EFFECT OF STORAGE CONDITIONS AND ANTIOXIDANT ADDITIVES ON THE DETERIORATION OF BIODIESEL AND BIODIESEL BLENDS

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DECLARATION

I hereby declare that the materials in this thesis are original except for quotations, summaries and references, each of which have been duly acknowledged.

7th October 2014 ....

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ABSTRACT

Biodiesel is often used as a substitute of diesel fuel in current market. However, the inherent structure remains a significant problem due to its oxidation stability. Most industries blend biodiesel in certain percentages of diesel to prolong the shelf life, which lead to the aims of this study, to clarify and to investigate the storage stability of biodiesel and biodiesel blends under various type of storage effect over storage time of 8 months with few different conditions. Results show that storage with exposure of ambient air deteriorate faster compare to sample without exposure. Deteriorated percentages were faster for B100 > B30 > B20 > B0. Biodiesel with different blending percentages with Ultra Low Sulphur Diesel (ULSD) were also investigated. Additives added during desulfurization process for ULSD gives different trend compare to normal diesel. Water content, peroxide value and total acid number increased with respect to time. Upon exposure to air and under high temperature (heat) condition during storage, biodiesel and biodiesel blend is more susceptible to deteriorate due to its chemical structure. 2 layers of fuel as upper layer and sludge as bottom layer were formed after deterioration. Fuel analysis showed a drastic increase in the acid value, viscosity, oxidation product compound when the fuel deteriorated after 24 hours. Deterioration compound were examined, which demonstrated that aldehyde, ketones, short chain carboxylic acids as dominant compounds. As oxidation cannot be completely prevented, biodiesel and biodiesel blends user can only slow down the deterioration by adding sufficient antioxidant. Therefore the efficacy of selected antioxidant additives, Ecotive, Petrolift, Butylated Hydroxytoluene (BHT), Tert-Butylhydroquinone (TBH), and 2,2'-methylene-bis(4-methyl-6-tert-butylphenol) (MBP), in soy methyl esters (SME), palm methyl esters (PME) and jatropha methyl esters (JME) was investigated. These five antioxidant additives were selected for further studies at dosage percentages from 0.1 wt%, 0.5 wt% and 1.0 wt% and effect on different blending percentages. The antioxidant additives were measured in EN14112 Oxidation Stability under EN standard method, and protection factor (PF). Results showed that phenolic additives TBH give a better PF to comparing to other additives. It possesses two hydroxyl groups (OH^-) attached to the aromatic ring, thus on the basis of its electronegativity offer more sites for the formation of the complex between the free radical and antioxidant radical for the stabilization of the ester chain. The present finding is able to provide general guideline on additives selection and information on their performance. Results shows that efficacy of antioxidant rank from Petrolift < BHT < Ecotive < TBH & MBP. Effectiveness and performance of antioxidants did not influence by biofuel feedstock. Oxidation of biodiesel is fully depending on unsaturated fatty acid and position of allylic and bis-allylic on fatty acid. Results also showed that additives able to perform better with the present of higher diesel percentages in biodiesel blends. The higher the diesel percentages in diesel the better the additive can improve its IP.These results are sufficient enough to provide a biodiesel and biodiesel blends storage and prevention guideline according to storage conditions, fuel types and blending percentages to end user and to support the products of Yanmar.

