The Effect of Using Hydrogen Peroxide as Fuel Oxygenates for Enhancing Combustion Performance

by

Ong Yu Han

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

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Approved by,

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TRONOH, PERAK

MAY 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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ONG YU HAN

ABSTRACT

The price of crude oil is increasing annually due to the depletion of hydrocarbon production. In order to cope with the high demand from the market, researchers are working on improving the performance of the fuels by applying fuel oxygenates. Fuel oxygenates are chemical compounds that has the function of increasing the oxygen content in the fuel. The presence of fuel oxygenates promotes more complete combustion and hence, better engine performance and fuel consumption can be achieved. Besides, better combustion process also lowers the emission of harmful gases.

In this research, the main objective is to determine the effects of applying hydrogen peroxide as diesel oxygenates. Due to the difference in polarity, the blending of hydrogen peroxide and diesel fuel requires emulsification process to achieve a stable mixture. After emulsification, stability test was conducted on the oxygenated diesel samples based on the separating layer. Characterization tests were then carried out to identify the effects of hydrogen peroxide application. The major parameters of the oxygenated diesel are cetane number, calorific value, oxygen and sulphur content. From the analysis of the characterization tests, the application of hydrogen peroxide increases the oxygen content of the diesel from 5.47 % to 7.01%. The presence of additional oxygen improves the combustion quality and simultaneously reduces the emission of harmful gases, such as carbon monoxide and sulphur dioxide by increasing the cetane number from 41 to 71.2. However, there are some tradeoffs for the application of hydrogen peroxide. The major disadvantage is the heating value of oxygenated diesel. It reduces from 39,581 kJ/kg to 38,322 kJ/kg due to the presence of hydrogen peroxide.

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CHAPTER 1

INTRODUCTION

1.1. Background

Fossil fuel is the major source of energy in the world. It is used in many industries, such as transportation, manufacturing and power generation. With the increasing development activities across the globe, the demand of fossil fuel from various industries is increasing annually. However, it is a known fact that fossil fuel is not a renewable energy where the production of crude oil and natural gas is decreasing every day. This leads to the phenomenon of demand exceeding production and results in increasing of crude oil price.

Other than the fuel pricing, environmental issue has become another major concern nowadays. Inefficiency of combustion process produces harmful greenhouse gases, such as carbon monoxide, sulphur dioxide and NO_x. The emission of greenhouse gases from vehicles, manufacturing factories and plants worsens the air condition. As time passes, the deterioration of air quality will eventually affect the health of human beings and contribute to global warming. Therefore, researchers have been working on finding the solution to improve the fuel performance. The studies conducted for the past few years have suggested the application of fuel oxygenates for fuel improvement.

Fuel oxygenate is a chemical compound which can supply more oxygen to the fuel. It has the functions of improving the combustion performance and lowering the emission of harmful gases (U.S. EPA, 2009). Better combustion process by oxygenated fuel also improves engine performance. Currently, the commercial fuel oxygenate used in the industry are ethanol, methyl tert-butyl ether (MTBE) and tert-butyl alcohol (TBA) (API, 2008).

In this project, the fuel selected for the research is diesel fuel, whereas the fuel oxygenate is hydrogen peroxide. Hydrogen peroxide is a strong oxidizer. With its strong oxidizing properties, the application of hydrogen peroxide as fuel oxygenates has been proven to be able to promote more complete combustion in some literatures. Thus, analysis was performed on the combustion performance of oxygenated diesel to identify the effects of hydrogen peroxide additive.

1.2. Problem Statement

There are several studies conducted on hydrogen peroxide as fuel oxygenates. However, the emphasis of the previous studies was on the output of the application of hydrogen peroxide as fuel oxygenate, such as combustion performance and engine efficiency without looking into the chemical properties of oxygenated fuel. Therefore, in this project, more emphasis will put on the study of the chemical properties of the oxygenated diesel, for example heating value, cetane number, sulphur content, oxygen content and flash point. In addition, the diesel pricing and the effects of diesel engine on environment have become the major concerns nowadays. Therefore, the study on the effect of hydrogen peroxide as diesel fuel oxygenate on combustion performance is crucial for fuel performance improvement. With the enhancement in fuel performance, the pollution caused by the emission of harmful flue gases can be minimized.

1.3. Objectives

The objectives of this project are as follows,

i. To produce stable hydrogen peroxide - diesel blend which has better combustion performance and more environmental friendly.
ii. To study the properties of the oxygenated diesel and the combustion effects of using hydrogen peroxide as fuel oxygenates.

1.4. Scope of Study

The scope of study for this project involves the emulsification of polar and non – polar solutions, combustion process and characterization of fuel. In this project, it is required to blend hydrogen peroxide with diesel. Hydrogen peroxide is a polar solution, whereas diesel is a non – polar compound. Due to the difference in polarity, the mixing of both solutions produces two immiscible layers. Hence, the application of emulsifier or surfactant is required in order to promote a stable blending which is known as emulsification.

It is also one of the objectives to study the effects of hydrogen peroxide as diesel oxygenates on combustion process. It is crucial to determine the completeness and performance of the fuel combustion process. This can be performed by measuring the calorific value and cetane number of the oxygenated diesel. Besides, characterization of oxygenated diesel is also a vital part of this project. The major parameters of oxygenated diesel are oxygen content, sulphur content and flash point. The characterization process will be performed on both diesel and oxygenated diesel for comparison purpose.

CHAPTER 2

LITERATURE REVIEW

2.1. Hydrogen Peroxide

Hydrogen peroxide is known as the simplest form of peroxide compound which consists of an oxygen-oxygen single bond. Hydrogen peroxide is a colourless liquid with a sharp odor. It is a weak acid and strong oxidizing agent. The specific gravity of hydrogen peroxide is 1.135. Hydrogen peroxide is soluble in water and it is a polar solution. It is slightly unstable and will decompose at a reasonably slow rate.

$$2\ H_2O_2 \longrightarrow 2\ H_2O + O_2$$

During the decomposition of hydrogen peroxide, one volume of hydrogen peroxide is able to release 10 volumes of oxygen. Due to this characteristic, hydrogen peroxide is currently utilized as rocket propellant fuel.

Hydrogen peroxide is a polar solution, whereas diesel is a non – polar solution. Due to the difference in polarity, the mixing with diesel creates a mixture with two immiscible layers. In order to produce a stable mixture of hydrogen peroxide – diesel blend, emulsifier or surfactant is required.

2.2. Diesel

Diesel is one of the major sources of fuel in the world. It is produced from fractional distillation process of crude oil at the boiling point range of 149 ℃ to 371 ℃. Diesel fuel mainly consists of paraffinic and naphthenic hydrocarbons. The specific gravity of diesel is in the range of 0.81 to 0.89. The cetane number of diesel fuel is approximately within the range of 40 – 55. Diesel has the heating value of approximately 44,800 kJ/kg. Like any other hydrocarbons, diesel is a non-polar solution.

