SUPERVISOR DECLARATION

"I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of the degree of Bachelor of Mechanical Engineering (Automotive)"

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Date: …………………………….

PARAMETRIC STUDY OF BIODIESEL PROPERTIES TO THE STORAGE CONDITION

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This report is submitted in partial fulfillment of the requirements for the award Bachelor of Mechanical Engineering (Automotive)

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DECLARATION

"I hereby declare that the work in this thesis is my own except for summaries and quotations which have been duly acknowledged."

Signature: …………………………….
Author: FARIS BIN AZMAN
Date: …………………………….

To my

Beloved father and mother

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ABSTRACT

Storage condition is important for biodiesel because it may affect the biodiesel properties which can lead to degradation of biodiesel. First of all, the test method to produce biodiesel standards need to be understood. Moreover, selected biodiesel properties were investigated by performing experimental work under storage condition and the results are analysed and compared with existing biodiesel standard. Next, simplest test methods need to be found to determine the biodiesel properties. In addition, the storages must be correctly set up to maintain the temperature which are hot, ambient and cold temperature of the storage conditions. Besides that, the biodiesel properties need to be determined under storage condition to know whether there are differences with the properties according to the existing biodiesel standard. In this project, Setaflash Series 3 Plus Closed Cup Tester instrument was used to determine the flash point, volumetric titration method to determine the acid number and Fourier Transform Infrared Spectroscopy to determine the ester content, in B100 and standard diesel samples under storage conditions. Flash point of B100 samples in storage conditions follow biodiesel standard but not in acid number. Furthermore, B100 sample in cold storage condition showed highest flash point, lowest acid number and lowest ester content which is better than other B100 samples in other storage conditions.

ABSTRAK

Kondisi penyimpanan penting untuk biodiesel kerana berkemungkinan memberi kesan kepada sifat biodiesel yang boleh membawa kepada degradasi biodiesel. Pertama sekali, kaedah ujian untuk menghasilkan biodiesel perlu difahami. Selain itu, sifat-sifat biodiesel yang dipilih telah diselidik dengan melakukan kerja eksperimen dalam kondisi penyimpanan dan hasil eksperimen dikaji dan dibandingkan dengan piawaian biodiesel yang sedia ada. Seterusnya, kaedah-kaedah ujian yang paling mudah perlu ditemui untuk menentukan sifat-sifat biodiesel. Di samping itu, penyimpanan mesti ditetapkan dengan betul sehingga dapat mengekalkan suhu iaitu pada suhu yang panas, suhu sekeliling dan suhu sejuk untuk kondisi penyimpanan. Selain itu, sifat-sifat biodiesel perlu ditentukan dalam keadaan konsdisi penyimpanan untuk mengetahui sama ada terdapat perbezaan dengan sifat-sifat mengikut piawaian biodiesel yang sedia ada. Dalam projek ini, instrumen 'Setaflash Seires 3 Plus Closed Cup Tester' telah digunakan untuk menentukan takat kilat, kaedah titratan volumetri untuk menentukan nilai asid dan 'Fourier Transform Infrared Spectroscopy' untuk mentukan kandungan ester, dalam sampel B100 dan diesel biasa dalam kondisi penyimpanan. Takat kilat sampel B100 dalam kondisi penyimpanan mengikuti piawaian biodiesel tetapi tidak dalam nilai asid. Tambahan pula, sampel B100 dalam kondisi penyimpanan sejuk menunjukkan takat kilat yang tertinggi, nilai asid yang paling rendah dan kandungan ester yang paling rendah iaitu lebih baik daripada sampel B100 dalam kondisi penyimpanan yang lain.

