Evaluation of Oxidizer Based Emulsifier for Diesel /Hydrogen Peroxide Blend

by

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CERTIFICATION OF APPROVAL

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Approved by,

____

(Dr. Iqbal Ahmed)

UNIVERSITI TEKNOLOGI PETRONAS

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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NUR SYAZWIN BINTI SALLEHUDDIN

ABSTRACT

The emission of pollutants like black smoke, particulate matter (PM), nitrogen oxide (NOx), sulphur oxide (SOx) and carbon monoxide generated by diesel engine poses a threat to the environment and is detrimental to human health. The use of emulsified diesel has been considered to be one of the possible approaches to reduce the production of harmful diesel emissions. This research has studied on the "Evaluation of Oxidizer Based Emulsifier for Diesel /Hydrogen Peroxide Blend", which simultaneously improved the fuel economic and increased the cetane number of diesel by using oxygenated chemical. Oxidizer based emulsifier which consists of 85% hydrogen peroxide as diesel oxygenate is introduced to crude diesel by using emulsification technique to form a considerable stable emulsion during the dissociation of different nature of solvents. This paper shown an experimental result carried out to evaluate pour point, cloud point, flash point, pH value, viscosity, cetane number, calorific value and density of emulsified diesel as compare to commercial diesel. On the whole, it is concluded that the diesel consumption, NOx, SOx, CO, PM and black smoke decrease in this emulsified diesel as emulsified diesel produced promote more complete combustion.

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CHAPTER 1
INTRODUCTION

1.1 Background of study

Diesel fuel is defined as a fuel obtained from petroleum distillation that is used in diesel engines. It has a relatively low ignition temperature (540°C) and is ignited by the heat of compression. Diesel fuel is more efficient than gasoline because it contains up to 30% more energy per gallon than gasoline. Gasoline usually is rated by its octane while for diesel; it is rated by its cetane number, which indicates how easy it is to ignite and how fast it burns.

Generally, diesel engine is more efficient than a spark-ignited petrol engine having the same power output when the engines are installed in a vehicle having a similar mass. This is due to the diesel that having lower fuel consumption, roughly 40% more km travelled for an efficient turbo-diesel engine as compared to gasoline. The calorific value of diesel fuel is roughly 45.5 MJ/kg, slightly lower than petrol which is 45.8 MJ/kg. However, diesel fuel is denser than petrol and contains about 15% more energy by volume. Accounting for the difference in energy density, the overall efficiency of the diesel engine is still some 20% greater than the petrol engine, despite the diesel engine also being heavier. [1]

Diesel has its own advantages and disadvantages. [2] The pros of using diesel are; it has greater fuel economy than petrol which is up to 20-30% and better performance in term of power to pull larger and heavier load. But the problem of diesel fuel is much more related to environmental and safety issue. The public are concern regarding the air pollution released by diesel engine such as gaseous pollutants, particulate matter and an obnoxious odor. The pollutants that are emitted into the atmosphere from diesel engine such as NOx, HC, CO, SOx, CO_2, PM, black smoke and others are often transformed into other noxious material that not only damage our ecology but threaten human health as well.

As a result, efforts are underway to minimize the emissions from diesel engine which are already in operation and include a strategy like fuel reformulations. Therefore, ways to reduce the emission of pollutants by diesel-powered vehicles are worldwide importance. There are several methods to reduce emissions from diesel engines, such as improving the engine design, enhancing the maintenance of engine and fuel system and the last one is by utilizing clean alternative fuels.[3]

An emulsion has been considered as one of the possible alternative fuels to reduce emissions from diesel engines without doing any modification. An emulsion is defined as two immiscible liquids wherein droplets of one phase (the dispersed or internal phase) are encapsulated within sheets of another phase (the continuous or external phase). These liquids do not mix or are mutually only slightly soluble. [4] Thus, an emulsifying agent is essential to stabilize the dispersed phase against coalescence and to lower the surface energy of the interface of the produced droplets.

This research will focus of the emulsification process between diesel and hydrogen peroxide. There are several studies that have been done by researchers to identify the potential of hydrogen peroxide as an oxygenated chemical in diesel fuel. In hydrogen peroxide, the excess oxygen will participate to reduce the unburned hydrocarbon and NO_X. Besides, it will help on early combustion inside compressor air other than enhanced the cetane number of diesel. M. P. Ashok, C. G. Saravanan (2008)[5] claimed that the hydrogen-peroxide-added emulsified fuel shows an increase in brake thermal efficiency and a decrease in specific fuel consumption, smoke density, particulate matter, oxides of nitrogen, hydrocarbon, and carbon monoxide than the diesel fuel and the emulsified fuel.

The emulsifying agent used in this research has tendency to absorb moisture which will help hydrogen peroxide to make a bridge with diesel fuel for longer period of time. Stabilized blend of diesel and hydrogen peroxide will be attained through the prepared emulsifier by reducing the density as well as the surface tension of both liquids.

1.2 Problem statement

Diesel fuel is widely used nowadays for transportation, manufacturing, power generation, construction and also farming. It is made of a blend of crude oil components called hydrocarbon. Diesel fuel is using diesel engine or compression-ignition engine which is an internal combustion engine that uses the heat of compression to initiate combustion. [6] Internal combustion engine is significant contributors to air pollution with emission of NOx, HC, CO, SOx, CO_2, PM and black smoke which will bring a bad impact towards human health and environment.

An alternative approaches should be find to increase fuel economic and reduce harmful emission from internal combustion energy due to the predicted shortness of conventional fuels as well as environmental concern. One of the choices is to add a right amount of oxygenated chemical and emulsifying agent into diesel. This stable mixture of components is known as emulsified oxygenated-diesel.

Using hydrogen peroxide as an oxygenated-fuel to enhance the conventional diesel engine performance has been investigated by several researches and the result is very promising. Hydrogen peroxide is used to increase in brake thermal efficiency of diesel engine, reduction in exhaust emission and also reduction in specific fuel consumption. The problem comes when hydrogen peroxide properties (polar) is totally different from the diesel fuel properties (non-polar), thus make them insoluble to each other. To get a stable emulsion, an emulsifying agent is mixed together in this blend solution. But, these three different mixtures (hydrogen peroxide, diesel, and emulsifying agent) able to sustain in stable phase for only two days.[7] So, this research will try to come out with different formulation of emulsifier in order to produce an acceptable stable emulsion.

1.3 Research Objectives

The objectives of this research are:

1. To prepare an emulsifier that is able to create a bridge between diesel/H_2O_2
2. To observed the stability of emulsified diesel/H_2O_2
3. To study the properties of emulsified diesel/H_2O_2

1.4 Scope of Study

This study is different from the ordinary works done since it is compromising of both economic and environmental sections. It will analyze the physicochemical properties of emulsified diesel by adding H_2O_2 into diesel which includes:

1. The ability of gelatine to absorb and hold excess of oxygen inside the diesel and hydrogen peroxide blend
2. The solubility limit of hydroxymethane in gelatine and hydrogen peroxide solution
3. Type of emulsifier and the ratio of diesel to emulsifier to be used
4. Stability of emulsified diesel fuel
5. Characterization and comparison of emulsified oxygenated-diesel

1.5 Feasibility of the Project within Scope and Time Frame

This project is feasible within the scope identified and the time allocated. The first half of this project will be focusing on the through literature review of the related researches to see the areas of improvement and to obtain the basic understanding and knowledge about the project. After that, planning will be done in order to determine the subjects to be studied, the way to conduct experiment and the results to be collected from the experiment, with reference to the research journals studied. The second half of the project mainly focuses on conducting experiments and collected results and data. These results collected will then be analyzed and investigated critically.

In terms of scope of study, the project is feasible to be carried out in UTP as it has the required apparatus and equipment to run the experiment. The glassware and characterization equipment are also available. Furthermore, types of chemical used which are diesel, gelatin, hydrogen peroxide, hydroxymethane and acetone can be easily obtained as well. As such, this research project is feasible within the time frame and the scope of study. Strategic planning on the execution is needed for this research project to be completed on time and successfully.

CHAPTER 2
LITERATURE REVIEW

2.1 Diesel fuel

2.1.1 Diesel Fuel Uses

The term diesel fuel is referring to any fuel for a compression ignition engine or so called internal combustion engine. Diesel fuel keeps the world economy moving as it is widely used in the society. The major uses of diesel fuel are: [8]

- On-road transportation
- Construction
- Electric power generation
- Agriculture
- Rail transportation
- Marine shipping

2.1.2 Diesel Fuel Air Quality

When hydrocarbon fuel is burned with the correct amount of air in diesel engine, the benign gases that are left are water vapour, carbon dioxide, and nitrogen. However it leads to production of harmful emissions such as VOCs, CO, NOx, SO2 and also PM. Diesel engine emits PM and NOx but only small amount of CO and VOCs. According to air quality expert, it is estimated that diesel engines produce particles at about 20 times the rate of petrol engines. NOx have also been linked to serious health problems, including asthma, respiratory disease, infections and reduced lung function in children. [8]

2.1.3 Diesel Consumption

The invention of the internal combustion engine has greatly increased the demand for gasoline and diesel oil, both made from fossil fuel. Fossil fuel is the fuel formed by natural process of buried organism which typically takes million of years to form. As the demand for the fossil fuel is increasing while the supply for fossil is decreasing, an alternative fuels need to be identified. [9] Figure 1 shows 80.6% of total world energy consumption by source is make up of fossil fuels.[10]

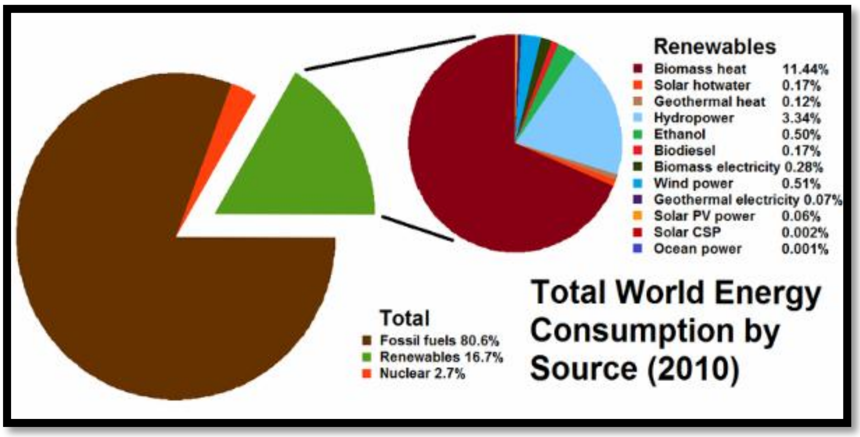


Figure 1 : Total World Energy Consumption by Source 2010[10]

Figure 2[11] represents the value for road sector diesel fuel consumption (kt of oil equivalent) in Malaysia was 4,988.00 as of 2009. As the graph below shows, over the past 38 years this indicator reached a maximum value of 5,354.00 in 2004 and a minimum value of 630.00 in 1971.

