

# CAB 4614 FINAL YEAR PROJECT 2

**JULY 2009** 

Development of methodology for long term stability of water-diesel emulsion

## **DISSERTATION REPORT**

Submitted in fulfilment of the requirement for the Bachelor of Engineering (Hons) Chemical Engineering

> JAFARINI BIN DAWAMI 7343

Lecturer AP DR. ISA BIN MOHD TAN

# CHEMICAL ENGINEERING DEPARTMENT UNIVERSITI TEKNOLOGI PETRONAS

#### CERTIFICATION OF APPROVAL

### Development of methodology for long term stability of water-diesel emulsion

by JAFARINI BIN DAWAMI (7343)

A project dissertation submitted to the Chemical Engineering Programme Universiti Teknologi PETRONAS in partial fulfilment of the requirement for the BACHELOR OF ENGINEERING (Hons) (CHEMICAL ENGINEERING)

Approved by,

(Assoc. Prof. Dr. Isa bin Mohd Tan)

## UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

July 2009

# 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.

## JAFARINI BIN DAWAMI

#### ABSTRACT

This project titles' long term stability of water-diesel emulsion in storage is to search for the best formula or method to ensure the stability of water-diesel emulsion in storage for a long period. Water-diesel emulsion is one of the ways to reduce diesel consumption in various sectors around the world. By reducing diesel consumption, the world can have better environment and cheaper industrial operation cost in the future. Water is immiscible in diesel and would be in two phase if both of them were mixed. But surfactant which acts as an emulsifier can be added to the mixture to emulsify the water and diesel.

The ratio of water and diesel in the mixture, the amount and types of emulsifier, the pressure and temperature during mixing, and the method use emulsify the mixture will be considered as the most important factors to be study. Experiment will be conducted to analyze the characteristic of the emulsion fuel in the storage and engine. And one of the most important characteristics of the emulsified fuel is the stability of the formation of the emulsified fuel. The emulsified fuel tends to be separating into two phases of mixture after awhile.

At the end of this project, the longest stability emulsified fuel with the optimum water-diesel ratio will be obtained with the formula. This can ensure that the emulsified diesel will be replacing the conventional diesel uses in the world today. As the conclusion, this project has the ability to help the world in facing the green house effect and the increment of operation cost.

# **TABLE OF CONTENTS**

ABSTRAC	Ti
LIST OF FIGURES.	ii
LIST OF TABLES	iv
1.0 INTRO	DUCTION
1.1	Background1
1.2	Problem Statement
1.3	Objectives
1.4	Scope of Study
2.0 LITER	ATURE REVIEW
2.1	Diesel
2.2	Water
2.3	Emulsifier
2.4	Co- surfactant
2.5	Emulsion Fuel12
2.6	Temperature and Pressure
2.7	Emulsion Optimization

3.0 METHODOLOGY/PROJECT WORK	
3.1 Project Work	19
3.2 Experiment Procedure	21
4.0 RESULTS AND DISCUSSION	
4.1 Result	22
4.2 Discussion	33
5.0 CONCLUSION	
6.0 REFERENCES	40
7.0 APPENDICES	41

# LIST OF FIGURES

1.	Figure 1: Diesel in An Erlenmeyer's Flask
2.	Figure 2: H <sub>2</sub> O Chemical Formula
3.	Figure 3: H <sub>2</sub> O Molecule Structure
4.	Figure 4: Hydrogen Bonding between Water Molecules
5.	Figure 5: A Micelle
6.	Figure 6: Emulsion Oil12
7.	Figure 7: 5-10 Microns Emulsion in 500X Magnification13
8.	Figure 8: Ternary diagram of water/surfactant/oil with phase classification regions
9.	Figure 9: Pseudo-ternary phase diagram obtained from microemulsions15
10. 11.	<ul> <li>Figure 10: Slope of turbidity ratio (R) X (-10<sup>-3</sup>) versus amount of water/wt%</li></ul>
12.	Figure 12: Slope of turbidity ratio (R) X (-10 <sup>-3</sup> ) versus HLB value
13.	. Figure 13: Final Year Project Gantts'Chart20
14.	. Figure 14: Experiment Procedure Flowchart
15.	Figure 15: Emulsion Particles Size Graph26
16.	Figure 16: Emulsion Clarity Graph27
17.	. Figure 17: Emulsion Corrosion effect Graph27

18. Figure 18: Torque of Engine at 5000rpm Graph	.28
19. Figure 19: Power of Engine at 5000rpm Graph	29
20. Figure 20 : BMEP of Engine at 5000rpm Graph	29
21. Figure 21 : SFC of Engine at 500rpm Graph	30
22. Figure 22 : Particular matter reduction Graph	31
23. Figure 23 : NOx Emission Graph	31
24. Figure 24 : CO Emission Graph	32
25. Figure 25: Ternary Diagram for Pure Surfactant (700 rpm)	33
26. Figure 26: Ternary Diagram for Surfactant 80% + Butanol 20% (700 rpm)	.34
27. Figure 27: Ternary Diagram for Pure Surfactant (3500 rpm)	36
28. Figure 28: Ternary Diagram for Surfactant 80% + Butanol 20% (3500 rpm)	.37
29. Figure 29: Preparing the aparatus and chemical for the experiment	.41
30. Figure 30: Preparing the emulsifier (Labsa) for the experiment	.41
31. Figure 31: Observing the emulsification process	42
32. Figure 32: Close look on the mixing of the water and diesel	42
33. Figure 33: Initial condition of the emulsion sample (1)	.43
34. Figure 34: Separated emulsion sample	43
35. Figure 35: Final Comparison between Pure Diesel, Macro Emulsified Diesel, Opaque Emulsified Diesel, and Micro Emulsified Diesel	, 44