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LIST OF SYMBOLS

$-OCH_3$	=	Methoxide ion
Na	=	Sodium
K	=	Potassium
Ca	=	Calcium
Mg	=	Magnesium
P	=	Phosphorus
NaOH	=	Sodium Hydroxide
KOH	=	Potassium Hydroxide

LIST OF ABBREVIATION

PSM	-	Projek Sarjana Muda
UTeM	-	Universiti Teknikal Malaysia Melaka
FKM	-	Faculty of Mechanical Engineering
BMCA	-	Bachelor in Mechanical Engineering Automotive
CFPP	-	Cold Filter Plugging Point
FAME	-	Fatty acid methyl ester
B5	-	5% biodiesel and 95% petroleum diesel
B100	-	100% biodiesel
EN	-	European Norm
ASTM	-	American Society for Testing and Materials
DIN	-	Deutsches Institut für Normung
GC	-	Gas chromatography
WCOT	-	Wall-coated open tubular
SCOT	-	Support-coated open tubular
FSOT	-	Fused silica open tubular
ICP-OES	-	Inductively coupled plasma and subsequent optical emission spectroscopy
AAS	-	Atomic absorption spectrometry
PMT	-	Photomultiplier tube
ICP	-	Inductively coupled plasma
FTIR	-	Fourier Transform Infrared
FKP	-	Faculty of Manufacturing Engineering
UTHM	-	Universiti Tun Hussein Onn Malaysia
PPE	-	Personal Protective Equipment
SD	-	Standard Diesel

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Biodiesel is defined as the mixture of monoalkyl esters of fatty acid methyl ester (FAME) such as vegetable oils, animal fats, cooking oil or algae oil which are parts of the renewable biological sources (Gog et al., 2014). Sharma et al. (2008) states that renewable fuel such as biodiesel with less exhaust emissions better than petroleum diesel which is a non-renewable fuel that emit many form of pollutants and last for limited period of time. Nowadays, petroleum prices keep rising as the result of its amount continue to decrease and higher demand in industry and high usage in daily life of people around the world. Therefore, the research and development of biodiesel is being focused on the optimization of process to meet the specification and standards required for the renewable energy source or fuel to be used commercially and worldwide without decreasing or reducing the durability and efficiency of engine parts. Biodiesel is now becoming one of the alternatives to partially fulfill expected future energy demands especially in transport sector.

Calero et al. (2014) states that biodiesel which is a mixture of fatty acid alkyl esters been produced by a chemical process called transesterification or alcoholysis of the parent oil or fat with an alcohol with the presence of basic catalyst usually a strong base such as sodium or potassium hydroxide. Transesterification process also producing other products which are glycerol, can also been called as glycerine with other small amount of unreacted materials, residual alcohol and residual catalyst.

Basically, there are three basics paths for the biodiesel production from oils and fats which are base catalysed transesterification of the oil, direct acid catalysed transesterification of the oil and lastly, enzymatic catalysed transesterification of the oil. Base catalysts are highly sensitive to moisture and free fatty acid contents which causes a partial reaction of saponification causing the consumption of the catalyst and reduction in catalytic efficiency. Acid catalysts are used when the acid value of the feedstock is higher than the performance range of the base catalysts. Both type of catalysts have disadvantages like being energy-intensive, difficult to recover glycerol, difficulty in removal of the excess catalyst from product, treatment of alkaline waste water and interference of free fatty acids and water in the reaction (Yan et al., 2014). Enzymatic transesterification on the other hand is better because of lower energy consumption, biodiesel easily separated from the reaction mixture and biodiesel purification is easier. However, in industry, base catalysts are most preferred because of the higher speed reaction, lower reaction temperature and higher conversion efficiency.