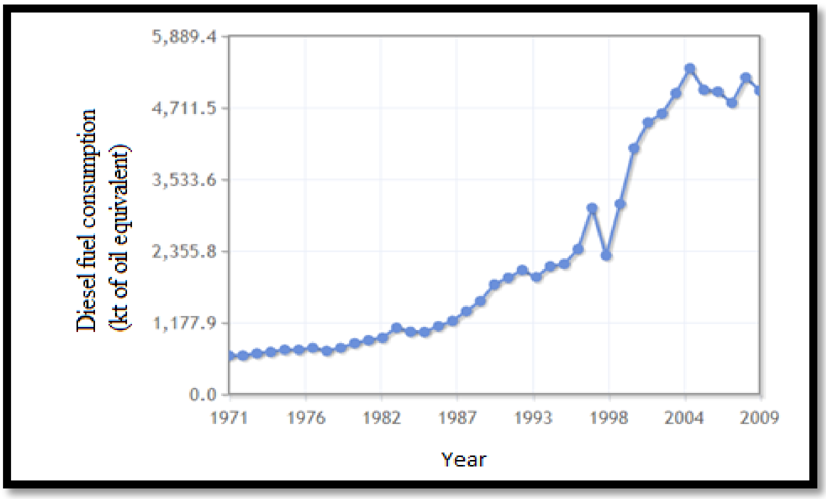


Figure 2 : Road sector diesel fuel consumption up to 2009 in Malaysia [11]

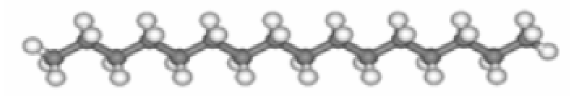
As a result of the current situation, an alternative should be identified which include:

- To enhance the fuel consumption
- To minimize the environmental impact related to the used of diesel fuel.

In this perspective, alternative oxygenated-diesel fuel blends are currently receiving renewed interest. [12]

2.1.4 Properties of diesel fuel

Table 1 : Properties of diesel fuel [13,14]

Properties	Diesel blend
Molecular formula	$C^{10}H^{15}$-$C^{15}H^{28}$ Commonly used $C^{12}H^{23}$
Molecular structure	
Molecular weight	≈200
Oxygen content	0
Specific gravity, 60° F/60° F	0.81-0.89
Cetane number	49
Density, g/cm3 @ room temperature	0.832
Boiling temperature, °F	370-650
Freezing point, °F	-40
Flash point (^{O}F)	165
Auto ignition temperature (^{O}F)	600
Viscosity, cp @ 60°F	2.6-4.1
Lower flammability limit, %	1
Upper flammability limit, %	6
Heating value	
Higher, BTU/gal @ 60°F	138,700
Lower, BTU/gal @ 60°F	128,400
Specific heat, Btu/lb °F	0.43
Energy content (Btu/gal) Lower heating value	128,450
Energy content (Btu/gal) Higher heating value	137,380

2.2 Oxygenated Chemical

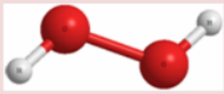
Oxygenated chemical is a chemical compound which can supply more oxygen to the fuel. It has the functions of improving the combustion performance and lowering the emission of harmful gases by promoting more complete combustion process (U.S. Environmental Protection Agency, 2009). [15] Better combustion process by oxygenated chemical leads to better fuel and engine efficiency. Currently, the commercial oxygenated chemical used in the industry are alcohols and ethers like ethanol, methyl tert-butyl ether (MTBE) and tert-butyl alcohol (TBA). [16]

Other than alcohol 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 to study the effect of introducing hydrogen peroxide in combustion of liquefied petroleum gas, LPG. The application of hydrogen peroxide increases the combustion performance and fuel efficiency. Simultaneously, hydrogen peroxide also reduces the ignition and burn off temperature [17]. Other than that, it is also found that injection of hydrogen peroxide in methane combustion can reduce the concentration of carbon monoxide and increase the production of carbon dioxide [18].

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 with a low rate.

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

Table 2 : Properties of 30 wt% Hydrogen Peroxide [19]

Molecular formula	H_2O_2
Molecular structure	
Boiling point, ºC	106
Freezing point, ºC	-26
Density @ 25ºC	1.11 g/cm3
Water solubility	Very miscible (polar solution)
Stability	Slightly unstable. May react with organic materials & metals Strong oxidizing & reducing agent
Application	Rocket propellant fuel (70-98 wt%) Water treatment

Hydrogen peroxide was blended with diesel at the concentration of 2%, 5% and 10% respectively in another research related to hydrogen peroxide-diesel mixture. Each chemical oxygenate 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 [20].

The advantages of using hydrogen peroxide instead of alcohol and esters are; it is considered as the most environmental friendly as compared to the other two, it does not reduce the viscosity and lubricity of diesel fuel and it is able to increase the cetane number and calorific value of diesel.

2.3 Emulsifying agent

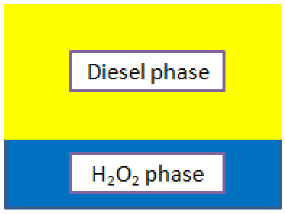


Figure 3 : Two immiscible layers between diesel and hydrogen peroxide

- Density of 30% hydrogen peroxide = 1.11 g/cm^3 at room temperature [21]
- Density of diesel = 0.832 g/cm^3 at room temperature [22]

Emulsifying agent are wetting agents that lower the surface tension of a liquid, allowing easier spreading, and lower the interfacial tension between two liquids. It is usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their "tails") and hydrophilic groups (their "heads"). Therefore, they are soluble in both organic solvents and water. [23]

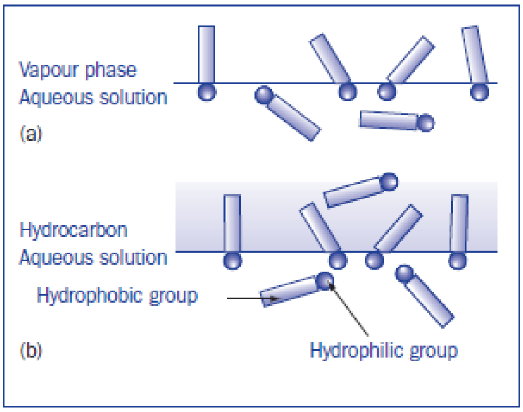


Figure 4 : Orientation of amphiphiles

(a) solution– vapours interface and (b) hydrocarbon–solution interface [21]

There are three emulsifying agents used in this project which are gelatine, acetone and hydroxymethane. All of these chemical will act to reduce the surface tension between diesel and hydrogen peroxide other than enhance the diesel properties.

2.3.1 Gelatine[24]

Gelatine has multiple functional properties which make it suitable as an emulsifying agent:

- Solubility: Gelatine swells in cold water and is completely soluble in hot water. A temperature of about 60°C is necessary in order to release the ordered structure of gelatine in its dry state.
- Emulsifying ability: The emulsifying ability of gelatine makes it possible to obtain, through mashing, a homogenous dispersal in a mixture of constituents which are not normally miscible for example, a mixture of oil and water.
- Stabilising ability: Gelling colloidal solutions and emulsions makes them stable. The stabilising power of gelatine is often greater than that of other natural polymers.

2.3.2 Hydroxymethane

An experimental investigation on effects of methanol blended diesel fuels to engine performance and emissions of a diesel engine has been done in 2011. It is proved that duel fuel operation with hydroxymethane and diesel fuel brings following advantages and disadvantages.[25] The relative advantages of hydroxymethane comparing with conventional diesel fuel include:

1. High stoichiometric fuel to air ratio
2. High oxygen content, high hydrogen to carbon ratio and low sulfur content
3. Higher latent heat of vaporization
4. Improving the combustion and reducing the soot and smoke
5. Higher cooling by evaporation of hydroxymethane blended diesel fuel relative to single diesel fuel. Thus required work input in the compression stroke is reduced.

The disadvantages are:

1. Poor ignition behaviour due to its low cetane number, high ignition temperature. Therefore it can produce longer ignition delay
2. More corrosive than diesel fuel on copper, brass, aluminum, rubber, and many plastics
3. Hydroxymethane has lower energy content and much lower flash point comparing with diesel engine

2.3.2 Acetone

Acetone is soluble in diesel and gasoline as well as water. It will emulsify or suspend water in diesel or gasoline, unless the amount of water is roughly equal to or greater than the amount of acetone, in which case, the water/acetone solution will “fall out” of solution with the fuel and drop to the bottom of the fuel tank. Water doesn’t dissolve in the fuel but rather the water dissolves in the acetone and the acetone dissolves in the fuel, to put it simply.[26] An emulsion can appear cloudy or clear depending upon the ration of fuel/acetone/water.