# LIST OF TABLES

1. Table 1: 5% Surfactant Labsa	22
2. Table 2: 10% Surfactant Labsa	22
3. Table 3: 15% Surfactant Labsa	22
4. Table 4: 4% Surfactant Labsa + 1% Butanol (5% surfactant mix)	23
5. Table 5: 8% Surfactant Labsa + 2% Butanol (10% surfactant mix)	23
6. Table 6: 9% Surfactant Labsa + 6% Butanol (15% surfactant mix)	23
7. Table 7: 5% Surfactant Labsa	24
8. Table 8: 15% Surfactant Labsa	24
9. Table 9: 25% Surfactant Labsa	24
10. Table 10: 35% Surfactant Labsa	24
11. Table 11: 45% Surfactant Labsa	24
12. Table 12: 5% Surfactant Labsa	25
13. Table 13: 15% Surfactant Labsa	25
14. Table 14: 25% Surfactant Labsa	25
15. Table 15: 35% Surfactant Labsa	25
16. Table 16: 45% Surfactant Labsa	25
17. Table 17: Comparison of 6 selected samples (Characteristics)	26
18. Table 18: Comparison of 6 selected samples (Engine Performance)	28
19. Table 19: Comparison of 6 selected samples (Pollution emitted)	30

# **<u>1.0 INTRODUCTION</u>**

# **1.1 Background**

Diesel had been widely use in many sectors since the era of industrialization. Even the first car commercial car in the world used diesel as fuel. Diesel is kind of oil with the hydrocarbon chains of 12 carbons to 14 carbons produced by cracking the petroleum recovered from the reservoir in the earth. Diesel usually appears in reddish golden colour which also emits some pleasant odour. Diesel which has large hydrocarbon chain could produce a large amount of energy with a small amount of diesel. That is why diesel had been a popular fuel for industrialization for centuries. But diesel fuel is categorized as dirty fuel which means burning diesel could cause heavy pollution the world and it is a non-renewable fuel or energy source.

Diesel most widely uses in heavy vehicles such as lorry and truck, electric generator in the some power plants, and factories. The worlds burn few billion litres of diesel every year which emit a lot of hazardous materials and hazardous smoke. Burning diesel the engine will produced huge amount of energy, carbon monoxide (CO), carbon dioxide (CO2), nitrogen oxide (NOx), and fine particles (which seen as black smoke from the exhaust of a running diesel engine). The cost of using diesel in the world fluctuates with the current oil price. Some time the diesel price could be very high that it is increases the cost of industry operation and transportation significantly. Diesel as energy source could be replaced with other energy source available in the world such as solar energy, wind energy, kerosene, or nuclear energy but the energy obtained would not be the same as diesel and the cost might be much higher. Apart from that, there are some alternative energy sources that could harm the world more that diesel such as nuclear energy.

This project is to mix the diesel with water in certain ratio to reduce the amount diesel burn in the world every day. Using the technology of emulsification, diesel and water could be mix in one phase with the presence of surfactant or emulsifier. Emulsification process is the same as mixing process but it involved immiscible substances. Emulsification process can be done in many ways such as centrifuging, spraying droplet, membranes, and normal mixing. Emulsion divided into two categories which are macro emulsion and micro emulsion. Emulsion happen through the process of emulsification with the presence emulsifier. Emulsifier is a type of chemical generally consists of hydrophile and lipophile part. The hydrophile part will dissolve in the water and the lipophile part will dissolve in the diesel. For an easier view, the emulsifier will be like 'glue' for the water and diesel or the bonding chain for the water and diesel.

The emulsifier play a big role in emulsification process where the properties of the emulsifier will influence the strength, stability, type, and properties of the emulsion. The main property of the emulsifier that would much influence the emulsion is the Hydrophile-Lipophile Balance (HLB). This property will indicate the emulsion produce would be water-in-oil emulsion or oil-in water emulsion. For water-in-oil emulsion, the HLB value should be 4 to 6. But the stability of the emulsion not only effected by the emulsifier properties but also the emulsion ratio, the emulsification method, and the size of the emulsion particle.

At the moment, no one could give the right solution for the problem of the instability of the water in diesel emulsion. Most of the water in diesel emulsion does not form to be very stabile and most likely to separate out some water or diesel or both. The stability of the emulsion remains a question mark until today. This project not only study on the emulsification process of water in diesel but also to find out the most stabile emulsion through few emulsification methods. The emulsified diesel would reduce the world's diesel consumption, reduce the cost of operation and transportation, and reduce the air pollution in the world while maintaining the performance of the engine and generator.

#### **<u>1.2 Problem Statement</u>**

The idea of emulsified diesel had been developed by some scientists to add water into diesel. The purposes of the idea to reduce the pollution cause by burning diesel. But the problem is the emulsified diesel is hardly to be in stabile form. From Johan Sjöblom, *Emulsions and emulsion stability Edition:* 2, 2006 by Johan Sjöblom, published by Taylor & Francis Group, there is still **no absolute answer** to emulsion stability. There is **no one** had ever come with the **right solution** for long emulsion stability. The stability of emulsion remains **mystery** until today.

The emulsified diesel would most likely separate into 2 phases or 3 phases after a period of time. From journal *Rapid Evaluation of Water-in-Oil (w/o) Emulsion Stability by Turbidity Ratio Measurements* by Department of Chemical Engineering, Korea Advanced Institute of Science and Technology from ideal library, the **phase separations** of emulsions prepared from different emulsifier content measured after **30 days** at room temperature. This statement support that the emulsion will undergoes phase separation within the 30 days.