ABSTRAK

KESAN KEADAAN PENYIMPANAN DAN BAHAN ANTI-PENGOKSIDAN TERHADAP KEMEROSOTAN BIODIESEL DAN CAMPURAN BIODIESEL

Biodiesel sering digunakan sebagai pengganti diesel dalam pasaran kini. Walau bagaimanapun, struktur asal biodiesel masih menyumbangkan masalah kestabilan pengoksidaan. Kebanyakan pengguna dalam industri sering mengabungkan biodiesel dengan peratusan diesel yang tertentu untuk menambah jangka hayatnya. Hal ini menjurus kepada tujuan penyelidikan, iaitu untuk menjelaskan dan mengkaji kestabilan pelbagai kesan penyimpanan biodiesel dan campuran biodiesel dalam tempoh 8 bulan dengan beberapa kaedah yang berbeza. Peratusan yang telah reput adalah lebih cepat untuk B100 > B30 > B20 > B0. Keputusan menunjukkan bahawa biodiesel terdedah pada udara berlebihan boleh mempercepatkan kadar penurunan kualiti biodiesel berbanding yang tidak terdedah. Pelbagai campuran biodiesel dan diesel sulfur rendah (ULSD) juga dikaji. Kandungan air, peroksida dan asid turut meningkat mengikut peredaran masa. Apabila terdedah dengan udara pada suhu tinggi (haba) semasa penyimpanan, biodiesel dan campuran biodiesel lebih cenderung untuk rosot disebabkan oleh stuktur kimianya. Keputusan menunjukkan pembentukan dua lapisan, iaitu minyak di lapisan atas dan mendapan di lapisan bawah. Keputusan analisis menunjukkan peningkatan asid, kelikatan, produk bahan pengoksidaan semasa minyak dirosotkan selepas 24 jam. Bahan pengoksidaan dikaji dan menunjukkan bahawa aldehid, keton, rantai asid karboksilik adalah bahan dominan. Disebabkan pengoksidaan tidak boleh dielakkan sepenuhnya, kemerosotan biodiesel dan campuran biodiesel hanya boleh dilambatkan dengan penggunaan anti-pengoksidaan yang secukupnya. Keberkesanan anti-pengoksidaan, Ecotive, Petrolift, butylated hydroxytoluene (BHT), tert-butylhydroquinone (TBH), dan 2,2-methylene-Bis (4-metil-6-tert-butilphenol) (MBP), dalam metil ester soya (SME), metil ester sawit (PME) dan metil ester jarak pagar (JME) dikaji. Kelima-lima dikajian dalam dos dari 0.1 wt%, 0.5wt% dan 1.0 wt% dan kesan terhadap peratus campuran yang berbeza. Kestabilan anti-pengoksidaan ditentukan dengan EN14112 iaitu oksidatif di bawah kaedah piawaian EN, dan faktor perlindungan (PF). Keputusan anti-pengoksidaan fenolik TBH menunjukkan PF yang lebih baik berbanding dengan pengawet lain. Ia mengandungi dua kumpulan hidroksil (OH-) terikat pada gelang aromatik, justeru pada asasnya kesan keelektronegatifan membuka ruang lebih untuk pembentukkan kompleks radikal bebas dan radikal antioksidan untuk kestabilan rantai ester. Ini berupaya untuk memberi petunjuk kepada pemilihan bahan anti-pengoksidaan dan maklumat prestasinya. Hasil menunjukkan keberkesanan antioksidan adalah Petrolift < BHT < Ecotive < TBH & MBP. Keberkesanan dan prestasi antioksidan tidak dipengaruhi bahan mentah biofuel. Pengoksidaan biodiesel bergantung sepenuhnya kepad asid lemak tak tepu dan kedudukan allylic dan bis - allylic asid lemak. Keputusan juga menunjukkan bahawa tambahan dapat melakukan yang lebih baik dengan masa kini peratusan diesel yang lebih tinggi dalam campuran biodiesel. Prestasi anti-pengoksidaan meningkat dengan lebih tinggi peratus diesel dalam biodiesel. Hasil ini cukup untuk memberi panduan penyimpanan biodiesel dan campuran biodiesel dan juga pencegahan menurut keadaan penyimpanan, jenis minyak dan peratus campuran kepada pengguna dan untuk membantu produk Yanmar.

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LIST OF ABBREVIATIONS

ASTM	-	American Society for Testing and Materials standard
B0	-	100% of diesel
B20	-	20% of biodiesel blends with 80% of diesel
B100	-	100% of biodiesel
BHA	-	Butylated Hydroxyanisole
BHT	-	Butylated Hydroxytoluene
BSTFA	-	N,O-Bis(trimethylsilyl)trifluoroacetamide
CJO	-	Crude Jatropha Oil
EIC	-	Extracted Ion Chromatogram
EN	-	European Standards
FD-MS	-	Field Desorption Mass Spectrophotometer
FFA	-	Free Fatty Acid
FTIR	-	Flourier Transmitted Infra-Red
GC	-	Gas Chromatograph
GC-MS	-	Gas Chromatograph Mass Spectrophotometer
GHG	-	Green House Gas
HPLC	-	High Performance Liquid Chromatography
IP	-	Induction Period
ISO	-	International Organization for Standardization
JME	-	Jatropha Methyl Esters
max	-	Maximum
MBP	-	2,2'-Methylene-Bis(4-Methyl-6-Tert-Butylphenol)
MD	-	Malaysia Diesel
MH	-	Methyl Hydroquinone
N-H	-	Amine Group
NIRS	-	Near Infrared Spectroscopy
PA	-	Pyrogallol
PE	-	Poly Ethylene
PF	-	Protection Factor
PG	-	Propyl Gallate
PME	-	Palm Methyl Esters

POV	-	Peroxide Value
PY	-	1,2,3 Tri-Hydroxy Benzene
SCAS	-	Sumika Chemical Analysis Service, Ltd.
SME	-	Soy Methyl Esters
TAN	-	Total Acid Number
TBH	-	Tert-Butylhydroquinone
ULSD	-	Ultra Low Sulfur Diesel
YKRC	-	Yanmar Kota Kinabalu R&D Center