2.4 Diesel/hydrogen peroxide blend fuel

An alternative ways should be find to increase fuel economic and reduce harmful emission from internal combustion energy due to the predicted shortness of conventional fuels and environmental concern. One of the choices is by creating a stable emulsified diesel instead of improving the burning facilities. According to Y.K Tseng and H.C Cheng (2011)[27] there are three world commonly used to get emulsified fuel. The first method is adding the chemical additives to heavy oil, and disturbing it while the second one is to use the homogeneous machines to homogenize heavy oil and break up the asphalt sludge which is easily to deposit. The last method is to add the right amount of water and additives into heavy oil with the proper mixing procedure to get a stable emulsified fuel. Among these three methods, the last method is the most cost effective as it improve the energy efficiency by 4-6% as compare to 2-3% for the first two methods.

According to M. Nadeem et.al (2006) [28] the application of emulsified diesel has been consider being one of the possible approaches to reduce the production of diesel engine pollutants and also rate of fuel consumption without reducing the engine's performance. C.Y. Lin, L.W. Chen [29] said that the pollutants that are emitted into the atmosphere from diesel engines, such as NO_X, HC, CO, SO_X, PM, black smoke and others, are often transformed into other harmful material that not only damage ecology system but threatens human health as well.

The use of emulsified increases the brake thermal efficiency and decreases the specific fuel consumption, particulate matter, smoke density, hydrocarbon, and carbon monoxide. However, there is much rising of NOx. Thus, the addition of hydrogen peroxide to the emulsified fuel is needed to improve the performance and reduces the emissions, including NOx. This is explained by M. P. Ashok, C. G. Saravanan (2008)[5] through their research.

H M. Herwan et al. (2012) claimed that when 20% of water is added into diesel, two immiscible layers of solution are formed in a short period of time. Thus, a surfactant is added into this solution to create water in oil emulsion fuel. Unfortunately, this emulsified diesel is able to in a stable phase for one week. [7]

Table 3 : Summary of Journals and Articles

Title of Journal/Article	Summary of Findings
NOx And HC Emission Control Using Water Emulsified Diesel In Single Cylinder Diesel Engine (2010)[30]	• Water emulsified diesel fuel has a potential to improve the performance and emission characteristics of diesel engine. • The NOx and hydrocarbon emissions were found to decrease with increase in water percentage in the emulsified diesel. • Corrosion problem: Kweonha Park et al., [31] argued that water in the oil was quickly evaporated by micro-explosion into extremely tiny droplets; this would make the water droplets not to reach directly to the combustion chamber wall, so there would be no corrosion on the cylinder surface.
Experimental Investigations of Diesel Emulsions as Fuel in Small Direct Injection Compression Ignition Engines (2012) [32]	• Addition of water in the form of emulsion improves the combustion efficiency in the diesel engine as the engine speed increases. • Emulsion with 20% of water content : ▪ Has the lowest exhaust gases temperature among the five tested fuels ▪ Has the highest brake specific fuel consumption considering diesel plus water as the total volume ▪ Has the lowest CO, CO2, HC, black smoke opacity and NOx emission over all loading condition
Effect of H2/O2 addition in increasing the thermal efficiency of a diesel engine (2010) [20]	Using hydrogen as an additive to enhance the conventional diesel engine performance in term of: • Increase in brake thermal efficiency • The emission of HC,CO2 and Co decreased while the NOx emission increased

Advantage of Using Water-Emulsified Fuel on Combustion and Emission Characteristics [33]	• Water addition to the fuel extends the combustible limit especially in high fuel equivalence ratio and high atomizing air ratio side. • NOx emission is drastically reduced by adding water. • Water addition to the fuel is effective to reduce PM emission.
Experimental Study of Exhaust Emissions of W/O Emulsion Fuel in DI Single Cylinder Diesel Engine (2011) [34]	The laboratory experiment project is using 10% water mixed with diesel oil and in a few inorganic surfactant by volume ratio (10% water, 89% diesel oil, 1% surfactant) • Emission of NO and SO2 concentration by emulsion fuel are lower than base diesel oil. • Effect of adding water in oil : high oxygen contain in fuel result in higher amount of fuel can burnt in a given lower fuel consumption.
Role of Hydrogen Peroxide in a Selected Emulsified Fuel Ratio and Comparing It to Diesel Fuel (2008) [5]	(1) The use of emulsified fuel increases the brake thermal efficiency and reduces the specific fuel consumption, smoke density, and particulate matter. However, there is much rising of NO*x* (2) The addition of hydrogen peroxide to the emulsified fuel improves the performance and reduces the emissions, including NO*x*. • Higher brake thermal efficiency is achieved • Specific energy consumption is reduced • Reduction in smoke density • A significant decrease in the particulate matter value • Lower the exhaust gas temperature, carbon monoxide and hydrocarbon value

CHAPTER 3
RESEARCH METHODOLOGY

3.1 Research method

This project is mainly about producing a new emulsifier for diesel/hydrogen peroxide blend fuel. The methodology is divided into three parts which are; 1) input and 2) methodology and 3) output of the project.

3.1.1 Input

i. Problem identification with the current scenario
ii. Define study objectives to solve the problem
iii. Study on published journals on effect of adding hydrogen peroxide as an additive in diesel engine
iv. Identify the study parameters
v. Prepare all chemicals and setup of equipment required for the experimental study

3.1.2 Methodology

The fuel utilized for this project is crude diesel and 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 gelatine and acetone.

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

1. Preparation of hydrogen peroxide/diesel blend.

Acetone and gelatine are the emulsifier major components to reduce the interfacial tension between the diesel and hydrogen peroxide. Gelatine was added to secure the oxygen content of the hydrogen peroxide and stabilize the emulsification process. In addition, calcium hydroxide was added to reduce the pH value of emulsified diesel produced.

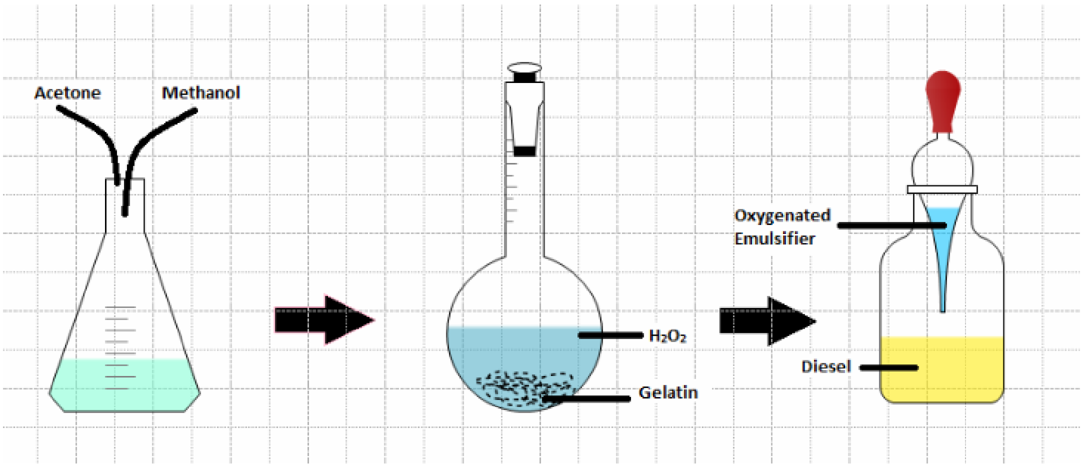


Figure 5: Experimental Setup

2. Stability test of hydrogen peroxide/diesel blend.

Hydrogen peroxide and diesel blend emulsion is obtained by mixing the two immiscible liquid in the presence of surfactant. The surfactant acted to stabilize the hydrogen peroxide droplet phase within the diesel continuous phase. The stability test aimed to observe the most optimum percentage of hydrogen peroxide in emulsifier to form homogeneous mixture with the crude diesel.

3. Characterization and study the effects 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 sulfur 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 sulfur 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.

3.1.3 Output

i. Comparative study on characterization of emulsified oxygenated-diesel based on calorific value, cetane number and economic value.
ii. Result analysis and documentation