The emulsified diesel also has to achieve certain quality in order to be use in the engine such as the viscosity and the micron size of the fluid. The most stabile emulsified diesel at the moment has high viscosity and big microns size (macro emulsion) which not suitable to be use in the engine.

In this project, the author will experiment the process of emulsification of water in diesel varying the composition of the mixtures, additives and method in order to achieve the certain qualities of emulsified diesel. The author believes that there would be some method and composition which would achieve the quality.

# **1.3 Objective**

This project has few objectives that needed to be achieves which will overcome all the problems stated in the problem statement. The objectives are:-

- 1. To develop stabile diesel micro emulsion.
- 2. To develop an experiment procedure to achieved stabile diesel micro emulsion.
- 3. To test the diesel micro emulsion produced on characteristics, engine performances and pollution emission to ensure the quality set achieved.

## **<u>1.4 Scope of Study</u>**

This project will take a year or two semesters to be completed. Therefore, this project will be done in two phases. In the first phase, the project will be more on studying and researching for information on the journal and experiment report available in the net and library. This first phase was mainly to ensure the author have full understanding and strong knowledge on the emulsified diesel project and all the related issues. The first phase had been completed last semester and now in going into the second phase.

In the second phase, the experimenting process will be taken it place. Using all the information and knowledge gain from the first phase, a proper experiment will be done to achieve all the objectives stated earlier. The experiment involves preparing the emulsified diesel, testing the emulsified diesel in the engine, and performing micron test and clarity test. In the end of the project, a proper method in preparing the emulsified diesel will be draft out including the right composition of water, diesel, surfactant and other additives require. A full report will be draft out to explain the emulsified diesel including the commercial value and the beneficiary of using emulsified diesel.

#### **2.0 LITERATURE REVIEW**

#### 2.1 Diesel



Figure 1: Diesel in An Erlenmeyer's Flask

Diesel fuel is derived from crude oil. It is a mixture of hydrogen and carbon molecules. It is developed for engines that provide energy for power, flow readily in cold temperature, provide low emission, provide good fuel economy, and allow easy start-up. Power generators are run by diesel fuel. The fuel also runs diesel-powered vehicles, such as ships, buses, or trucks. Diesel engines of these types of vehicles are internal combustion engines.

Diesel is used in a high-compression engine. Air is compressed until it is heated above the autoignition temperature of diesel. Then the fuel is injected as a high pressure spray. There is no ignition source. As a result, diesel is required to have a high flash point and a low autoignition temperature. The flashpoint of a fuel is the lowest temperature at which it can form an ignitable mix with air. The high flash point in diesel fuel means that it does not burn as easily as gasoline, which is a safety factor. Too low of a flash point is a fire hazard because ignition may continue and lead to explosion. Autoignition temperature is the temperature at which a substance can be brought to flames without any sort of external force, such as a flame or spark.

In diesel engines, fuel is injected directly into the combustion chamber using a volume based metering system (in most cases). The energy content of fuel is approximately proportional to the mass of fuel injected. Thus, for a constant volume

injection system, variations in fuel density can result in variations in the energy content of the fuel injected. Consequently engine power, emissions and fuel consumption may be affected. In order to optimize the engine performance and exhaust emissions, fuel density must be controlled within a fairly narrow range.

Black smoke emissions from diesel engines occur primarily at full load operation. They normally arise when the mixture is over-rich or there is incomplete mixing of fuel and air. Limits on smoke emissions therefore limit the maximum power output of engines. Although there is some relationship between visible smoke and particulates, the optical and size characteristics, and number density of particles vary greatly, and hence the relationship between them is not well understood.

If the fuel being used is denser than the fuel for which the engine is calibrated, this may lead to generation of smoke through over fuelling. Conversely, lower density fuel should reduce the level of smoke, but will reduce power as well if the fuel injection system is not set up for that lower density. For a constant maximum power output (constant mass of fuel injected) volumetric fuel consumption will increase with lowering density and decrease with increasing density.

The volumetric quantity of fuel injected can also be used as a parameter in some advanced emission control systems such as exhaust gas re-circulation (EGR) so variations in fuel density may affect their efficiency.

24/08/09

#### 2.2 Water

Water is the most abundant molecule on Earth's surface, constituting about 70% of the Earth's surface in liquid, solid, and gaseous states. Water is the chemical substance with chemical formula  $H_2O$ : one molecule of water has two hydrogen atoms covalently bonded to a single oxygen atom. Water is a tasteless, odorless liquid at standard temperature and pressure. The color of water and ice is, intrinsically, a very light blue hue, although water appears colorless in small quantities. Ice also appears colorless, and water vapor is essentially invisible as a gas. The maximum density of water is at 3.98 °C (39.16 °F). Water becomes even less dense upon freezing, expanding 9%.



Figure 2: H<sub>2</sub>0 Chemical Formula



Figure 3: H<sub>2</sub>0 Molecule Structure

Pure water has a low electrical conductivity, but this increases significantly upon solvation of a small amount of ionic material such as sodium chloride. Water has the second highest specific heat capacity of any known chemical compound, after ammonia, as well as a high heat of vaporization (40.65 kJ mol<sup>-1</sup>), both of which are a result of the extensive hydrogen bonding between its molecules. These two unusual properties allow water to moderate Earth's climate by buffering large fluctuations in temperature.

