating "v" using formula in equation....
- 9. There is need to repeat steps 6 to 8 about 3 or 4 times without recharging the viscometer to ascertain maximum accuracy.
- 10. The viscometer used in this experimental set up is Ic for measuring range from 6-30, I for measuring range from 2-10, and Oc for measuring range 0.6-3.
- 11. Clean back, all equipment used and make sure they are appropriately stored in a good place.

3.6.2 Procedure ii (density)

Step 1: This is the start of the experiment and this is when the weight of the pycnometer is first checked. At this stage, I made sure that the pycnometer is dry and free of any particulate. I also ensured that the electronic balance is set in a position free from vibration and every other thing that may cause in balances in the measurement before checking the weight of the empty pycnometer. At this stage is also when you clean the pycnometer with the cleaning materials, followed by acetone, and make sure it is dry before introducing samples into it.

Step 2: This is the stage at which the sample is introduced into the pycnometer until the throat level. At this stage, I made sure that the pycnometer is filled up leaving no space for air bubbles. There is a glass stopper attached to this pycnometer, which helps to remove excess samples from the pycnometer. At every intervals always check the pycnometer to be sure that the samples does not reduce below the throat level as any slight changes in this will directly change the density measurement.

Step 3: I made sure that that the electronic balance device is working perfectly and I know this by its ability not to deviate from its default reading of 0.000 by any minimum surrounding factors at this stage.

Step 4: This is the stage at which the already filled up pycnometer with sample is placed in the cold bath containing alcohol or in the glass beaker containing water. The most important factor to be considered at this stage is that, when the temperature gets lower there is every tendency that the molecules of the samples in the pycnometer binds or clot together and as such reduce the content level below the throat level and so when this happens you need to refill and make

sure that it gets back to the required level. Another important factor at this level is that I made sure I have homogenous temperature before taking my measurement and this is explained in 3.1.3.

Step 5: After been assured that there is homogenous temperature all through the experimental set up and that the sample is at the required throat level and lastly the electronic device is working properly, then the measurement can be carried out. What to take note of at this stage is that the electronic balance must not be far from where the pycnometer because this is highly temperature dependant and also make sure you wipe excess liquid content outside of the pycnometer before placing it on the electronic balance.

Step 6: This is the last stage of the measurement after the measurement has been recorded. At this stage is when you make sure that the pycnometer and electronic balance are kept safe.







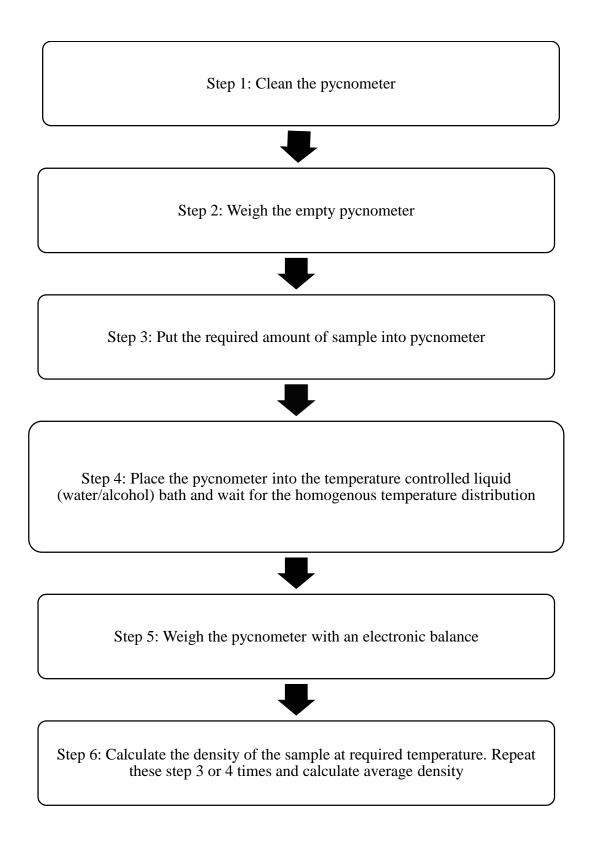






Figure 3.6: Diagrammatic representation of measuring density-using pycnometer

3.6.3 Flow chart on density



For example:

Determine the density of 5%BD + 95%ED at 15° C

Temperature = 15° C $M_E = 42.763g$ $M_F = 125.782g$ $M_N = M_F - M_E$ $M_N = (125.782 - 42.763) g = 83.019g$ $\rho = M_N / V_P$ $\rho = 83.019/99.693 = 0.8327g/1$ $\rho = 0.8327 x 1000 = 832.7465 kg/m^3$

3.6.4 Procedure iii (pour Point and cloud Point, cfpp)

Figure 3.7 and 3.8 explains the procedures involved in determining the cloud point and the pour point.