3.2.2 Chemicals required

In the experiments that are going to be conducted, several chemicals are needed which are:

i. Diesel
ii. Gelatine
iii. Hydrogen peroxide
iv. Hydroxymethane
v. Acetone

3.2.3 Some of the equipment used

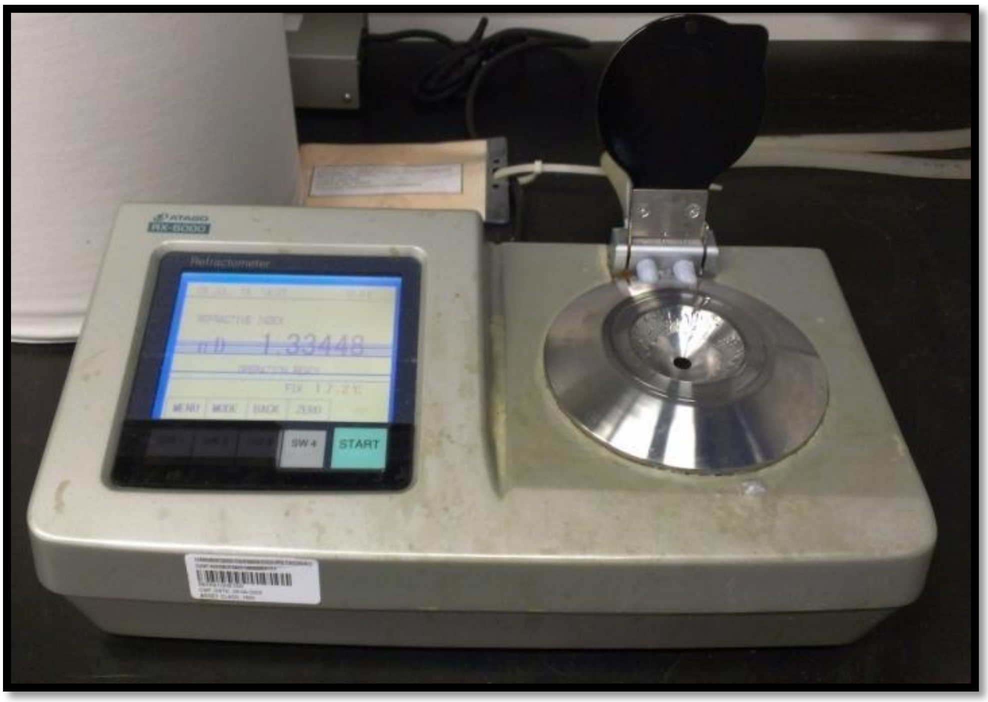


Figure 6 : Refractometer to measure refractive index

Figure 7 : Spinning drop tensiometer to measure interfacial tension

Figure 8 : Viscometer to measure viscosity

Figure 9 : Microscope to measure droplet size

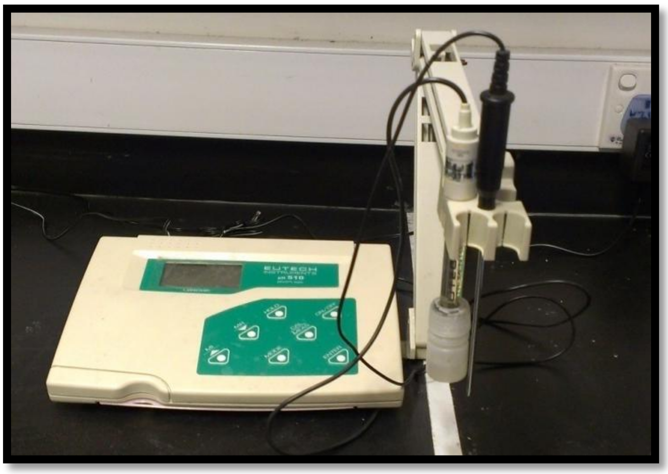


Figure 10 : pH meter to measure the pH value

3.2 Key milestone & Gantt Chart

Problem Statement and Objective of the project

Identifying the purpose of this research project

Literature Review

Gathering as much information as possible from various sources such as journals and websites

Experiment Design

Identifying the subjects that need to be investigated and the experimental procedures, as well as the chemicals needed and the collection of results

Data Analysis and Interpretation

The findings obtained are analyzed and interpreted critically. Comparison with other literature readings will also be done.

Documentation and Reporting

The whole research project will be documented and reported in detail. Recommendations or aspects that can be further improved in the future will also be discussed.

Table 4 : FYI 1 Gantt Chart and Key Milestone

NO	DETAIL WEEK	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Selection of Project Title	■	■													
2	Preliminary Research Work and Literature Review		■	■	■	■										
3	Submission of Extended Proposal Defense						●									
4	Preparation for Oral Proposal Defense							■								
5	Oral Proposal Defense Presentation									■						
6	Detailed Literature Review									■	■	■	■	■		
7	Preparation of Interim Report			■	■	■	■	■		■	■	■	■	■		
8	Submission of Interim Draft Report														●	
9	Submission of Interim Final Report															●

● Key milestone

■ Process

Table 5 : FYI II Gantt Chart and Key Milestone

NO	DETAIL WEEK	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Project Work Continues (Sample preparation)																
2	Characterizations : pH, Density, Viscosity, Droplet Size																
3	Submission of Progress Report									●							
4	Characterization : FTIR, Pour point, cloud point, flash point, CHNS, cetane number																
5	Pre-SEDEX												●				
6	Submission of Draft Report													●			
7	Submission of Dissertation (soft bound)														●		
8	Submission of Technical Paper														●		
9	Oral Presentation															●	
10	Submission of Project Dissertation (Hard Bound)																●

• Key milestone

Process

CHAPTER 4

RESULT AND DISCUSSION

4.1 Crude diesel properties

Stable emulsion is defined as the presence of only one phase as there is no separate phase between hydrogen peroxide and diesel. The emulsion is prepared by gradually adding certain amounts of emulsifier that contains hydrogen peroxide into diesel.

Diesel fuel from PETRONAS Refinery Terengganu is used in all emulsion investigations. Table 7 shows the physical properties of the crude diesel fuel used. Density, viscosity, and surface tension of diesel fuel were measured by densitometer, rotational viscometer, and the spinning drop tensiometer respectively.

Table 6 : Physical properties of PETRONAS Refinery crude diesel fuel

Density at 25^{o}C, kg/m^{3}	0.832
Kinematic viscosity, cSt	2.1
Surface Tension at 25^{o}C, mN,m	21.776
Flash point, ^{o}C	43
Cloud Point, ^{o}C	-9
Pour Point, ^{o}C	-17
Sulphur content ,%	1.043

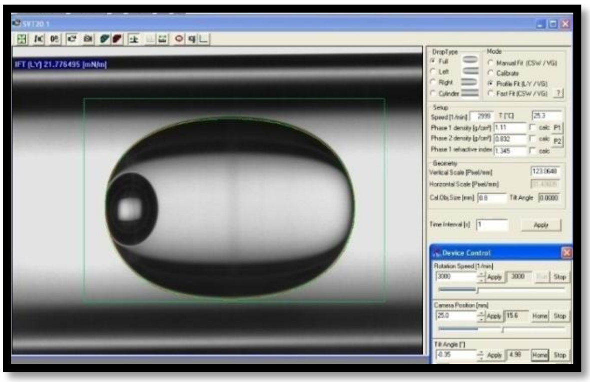


Figure 11 : Interfacial Tension Result for H_2O_2/Diesel

Hydrogen peroxide and diesel emulsion can be obtained by mixing the two immiscible fluids in the presence of an emulsifying agent. The dispersion mechanism produces a very small hydrogen peroxide droplet phase dispersed within the diesel continuous phase. An emulsifying agent is added to reduce the interfacial tension between hydrogen peroxide and diesel to produce the emulsion and to stabilize the hydrogen peroxide droplet phase within the continuous phase of diesel.

4.2 Stability Investigation

The stability of hydrogen peroxide and diesel emulsion is screening under the influence of the different emulsifier formulation. The best formulation will be used for further stability experiments.

4.2.1 Different emulsifier formulation

The emulsifier formulation is formulating using trial and error method. 15 ml of hydrogen peroxide, 1 g of gelatine and 0.1 g of Ca(OH) are kept constant for all the emulsifier formulation. The mixing speed and mixing time are fixed, which is 3 rpm and 30 minutes respectively. 2 ml of each emulsifier formulation is added into 10 ml diesel is studied in this experiment. The approximate time taken for the blend diesel and hydrogen peroxide to form two immiscible layers is noted as per below:

Table 7 : Different emulsifier formulations

Emulsifier Name	Emulsifier formulation
A	1 g Gelatine + 15 ml H_2O_2 + 5 ml Methanol + 0.1 g $Ca(OH)_2$
B	1 g Gelatine + 15 ml H_2O_2 + 3 ml Methanol + 2 ml Butanol + 0.1 g $Ca(OH)_2$
C	1 g Gelatine + 15 ml H_2O_2 + 2 ml Methanol + 1 ml Turpentine + 2 ml Acetone + 0.1 g $Ca(OH)_2$
D	1 g Gelatine + 15 ml H_2O_2 + 2 ml Methanol + 3 ml Acetone + 0.1 g $Ca(OH)_2$
E	**1 g Gelatine + 15 ml H_2O_2 + 5 ml Acetone + 0.1 g $Ca(OH)_2$**

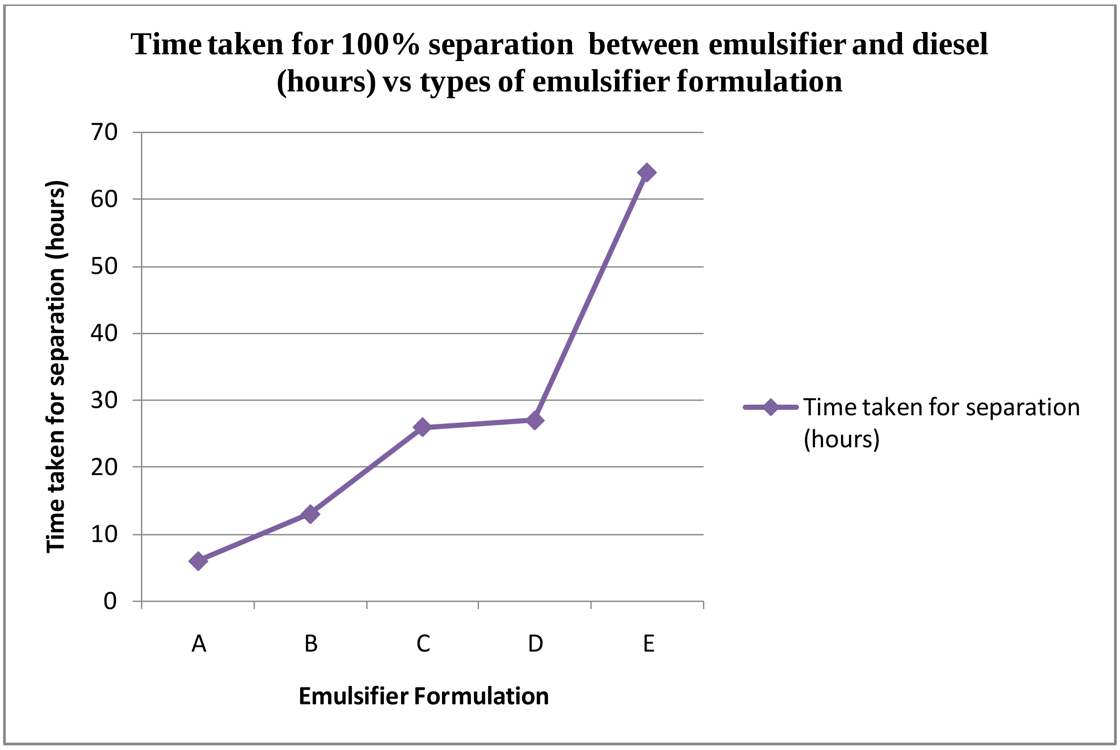


Figure 12 : Time taken for 100% separation between emulsifier and diesel (hours) vs types of emulsifier formulation