Water is a very strong solvent, referred to as the universal solvent, dissolving many types of substances. Substances that will mix well and dissolve in water, e.g. salts, sugars, acids, alkalis, and some gases: especially oxygen, carbon dioxide (carbonation), are known as "hydrophilic" (water-loving) substances, while those that do not mix well with water (e.g. fats and oils), are known as "hydrophobic" (waterfearing) substances. Water is also miscible with many liquids, for example ethanol, in all proportions, forming a single homogeneous liquid. On the other hand, water and most oils are immiscible usually forming layers according to increasing density from the top. As a gas, water vapor is completely miscible with air. Elements which are more electropositive than hydrogen such as lithium, sodium, calcium, potassium and caesium displace hydrogen from water, forming hydroxides. Being a flammable gas, the hydrogen given off is dangerous and the reaction of water with the more electropositive of these elements is violently explosive.



Figure 4: Hydrogen Bonding between Water Molecules

Water has a high surface tension caused by the weak interactions, (Van Der Waals Force) between water molecules because it is polar. The apparent elasticity caused by surface tension drives the capillary waves. Since oxygen has a higher electronegativity than hydrogen, water is a polar molecule. The oxygen has a slight negative charge while the hydrogens have a slight positive charge giving the article a strong effective dipole moment. The interactions between the different dipoles of each molecule cause a net attraction force associated with water's high amount of surface tension. Another very important force that causes the water molecules to stick to one another is the hydrogen bond. The water surface tension force can be reduced by adding some surfactant such as detergent. This will enable the water to be miscible with hydrophobic substance such as oil. Water also has high adhesion properties because of its polar nature. Capillary action refers to the tendency of water to move up a narrow tube against the force of gravity by the help of water surface tension force.

# 2.3 Emulsifier

Emulsifier is a chemical that help to form emulsion. In this project, the emulsifier is also known as surfactant. The term surfactant is a blend of "surface active agent". Surfactants are 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. The term surfactant was coined by Antara Products in 1950.

Surfactants reduce the surface tension of water by adsorbing at the liquid-gas interface. They also reduce the interfacial tension between oil and water by adsorbing at the liquid-liquid interface. Many surfactants can also assemble in the bulk solution into aggregates. Some of these aggregates are known as micelles. The concentration at which surfactants begin to form micelles is known as the critical micelle concentration or CMC. When micelles form in water, their tails form a core that is like an oil droplet, and their (ionic/polar) heads form an outer shell that maintains favorable contact with water. When surfactants assemble in oil, the aggregate is referred to as a reverse micelle. In a reverse micelle, the heads are in the core and the tails maintain favorable contact with oil. Surfactants are also often classified into four primary groups; anionic, cationic, non-ionic, and zwitterionic (dual charge).

Thermodynamics of the surfactant systems are of great importance, theoretically and practically. This is because surfactant systems represent systems between ordered and disordered states of matter. Surfactant solutions may contain an ordered phase (micelles) and a disordered phase (free surfactant molecules and/or ions in the solution).



Figure 5: A micelle - The lipophilic ends of the surfactant molecules dissolve in the oil, while the hydrophilic charged ends remain outside, shielding the rest of the hydrophobic micelle

A micelle (rarely micella, plural micellae) is an aggregate of surfactant molecules dispersed in a liquid colloid. A typical micelle in aqueous solution forms an aggregate with the hydrophilic "head" regions in contact with surrounding solvent, sequestering the hydrophobic tail regions in the micelle centre. This type of micelle is known as a normal phase micelle (oil-in-water micelle). Inverse micelles have the head groups at the centre with the tails extending out (water-in-oil micelle). Micelles are approximately spherical in shape. Other phases, including shapes such as ellipsoids, cylinders, and bilayers are also possible. The shape and size of a micelle is a function of the molecular geometry of its surfactant molecules and solution conditions such as surfactant concentration, temperature, pH, and ionic strength. The process of forming micelles is known as micellisation and forms part of the phase behaviour of many lipids according to their polymorphism. rom the book *Modern aspects of emulsion science*, 1998 by Bernard P. Binks, published by RSC Publishing, surfactant available in the market can be in **solid or liquid**. Both are almost equal. Surfactant may be **use in pair** depending on their type for example tween and span.

All surfactants or emulsifiers characteristic are greatly influence by hydrophile-lipophile balance (HLB). Different ingredient of emulsion required different value of HLB. Basicly, water-oil emulsifiers have low HLB value, oil-water emulsifiers have intermediate HLB value and solubilizing agents have high HLB value. So in this project of water-oil emulsified fuel, a surfactant with low HLB value will be used to emulsify the water in diesel and to remain them stabile in emulsion form. From journal *Rapid Evaluation of Water-in-Oil (w/o) Emulsion Stability by Turbidity Ratio Measurements* by Department of Chemical Engineering, Korea Advanced Institute of Science and Technology from ideal library, the results of the turbidity ratio measurements, the maximum stability was shown at the **6.0 of HLB**, and the stability of emulsion was **increased** with the **amount** of emulsifier. Apart from HLB value, the stability of the emulsion also depends on temperature, viscosity, specific gravity, water contents and the method of emulsification.

24/08/09

# 2.4Co-surfactant

Co-surfactant is a substance to be use along side with surfactant to increase the effectiveness of the surfactant in emulsification process. The co-surfactant also will enhance the stability of the emulsion. The co-surfactant can be either heavy metal or alcohol. The examples of heavy metal co-surfactant are Zink, potassium, and sodium. The examples of alcohol co-surfactant are propanol, butanol, and pentanol. From Johan Sjöblom, *Emulsions and emulsion stability Edition: 2*, 2006, published by Taylor & Francis Group, he stability of the emulsion could be enhance by using some additive which is called co-surfactant that will enhance the emulsification process and increase the stability of the emulsion, and the co-surfactants are usually heavy metals, alcohols and polymers. Each use for specific emulsification process

The different between co-surfactant of heavy metal and alcohol is heavy metal is slightly better co-surfactant in case of emulsion stability compared to alcohol but some heavy metal doesn't dissolved in the emulsion and needed to be separate before commercialize. The heavy metal only is a co-surfactant if the heavy metal present in the emulsion. If the heavy metal being removed, the emulsion will lost it stability drastically. Some heavy metal could be very reactive in the mixture which could lead to explosion. The heavy metal co-surfactant acts more like a catalyst for the emulsification process. Basically all alcohol can be a co-surfactant. The longer the alcohol carbon chain, the better co-surfactant the alcohol is. Alcohol co-surfactant would dissolve in the emulsion and also will prolong the stability of the emulsion.