One of the disadvantages of using diesel fuel is the sulphur content. The sulphur content in the fuel can cause corrosion of engine and emission of sulphate particulates. With the introduction of Ultra Low Sulphur diesel, the demand and consumption of diesel of the world remain high. For instance, in Europe, most of the on-road vehicles are running on diesel engines (NACS, 2012). Other than transportation sector, the machineries in the industrial sector are majority relying on diesel fuel for power generation.

2.3. Solvent for Emulsification Process

Due to the difference in polarity, the mixing of hydrogen peroxide and diesel requires the application of emulsifier in order to produce a stable mixture. In this project, N, N – diethylmethylamine (DEMA) and N–methyl–2–pyrrolidone (NMP) are the emulsifiers used for emulsification process. They have the function of reducing the interfacial tension between two immiscible solutions which enhances the mixing process. DEMA is highly flammable with the flash point of -23 ℃, corrosive and has very strong odor. DEMA is soluble in water and it is also proven soluble in diesel during the experimental session. N–methyl–2–pyrrolidone has low flammability with the flash point of 91 ℃. It can dissolve completely in water and soluble in hydrocarbon compounds. Therefore, both chemicals are suitable solvents for emulsification process between hydrogen peroxide and diesel due to their solubility in polar and non – polar solutions.

2.4. Fuel Oxygenates

Fuel oxygenates are developed with the aim to improve fuel performance. It is defined as the chemical that can increase the oxygen level in a fuel in order to promote more complete combustion process (U.S. EPA, 2009). Currently, the common oxygenate fuel additives are alcohols and ethers, such as methyl tertiary butyl ether (MTBE), methanol and ethanol.

For the past few years, many studies were conducted for further understanding the concept of oxygenated fuel. In China, a group of researchers from Xi'an Jiaotong University has found that methanol-diesel blend has the ability to increase the thermal efficiency and reduce the brake specific fuel consumption as fuel delivery advanced angle increases (Huang et al., 2005). However, there is a downside of methanol application as fuel oxygenate. It is found that methanol fuel blend is very corrosive and hence, increases the risk of leakage of the fuel tank (U.S. EPA, 2009).

Similarly, ethanol is also applied as fuel oxygenate in the industry. In the University of Zagreb, Crotia, a study was conducted on different blends of gasoline, for example ethanol, hydrogen peroxide – water – ethanol and 10% and 20 % hydrogen peroxide. The results showed that 20% ethanol-gasoline blend has better fuel performance than normal gasoline and other blends. However, the concentration of ethanol in oxygenated fuel is vital. Another research showed that increasing the amount of ethanol in gasoline beyond 20% apparently increases the fuel consumption (Puskaric & Oros, 2012). Same trend was determined by Daheriya and Shrivastav (2012) that increasing of ethanol volume from 10% to 30% in diesel reduces the brake thermal efficiency of the diesel engine.

Another research conducted by Engine Manufacturers Association in 2010 has similar findings with the earlier studies. It is stated that different amount of ethanol blending with gasoline yields different fuel properties. With the fact that the energy value of ethanol is 35% lower than gasoline in volume basis, mixing ethanol with gasoline will reduce the energy content. However, if the volume of ethanol in the oxygenated gasoline is less than 10%, the reduction of energy is not a major concern (EMA, 2010). Barnes et al. (n.d.) conducted a research on the effect of acetals as fuel oxygenate. The results show that the addition of acetals in diesel reduces the emission of NO_x and engine particles due to better combustion process.

In University Californa, a cost-benefit analysis of oxygenated gasoline was conducted. The study shows that the application of Methyl-tert-butyl ether (MTBE) is not cost effective taking the consideration of its potential of water pollution. Besides, blending ethanol with gasoline is slightly more cost effective than MTBE. However, it is not as efficient as the non – oxygenated fuel (Keller & Fernandez, 2000).

Other than alcohol and ether based oxygenate compounds, researchers are currently working on the alternative fuel oxygenates. As a strong oxidizer, hydrogen peroxide is a suitable candidate. The oxidizing characteristics of a peroxide compound are found to be useful in enhancing fuel and combustion efficiency. In 2009, a research was conducted in Universiti Malaysia Pahang to study the effect of introducing hydrogen peroxide in liquefied petroleum gas combustion. The application of hydrogen peroxide increases the combustion performance and fuel efficiency. The improvement of combustion process leads to the reduction of carbon monoxide production with the presence of additional oxygen. Simultaneously, the application of hydrogen peroxide also decreases the ignition and burn off temperature (Muhammad Saad et al., 2009). In addition, a similar research was also conducted in Universiti Malaysia Pahang in 2010. The research is about applying hydrogen peroxide in methane gas combustion. The research results show that the injection of hydrogen peroxide improves the lean burn ability. With the enhancement of combustion process, the production of greenhouse gases, such as carbon monoxide is decreased with the presence of hydrogen peroxide (Muhammad Syukri, 2010).

In 2008, a similar research was conducted in Annamalai University to study the effect of hydrogen peroxide in emulsified diesel. The methodology of this research was performed by adding 12 % of hydrogen peroxide in volume basis into emulsified diesel with 50% diesel and 50% ethanol (50D50E). From the experiment, the results showed that the application of hydrogen peroxide enhances the brake thermal efficiency from 36% (50D50E) to 41%. Besides, the presence of hydrogen peroxide in the emulsified diesel decreases the emission greenhouse gases (Ashok & Saravanan, 2008). In April 2012, a research was conducted by mixing hydrogen peroxide with diesel at the concentration of 2%, 5% and 10% respectively. Each oxygenated fuel blend was tested using a diesel engine working on different loads. The study has shown that the brake thermal efficiency is increased and exhaust gases temperature is reduced with the presence of hydrogen peroxide (Nagaprasad & Madhu, 2012). In addition, a similar study was performed in Amravati University, India. The study has the objective to conduct analysis on hydrogen peroxide – diesel blend in compression ignition direct injection (CIDI) engine. This experiment gained the similar results where the mechanical efficiency of CIDI engine is higher and combustion process is better (Prof. Kongre et al., 2012).

2.5. Emulsification

The mixture of hydrogen peroxide and diesel is always in heterogeneous system due to their difference in polarity. Thus, emulsification process is required to produce a stable mixture of oxygenated fuel. Emulsion is defined as a heterogeneous system of two immiscible liquid phases where one is dispersed in another one in colloidal size (Binks, 1998).

A stable emulsion requires the aid of emulsifier or surfactant. The function of emulsifier is to reduce the interfacial tension between two liquids. By lowering the interfacial tension, surfactant can promote droplets break-up (Binks, 1998). The main criterion of emulsifier or surfactant is to have the balance of hydrophobic and hydrophilic properties (Feuerman & Bloomfield, 1979). The hydrophilic portion of emulsifier is water-soluble and attracted to polar and ionic compounds, whereas hydrophobic has opposite characteristics which it favours non water-soluble compounds like hydrocarbons (Dow Chemicals, 2010).