LIST OF SYMBOLS

±	- Plus minus
<	- Less than
>	- More than
%	- Percent
^oC	- Degree Celsius
$-CH_2-$	- Methylene Group
$g\ I^2/100g$	- Gram of Iodine per 100 gram
h	- Hour
L/h	- Liter per Hour
L	- Liter
m.z	- Mass Number per Charge Number
meq/kg	- Miliequivalent per Kilogram
mg KOH/g	- Milligrams of Potassium Hydroxide per Gram
min	- Minimum
ml	- Milliliter
mm^2/s	- Square Millimeter per Second
m/z	- Mass-to-charge Ratio
N-H	- Amine Group
NIRS	- Near Infrared Spectroscopy
NO_x	- Nitrous Oxide (x = Oxygen Number)
O-H	- Hydroxyl Groups
ppm	- Parts per Million
rpm	- Round per Min
wt %	- Weight per Volume

CHAPTER 1

INTRODUCTION

1.1 Introduction of Biodiesel

Biodiesel is an alternative diesel fuel consisting of monoalkyl esters of long chain fatty acids (Aricetti & Tubino, 2012a; Pinzi *et al*., 2013; Salamanca *et al*., 2012; Vicentim *et al*. 2009) derived from vegetable oilsand animal fats for the use in diesel engine as an alternative of diesel fuel (Shahabuddin *et al*., 2012).Due to its renewability and applicability to existing compression ignition diesel engine technologies (Knothe, 2007), biodiesel has gained considerable attention, offering improved lubricity and exhaust emissions (Guzman *et al*., 2009).

Biodiesel has similar physical and chemical properties with diesel fuel. However, biodiesel properties can sometimes be more superior than diesel fuel because it has higher flash point, low sulphur concentration, better lubricating efficiency, and better cetane number (Demirbas, 2008a;Koh & Ghazi, 2011; Silitonga *et al*., 2013). Currently, biodiesel can be used in the existing diesel engine with little or no modifications (Knothe *et al*., 2005). In 2012, many countries provide B20 (20% of biodiesel mixted with 80% of diesel) for commercial diesel car and some diesel engine manufacturer have approved to use biodiesel with concentration up to 100%. Such biodiesel fuel should be comply with the European Standard, EN14214 (2003) and/or the American Standard ASTM D6751 (2001).

1.2 Advantages of Biodiesel

Biodiesel has several advantages over regular petroleum diesel and become more and more attractive recently because of its environmental benefits. First, it is not a petroleum-based fuel, which means that using biodiesel would reduce dependency on petroleum. Second, biodiesel is domestically produced, which means that using biodiesel will create jobs and contribute to local economies. The third major advantage of biodiesel is that it is cleaner than conventional diesel, including proper lubricity, good biodegradability, excellent combustion efficiency and low toxicity (Wang *et al.*,2013); biodiesel produces significantly less harmful emissions than regular petroleum diesel when burned in a combustion engine (Zuleta *et al.,* 2012).

1.3 Disadvantages of Biodiesel

The performance of biodiesel in cold conditions is markedly lower than that of petroleum diesel. At low temperatures, biodiesel forms wax crystals, which can clog fuel lines and filters in a vehicle fuel system. Presence of a high amount of mono-unsaturated components in biodiesel impedes agglomeration attributed to their bent structure (Demirbas, 2008a). The oxidative stability of biodiesel is also lower than the oxidative stability of diesel. This is a critical issue in industry because it affects the quality of the fuel and the materials in contact with it (Zuleta *et al.,* 2012). Due to their chemical composition, biodiesel are easily deteriorated (Mittelbach & Remschmidt, 2006). A deteriorated biodiesel contained high levels of free fatty acids can cause many problems in engine, such as sludge formation (Zuleta*et al.*, 2012). It has been the focus of a considerable amount of recent research because it is renewable, reduces the emission of some pollutants, and is also readily biodegradable in the environment (Bouaid *et al.,* 2007). Therefore their concentration must be controlled and maintained at low levels (Aricetti & Tubino, 2012a).

1.4 Problems Statement

The problems encountered in biodiesel are its stability. This problems arising from the deterioration of biodiesel fuel properties during storage are expected to be more severe than for diesel fuel. Therefore it is essentials to understand the mechanism of deterioration on biodiesel and biodiesel blends so we could identify the main reason of sludge formation, and provide a solution of biodiesel and biodiesels blends user. The present study investigates the effect of biodiesel and biodiesel deterioration on storage and its deterioration mechanism and the sludge formation. This information will be useful to both biodiesel producers and biodiesel users for designing their biodiesel storage system, for maintaining the quality of biodiesel in the fuel or storage tank, and to delay the deterioration of biofuels.