The amount of co-surfactant in the mixture of surfactant/co-surfactant will affect the stability of the emulsion. The ratio of surfactant and co-surfactant should not exceed more than 1:1. However, the ratio of surfactant to co-surfactant depending on the carbon chain in the alcohol. The longer the carbon chain of the alcohol, the lesser amount of co-surfactant needed to be mix with the surfactant. But alcohol with longer carbon chain will be much more expensive and it will be very costly. For an alcohol of carbon chain of 3-5, the ratio of surfactant to co-surfactant vary from 7:3 to 8:2.

## 2.5 Emulsion Fuel



Figure 6: Emulsion Oil – (A) microemulsion (<10 microns) & (B) macroemulsion (>100microns)

Water-diesel emulsion is an idea to mix the water and diesel in one phase mixture. Thus, the water needs to be emulsified with diesel into one phase mixture. With this emulsified fuel, the amount of diesel burn in the engine can reduce. For example of water-diesel ratio 10-90, the amount of diesel had reduced 10% by adding 10% of water. Then the operating and transportation cost also will reduce approximately 10% as water price is very cheap and it almost free. This also will reduce the amount of harmful gas release in the air without compensating the engine performance due to the reports of experiments and analyzes done by scientists around the world. These two main points had motivated more study and research on water-diesel emulsion fuel or emulsified fuel.

Water and diesel to be mix in one phase mixture mean to emulsified water with diesel. As natural characteristic of water and diesel, water is immiscible in diesel. Thus, water need to be emulsified with diesel. But Water-diesel emulsion will not emulsified naturally especially in a big amount under atmospheric pressure and temperature. Water-diesel emulsion is very unstable and would most likely to separate into two phase. The water-diesel emulsion can be obtained by adding some emulsifier which most likely surfactants that will reduce the surface tension of the water and natural the cas of water. But this still couldn't guarantee that the emulsion will remain stable for a long period. The stability of the water-diesel emulsion is very important to ensure the commercial value and the ability to be use in the engine. The stability of the emulsion affect by few factors such as the water-diesel ratio, the micron of water

emulsified in the diesel, amount and types of emulsifier, and mixing method. At the moment, the best emulsion was 15-85 water diesel ratio using Gemini surfactant as emulsifier and the micron of water for this particular emulsion is 5 micron mixing at a speed of 3000 rpm. From journal Diesel engine performance and emission evaluation using emulsified fuels stabilized by conventional and gemini surfactants by M. Nadeem et al and Universiti Teknologi PETRONAS (UTP) from Science Direct, the ratio of oil to water 95:5,90:10,85:15, stirring intensity, 2500 rpm, mixing time 15 minutes, emulsifying temperature, 30°C, and pH value 6.0. The emulsified fuel size had to be ensured as low as possible to avoid any blockage in the filter and also to minimize incomplete burning in the engine which may lead to harmful gas emission. From journal Diesel engine performance and emission evaluation using emulsified fuels stabilized by conventional and gemini surfactants by M. Nadeem et al and Universiti Teknologi PETRONAS (UTP) from Science Direct, predetermined amount of oil, water and surfactants were introduced to an atomizer for **homogenous mixing** to produce the stable dispersed water droplets in range within 5-10 micro meter. There might be other type of surfactant to be considered apart from the conventional and Gemini surfactant.



Figure 7: 5-10 Microns Emulsion in 500X Magnification

The emulsified fuel required many others consideration such as the foaming characteristic. The emulsified fuel tends to foam during mixing. This is because the presence of the surfactant in the process. If the mixer speed use is higher than 3500 rpm, foam started to form in huge amount and the emulsified fuel being separated during mixing due the vortex force instead of centrifuge force created by the mixer.

But if the mixer speed is too slow, the mixing process couldn't break up the Van Der Waals force of the water easily. This will make the mixing of the water into the diesel incomplete and uneven which most likely to form macro emulsion which relatively instable. When this happen, the emulsified fuel will lose it quality and will be separated into two phase easily. And if the macro emulsions fuel use in the engine, it will damage the engine during combustion due the presence of water. Water will erode the engine surface as well as increase the unnecessary load onto the engine.



Figure 8: Ternary diagram of water/surfactant/oil with phase classification regions

#### 2.6 Temperature and Pressure

The process of emulsification water in diesel much influence by temperature factor. The higher the temperature the faster and better the emulsification process. High temperature will help to reduce the surface tension of the water. The temperature must not be too high otherwise the surfactant will loss it efficiency, and the diesel and alcohol use might be possible to be on fire.

Pressure does not affect the emulsification process as pressure had slight effect on liquid phase. All the materials use for the process is in liquid phase and the final product also in liquid phase. Increasing pressure will only cause difficulty and unnecessary procedure to the emulsification process.

# **2.7 Emulsion Optimization**



Figure 9: Pseudo-ternary phase diagram obtained of microemulsions. (System A) Whithout Cosurfactant (System B) Whith cosurfactant. Key: (LME) Liquid microemulsions; (GME) Gel microemulsions; (OE) Opaque emulsions; (ST) Semi-transparent emulsions; (PS) Phase separation; (O) Experimental points; Temperature  $25 \pm 0.1^{\circ}$ C.