Figure2.0.Structure of surfactant or emulsifier.

There are various emulsifiers used for different types of mixtures. For emulsified fuel, the typical surfactant is C_4 – C_{14}alkylphenol. In a U.S. Patent 6,280,486, alkylphenolemulsifier was used for water-gasoline blend with hydrogen peroxide additives. The suggested amount of emulsifier utilized is approximately 0.5% to 1 % in weight basis (Dessauer et al., 2001). The stability of an emulsion has to be tested to ensure no separation will occur after certain period. Particle Science has shown and summarized the common test conditions for emulsion stability test in Figure 1. For example, storage of emulsion at room temperature, 25 ℃ can last approximately 36 months (Particle Sciences, 2011).

Table 2.0. Common test conditions for emulsion stability testing.

Storage Conditions	Storage Period
Ambient temperature	25 ℃ for 3 years.
Elevated temperature	37 ℃ for 6 months and 45 ℃ for 6 months.
Refrigerator	Approximately 4 ℃ for 3 months.
Freeze/thaw cycles	Approximately -10 ℃ to ambient.
Cycling chamber	4 ℃ to 45 ℃ in 48 hours for 1 month.
Light exposure	1 month exposure to north-facing daylight or light cabinet.

2.6. Combustion

Combustion is a chemical reaction between fuel and oxygen with the presence of ignition source and the mixture produces heat, water and carbon dioxide. However, by-product such as carbon monoxide can be produced from an incomplete combustion reaction normally due to insufficiency of oxygen. Combustion efficiency is a measure of how well a fuel is burned in a combustion reaction. There are few methods to determine the performance of a combustion process. The first method is the measure of heat loss carried by the exhaust gases and moisture. This can be measured by determining the temperature of the flue gases leaving from the combustion chamber. The second method is the study of the component of exhaust gas produced by combustion. For instance, the presence of carbon monoxide is an indication of incomplete combustion (Bergmann, 2005).

Other than the physical measurements of the combustion process, the combustion performance can be measured through calorimetric method. This method provides the information of the heating value or heat of combustion of the fuel. Heat of combustion is defined as the energy change when a complete combustion process of one mole of compound takes place (Clark J., 2010). Theoretically, fuel with higher heat of combustion tends to release more energy in a combustion process and hence, increases the fuel efficiency. However, high in heating value is also an indication that the fuel is less stable due to the release of higher amount of energy (Columbia Electronic Encyclopedia, 2012).

CHAPTER 3

METHODOLOGY/PROJECT WORK

3.1. Research Methodology

The research methodology of this project is divided into 4 major parts – literature review, experiment design, experimental work and analysis of experimental findings. FYP 1 covers the part of literature review and design of experimental approach. In FYP 2, the experimental work and the analysis of experimental findings were conducted.

3.2. Experiment Procedure

The experiment of this project is divided into three main parts,

I. Preparation of hydrogen peroxide - diesel mixture.
II. Stability test of hydrogen peroxide - diesel mixture.
III. Characterization and study the effects of hydrogen peroxide - diesel mixture.

3.2.1. Raw Materials, Chemicals and Apparatus

The fuel utilized for this project is PETRONAS commercial diesel and the oxygenate is hydrogen peroxide. In order to create stable emulsion of oxygenated diesel, surfactant or emulsifier is required. The emulsifiers used in the oxygenated diesel preparation are N, N – diethylmethylamine (DEMA) and N – methyl – 2 pyrrolidone (NMP). Carboxyl methyl cellulose (CMC) and sodium hexametaphosphate (SHMP) are also added to secure the oxygen content of hydrogen peroxide and stabilize the emulsion.

The apparatus setup of the experiment is as shown in the Figure 3.0 below which consists of 3 – neck bottom flask, magnetic stirrer and retort stand.

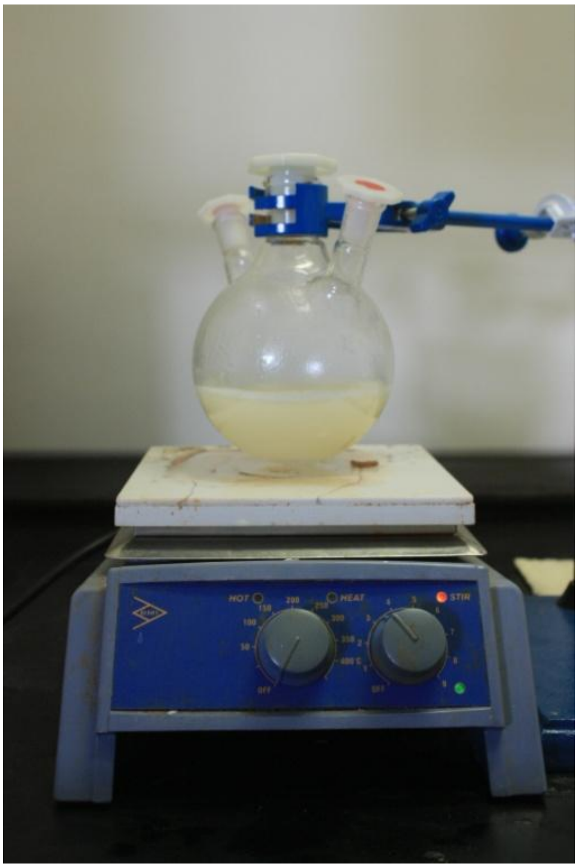

Figure 3.0.Apparatus setup for hydrogen peroxide and diesel mixing.

The characterization of the oxygenated diesel includes the study of the major parameters of the diesel. Calorific value and cetane number are the important parameters to determine the combustion quality of the fuel. In addition, CHNS analyzer was used to determine the composition of the diesel after the addition of hydrogen peroxide and emulsifier. Besides, the flash point, cloud point and pour point act as a measurement for the quality of diesel.

3.2.2. Preparation of Hydrogen Peroxide – Diesel Mixture

N, N – diethylmethylamine (DEMA) and N – methyl – 2 – pyrrolidone are the emulsifiers to reduce the interfacial tension between the diesel and hydrogen peroxide.

Carboxyl methyl cellulose (CMC) was added to secure the oxygen content of the hydrogen peroxide and stabilize the emulsification process. In addition, sodium hexametaphosphate (SHMP) was added to reduce the sulphur content in the diesel for further improvement of the diesel.

Preparation of 25 ml of hydrogen peroxide and emulsifier mixture

a. 0.2 g of SHMP and 0.3 g of CMC were added into 4 ml of N – methyl – 2-pyrrolidone (NMP).
b. The mixture was stirred and heated at a constant temperature of 50 ℃ for 30 minutes.
c. The mixture was cooled to room temperature for 20 minutes.
d. 1 ml of N, N – diethlymethylamine (DEMA) was added to the mixture. The mixture was stirred for 30 minutes at room temperature.
e. 20 ml of hydrogen peroxide was added into the mixture slowly and stirred for 30 minutes.