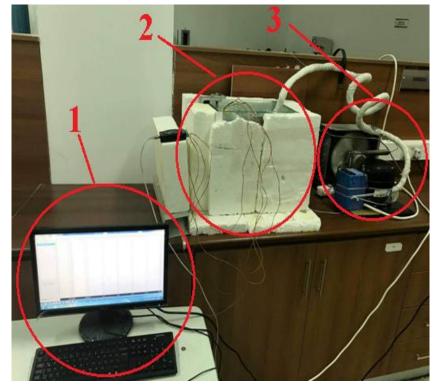


Figure 3.7: Cloud point and pour point measurement apparatus

From figure 3.7, point1 indicates the data system while point 2 indicates the cooling bath and point 3 indicates the compressor system.

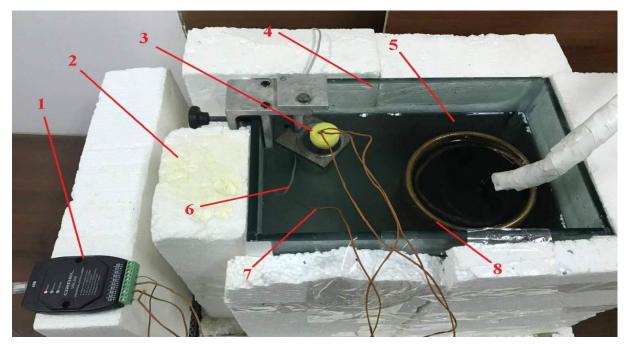


Figure 3.8: Data logger and thermocouples

From figure 3.8, we have various points, which are listed and explained below

- Data logger- This is a device, which is connected to a computer where the outputs can be read and connected to the glass jar with thermocouples. The various thermocouples connected to the device are for determining temperature inside the cooling bath, also for determining the cloud point, which is placed on the down part of the glass test jar and for determining the pour point, which is placed on the top part inside the glass jar.
- 2. A block of Insulator (Styrofoam): This is used to maintain a steady temperature range.
- 3. Glass test jar: 45ml of the test sample was discharge into the glass jar. Three thermocouples are been placed in the glass jar as shown in figure 3.9. The lower thermocouple is for measuring the cloud point while the upper thermocouple is for measuring the pour point. The thermocouple in between is for determining the cooling curve.
- 4. Cooling bath: This is an apparatus used in maintaining low temperature; it is secluded by a thick layer of Styrofoam block of 11cm inside a wooden box.
- 5. Alcohol: This is used because of its ability to freeze at a very low temperature of -114°C.

- 6. Thermocouple of compressor system: It sends temperature signal to the compressor.
- 7. Fourth thermocouple of data logger: Determines the readings of the entire system and displays on the software already installed on the computer.
- 8. Coil of compressor system: Enhances the cooling rate.

The set-up consists of a glass test jar, which was placed into an aluminium cylinder inside the cooling liquid bath (in this case, alcohol was used as the cooling liquid). The glass test jar was isolated from the aluminium cylinder by means of a cork stopper and ring assembly. The cylinder has been engrossed into an 8-liter stainless steel cooling bath-containing alcohol at a low temperature and sample already heated to 65°C before introduced into the glass jar. The cooling bath was placed inside an 11cm thick of Styrofoam block in order to isolate it from any vibrations and heat transfer to keep the cooling bath at low temperature for a long period and for the cooling curve to be achieved. This same sample was also used for determining the kinematic viscosity checked with ASTM D445-06

A new sample was used for assessing the cloud point and pour point. The samples were tested as per American standard test method for cloud point and pour point, ASTM D2500 and ASTM D97 respectively.

After preparing the apparatus and cooling down the liquid bath, the cloud point test consist of the cooling of the sample in the glass test jar under prescribed conditions and inspected at stepwise of 1°C until a cloud (fog) appeared on the sample, then the degree was recorded as cloud point for that sample when the reading was taken from that thermocouple which was placed on the down part of the test jar because temperature at the down part of the jar is normally higher than the upper part.