The process of emulsification water in diesel which required the surfactant and co-surfactant need to be tuned properly. The diesel should be varying from 95/wt% to 55/wt%. The most optimum amount of diesel in the emulsion is 75/wt% with the presence of the right amount of water, surfactant, and co-surfactant.



Figure 10: Slope of turbidity ratio(R) X (-10<sup>-3</sup>) versus amount of water/wt%

The optimum amount water should be varying from 0/wt% to 25/wt%. From journal *Rapid Evaluation of Water-in-Oil (w/o) Emulsion Stability by Turbidity Ratio Measurements* by Department of Chemical Engineering, Korea Advanced Institute of Science and Technology from ideal library, the **increasing** amount of the **water** showed a **negative effect** on emulsion stability The water amount in the emulsion less than the amount supposedly to be filled up by the water because of trade-off with the amount surfactant and co-surfactant. The most optimum amount of water in the emulsion is 15/wt%. The water is insoluble in diesel and thus the emulsion needed a huge amount of surfactant mixture for emulsification.



Figure 11: Slope of turbidity ratio(R) X (-10<sup>-3</sup>) versus amount of emulsifier/wt%

The amount of surfactant mixture should vary from 5/wt% to 55/wt%. The optimum amount of surfactant mixture is 20/wt%. The exact amount of surfactant is depending on the amount of co-surfactant which the amount of co-surfactant should not be more than 50/wt% of the surfactant mixture. The ratio surfactant to co-surfactant should vary from 7:3 to 8:2. The surfactant uses for this emulsification process varying from the surfactant having HLB value of 2 to 10. The most optimum surfactant HLB value is 6 according to bar chart below.



Figure 12: Slope of turbidity ratio(R) X (-10<sup>-3</sup>) versus HLB value

The temperature gives some effect to the emulsification process especially in the mixing process. The heat up process should be on the water and not on the diesel for safety purposes. The water that was mix initially with the surfactant mixture was heat up to reduce the surface tension of the water in order to ease the emulsification process. The water was heat up to 60°C and not higher because the flash point for diesel is about 65°C. During mixing, the temperature would drop to approximately 45°C as the initial temperature of the diesel is 25°C. The mixing speed has effect on the emulsification process. If the mixing speed is too slow, the mixing process would not be even and will produce turbid emulsion. If the mixing speed is too fast, the mixing process would not be efficient and the foam will start to form due to the surfactant characteristic. The most optimum mixing speed would be 2500rpm to 3500 rpm.

# **3.0 METHODOLOGY/PROJECT WORK**

24/08/09

#### 3.1 Project Work

The main objective of this project is to develop a formula and method to obtain the most stable water-diesel emulsion for a long period of time. The projects will be done in two main phases. The first phase is information and data collection process and the second phase is experimenting and analyzing process. In the first phase, the author will collect information and data from the journal and report of experiment done by people before. With the information collected, the author could understand the characteristic of water, diesel, emulsified fuel and engine. By understanding those characteristic, the author could be able to develop a theory on how to emulsify diesel which can be use in the engine and how to prolong it stability in storage.

In the second stage which experimenting and analyzing process, the author will first use the theory develop from the information and data collection process as a stepping stone for this project. Then the author will vary the water-diesel ratio, and the amount and type of emulsifier use for emulsification process. The varying process is to obtain the most optimum ratio and most stable emulsion. The varying process will be compared with the first emulsion develop base on theory. All the emulsions developed will be tested on the diesel engine to check on the engine performance. The author will analyze the data collected from the experimenting process by draft graph. In the end, the author could be able to come out with the most optimum formula and method to emulsify the water with diesel in developing emulsified fuel.

#### Final Year Project Gantts' Chart

19

No.	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project Work Continue														
2	Submission of Progress Report 1														
3	Project Work Continue														
4	Submission of Progress Report 2														
	ŭ .														
5	Seminar (compulsory)														
5	Project work continue														
	,														
6	Poster Exhibition														
7	Submission of Dissertation (soft bound)														
	,														
8	Oral Presentation														
9	Submission of Project Dissertation (Hard Bound)														

Figure 13: Final Year Project Gantts' Chart

# **<u>3.2 Experiment Procedure</u>**

## Apparatus

Equipment:

- 1. Blade mixer capable of 4000 rpm speed
- 2. Magnetic mixer capable of 3000 rpm speed
- 3. Beakers
- 4. Containers with cover
- 5. Stirrer
- 6. Volumetric cylinders
- 7. Light intensity detector
- 8. Micron microscope
- 9. Diesel engine tester

#### **Procedure:**

Chemical:

- 1. Diesel
- 2. Water
- 3. Conventional surfactant
- 4. Butanol

PPE

- 1. Lab coat
- 2. Covered shoe
- 3. Goggle
- 4. Gloves



Figure 14: Experiment Procedure Flowchart

# **4.0 RESULT AND DISCUSSION**

# **4.1 RESULT**

## <u>At 700 rpm</u>

Pure Surfactant

Diesel (%)	Water (%)	Phase	Diesel	Water	Emulsion
			(ml)	(ml)	(ml)
90	5	OEW	50	15	35
85	10	OEW	40	15	45
80	15	OEW	25	10	65
75	20	OEW	5	10	85
70	25	OEW	50	40	10

Table 1: 5% Surfactant Labsa

Diesel (%)	Water (%)	Phase	Diesel	Water	Emulsion
			(ml)	(ml)	(ml)
85	5	OEW	5	5	90
80	10	OEW	1	2	97
75	15	OEW	2	4	94
70	20	OEW	3	5	92
65	25	OEW	3	7	90