From the figure 12, 2 ml of Emulsifier E which consists of 1 g Gelatine, 15 ml H_2O_2, and 5 ml Acetone is the most stable emulsifier as compared to Emulsifier A,B,C and D. It takes about 64 hours for Emulsifier E to form two immiscible layers. Emulsifier E is few times more stable than Emulsifier A, B, C and D because there is an absent of methanol in the emulsifier formulation. From the test that is conducted, methanol is dissolved in hydrogen peroxide but it is immiscible in diesel; while acetone is dissolved in both hydrogen peroxide and diesel.

Thus, the formulation of Emulsifier E with 75% of hydrogen peroxide will be use to find the most optimum conditions to create the most stable emulsion between hydrogen peroxide and diesel.

4.2.2 Optimum volume of hydrogen peroxide to acetone

Table 8 : Optimum percentage of H_2O_2 in emulsifier

Emulsifier E	Volume of H_2O_2 (ml)	Volume of Acetone (ml)	% of H_2O_2 in emulsifier	Time taken for separation (hours)
E.1	15	5	75%	± 60
E.2	16	4	80%	± 60
E.3	**17**	**3**	**85%**	**± 60**
E.4	18	2	90%	± 45
E.5	19	1	95%	± 40

From the stability investigation, it is shown that emulsifier that contains only hydrogen peroxide and acetone is the most stable. Table 9 shows the time taken for the separation to take place when volume of hydrogen peroxide to acetone is varies. Emulsifier E.1 to E.3 with 75% to 85% of hydrogen peroxide content shows almost the same time for separation to occur which is approximately 60 hours. When the percentage of hydrogen peroxide is increased to 90% and 95%, the time taken for the emulsion to separate is decreased to 45 hours and 40 hours respectively.

As Emulsifier E.3 has the highest percentage of hydrogen peroxide with reasonable stability, 17 ml of hydrogen peroxide with 3 ml of acetone is chosen as an optimum volume for this emulsifier formulation.

4.3 Solubility limit for oxygenated emulsifier (Emulsifier E.3) to crude diesel

4.3.1 Procedures

1. Preparation of emulsifier.
   1 gram of gelatin is dissolved in 17 ml of hydrogen peroxide to hold excess oxygen content. The solution is stirred at 3 rpm and 30 minutes. Then, 3 ml of acetone is added. Figure 13 shows the oxygenated emulsifier prepared.

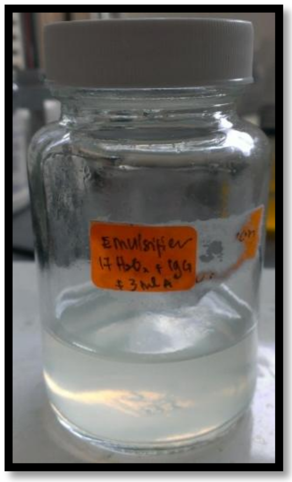


Figure 13 : 20 ml of oxygenated emulsifier with 85% H_2O_2

2. Adding oxygenated emulsifier into 100 ml crude diesel.

   Oxygenated emulsifier, E.3 is added slowly into 100 ml crude diesel. The solution is stirred at 3 rpm for 30 minutes. 1 gram of $Ca(OH)_2$ is added to reduce the pH value of the solution. The solution is continuously stirred for another 30 minutes.

3. Filtration.

   The solution is then filtered.

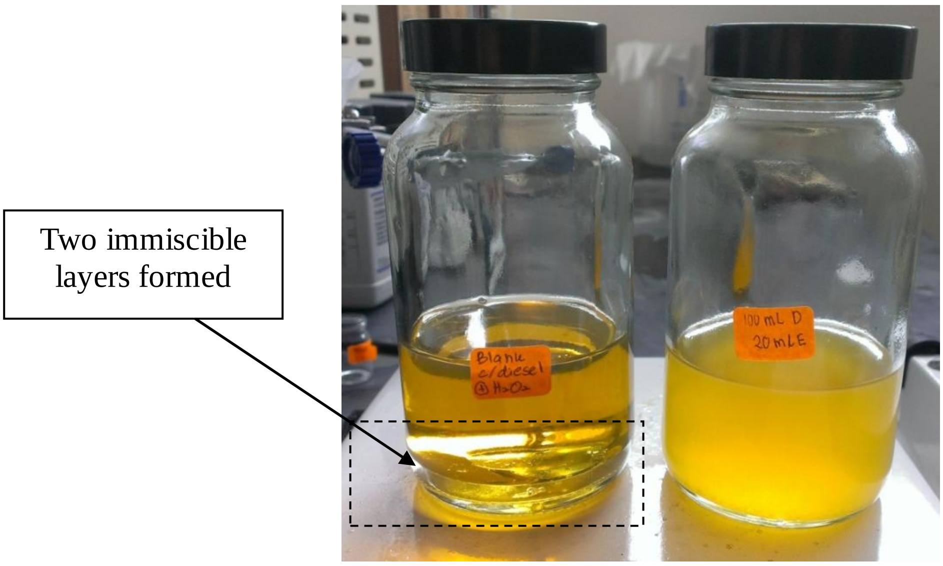


Figure 14 : Different between crude oil with hydrogen peroxide (left) and emulsified crude oil (right)

The left-hand side of figure 14 shows 20 ml hydrogen peroxide is added directly into 100 ml of crude diesel; while the right-hand side of the figure shows 20 ml of oxygenated emulsifier (85% hydrogen peroxide) in 100 m crude diesel. There are three obvious differences between these two samples:

i. Color : Emulsified diesel with 85% hydrogen peroxide in emulsifier seems to be more cloudy as compared to the crude diesel with 20 ml diesel.
ii. Direct adding hydrogen peroxide into diesel will form two immiscible layers as shown on the left side of Figure 14; while emulsified diesel formed homogeneous mixture between emulsifier with 85% hydrogen peroxide and diesel.
iii. Odor : Crude diesel with hydrogen peroxide has stronger smell than emulsified diesel.

4.4.2 Varying volume of emulsifier in 100 ml diesel

In order to get the maximum solubility of emulsifier in 100 ml diesel, five samples with different emulsifier volume are conducted. Volume of emulsifier is varies from 20 ml to 60 ml by 10 ml increment for each sample. Details of the result and observation are discussed in the table below. 85% of hydrogen peroxide in the emulsifier will be used throughout all the experiments. Percentage of emulsifier and hydrogen peroxide in 100 ml of crude diesel will be calculated as follows:

Percentage of Emulsifier in 100 ml diesel = [Weight of emulsifier/(Total Weight)]

Percentage of H_2O_2 in 100 ml diesel = [Weight of H_2O_2/(Total weight)]

Where;

Total Weight = Weight of H_2O_2+ weight of gelatine + weight of acetone + weight of 100 ml diesel + weight of $Ca(OH)_2$)]

Table 9 : Result for varying volume of emulsifier in 100 ml diesel

Sample number	Sample picture	Result
B	20ml of Emulsifier E.3	
	 Figure 15 : 20 ml Emulsifier	Content in 100 ml crude diesel : • 16.17 % Emulsifier E.3 • 14.17 % hydrogen peroxide Physical observation : • Color – cloudy yellow • Odor – less sharp than crude diesel • Very small bubbles formed after some times
C	30ml of Emulsifier E.3	
	 Figure 16 : 30 ml Emulsifier	Content in 100 ml crude diesel : • 23.08 % Emulsifier E.3 • 19.62 % hydrogen peroxide Physical observation : • Color – cloudy yellow • Odor – less sharp than crude diesel • Bubbles formed after some times
D	40ml of Emulsifier E.3	
	 Figure 17 : 40 ml Emulsifier	Content in 100 ml crude diesel : • 28.57 % Emulsifier E.3 • 24.29 % hydrogen peroxide Physical observation : • Color – cloudy yellow • Odor – less sharp than crude diesel • Two immiscible layers formed after some times

E	50ml of Emulsifier E.3	
	 Figure 18 : 50 ml Emulsifier	Content in 100 ml crude diesel : • 33.33 % Emulsifier E.3 • 28.33 % hydrogen peroxide Physical observation : • Color – cloudy yellow • Odor – less sharp than crude diesel • Two immiscible layers immediately formed
F	60ml of Emulsifier E.3	
	 Figure 19 : 60 ml Emulsifier	Content in 100 ml crude diesel : • 37.50 % Emulsifier E.3 • 31.88 % hydrogen peroxide Physical observation : • Color – cloudy yellow • Odor – less sharp than crude diesel • Two immiscible layers immediately formed

Figure 20 : Result of varying volume of emulsifier in 100 ml crude diesel

4.5 Characterization of emulsified diesel

4.5.1Morphology of emulsified diesel

Diesel and hydrogen peroxide emulsion's size is investigated by using the microscope and computer image analyzer system as in Figure 9. Five samples with different volume of emulsifier as shown in Figure 22 to 25 are used to be analyzed.