The transesterification process is the reaction of a triglyceride with an alcohol and helped from catalyst to form esters and glycerine. A triglyceride has a glycerine molecule as base with three long chain fatty acids. The alcohol used is usually methanol where excess quantity of alcohol is added in the process to produce equilibrium towards the products since the process is reversible. Sufficient quantity of alcohol for the chemical reaction is 3:1 alcohol to oil molar ratio as per stoichiometry (Mythili et al., 2014). The presence of catalyst aid the process because the catalyst like sodium hydroxide react with methanol to produce methoxide ion, $^{-}OCH_3$, that is required to produce the esters. The products formed are ester which is the biodiesel and glycerine, the co-product of the chemical reaction. Esters that are produced is dependent on the alcohol used (using methanol will produce methyl ester and using ethanol will produce ethyl ester). However, the glycerine produced is contaminated with the unreacted material which is the glycerides, residual alcohol and residual catalyst. The following Figure 1.1 shows the transesterification process:

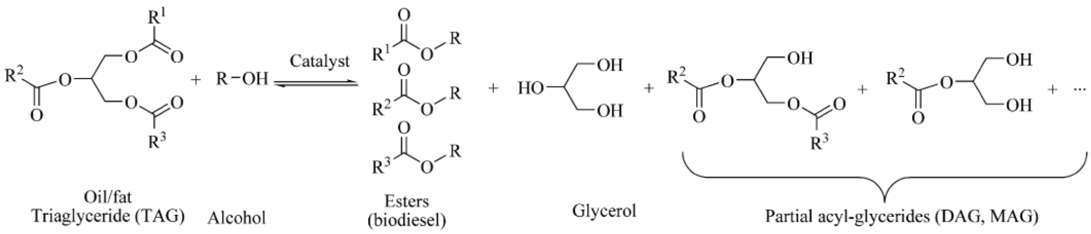

Figure 1.1: Chemical Reaction in Producing Biodiesel

(Source: Gog et al., (2014))

A successful transesterification reaction is determined by the separation of the biodiesel and glycerine layers after the reaction time. The glycerine produced is useful in other industry such as food industry and pharmaceutical but the contaminants need to be removed to obtain the pure glycerine and attain commercial value. In addition, automation industry especially for the diesel engine industry, the engine combustion also benefits from the good and completed process of the transesterification of the oil.

The completed biodiesel must be analysed using appropriate and suitable equipment in order to ensure that it meets the specific requirements needed. The most important aspects of biodiesel production to ensure smooth and good operation in diesel engine are:

1. Complete reaction
2. Removal of glycerine
3. Removal of catalyst
4. Removal of alcohol
5. Absence of free fatty acids

Comparison between biodiesel and petroleum diesel shows that biodiesel is better than the fossil fuel. First and foremost, it is a clean energy source which is environmentally friendly because of reduces in emission of carbon dioxide, sulphur dioxide and carbon monoxide (Huang et al., 2012). Biodiesel has low sulphur content and contains oxygen that promotes clean burning. Biodiesel has a better flammability so that it can be transported conveniently and more safely, high viscosity which is good for lubrication to extend the life span of engine.

The storage condition of the biodiesel is also important. One of the aspects that are hard to control in storage condition is temperature. Whether its the heat during day or cold during night, the change in temperature may affect the biodiesel inside the storage that possibly contribute to the degradation of biodiesel.

Biodiesel has a number of standards for its quality. Most commonly standards seen are B5, B20 and B100. The “B” alphabet of the acronyms shows the percentage of biodiesel blend like B5 shows the diesel oil is 5% biodiesel and 95% petroleum diesel. Each of the standards has its own usage especially B5 which is now widely use in vehicle that use diesel engine.

Based on the advantages of biodiesel and now that it is gaining global intention and market, few countries made their own biodiesel standard like European standard or European Norm (EN) and American Society for Testing and Materials (ASTM) standard. This is because vehicle manufacturers need a standard to approve vehicles to be operated using biodiesel which shows an approved biodiesel standard is important to the producers, suppliers and users. The following Table 1.1 to Table 1.3 show few standards that already exist in the world:

Table 1.1: European Standard for Biodiesel (EN 14214)
(Source: Barabas and Todorut, (2011))