Table 2: 10% S	Surfactant Labsa
----------------	------------------

Diesel (%)	Water (%)	Phase	Diesel	Water	Emulsion
			(ml)	(ml)	(ml)
85	0	OEW	60	15	25
80	5	OE	1	0	99
75	10	OEW	1	5	94
70	15	OEW	2	7	91
65	20	OEW	2	10	88

Table 3: 15% Surfactant Labsa

80% Surfactant

Diesel (%)	Water (%)	Phase	Diesel	Water	Emulsion
			(ml)	(ml)	(ml)
90	5	OEW	40	3	57
85	10	OE	3	0	97
80	15	OE	1	0	99
75	20	OEW	3	3	94
70	25	OEW	3	5	92

Table 4: 4% Surfactant Labsa + 1% Butanol (5% surfactant mix)

Diesel (%)	Water (%)	Phase	Diesel	Water	Emulsion
			(ml)	(ml)	(ml)
85	5	OE	25	0	75
80	10	OE	20	0	80
75	15	OEW	15	1	84
70	20	OEW	10	3	87
65	25	OEW	5	5	90

Table 5: 8% Surfactant Labsa + 2% Butanol (10% surfactant mix)

Diesel (%)	Water (%)	Phase	Diesel	Water	Emulsion
			(ml)	(ml)	(ml)
85	0	OW	95	5	0
80	5	OEW	10	3	87
75	10	OEW	5	0	95
70	15	OEW	0	5	95
65	20	OEW	5	15	80

Table 6: 12% Surfactant Labsa + 3% Butanol (15% surfactant mix)

# <u>At 3500 rpm</u>

# Pure Surfactant

Diesel (%)	Water (%)	Phase	Diesel	Water	Emulsion
			(ml)	(ml)	(ml)
90	5	Opaque	40	5	50
80	15	2 phase	78	15	2
70	25	2 phase	70 30		0
60	35	2 phase	60	40	0
50	45	2 phase	50	50	0

Table 7: 5% Surfactant Labsa

Diesel (%)	Water (%)	Phase	Diesel	Water	Emulsion
			(ml)	(ml)	(ml)
80	5	Micro	15	1	74
70	10	Micro	0	0	100
60	15	Opaque	21	3	76
50	20	2 phase	50	25	0

Table 8: 15% Surfactant Labsa

Diesel (%)	Water (%)	Phase	Diesel	Water	Emulsion
		(ml)		(ml)	(ml)
70	5	Micro	8	3	89
60	15	Macro	4	1	95
50	25	2 phase	50	50	0

Table 9: 25% Surfactant Labsa

Diesel (%)	Water (%)	Phase	Diesel	Water	Emulsion
			(ml)	(ml)	(ml)
60	5	Micro	11	3	86
50	15	2 phase	49	49	2

Table 10: 35% Surfactant Labsa

Diesel (%)	Water (%)	Phase	Diesel	Water	Emulsion
		(ml) (ml)		(ml)	
50	5	Opaque	34	37	29

Table 11: 45% Surfactant Labsa

80% Surfactant

Diesel (%)	Water (%)	Phase	Diesel	Water	Emulsion
			(ml)	(ml)	(ml)
90	5	Micro	20	2	78
80	15	Opaque	34	4	62
70	25	2 phase	70	30	0
60	35	2 phase	60	60 40	
50	45	Opaque	42	48	10

Table 12: 5% Surfactant Labsa

Diesel (%)	Water (%)	Phase	Diesel Water		Emulsion
			(ml) (ml)		(ml)
80	5	Micro	5	0	95
70	10	Micro	0	0	100
60	15	Macro	14	2	84
50	20	2 phase	50	25	0

Table 13: 15% Surfactant Labsa

Diesel (%)	Water (%)	Phase	Diesel	Water	Emulsion
			(ml) (m		(ml)
70	5	Micro	9	2	89
60	15	Macro	Macro 18		81
50	25	2 phase	50	50	0

Table 14: 25% Surfactant Labsa

Diesel (%)	Water (%)	Phase	Diesel	Water	Emulsion
			(ml)	(ml)	(ml)
60	5	Micro	10	2	88
50	15	2 phase	49	49	2

Table 15: 35% Surfactant Labsa

Diesel (%)	Water (%)	Phase	Diesel	Water	Emulsion
			(ml)	(ml)	(ml)
50	5	Opaque	34	35	31

Table 16: 45% Surfactant Labsa

#### JAFARINI BIN DAWAMI CAB 4614 – FYP 2

24/08/09

From the table and graph, the author had cut down the amount of sample needed for further quality testing to five which achieved the best quality for further testing. He author also will test pure diesel as for comparison with the emulsified diesel. The testing would be on micron test, clarity, corrosion, and engine performance.

No.	Diesel, %	Water, %	Size, microns	Clarity, %	Corrosion, mg
1	100	0	7.0	72	0.02
2	90	5	5.2	89	0.07
3	80	5	5.3	87	0.08
4	70	5	5.5	86	0.09
5	70	10	6.2	78	0.11
6	60	5	5.7	80	0.09

Table 17: Comparison of 6 selected samples (Characteristics)



Figure 15: Emulsion particles size graph



Figure 16: Emulsion Clarity Graph



Figure 17: Emulsion Corrosion Effect Graph

## JAFARINI BIN DAWAMI CAB 4614 – FYP 2

No.	Diesel, %	Water, %	Torque, Nm	Power, BHP	BMEP, Bar	SFC, g/kWh
1	100	0	74.7	49.6	5.20	350
2	90	5	73.8	48.9	5.18	358
3	80	5	73.1	48.5	5.05	368
4	70	5	72.5	47.8	4.98	373
5	70	10	70.1	46.9	4.92	387
6	60	5	71.1	47.4	4.96	378