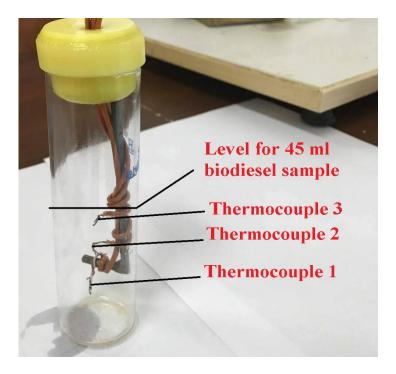
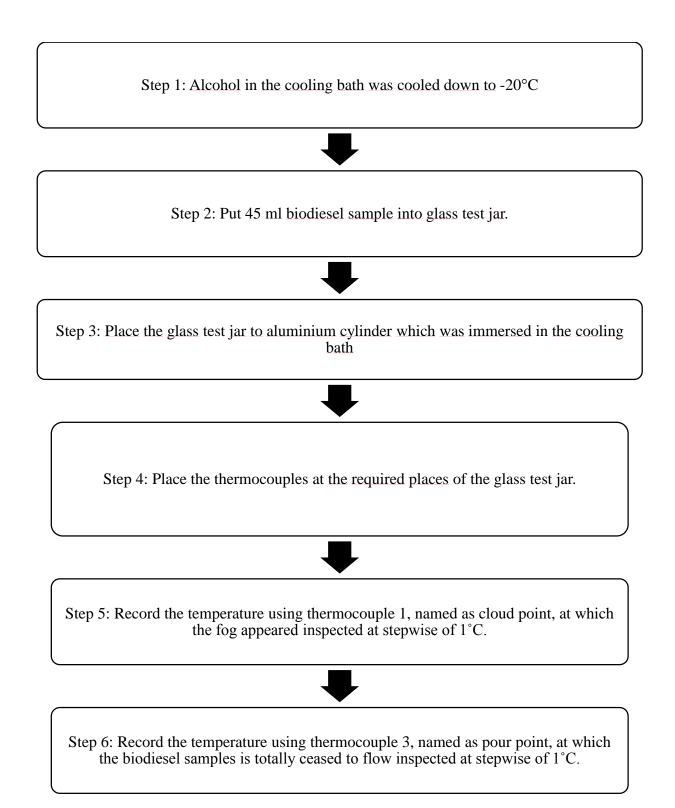


Figure 3.9: Glass jar and thermocouples

For determining the pour point, the observation of the samples starts at a temperature that is at least above the expected pour point. The same sample was immersed in an extremely low temperature cooling bath and inspected at stepwise of 1°C until the sample totally ceased to flow. Reading of the test thermometer was taken and the degree before this reading was recorded as pour point but the reading was taken from that thermocouple which was placed at the top layer of the sample. All the measurements were done three times for each sample and the results averaged (The standard deviation of the test results is $\pm 2^{\circ}$ C).

3.6.5 Flow chart for measuring cloud point and pour point



3.6.6 Procedure IV (blend temperature stability and storage)

A blend of 5% BD + 95% ED is stored at a constant temperature over a long period in order to be able to measure and calculate both the kinematic viscosity, density and cold flow properties. This is achieved by storing the bio-diesel and euro-diesel blends in an oven that it is regulated to 40° C by a thermostat, which opens and closes the lamps fitted to the oven. The thermostat is the part of the oven that is charged with regulating the oven temperature. The thermostat monitors the interior temperature of the oven, turning on and shutting off the heat source according to the temperature setting. The top of the thermostat extends up behind the knob that is used to set the oven temperature. The thermostat is connected to a long hollow copper tube that extends into the body of the oven. The tube senses the temperature of the oven by heating up and relaying the heat back to the thermostat. When the thermostat is informed that the oven has reached the desired temperature setting, it shut off the heat source. When the temperature in the oven cools, the thermostat triggers the heat source allowing the oven to re-heat.

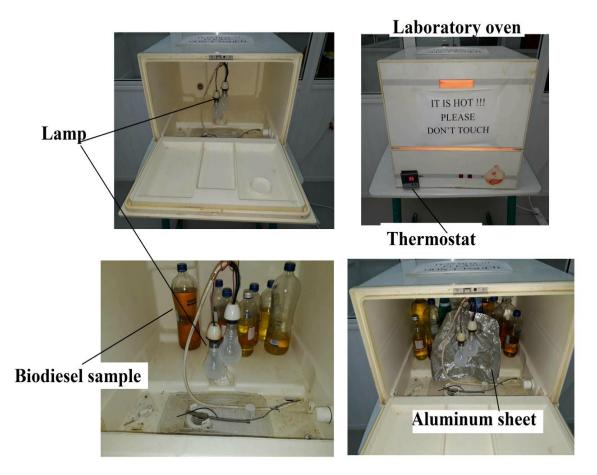


Figure 3.10: Bio-diesel and euro-diesel blends in an oven

CHAPTER 4 RESULT AND DISCUSSION

Viscosity is simply one of the important factors when determining how liquids and fluids will behave. It is a proved analysis that viscosity is also the factor, which determines the measurement of fluids or liquid resistance to flow. By virtue of this, kinematic viscosity is highly dependent on the reference temperature and that is why for every liquid; kinematic viscosity decreases with increase in temperature and kinematic viscosity increases with decrease in temperature.