Preparation of hydrogen peroxide – diesel mixture

a. 100 ml of diesel was poured into 3 – neck bottom flask.
b. 10 ml of hydrogen peroxide and emulsifier was added slowly into the flask and stirred for 30 minutes.
c. The oxygenated diesel was then filtered.
d. The steps were repeated for 20 ml, 30 ml, 40 ml, 60 ml and 80 ml of hydrogen peroxide and emulsifier.

3.2.3. Stability Test

Due to the difference in polarity between diesel and hydrogen peroxide, the mixture has the tendency to form two immiscible layers. The stability test was conducted by observing the boundary of the separating layer in the diesel. The separating immiscible layer in the mixture is formed by the undissolved hydrogen peroxide.

The separating layer in each oxygenated diesel sample was observed to have lower amount than the amount of hydrogen peroxide added. The observation shows that a certain amount of hydrogen peroxide has been dissolved in the diesel. In order to determine the amount of hydrogen peroxide dissolved in the diesel, funnel separation method was utilized as shown in Figure 3.1.

a. Oxygenated diesel sample was poured into the separation funnel.
b. It was left for 5 minutes in the funnel for the mixture to settle into two immiscible layers.
c. The separating layer of undissolved hydrogen peroxide was drained by opening the funnel slowly.
d. The separation process was ceased after the separating layer was drained.
e. The separating layer and the oxygenated diesel were weighed.
f. The steps were repeated for other samples.
g. In order to determine the stability of the mixtures, the separated oxygenated diesel samples were put under observation for any further separation.

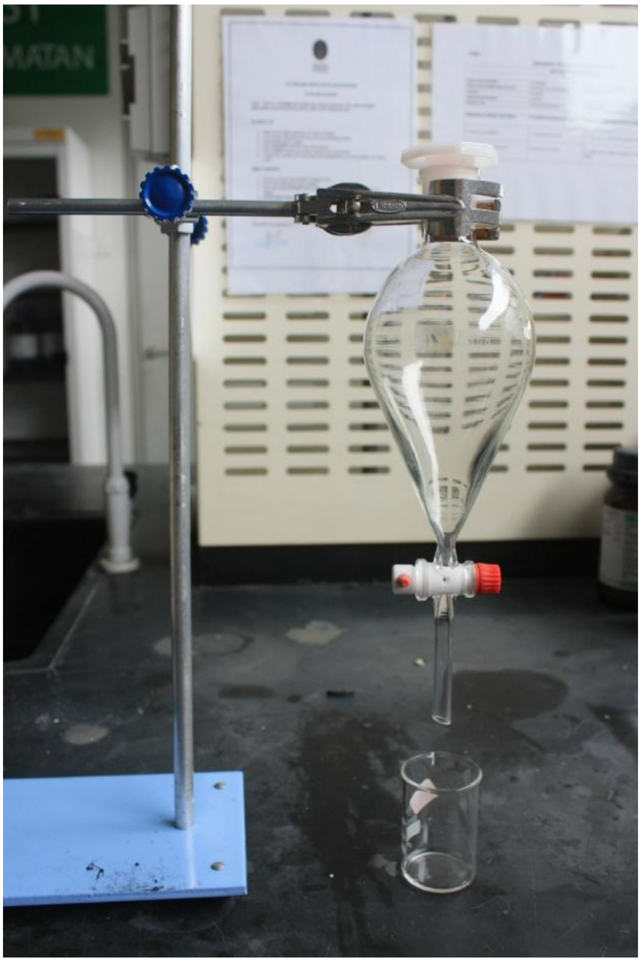

Figure 3.1.Apparatus setup for separation process.

3.2.4. Characterization of Hydrogen Peroxide – Diesel Blend

The characterization of the oxygenated diesel was performed by studying the following parameters.

a. Heating value
b. Cetane number
c. Oxygen and sulphur content
d. Flash point
e. Cloud point and pour point
f. Density
g. Viscosity
h. pH value

Heating value is a measurement of the heat energy released of a complete combustion, whereas cetane number is a measurement of the compression ignition delay of diesel. Calorific value and cetane number analysis can determine the combustion performance and quality of the oxygenated diesel. Theoretically, diesel with higher calorific value and cetane number has better combustion efficiency due to more complete combustion.

The addition of hydrogen peroxide and emulsifier alters the composition of the diesel. The composition of the oxygenated fuel, such as oxygen and sulphur content are significant for the understanding of the application of hydrogen peroxide. The composition of the diesel sample was determined using CHNS analyzer.

The flash point, cloud point and pour point of the diesel samples provide the understanding on fuel quality. Flash point provides the information of the flammability of the diesel samples. It acts as a safety indication of the diesel. Cloud point and pour point are the temperature where the diesel forms wax precipitate and losses its flow properties. By understanding the important parameters of the oxygenated diesel, the effects of hydrogen peroxide as fuel oxygenates can be determined.

3.3. Key Milestones

The major key milestones of this research are as follows.

a. Proposal defense.
b. Design of experimental work.
c. Preparation of oxygenated diesel and stability test.
d. Characterization of oxygenated diesel.
e. Final presentation.
f. Dissertation and technical paper.

3.4. Gantt Chart

No	Detail /Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
	FYP 1																
1	Selection of Project Topic																
2	Preliminary Research Work																
3	Submission of Extended Proposal						●										
4	Proposal Defence																
5	Perform experimental work													●			
6	Submission of Interim Draft Report														●		
7	Submission of Interim Report															●	
	FYP 2																
1	Preparation of oxygenated diesel.																
2	Submission of progress report.									●							
3	Characterization of oxygenated diesel.																
4	Pre – SEDEX.												●				
5	Submission of draft report.													●			
6	Submission of dissertation (soft bound).														●		
7	Submission of technical paper.														●		
8	Oral presentation.															●	
9	Submission of dissertation (hard bound).																●

● Suggested milestone

Process

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Oxygenated Diesel Samples

The oxygenated diesel samples were prepared by manipulating the concentration of emulsifier added. The emulsifier consists of 2.60 % of N, N - diethylmethylamine (DEMA), 15.20 % of N–methyl–2–pyrollidone (NMP), 1.10 % of carboxyl methyl cellulose (CMC), 0.70 % of sodium hexametaphosphate and 80.30 % of hydrogen peroxide. Table 4.0 shows the information of oxygenated diesel samples.

Table 4.0 Hydrogen peroxide content and stability status of oxygenated diesel samples.

Sample	Diesel (ml)	Emulsifier (ml)	H_2O_2 Mass %	Stability
A	100	0	0.00	Stable
B	100	10	2.53	Stable
C	100	20	3.50	Stable
D	100	40	6.34	Stable
E	100	60	10.92	Stable
F	100	80	15.75	Stable

Table 4.0 shows that the hydrogen peroxide content in the diesel increases with the increasing amount of emulsifier added for the emulsification process. Sample A is

pure diesel without any addition of hydrogen peroxide. Sample F has the highest amount of hydrogen peroxide dissolved in the diesel, 15.75 % among all the samples, whereas sample B has the lowest amount of hydrogen peroxide, 2.53%.