Sample	Content in 100ml crude diesel		pH	Droplet size,µm
	Emulsifier,%	H_2O_2, %		
A (Crude diesel)	-	-	5.32	-
B	16.17	14.17	5.16	0.4
C	23.08	19.62	5.13	0.7
D	28.57	24.29	5.12	1.0
E	33.33	28.33	5.13	1.4
F	37.50	31.88	5.14	3.0

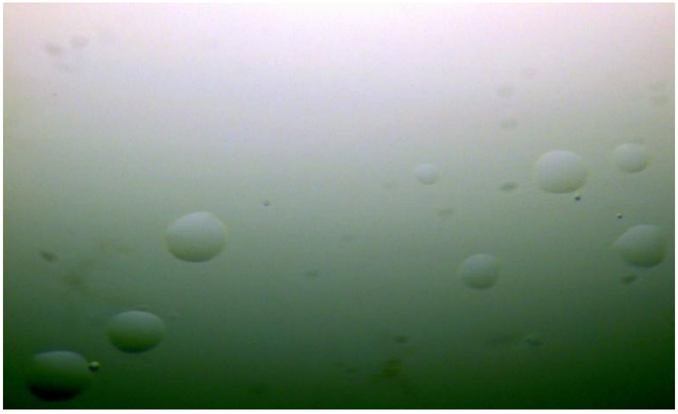


Figure 22 : Droplet Size Sample number B

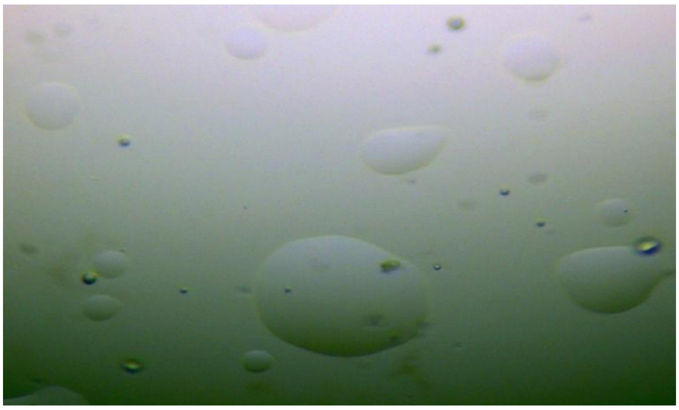


Figure 21 : Droplet Size Sample number C

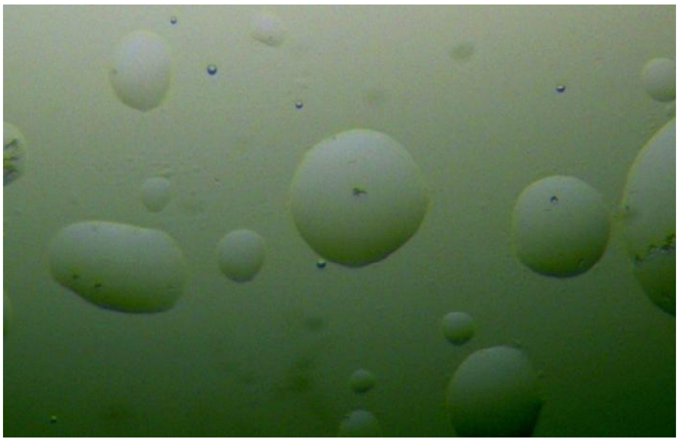


Figure 23 : Droplet Size Sample number D

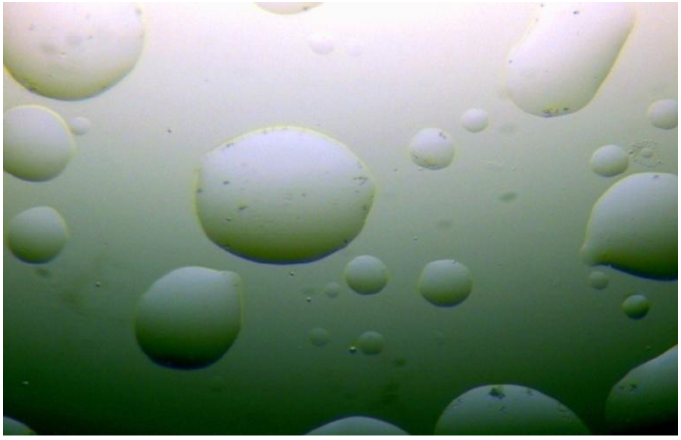


Figure 24 : Droplet Size Sample number E

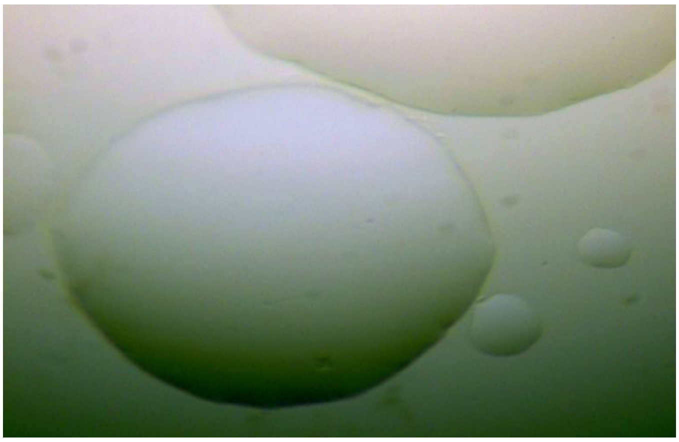


Figure 25 : Droplet Size Sample number F

Figure 22 to Figure 25 shows the variation of the droplet size in different volume of emulsifier used. Referring to the figures, the higher the percentage of emulsifier in 100 ml diesel, the bigger the size of average droplet formed. Figure 25 with the highest volume of emulsifier (60ml) gives the largest droplet size. The result indicates that the solubility of the emulsifier in diesel has achieved its limitation when the droplet size dominates the whole solution. Thus, this is the main reason of immediate separation for emulsifier and diesel when 50 ml and 60 ml of emulsifier are used. As a conclusion, average bubble size increased as percentage of H_2O_2 increased.

4.5.2 Density and surface tension of emulsified diesel

Table 10 Density and Surface Tension at room temperature (25^{o}C)

Volume of emulsifier (ml)	Density (kg/m^3)	Average Surface Tension (mN/m)
0	0.832	21.78
20	0.804	Undefined
30	0.791	Undefined
40	0.793	17.61
50	0.787	16.83
60	0.789	17.15

The density of crude diesel without emulsifier is 0.832 kg/m^3. The density is slightly increased which is about 0.02 from 30ml to 40ml emulsifier. Then, it is reduced again from 0.793 kg/m^3 to 0.787 kg/m^3 before it increased again to 0.789 kg/m^3 for 60 ml of emulsifier. Overall, the density is reduced for emulsified diesel as compared to density of crude diesel.

21.78 mN/m is obtained for the surface tension value between crude oil and hydrogen peroxide. The value becomes undefined for the sample with 20 ml and 30 ml of emulsifier in crude diesel. The spinning drop tensiometer is unable to read the surface tension values for these two samples because there is no obvious immiscible layers existed in the samples. On the whole, the surface tension for emulsified diesel is decreased.

4.5.3 Kinematic viscosity of emulsified diesel

Viscosity is a measure of a liquid's resistance to flow. High viscosity means the fuel is thick and does not flow easily. The optimum viscosity for commercial diesel is between 1.6 to 5.8 cSt. Fuel with the wrong viscosity can cause engine or fuel system damage. If the fuel is too viscous which exceeding the range, it may become difficult to pump, hard to light the burner, and difficult to handle.

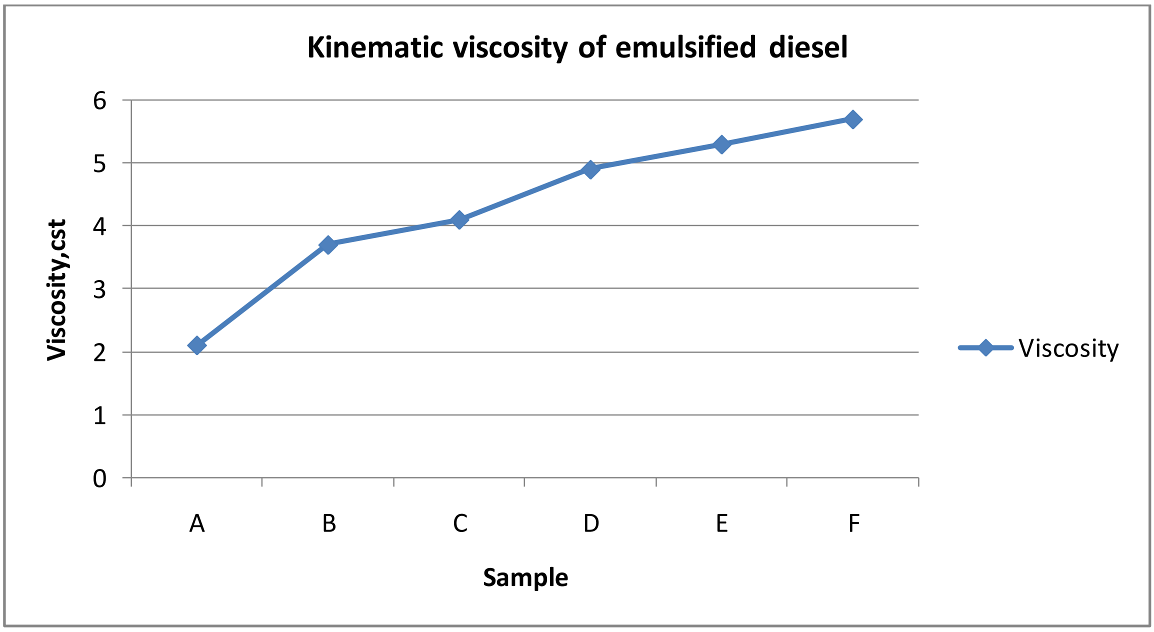


Figure 26: Kinematic viscosity value for different emulsified diesel sample

Figure 26 represents the kinematic viscosity value for the crude oil with different volume of emulsifier. Crude oil without an emulsifier gives the lowest kinematic viscosity value which is 2.1 cSt (Sample A). Once 20 ml of the emulsifier is added, the kinematic viscosity is increased to 3.7 cSt (Sample B), then increased to 4.1 cSt (Sample C), 4.9 cst (Sample D), 5.3 cSt (Sample E) and 5.7 cSt (Sample F) for every 10 ml increment of emulsifier consecutively. Kinematic viscosity of the emulsified diesel is increased due to the high viscosity of the emulsifier which is 6.2 cSt.