Relatively, density which is also another factor which is used to determine how efficient blends of bio-diesel and euro- diesel is also time dependent and that is why lots of measurement were carried out to determine the relationship between kinematic viscosity at constant temperature of 40°C over a storage period of 90 days and also kinematic viscosity for 12 weeks over testing temperature ranging from -11°C to 90°C and likewise the relationship between density at constant temperature of 15°C over a storage period of 90 days and density for 12 weeks over testing temperature also ranging from -11°C to 90°C when 5% of bio-diesel is mixed with 95% of euro-diesel.

The essence of this is simply to predict experimentally at what rate this blends will degenerate which will help to know how long this blends should be efficient to use and at what temperature should not be reliable to use.

At the end we should be able to establish that the experimental values achieved correlates with standard test methods which will also prove that the experiments were carried out with much accuracy and also that the instruments used are properly calibrated.

4.1 Kinematic Viscosity over a Storage Period of 90 days at Temperature 40°C

Table 4.1 below contains the experimentally result obtained for kinematic viscosity in a blend of 5% BD + 95% ED when measured at a temperature of 40°C over a storage time of 90 days.

Table 4.1: Kinematic Viscosity (mm²/s) for Storage Period 90days at 40°c

Days	0	10	20	30	40	50	60	70	80	90
B5	3.080	3.105	3.129	3.200	3.226	3.251	3.319	3.325	3.332	3.448

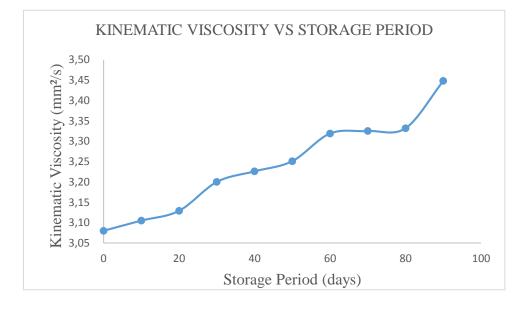


Figure 4.1: Kinematic viscosity (mm²/s) for storage period 90 days at 40°C

From figure 4.1, kinematic viscosity increased over the storage time because total acidic number in fuel increases which is also known as oxidation, which increased the impurities in the fuel system such as polymer and fatty acid chains.

4.2 Kinematic Viscosity over Testing Temperatures

Table 4.2 below contains the experimentally result for kinematic viscosity in a blend of 5% BD + 95% ED for testing temperatures from -11°C to 90°C at weekly intervals.

		Weeks							
T(°C)	0 weeks	4 weeks	8 weeks	12 weeks					
-11	21.888	23.737							
-10	18.471	18.473	19.155	19.316					
-8	14.374	14.376	14.907	15.032					
-7	12.291	12.292	12.746	12.853					
-5	10.613	10.820	11.220	11.315					
-3	9.244	9.525	9.877	10.245					
0	8.493	8.385	8.695	8.920					
2	7.801	7.787	8.075	8.203					
5	7.374	7.692	7.976	7.965					
8	6.785	6.771	7.021	7.011					
10	6.402	6.389	6.625	6.616					
15	5.386	5.375	5.573	5.566					
20	4.929	4.919	5.101	5.094					
30	3.721	3.713	3.851	3.845					
40	3.080	3.200	3.319	3.448					
50	2.853	2.965	3.074	3.070					
60	2.744	2.851	2.956	2.952					
70	2.688	2.793	2.897	2.893					
80	2.606	2.708	2.808	2.804					
90	2.543	2.642	2.740	2.736					