In the emulsification process, it is found that only certain amount of hydrogen peroxide is dissolved in the diesel. In order to determine the amount of hydrogen peroxide that has been dissolved in the diesel, separation process was performed to extract the undissolved hydrogen peroxide layer as shown in Figure 3.1. 80 ml of emulsifier originally has 62.7 ml of hydrogen peroxide. However, only 15.3 ml of hydrogen peroxide is managed to be dissolved in the diesel. For 10 ml emulsifier, the hydrogen peroxide content is 7.84 ml, but only 4.1 ml is dissolved. This phenomenon can be explained that the emulsifier has limited ability to blend hydrogen peroxide with diesel. Judging from data for all the samples, the emulsifier is observed to be able to dissolve only approximately 14 % of hydrogen peroxide added into the diesel. The other 86 % of hydrogen peroxide which is not dissolved is present as immiscible layer in the samples.

The oxygenated diesel samples have good stability. After the separation of the undissolved hydrogen peroxide from the oxygenated diesel, the sample did not show any sign of separation or presence of bubbles which is shown in the figures below.

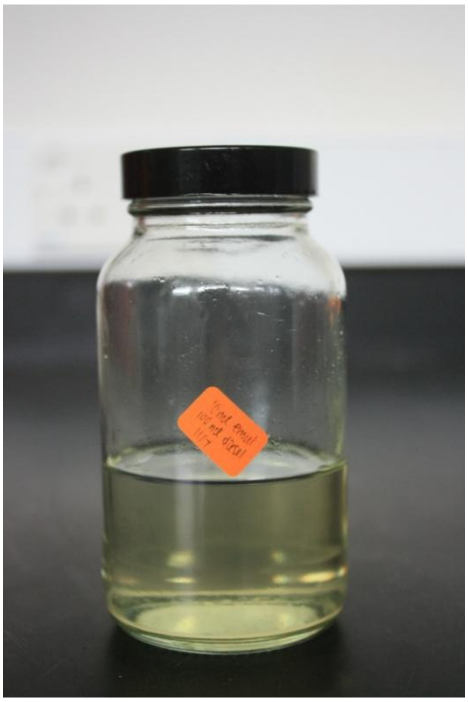

Figure 4.0.Sample B with 10 ml emulsifier (2.53% of H_2O_2).

Figure 4.1.Sample C with 20 ml emulsifier (3.50% of H_2O_2).

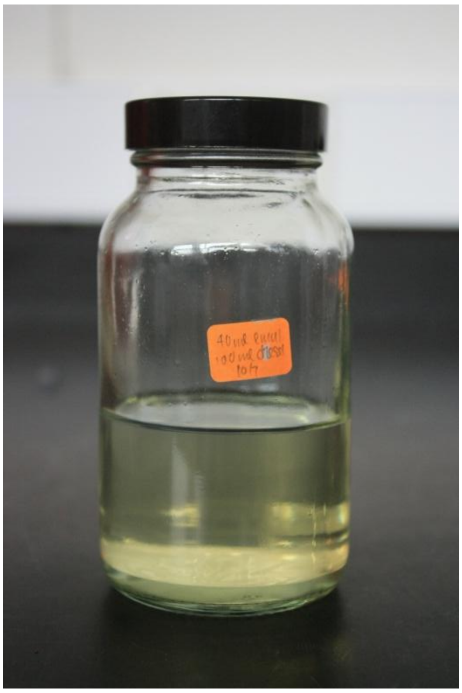

Figure 4.2.Sample D with 40 ml emulsifier (6.34% of H_2O_2).

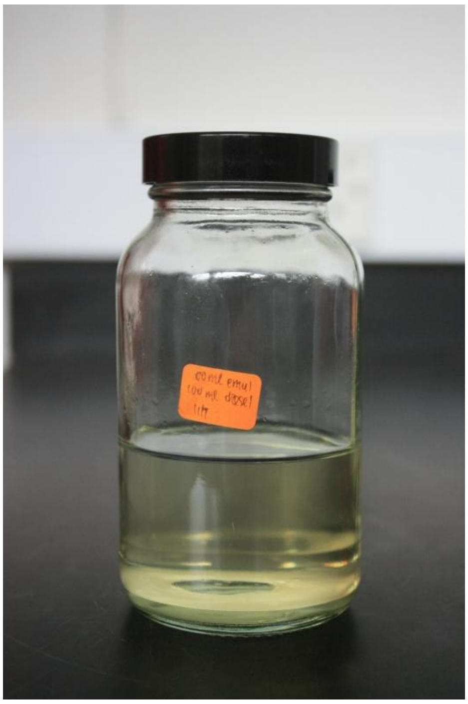

Figure 4.3 Sample E with 60 ml emulsifier (10.92% of H_2O_2).

Figure 4.4 Sample F with 80 ml emulsifier (15.75% of H_2O_2).

4.2. Density and Viscosity

It is important to study the density and viscosity of the oxygenated diesel to identify the effects of the presence of hydrogen peroxide in the diesel. Table 4.1 shows the density and viscosity of each sample.

Table 4.1 Density and viscosity of the oxygenated diesel.

Sample	Density (kg/m^3)	Viscosity (cst)
A	842.21	2.22
B	836.39	2.65
C	846.04	2.74
D	842.21	3.12
E	833.47	3.55
F	830.51	4.71

The density values of the oxygenated diesel samples are similar with the pure diesel, sample A. Pure diesel has the density of 842.21 kg/m^3. The density range of the oxygenated diesel samples lies between 830 kg/m^3 to 850 kg/m^3. The small density range is a good indication as the process of adding fuel oxygenates does not cause drastic effects on the physical properties of the diesel and simultaneously, improves the combustion performance.

However, Table 4.1 shows an increasing trend of diesel viscosity with the increasing of emulsifier added into the diesel. Pure diesel, sample A has viscosity of 2.22 cst. The addition of emulsifier causes increment in diesel viscosity. This is due to the presence of carboxyl methyl cellulose (CMC) in the emulsifier. CMC is a thickener with the function of stabilizing the emulsification process. CMC is also used to prevent the oxygen in hydrogen peroxide from escaping to the atmosphere by increasing the viscosity of the emulsifier. This causes the diesel to be more gel-like where the oxygen is trapped. From Table 4.1, sample F has the highest viscosity of 4.71 cst among all the samples because it has the highest amount of CMC. Viscosity is the measure of flow motion of a fluid. Oxygenated diesel with higher viscosity has disadvantage in term of fluid motion in the diesel engines as compared with the pure diesel.