Propert	Test method	Limits		Unit
		min		
Density at 15°C	EN ISO 3675, EN ISO	860	900	kg/m^3
Viscosity at 40°C	EN ISO 3104, ISO 3105	3.5	5.0	mm^2/s
Flash point	EN ISO 3679	120	–	°C
Sulfur content	EN ISO 20846, EN ISO	–	10.0	mg/kg
Carbon residue (in 10% dist. residue)	EN ISO 10370	–	0.30	% (m/m)
Cetane number	EN ISO 5165	5 1	–	–
Sulfated ash	ISO 3987	–	0.02	% (m/m)
Water content	EN ISO 12937	–	500	mg/kg
Total contamination	EN 12662	–	24	mg/kg
Copper strip corrosion (3 hours,50°C)	EN ISO 2160	–	1	class
Oxidative stability, 110°C	EN 14112	6.0	–	hours
Acid value	EN 14104	–	0.50	mg
Iodine value	EN 14111	–	120	g I/100 g
Linolenic acid content	EN 14103	–	12	% (m/m)
Content of FAME with ≥4 double bonds		–	1	% (m/m)
Methanol content	EN 14110	–	0.20	% (m/m)
Monoglyceride content	EN 14105	–	0.80	% (m/m)
Diglyceride content	EN 14105	–	0.20	% (m/m)
Triglyceride content	EN 14105	–	0.20	% (m/m)
Free glycerine	EN 14105; EN 14106	–	0.02	% (m/m)
Total glycerine	EN 14105	–	0.25	% (m/m)
Alkali metals (Na + K)	EN 14108; EN 14109	–	5.0	mg/kg
Earth alkali metals (Ca + Mg)	EN 14538	–	5.0	mg/kg
Phosphorus content	EN 14107	–	10.0	mg/kg

Table 1.2: ASTM Standard for Biodiesel (ASTM D6751)
(Source: Alternative Fuels Data Center, (2014))

Property	Test Method	Limits	Units
Calcium and magnesium combined	EN14538	5 max	ppm
Flash point	D93	93.0 min	°C
Water and sediment	D2709	0.050 max	vol %
Kinematic viscosity, 40°C	D445	1.9-6.0	mm^2/s
Sulfated ash	D874	0.020 max	% mass
Sulfur	D5453	0.0015 max (S15) 0.05 max (S500)	% mass
Copper strip corrosion	D130	0.020 max	-
Cetane number	D613	47 min	-
Cloud point	D2500	Report to customer	°C
Carbon residue[a]	D4530	0.050 max	% mass
Acid number	D664	0.50 max	mg KOH/g
Free glycerin	D6584	0.020	% mass
Total glycerin	D6584	0.240	% mass
Phosphorus content	D4951	0.001 max	% mass
Distillation temperature, 90% recovered (T90)[b]	D1160	360 max	°C
Oxidation stability	EN15751	3 min	hours
Cold Soak filterability	D7501	360 max[c]	seconds
Alcohol control - One of the following must be met:			
(1) Methanol content	EN14110	0.2 max	vol %
(2) Flash point	D93	130 min	°C

Table 1.3: Comparison Between European, Germany, American and Petroleum Diesel for Biodiesel

(Source: Biofuel Systems, (2014))