 Table 4.2: Kinematic Viscosity (mm²/s) for 12 weeks over Testing Temperatures °C

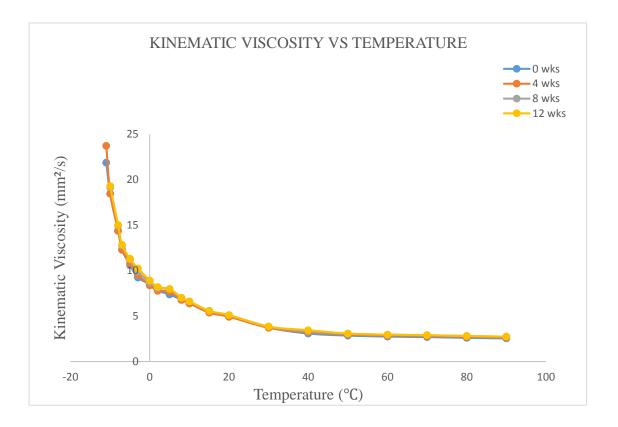


Figure 4.2: Kinematic viscosity (mm²/s) for 12 weeks over testing temperatures °C

From figure 4.2, kinematic viscosity decreases with the increase in temperature because Cohesive forces between the molecules of fuel losses its power with temperature rise.

4.3 Density over a Storage Period of 90 days at Temperature 15°C

Table 4.3 below contains the experimentally result obtained for density in a blend of 5%BD+95%ED when measured at a temperature of 15°C over a storage time of 90 days.

Table 4.3: Density (kg/m³) for Storage Period of 90 days at 15°C

Days	0	10	20	30	40	50	60	70	80	90
B5+D	828.7	829.9	831.1	832.3	833.6	834.8	836.0	837.2	838.5	839.6
95	09	52	97	97	45	96	17	71	26	13

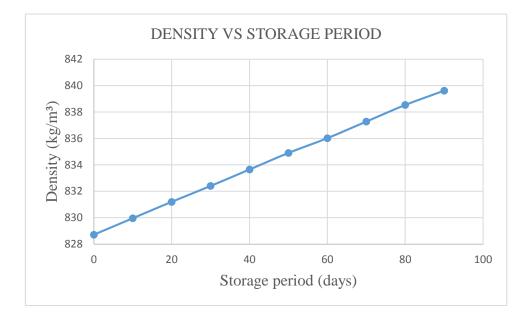


Figure 4.3: Density (kg/m³) for storage period 90 days at 15°C

From figure 4.3, density increased also with the storage time because of oxidation processes causing increase in polymer and fatty acid chains. All of these impurities makes the fuel more viscous and heavier.

4.4 Density over Testing Temperatures

Table 4.4 below contains the experimentally result for density in a blend of 5%BD+95%ED for testing temperatures from -11°C to 90°C at weekly intervals.

T(°C)	Weeks							
	0 weeks	4 weeks	8 weeks	12 weeks				
-11	917.81	918.581						
-10	909.70	910.468	914.428	918.36				
-8	901.59	902.354	906.279	910.18				
-7	893.49	894.240	898.130	901.99				
-5	885.38	886.126	889.981	893.81				
-3	877.27	878.013	881.831	885.62				
0	869.17	869.899	873.682	877.44				
2	861.06	861.785	865.533	869.26				
5	852.95	853.672	857.384	861.07				
8	844.85	845.558	849.235	852.89				
10	836.74	837.444	841.086	844.70				
15	828.71	832.397	836.017	839.61				
20	820.68	821.372	824.945	828.49				
30	812.65	813.336	816.874	820.39				
40	803.05	803.727	807.222	810.69				
50	801.21	801.884	805.372	808.84				
60	792.38	793.052	796.502	799.93				
70	785.82	786.479	789.900	793.30				
80	772.85	773.500	776.864	780.20				
90	766.80	767.445	770.783	774.10				

Table 4.4: Density (kg/m³) for 12 weeks over Testing Temperature $^{\circ}C$

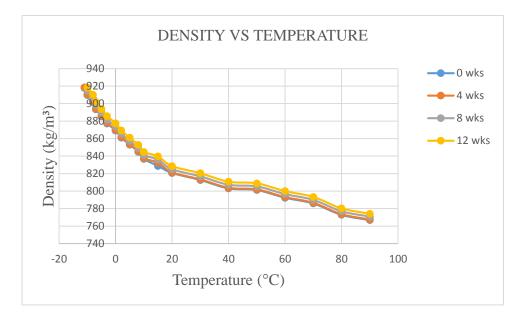


Figure 4.4: Density (kg/m³) for 12 weeks over testing temperatures °C

From figure 4.4, density is decreasing with the increasing temperature because the kinetic energy of the fuel is increasing thereby making the molecules in the fuel system moving faster.

4.5 Total Acidic Number and Oxidation Stability

Table 4.5 below shows the test method and test result for total acid number and oxidation stability of 5%BD+95%ED blend and this analysis was carried out two times within a period of 30 days by Nortest inspection and certification. The specimen is marked satisfactory at the time of receiving the specimen.