4.3. pH Value

The pH value of the diesel changes due to the addition of hydrogen peroxide. Table 4.2 shows the pH values of the samples.

Table 4.2 pH values of the samples.

Sample	pH
A	5.09
B	5.28
C	5.46
D	5.56
E	5.67
F	5.72

Pure diesel, sample A has pH of 5.09. The pH value of the oxygenated diesel samples increase with increasing emulsifier content in the diesel. The emulsifier consists of chemicals, such as NMP, CMC and SHMP. These chemicals have higher pH value than diesel and hydrogen peroxide. NMP, CMC and SHMP have pH values from 7 to 8.5, whereas diesel and hydrogen peroxide have pH values of 5 and 3.3 respectively. The addition of the emulsifier neutralizes the acidity of oxygenated diesel. The higher the amount of emulsifier added into the diesel, the higher the pH value of the oxygenated diesel. The application of emulsifier increases the pH from 5.09 to 5.72.

4.4. Oxygen and Sulphur Content

The function of fuel oxygenates is to increase the oxygen content of the fuel to promote more complete and better combustion. The oxygen and sulphur content of the samples are significant parameters to measure the quality of the diesel. Figure 4.5 shows the oxygen and sulphur content of the pure and oxygenated diesel.

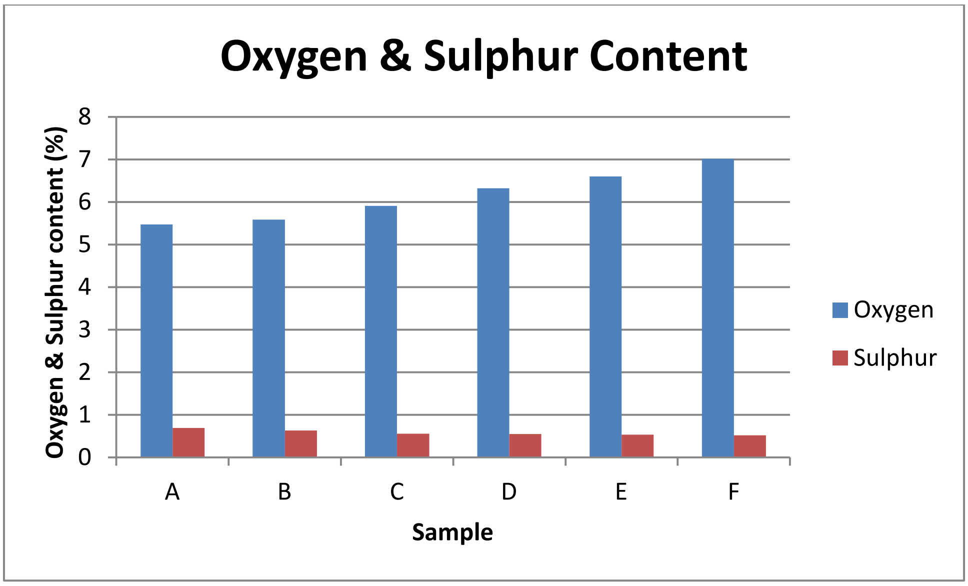

Figure 4.5. Oxygen and sulphur content of the samples.

Figure 4.5 shows an increasing trend for the oxygen mass percentage in the samples. Sample A, the pure diesel has 5.467 % of oxygen which is the control of the analysis. Sample F with 15.75 % of hydrogen peroxide has the highest mass percentage of oxygen, 7.012 %, whereas sample B with 2.53 % of hydrogen peroxide has the lowest mass percentage of oxygen, 5.587 %. Samples C, D, E with 3.50 %, 6.34 % and 10.92 % of hydrogen peroxide have 5.906 %, 6.323 % and 6.598 % of oxygen in mass basis respectively. The chart shows a steady increment of oxygen content in the diesel as the amount hydrogen peroxide added increase. This has proven the function of hydrogen peroxide as fuel oxygenates to increase the oxygen content in the diesel. The increasing of oxygen content results in more complete combustion of diesel especially in compression combustion. Simultaneously, the addition of oxygen content in the oxygenated diesel also reduces the emission of greenhouse gases which will be discussed in cetane number section.

One of the biggest disadvantages of using diesel is the sulphur content. Figure 4.5 also shows an opposite trend for sulphur content in the samples. The sulphur content of the samples decreases with the increasing amount of emulsifier added. The sulphur content of the pure diesel is 0.69 %. The sample F with 80 ml of emulsifier added has 0.516 % of sulphur which is the lowest among all. The sulphur contents of samples B, C, D and E are 0.632 %, 0.553%, 0.544% and 0.531% respectively. The sulphur content of the diesel reduces due to the usage of sodium hexametaphosphate, SHMP and carboxyl methyl cellulose, CMC. During the emulsification process, the SHMP strips the sulphur from diesel. Next, CMC traps the sulphur in the residue during filtration and hence, the sulphur content in the oxygenated diesel is lower than the pure diesel. The reduction of sulphur content in the oxygenated diesel is a good improvement as the emission of sulphur dioxide is reduced simultaneously. Reduction of the sulphur content in oxygenated diesel is a major improvement for the current diesel. The objective of harmful gasses reduction of the oxygenated diesel is achieved.

4.5. Cetane Number

Cetane number is a measurement of time taken for diesel to ignite after injection. It is used to determine the compression combustion quality of diesel in the engine. Figure 4.6 shows the trend of cetane number of each oxygenated diesel samples.

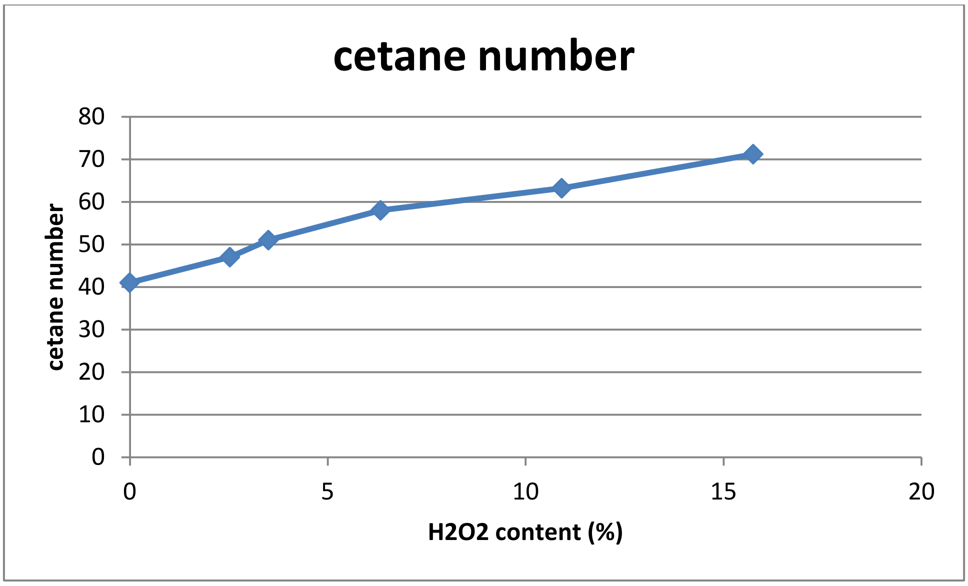

Figure 4.6.Cetane number versus hydrogen peroxide content graph.