4.5.4 Carbon, Hydrogen, Nitrogen and Sulfur Content

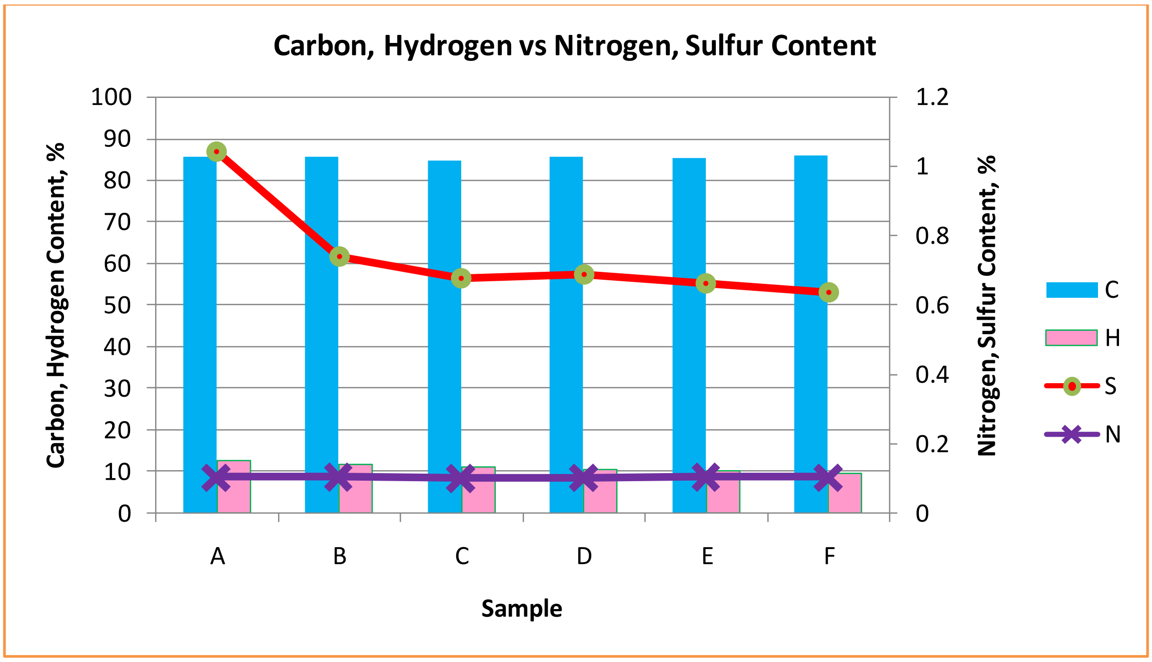


Figure 27: Carbon, Hydrogen, Nitrogen and Sulfur Content for different samples

Figure 27 shows carbon, nitrogen, hydrogen and sulfur content in crude diesel and emulsified diesel. Percentage of carbon all emulsified diesel is varies from 84% to 86% for emulsified diesel (sample B to sample F) as compared to crude diesel, 85% (sample A). So, the uses of oxygenated emulsifier do not change the carbon content in the diesel. For the hydrogen content, crude diesel consists of the highest percentage of hydrogen which is about 12.58%. Once 20ml of emulsified diesel is added in sample A, hydrogen content is decreased to 11.55%. Hydrogen content for emulsified diesel B, C, D, E and F are decreasing 11.18%, 10.38%, 10.01% and 9.401% respectively.

Apart from that, the sulfur and nitrogen content are decreasing for emulsified diesel compared to crude diesel. Sulfur in diesel fuel forms sulfur dioxide (SO_2) and sulfate (SO_4) particulate matter (PM) during combustion. SO_2 can affect the respiratory system and the functions of the lungs. Other than air quality and environmental impacts, sulfur in diesel fuel contributes to increased acid levels in the engine and causes serious damage on engine and emission control system. Therefore, using low sulfur and nitrogen diesel fuel directly reduces ambient SO_2, NO_x and fine PM levels, improves engine and after treatment system durability, and enables new technologies to be commercially viable.

4.5.5 Flash point, pour point and cloud point of emulsified diesel

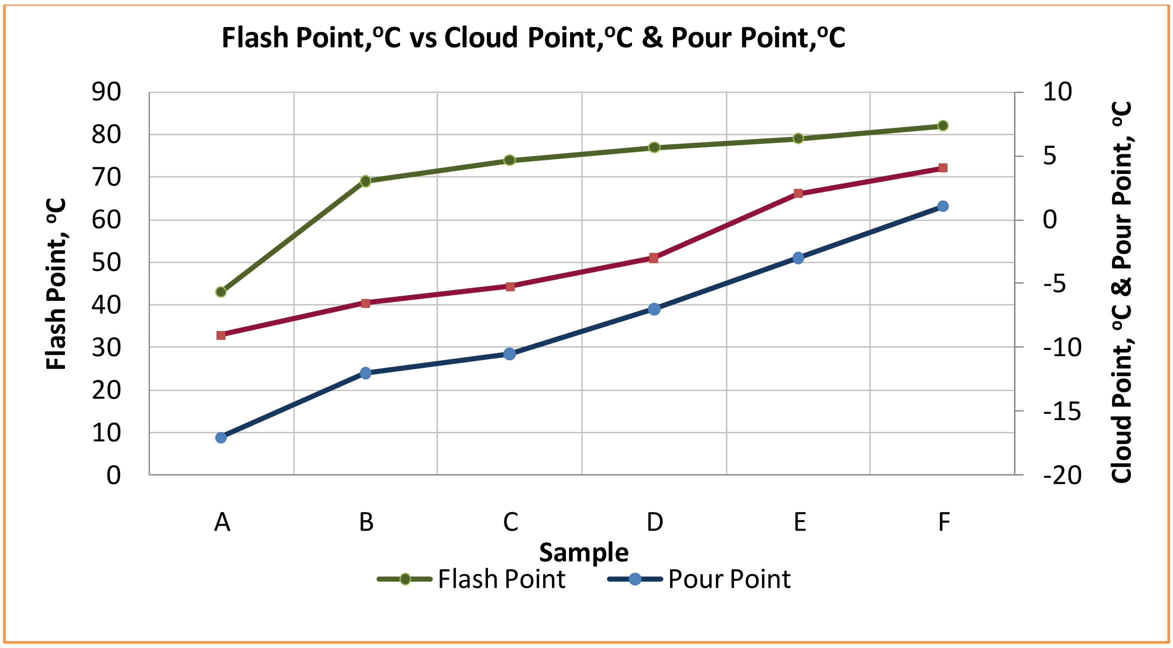


Figure 28: : Flash Point, Cloud Point and Pour Point for different samples

Flash point is the lowest temperature at which the vapour pressure of a liquid is sufficient to produce a flammable mixture in the air above the liquid surface in a vessel. It is important from both a fire safety standpoint and from the standpoint of evaporative hydrocarbon emissions. The minimum flash point required for commercial purpose is 60^0C. The flash point for emulsified diesel is increasing from 43^0C for crude diesel Sample A to 82^0C for emulsified diesel Sample F. Due to its higher flash point temperature, emulsified diesel fuel is inherently safer than crude diesel.

Cloud point is the temperature at which initial crystallization or phase separation (freezing) of the fuel begins. As diesel fuel is a mixture of many components, it does not have a well defined freezing point but solidifies over a wide temperature range. The maximum cloud point temperature for commercial diesel is 15^0C. Figure 28 shows that the cloud point for emulsified diesel is within the limit as it increased from -17^0C to 1^0C.

The pour point of a fuel is the lowest temperature at which it will pour or flow when cooled under prescribed conditions. It is a very rough indication of the lowest temperature at which fuel oil is ready to be pumped. The pour point is also increasing with respect to increased in emulsifier volume in each sample.

4.5.6 Cetane Number

Similar to the octane number seen on a retail gasoline dispenser, a cetane number rates a diesel fuel's quality of ignition. A diesel fuel's cetane number, however, is actually a measure of the fuel's ignition delay; the time period between the start of the injection of the fuel and the start of the combustion of the fuel. In general, a higher cetane fuel will have a shorter ignition delay period than a lower cetane fuel [35]

The objective of producing oxygenated diesel requires a minimum cetane number of 40 for a diesel fuel. There is considerable evidence that cetane numbers below 40 cause poor engine operation and increasing cetane number can improve engine performance and reduce emissions. Figure 29 shows Sample A which is a crude diesel consist of 43 cetane numbers. When the volume of emulsifier is increasing, cetane number is increasing significantly up to 65.