TEST DESCRIPTION	TEST	SPEC	TEST	
UNITS	METHOD	LIMIT	RESULTS	
Total Acid Number (mgKOH/gr)	D664-04(2017)	-	0.05 0.1	
Oxidation Stability (hours)	EN15751:2014	-	>20 17	

Table 4.5: Total Acidic Number (mgKOH, gr) and Oxidation Stability (hours)

The total acidic number or acidic value also increased with the storage period because the hydro-peroxide produced during degradation is increased due to reactions thereby producing more acids by oxidation, which increased the acidic number. An increase in total acidic number over the storage period decreases the oxidation stability of fuel system.

4.6 Cloud point, Pour point, Cold filter plugging point, Calibration curves and Cooling curve.

Table 4.6, figure 4.5 and figure 4.6 below respectively indicates the results obtained for cloud point, pour point, cold filter plugging point, calibration curves and cooling curves.

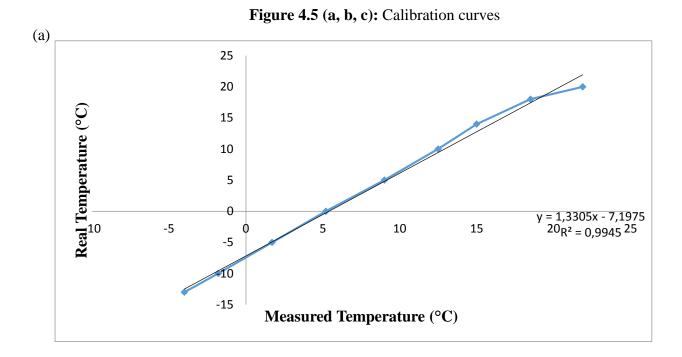
Cloud point °C	Pour point °C	Cold filter plugging point
		°C
-1	-15	-6.5

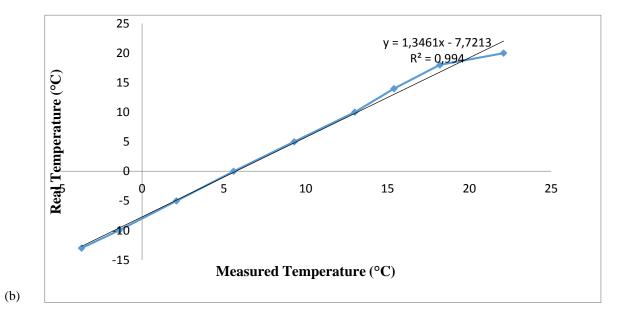
Table 4.6: Experimental Result of Cp, Pp and Cfpp

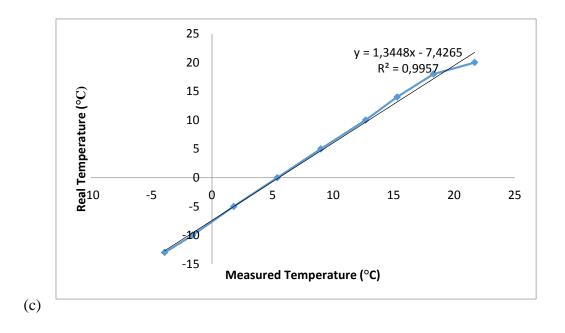
A blend of 5% BD + 95%ED is observed to have a cloud point of -1°, which is the temperature at which wax begins to precipitate which is known to be the cloud point. The pour point is observed to be -15° , which is the temperature at which the fuel becomes a gel and does not flow anymore. The cfpp is observed to be -6.5° but this cannot be visually determined but could be determined using the cooling curve.

4.6.1 Calibration curves

Figure 4.5 (a, b, c) indicates the calibration curves derived when comparing temperatures







The calibration curve allows for comparison between the real temperature measured by the thermostat and the temperature measured using the data logger device.