		EUROPE	GERMANY	USA	PETROLEUM DIESEL
Specification		EN 14214:2003	DIN V 51606	ASTM D 6751-07b	EN 590:1999
Applies to		FAME	FAME	FAAE	Diesel
Density 15°C	g/cm^3	0.86-0.90	0.875-0.90		0.82-0.845
Viscosity 40°C	mm^2/s	3.5-5.0	3.5-5.0	1.9-6.0	2.0-4.5
Distillation	% @ °C			90%,360°C	85%,350°C - 95%,360°C
Flashpoint (Fp)	°C	120 min	110 min	93 min	55 min
CFPP	°C	* country specific	summer 0 spr/aut -10 winter -20		* country specific
Cloud point	°C			* report	
Sulphur	mg/kg	10 max	10 max	15 max	350 max
CCR 100%	%mass		0.05 max	0.05 max	
Carbon residue (10%dist.residue)	%mass	0.3 max	0.3 max		0.3 max
Sulphated ash	%mass	0.02 max	0.03 max	0.02 max	
Oxid ash	%mass				0.1 max
Water	mg/kg	500 max	300 max	500 max	200 max
Total contamination	mg/kg	24 max	20 max		24 max
Cu corrosion max	3h/50°C	1	1	3	1
Oxidation stability	hrs;110°C	6 hours min		3 hours min	N/A (25 g/m3)
Cetane number		51 min	49 min	47 min	51 min
Acid value	mgKOH /g	0.5 max	0.5 max	0.5 max	
Methanol	%mass	0.20 max	0.3 max	0.2 max or Fp <130°C	
Ester content	%mass	96.5 min			
Monoglyceride	%mass	0.8 max	0.8 max		
Diglyceride	%mass	0.2 max	0.4 max		
Triglyceride	%mass	0.2 max	0.4 max		
Free glycerol	%mass	0.02 max	0.02 max	0.02 max	
Total glycerol	%mass	0.25 max	0.25 max	0.24 max	
Iodine value		120 max	115 max		
Linolenic acid ME	%mass	12 max			
C(x:4) & greater unsaturated esters	%mass	1 max			
Phosphorus	mg/kg	10 max	10 max	10 max	
Alkalinity	mg/kg		5 max		
Gp I metals (Na,K)	mg/kg	5 max		5 max	
GpII metals (Ca,Mg)	mg/kg	5 max		5 max	
PAHs	%mass				11 max
Lubricity / wear	µm at 60°C				460 max

1.2 OBJECTIVE

The following are the objectives to be achieved in this project:

1. To understand the test method used to produce biodiesel standards
2. To investigate the selected biodiesel properties by performing experimental work under storage condition
3. To analyse and to compare the results with existing biodiesel standard under storage condition

1.3 PROBLEM STATEMENT

Throughout this project, there are several aspects need to be considered. First of all is to find the simplest method to determine the biodiesel properties. Next, the storages must be correctly set up to maintain the temperature which are hot, ambient and cold storage conditions. Besides that, the biodiesel properties need to be determined under storage condition to know whether there are differences with the properties according to biodiesel standard.

1.4 SCOPE

This project will only focus on test methods to determine the properties in biodiesel which are free glycerine, total glycerine, sodium and potassium, calcium and magnesium, maximum phosphorus and cold filter plugging point (CFPP), acid number, flash point and ester by storage condition. Few properties will be selected to be determined in biodiesel and to be compared with existing standard by storage condition with conducting experiment to collect the data, analyse and to find the final result.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

From the all of the properties listed in the biodiesel standards, the properties that are been investigated to be determined the value or the amount of the contents inside the biodiesel are the first group of alkali metals, sodium and potassium (Na + K), the second group of alkali metals, calcium and magnesium (Ca + Mg), phosphorus (P), free glycerine, total glycerine, cold filter plugging point, acid number, flash point and ester. The following Table 2.1 shows the properties with its test method, limits and units based on European Biodiesel Standards EN14214:

Table 2.1: European Biodiesel Standards EN 14214

Properties	Test method	Limits	Unit
Free glycerine	EN 14105, EN 14106	0.020 max	% (mol/mol)
Total glycerine	EN 14105	0.25 max	% (mol/mol)
Sodium and potassium	EN 14108, EN 14109	5.0 max	mg/kg
Calcium and magnesium	EN 14108	5.0 max	mg/kg
Phosphorus	EN 14107	10.0 max	mg/kg
Cold filter plugging point	EN 116	-	℃
Flash point	EN ISO 3679	120 min	℃
Acid number	EN 14104	0.50 max	mg KOH/g