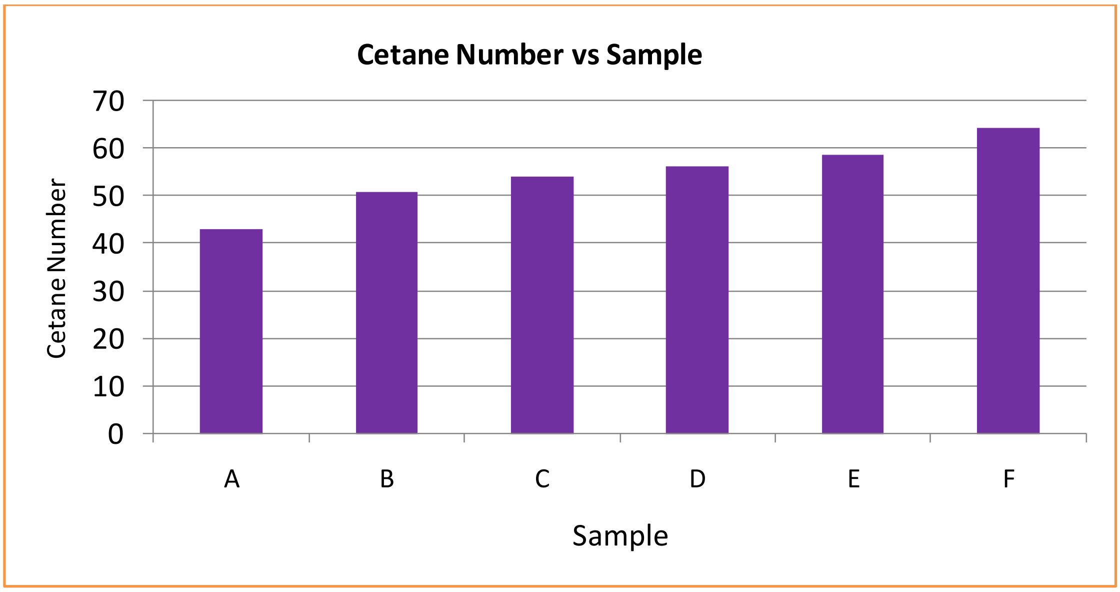


Figure 29: Value of cetane number for different samples

A higher cetane number, indicating a shorter ignition delay time which means more complete combustion of the fuel. Thus, it is believed that the emulsified diesel has the ability to improve the fuel efficiency, reduce the harmful emission as well as quicker starting by increasing the cetane number.

4.5.7 Calorific Value

Calorific value or 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 calorific value, the combustion process is said to be have better combustion efficiency due to higher energy released. Figure 30 shows the calorific values of the oxygenated diesel samples.

The calorific values are obtained by using the formula below (Channiwala, 2001). $HHV = 0.3491\,C + 1.1783\,H + 0.1005\,S - 0.1034\,O - 0.0151\,N - 0.0211\,A\ (MJkg)$

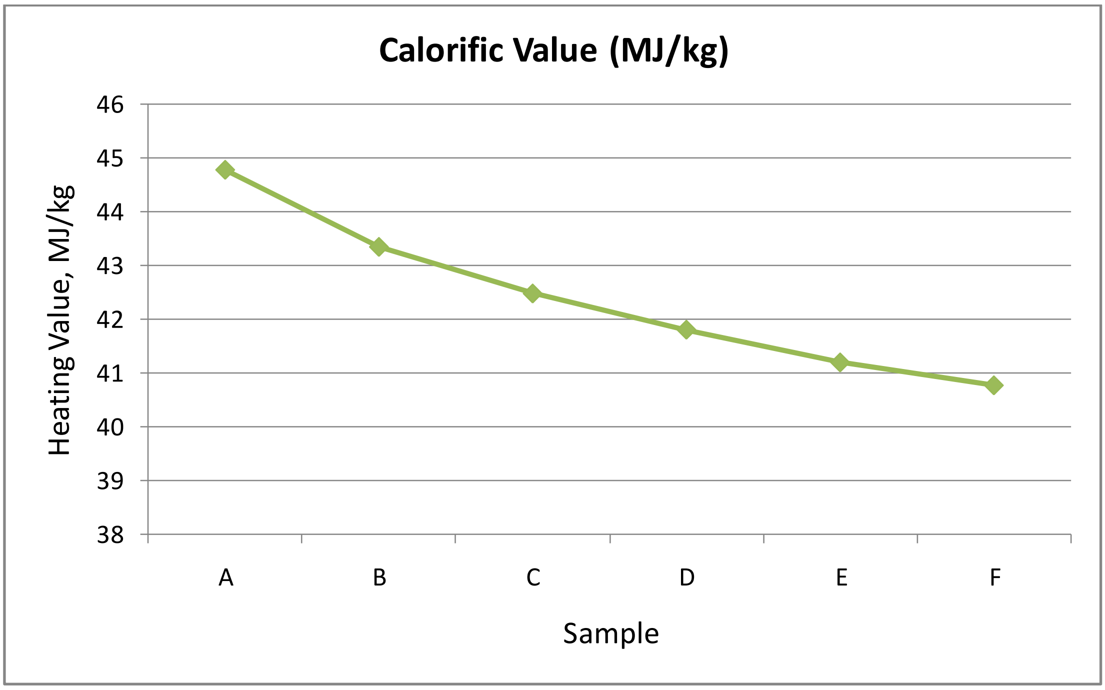


Figure 30: Calorific value of different samples

where,

C = carbon mass percentage

H = hydrogen mass percentage

S = sulfur mass percentage

O = oxygen mass percentage

N = nitrogen mass percentage

A = ash mass percentage

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 30 shows a decreasing trend of calorific value of the samples. Crude diesel has the calorific value of 44,767 kJ/kg. Sample B with 20ml of emulsifier has calorific value of 43,340 kJ/kg which is lower than the crude diesel, whereas, the sample of 60 ml emulsifier has the lowest calorific value of 40,777 kJ/kg. The decrement in calorific values of the samples is declining as the amount of emulsifier added into the samples. Calorific values of oxygenated diesel samples are lower than crude diesel is due to the presence of excessive water content as water is not a combustible molecule. The addition of hydrogen peroxide 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 calorific value. This results in the samples with higher hydrogen peroxide amount have lower calorific value. The drop in calorific value is a disadvantage to oxygenated diesel as it has lower energy content.

Although the calorific value of oxygenated diesel is lower than crude diesel, it is still higher than the commercial diesel which is 39,581 kJ/kg. Besides, the calorific 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 calorific value.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In conclusion, this project served to enhance the research and development of the non-renewable energy sources towards the sustainability of energy. In this context, oxygenated diesel fuel is gaining more significance as an alternative in view of the global depletion of petroleum. Diesel/hydrogen peroxide blend fuel through emulsification process can be promising substitute to the conventional diesel fuels that we are heavily depending on as it is able to increase cetane number of diesel without altering its properties, reduce main fuel consumption and reduce CO and NOx emission.

Study of potential mixture of chemical compounds (acetone, hydroxymethane and gelatine) that are able to reduce the surface tension as well as density, and increase the solubility between two immiscible layers will result in considerable stable emulsion of diesel and hydrogen peroxide blend. An emulsifier with 85% hydrogen peroxide, 18 % of acetone and 2 % of gelatin is the most stable emulsifier created in this experiment. Then, the solubility test is run by using different volume of emulsifier in 100 ml of diesel. The oxygenated diesel is characterized and compared with the properties of crude diesel. Besides, attempt will be given in trying to analyze the results and data obtain in order to further comprehend the insight producing the most stable oxygenated-emulsifier for diesel. The results for characterization are as follows:

i. Morphology test of emulsified diesel. Average bubble size increased as volume of emulsifier in the sample increased.
ii. Density and surface tension for emulsified diesel is lower as compared to crude diesel.

iii. Kinematic viscosity of the emulsified diesel is increased due to the high viscosity of the emulsifier which is 6.2 cSt, but it is still within the range for commercial diesel.

iv. Carbon, Hydrogen, Nitrogen, Sulfur content. Emulsified diesel does not change the percentage of Carbon content as it varies from 84% to 86% compare to crude diesel which id 85%. Sulfur and nitrogen content are decreasing for emulsified diesel compared to crude diesel thus reduced the emission of SOx and NOx.

v. Pour point, cloud point and flash point for emulsified diesel is increased within the limit of commercial diesel.

vi. Cetane number for emulsified diesel increase significantly, thus reduces the harmful emission and increase the fuel efficiency.

vii. Calorific value which is one of the factors to determine the combustion performance. The result showed that the calorific value of oxygenated diesel is lower than crude diesel (44,767 kJ/kg) but it is still higher than the commercial diesel which is 39,581 kJ/kg.

Overall, the objectives of this research are achieved.

5.2 Recommendations

As the research of diesel/hydrogen peroxide blend is indefinitely wide, various future works can be done to further expand and continue the research in various aspects. In order to commercialize the production of emulsified oxygenated-diesel in a big scale, the optimum ratio and reaction parameters has yet to be established. As such, the researches in the laboratory scale are being carried out actively in order to explore the possible and best ways to enhance the diesel consumption and minimizing the environmental impact. Some of the recommendations that can be expanded in the future are:

i. Explore the possibility of using other chemicals as an emulsifier.
ii. Detail study of the reaction mechanism of emulsifying agents; gelatine, acetone and hydroxymethane to obtain the most optimum parameters to create the most stable emulsifier.
iii. Further study on the corrosion test for diesel/H_2O_2 blend.
iv. Evaluate the density of the samples with respect to different temperature

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