4.6.2 Cooling curve

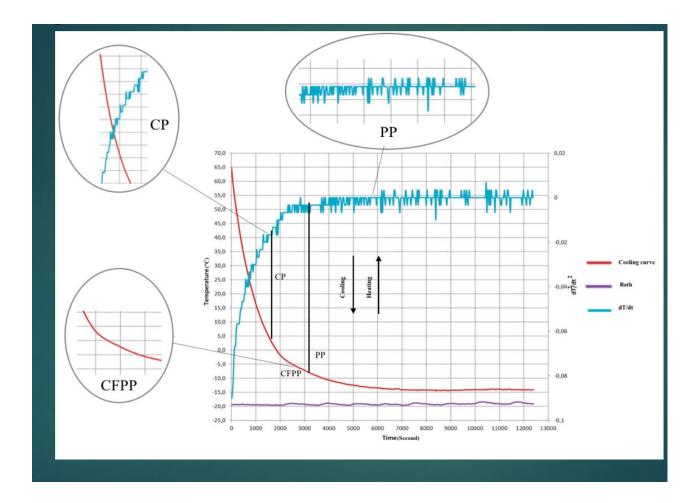


Figure 4.6: Cooling curve

Low temperature properties of the blends was also investigated using DSC. Figure 4.6 shows the cooling curve and bath temperature during both the cooling and heating cycle scans. In order to know the values of cold flow properties, the second derivative of temperature (as function of time) has been calculated and plotted as shown in figure 4.6. It is observed that, the value of CP, CFPP and PP from cooling curve and observation data are almost equals which are (-1, -6.5 and -15) °C respectively.

CHAPTER 5

CONCLUSION, POSSIBLE ERRORS AND RECOMMENDATION

5.1: Conclusion

The concentration of FAME in euro-diesel fuel may affect the ageing flow behaviour, i.e. density and kinematic viscosity of this blend, and based in the results obtained, the following conclusion can be relatively drawn.

The kinematic viscosity will always decrease with increase in temperature and will increase with decrease in temperature for every temperature composition blend of bio-diesel and eurodiesel.

For kinematic viscosity of this blend which is used in this work (5% bio-diesel + 95% eurodiesel), it cannot be determined at less than -15°C because of crystallization.

The cloud point of every blend of bio-diesel and euro-diesel will always occur a few degree above the CFPP (cold filter plugging point) before the pour point.

The blend used in this report can be used in car engines in cold regions that do not exceed - 15°C.

5.2 Possible errors

- There are uncertainties in the experiment putting into consideration the equipment has used and to probabilities of human error ranging from difficulty in reading, using the stopwatch accurately etc.
- There are possibility of non-homogenous temperature in the cold bath or the glass beaker.
- There are challenges of heat loss from the glass beaker into the environment when carrying out experiment at elevated high temperature and also heat gain from the environment into the cold bath when measurement are carried out at required low temperatures.
- There are also mechanical vibration from the cold bath at interval, which might alter the electronic balance used in measuring the density.
- There are situations when the samples in the pycnometer as reduced below the throat level and possible you did not take note of this, which will in turn give error in the density measurement.

- There are possibilities of the thermostat in the oven not working properly or the entire system out of power supply for some period.
- Presence of water content in the sample.

5.3 Recommendation

Further investigation to determine the properties of this same blend if additives are added to it since additives will enhance the behaviour of fuel system. Also, further investigation to determine the iodine value, cetane number, heat of combustion of 5% BD + 95% ED.

REFERENCES

- Akhlaghi, S., Pourrahimi, A.M., Sjostedt, C., and Bellander, M.S. (2017) Effects of ageing conditions on degradation of acrylonitrile butadiene rubber filled with heat-treated ZnO star-shaped particles in rapeseed biodiesel.
- Ali, H.A., Chughtai, A., Sattar, A., Bodla, A.R., and Butt, M.A. (2011). Waste Frying Oil as a Source of Biodiesel. *Pakistan Journal of Science*, 63(4).
- Anastopoulos, G., Zannikou, Y., Stournas, S. and Kalligeros, S. (2009). Transesterification of Vegetable Oils with Ethanol and Characterization of the Key Fuel Properties of Ethyl Esters. *Energies*, Vol.2, No.2 (2009), pp. 362-376.
- Atabani, A.E., Silitonga, A.S., Badruddin, I.A., Mahlia, T.M.I, Masjuki, H.H., and Mekhilef, S. (2012). A Comprehensive Review on Biodiesel as an Alternative Energy Resource and Its Characteristics. *Renewable and Sustainable Energy Reviews*, 16, 2070-2093.
- Azhari Muhammad Syam, Leni Maulinda, Ishak Ibrahim1, and Syafari Muhammad. (2013).
 Waste Frying Oils-Based Biodiesel: Process and Fuel Properties Smart Grid and Renewable Energy, 4, 281-286
- Barabás, I. and Todorut, A. (2010). Combustibili pentru automobile: testare, utilizare, evaluare. *Cluj-Napoca, Romania*.
- Barabás, I., and Todoruţ, I. (2011). Biodiesel Quality, Standards and Properties. *Technical University of Cluj-Napoca, Romania*.
- Barabás, I., Todorut, A. and Baldean, D. (2010). Performance and emission characteristics of an CI engine fueled with diesel-biodiesel-bioethanol blends. *Fuel*, 89(12), 3827-3832.
- Bățaga, N., Burnete, N. and Barabás, I. (2003). Combustibili, lubrifianți, materiale
- Berthiaume, D. and Tremblay, A. (2006). Study of the Rancimat Test Method in Measuring the Oxidation Stability of Biodiesel Ester and Blends. *NRCan* project No. CO414