Figure 4.6 shows an increasing trend of cetane number with increasing emulsifier added into the diesel. Pure diesel has the cetane number of 41, which serves as the control of the experiment. Sample B with 2.53% of hydrogen peroxide has cetane number of 47 which is the lowest among the oxygenated diesel samples. Sample F with 15.75% of hydrogen peroxide has the highest cetane number of 71.2. The increasing trend of cetance number shows that the addition of hydrogen peroxide results in combustion improvement.

Higher cetane number indicates that the diesel has shorter time delay between injection and ignition in the engine. Oxygenated diesel with shorter compression ignition delay leads to more complete combustion in the diesel engine as the diesel have more time to undergo combustion. Thus, improvement in ignition delay results in less fuel loss. In addition, more complete combustion process of the oxygenated diesel decreases the emission of harmful greenhouse gases, such as carbon monoxide and NOx.

The addition of hydrogen peroxide as fuel oxygenates improves the combustion quality of the diesel by increasing the cetane number. Improvement in cetane number also eases the process of starting an engine and provides smoother and better engine running on road. For example, most of the vehicles have problems of starting the engine in the morning due to the cold surrounding. Oxygenated diesel with higher cetane number is easier to undergo compressible ignition in the engine as compared with the pure diesel.

4.6. Heating Value

Heating value is a measure of the quantity of heat released by the combustion process of fuel. It is used to determine the fuel combustion performance. Theoretically, the higher the heating value, the combustion process is said to be have better combustion performance due to higher energy released. Figure 4.7 shows the heating values of the oxygenated diesel samples.

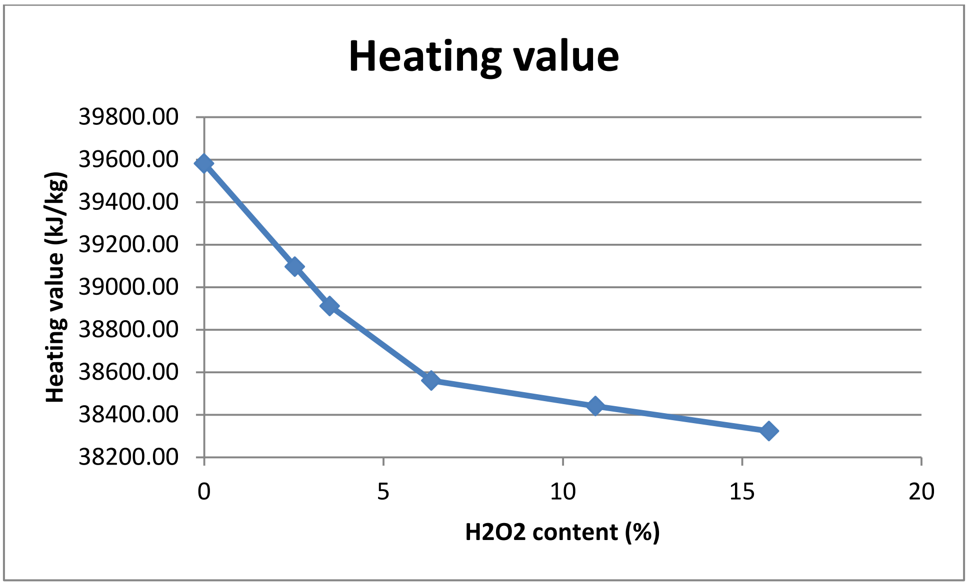

Figure 4.7. Heating value versus hydrogen peroxide content graph.

The heating values are obtained by using the formula below (Channiwala, 2001).

$$HHV = 0.3491\,C + 1.1783\,H + 0.1005\,S - 0.1034\,O - 0.0151\ - 0.0211\,A\ (\frac{MJ}{kg})$$

where,

C = carbon mass percentage

H = hydrogen mass percentage

S = sulphur mass percentage

O = oxygen mass percentage

N = nitrogen mass percentage

A = ash mass percentage

The calculation has the absolute error of 1.45 %. The values of C, H, N, S and O are obtained using CHNS equipment. Ash is assumed to be absent in the sample as the samples are all liquid fuels.

Figure 4.7 shows a decreasing trend of heating value of the samples. Pure diesel has the heating value of 35,581 kJ/kg. Sample B with 2.53% of hydrogen peroxide has heating value of 39,095 kJ/kg which is lower than the pure diesel, whereas, sample F with 15.75% of hydrogen peroxide has the lowest heating value of 38,322 kJ/kg. The decrement in heating values of the samples is declining as the amount of hydrogen peroxide added into the samples increases. The heating values of oxygenated diesel samples are lower than pure diesel due to the presence of hydrogen peroxide. Hydrogen peroxide has lower heating value of approximately 12,000 kJ/kg. The addition of hydrogen peroxide into diesel causes the drop in heating value of the diesel. In addition, hydrogen peroxide also causes the presence of excessive water content in the diesel. Hydrogen peroxide application causes the increase in oxygen content and water content in the diesel simultaneously. From the formula of HHV, it is also shown that increase in oxygen content reduces the heating value. This results in the samples with higher hydrogen peroxide amount have lower heating value. The drop in heating value is a disadvantage to oxygenated diesel as it has lower energy content.

Although the heating value of oxygenated diesel is lower than diesel, the heating value is not the only factor to determine the combustion performance. The cetane number and gases emission of the oxygenated diesel samples are taken into consideration also. The presence of additional oxygen in the diesel is a tradeoff between cetane number and heating value.

4.7. Flash Point, Cloud Point and Pour Point

Flash point is the lowest temperature where the evaporation of a chemical can produce combustible vapor. Flash point is significant as it is used as a safety indicator for fuels for handling and storage. It shows the temperature where the fuel forms vapor which is sufficient to support combustion. Cloud point and pour point are temperature measurement for the fuels too. Cloud point is the temperature where the crystallization of wax started in the diesel, whereas pour point is the temperature where the diesel losses its flow motion. Figure 4.7 shows the flash point, cloud point and pour point of the diesel samples.

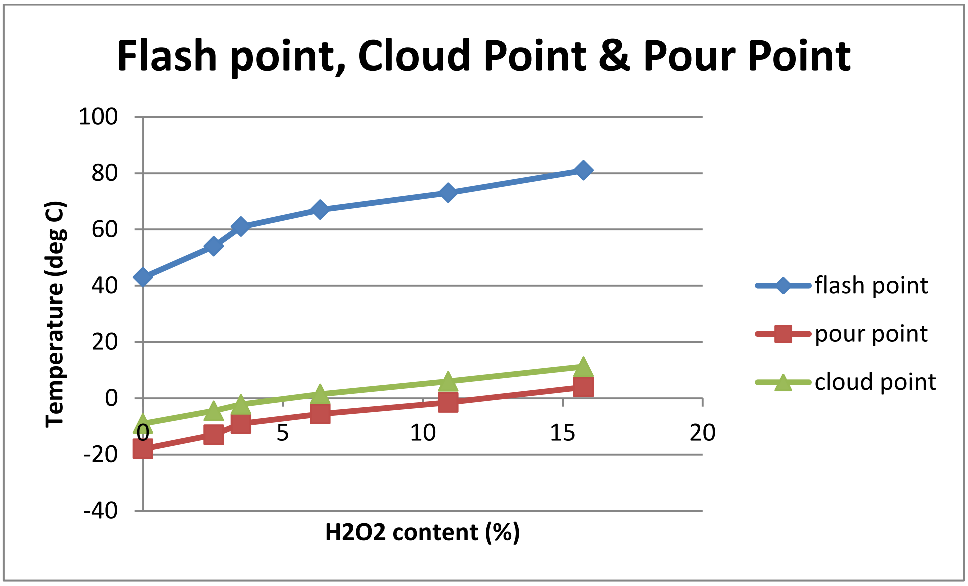

Figure 4.8. Flash point, cloud point and pour point of the samples.

Figure 4.8 shows an increasing trend of the flash point of the samples. Pure diesel has the flash point at 43 ℃. The addition of hydrogen peroxide into the diesel increases the flash point. Sample B with 2.53% of hydrogen peroxide has the lowest flash point of 54 ℃, whereas, Sample F with 15.75% of hydrogen peroxide has the highest flash point of 81 ℃. All of the oxygenated diesel samples have higher flash point than the pure diesel. Fuel with higher flash point is harder to form combustible vapor as compared to the fuel with lower flash point. Hence, oxygenated diesel is less flammable and it is safer for handling and storage. Higher flash point is a great advantage for oxygenated diesel.

Cloud point and pour point of the samples have the similar trend with the flash point. Pure diesel has the cloud point and pour point at -9 ℃ and -18 ℃. With the increasing amount of emulsifier added from 10 ml to 80 ml, the cloud point and pour point increase from – 4.5 ℃ to 11.2 ℃ and from -13 ℃ to 4 ℃ respectively. The addition of the emulsifier increases both of the cloud point and pour point where the oxygenated diesel forms wax precipitate and stops flowing at higher temperature. These are the downsides of oxygenated diesel where the blockage in the engine happens at higher possibility. However, the climate in Malaysia is hot and humid. The highest cloud point and pour point are 11.2 ℃ and 4 ℃. The oxygenated diesel is less likely to reach the cloud point and pour point due to the local climate. Therefore, the increment in cloud point and pour point is not a major concern.

4.8. Overview of Oxygenated Diesel

The application of hydrogen peroxide as fuel oxygenates leads to several changes of diesel properties. The hydrogen peroxide is proven to be able to increase the oxygen content from 5.47% to 7.01%. This results in the increment of oxygenated diesel cetane number from 41 to 71.2. Oxygenated diesel with higher cetane number has less ignition delay in the engine and leads to more complete combustion. Besides, the application of oxygenated diesel provides smoother engine running and reduces the environmental impacts.

In addition, the sulphur content of the oxygenated diesel is lower than the pure diesel. The reduction in sulphur content from 0.69% to 0.52% is a major improvement where the emission of sulphur dioxide can be minimized. The oxygenated diesel also has the advantage of having higher flash point than the pure diesel. Thus, the oxygenated diesel is less flammable and it is safer in handling and storage.

On the other hand, there are several disadvantages of the application of hydrogen peroxide as fuel oxygenates. The heating values of the oxygenated diesel samples are found to be lower than the pure diesel. The addition of hydrogen peroxide reduces the heating value from 39,581 kJ/kg to 38,322 kJ/kg. However, the combustion performance of a fuel is not judged solely based on heating value, the completeness of combustion process and the gasses emission are taken into consideration too. The higher cetane number has proven that the completeness of combustion of the oxygenated diesel is better than pure diesel and this also leads to less emission of carbon monoxide. It is true that pure diesel has higher calorific value of 39,581 kJ/kg, but its combustion process is not as complete as the oxygenated diesel samples due to lower cetane number. Hence, the possibility of having unburn fuel and loss of energy in pure diesel combustion is higher than oxygenated diesel. Thus, there is a tradeoff for the application of hydrogen peroxide as diesel oxygenates. By doing comparison between both parameters of cetane number and heating value, oxygenated diesel has better combustion performance despite the lower heating value.

In addition, the cloud point and pour point of the oxygenated diesel are higher than pure diesel. The oxygenated diesel losses its flow properties and forms wax precipitate more easily. But, the increment in cloud point and pour point is not a major concern due to the local climate.

Overall, the advantages of the oxygenated diesel outweigh the minor disadvantages. Although there are some tradeoffs in applying hydrogen peroxide, the oxygenated diesel has better overall combustion performance as compared with the current diesel.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1. Conclusion

The application of hydrogen peroxide as fuel oxygenates improves the performance of the diesel in several ways. Oxygenated diesel samples are found to have better combustion performance and more environmental friendly due to higher centane number.

The sulphur content of the oxygenated diesel reduces with the application of emulsifier. This results in less formation and release of sulphur dioxide into the atmosphere. In addition, oxygenated diesel with higher flash point is safer for handling and storage as it is less flammable.

Although there are a few minor disadvantages, such as lower heating value, higher cloud point and pour point, the improvements of the oxygenated fuel outweigh the disadvantages. The objective of studying the effects of applying hydrogen peroxide as fuel oxygenates is achieved.

In addition, the oxygenated diesel samples do not show any sign of separation. The good stability of the oxygenated diesel is achieved in this research with the application of emulsifier. All in all, the oxygenated diesel is proven to be stable, have better combustion performance and more environmental friendly. The objectives of the research are achieved.

5.2. Recommendation

The research can be continued with more analysis for better understanding of hydrogen peroxide as fuel oxygenates.

a. Corrosion test for the oxygenated diesel to study the effect of hydrogen peroxide. Hydrogen peroxide is a strong oxidizer. It is very reactive with the metals. Therefore, it is important to determine the effect of hydrogen peroxide on the engine material.
b. Moisture content analysis to determine the amount of water in the oxygenated diesel. Water content in the diesel has huge impact on the combustion performance. Theoretically, small amount of water in the diesel improves the combustion efficiency. However, once the water content exceeds the threshold value, it has inverse effects on the combustion performance.
c. Apply the oxygenate diesel in the diesel engine to determine the effects on the engine performance. Although the characterization of the oxygenated diesel provides the understanding on the application of hydrogen peroxide, applying the diesel in engine provides better and more accurate results to support the theoretical studies.

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