- Blangino, E., Riverós, A.F. and Romano, S.D. (2008). Numerical Expressions for Viscosity, Surface Tension and Density of Biodiesel: Analysis and Experimental Validation. *Physics and Chemistry of liquids*, 46(5), 527-547.
- Batts B.D. and Zuhdan Fathoni, A. (1991). A literature review on fuel stability studies with particular emphasis on diesel oil. Energy Fuels; 5(1) 2-21
- Dabir, S. V., Dasika H. L. P., Nidamartyv. K. D. and Kalipatnapu Y. R. (2007). Viscosity of Liquids Theory, Estimation, Experiment and Data.
- Engelen, B. (2009). Guidelines for handling and blending FAME. *Fuels Quality and Emissions Management Group. CONCAWE* report no. 9/09.
- Geacai, S., Iulian, O., Nita, I. (2015). Measurement, correlation and prediction of biodiesel blends viscosity. *Fuel 143*, 268–274.
- Gerpen, J.V. (2005). Biodiesel Production and Fuel Quality.
- Joshi, R.M., and Pegg, M.J. (2007). Flow Properties of Biodiesel Fuel Blends at Low Temperatures. *Fuel*, 86, 143-151.
- Knothe, G. (2005). Dependence of Biodiesel Fuel Properties on the Structure of Fatty Acid Alkyl Esters," *Fuel Processing Technology*, 86, 1059-1070.
- Knothe, G. (2010). Biodiesel: Current Trends and Properties. Top Catal, 53, 714-720.
- Knothe, G., and Steidley, K.R. (2005). Kinematic Viscosity of Biodiesel Fuel Components and Related Compounds. Influence of Compound Structure and Comparison to Petrodiesel Fuel Components. *Fuel*, 84, 1059-1065.
- Knothe, G., and Steidley, K.R. (2009). A Comparison of Used Cooking Oils: A very Heterogeneous Feedstock for Biodiesel. *Bioresource Technology*, 100, 5796-5801.
- Kulkarni, M.G., and Dalai, A.K. (2006). Waste Cooking Oil-an Economical Source for Biodiesel: A Review. *Industrial and Engineering Chemical Research*, 45, 2901-2913.
- Lima, L. S., Barbosa, T. P., Silva, L. F. B., Santo, D. M. E., Castro, C. S. C., Dos Santos, J. J. P., Siqueira, J. R R., Barbosa, A. P. F., Marteleto, P. R., Rodrigues, C. R. C. and

Pereira, R. G. (2010). Biodiesel density Characteristics using a pycnometer. *Centro Nacional de Metrologia*.

- Mejía,J.D., Salgado, N. and Orrego, C.E. (2013). Effect of Blends of Diesel and Palm-Caster Biodiesels on Viscosity, Cloud Point and Flash Point. *Industrial Crops and Products*, 43, 791-797.
- National Institute of Automotive Service Excellence (NIASE). (2007). Changes in Diesel Fuel; The Service Technician Guide to Compression Ignition Quality.
- National Renewable Energy Laboratory (NREL). (2009). Biodiesel Handling and Use Guide Fourth Edition.
- Saltas, E., Bouilly, J., Geivanidis, S., Samaras, Z., Mohammadi, A. and Iida, Y. (2017). Investigation of the effects of biodiesel aging on the degradation of common rail fuel injection systems. *Fuel 200*, 357–370.
- Sangita Banga and Pradeep, .K. Varshney. (2010). Effect of impurities on performance of biodiesel: *A review Journal of Scientific & Industrial research*, 69, 575-579.
- Ullah, K. (2013). Aging of polymer in diesel and biodiesel blended fuel.
- World Fuel Charter Committee (WFCC). (2009). Biodiesel Guidelines (Washington D.C.: Alliance of Automobile Manufacturers.
- Zhou, J., Xiong, Y., Gong, Y. and Liu, X. (2017). Analysis of the oxidative degradation of biodiesel blends using FTIR, UV–Vis, TGA and TD-DES methods.

APPENDICES