 Table 18: Comparison of 6 selected samples (Engine Performance)



Figure 18: Torque of Engine at 5000rpm Graph



Figure 19: Power of Engine at 5000rpm Graph



Figure 20: BMEP of Engine at 5000rpm Graph



Figure 21: SFC of Engine at 5000rpm Graph

No.	Diesel, %	Water, %	Particulate matter reduction, %	NOx Emission, ppm	CO Emission, ppm
1	100	0	0	800	2200
2	90	5	38	748	2023
3	80	5	40	734	1987
4	70	5	43	728	1961
5	70	10	47	702	1918
6	60	5	50	721	1953

 Table 19: Comparison of 6 selected samples (Pollution emitted)



Figure 22: Particular matter reduction Graph





Figure 23: NOx Emission Graph



# **4.2 DISCUSSION**

<u>At 700 rpm</u>



Figure 25: Ternary Diagram for Pure Surfactant (700 rpm)

For pure surfactant of labsa, the best percentage of surfactant in the emulsification process of water in diesel is 10% of the total volume. According to the tables above, using 10% surfactant for emulsification process produce stabile emulsion with more than 90% emulsion volume of the total volume. However, pure surfactant experiment has a small region of stabile emulsion (>95% emulsion volume) which within the range of mixture of 80% diesel with 5-10% of surfactant.



Figure 26: Ternary Diagram for Surfactant 80% + Butanol 20% (700 rpm)

For 80% surfactant labsa mix with 20% butanol, there are some improvement in the 5% surfactant set. The emulsion produced turnout to be very stabile which for 80% diesel with 15% water, only 1% of diesel separated out after 60 days. Hence, by using butanol as co-surfactant could reduce the amount of surfactant use in the emulsification process. But when there are too much of butanol in the emulsification process, the emulsion produce would be unstable just like in the 10% surfactant for example. Thus, adding butanol could increase the stability of the emulsion but only valid with small amount butanol.

This 700 rpm mixer rotation speed experiment was done in 16/06/09 which last for three days. Observation been done every day for 60 days on every emulsion samples. The most critical time is within 10 days after the emulsification process. The emulsion will separated or not within the first 10 days. The separation process happens drastically in the first 10 days, and then it started to slow down and finally stop after first 15 days. These phenomena happen because the emulsification process was initially help by the centrifuge force during the mixing. In fact, the mixing process is the main process in the emulsification then the emulsifier. So whichever molecules of diesel or water that does not bind with the emulsifier are most likely to find it ways within the emulsion molecules to float or to sink.

The experiment also was not done using proper equipment due to unavailability. The mixing process in the experiment does not reach 3000 rpm but only700 rpm. This mean that the centrifuge force uses in the emulsification process was inadequate. The emulsion sample produce from the experiment was not a micro emulsion but a macro emulsion where the micron size of the emulsion is more than 100 microns. Due to the big micron size of the emulsion, the emulsion was expected to very unstable and easy to be separated to two or three phase mixture. These phenomena happen because when the size of the diesel particles or the water particles is big, they would easily combine with each other to form a bigger group of diesel or water that would separate according to the buoyancy force. But however, the emulsion produced has high viscosity which most likely to have a form like gel. This is what that provided stability to the emulsion produced because high viscosity emulsion or gel emulsion could somehow render the particles from moving due to buoyancy force or forms a big combination of particle. The result of the experiment could be improved if proper equipment is use in the experiment.

There were foam forms during the emulsification process. The foam form in the emulsion was due to the characteristic of the surfactant. The surfactant has high pH value which indicate high alkaline characteristic. The foam started to form when the emulsion started to form. The foaming happens in the emulsion region. The foam also form due to the improper mixing process which the blade used in the experiment was a blind blade. The foam last in the emulsion for about 3-4 days only. The foam that forms in the emulsion was decreasing drastically everyday in the emulsion. The foaming also happen if there was an excess of surfactant in the emulsion.

#### At 3500 rpm



Figure 27: Ternary Diagram for Pure Surfactant (3500 rpm)

For pure surfactant of labsa, the best percentage of surfactant in the emulsification process of water in diesel is 15% of the total volume. According to the tables above, using 15% surfactant for emulsification process produced more micro emulsion. However, pure surfactant experiment has a small region of micro emulsion which within the range of mixture of 70-80% of diesel with 10-15% of surfactant.



Figure 28: Ternary Diagram for Surfactant 80% + Butanol 20% (3500 rpm)

For 80% surfactant labsa mix with 20% butanol, there are some improvement in the emulsification process. The region of micro emulsion became larger where the ranges of micro emulsion contain mixture of 60-90% of diesel with 5-25% of surfactant mixture. Hence, by using butanol as co-surfactant could reduce the amount of surfactant used but could also increase the amount water that could be added in the emulsification process.

This 3500 rpm mixer rotation speed experiment was done in 16/09/09 which last for a week. Observation been done every day on every emulsion samples. The most critical time is within 10 days after the emulsification process. The emulsion will separated or not within the first 10 days. The separation process happens drastically in the first 10 days, and then it started to slow down and finally stop after first 15 days. These phenomena happen because the emulsification process was initially help by the

centrifuge force during the mixing. In fact, the mixing process is the main process in the emulsification then the emulsifier. So whichever molecules of diesel or water that does not bind with the emulsifier are most likely to find it ways within the emulsion molecules to float or to sink.

For this experiment, micro emulsion had been able to be produce by using high speed mixer which 3500 rpm. The theory of micro emulsion could only be produce using high speed mixer proven. And in addition, spraying method was applied to transfer the diesel and water into the mixer. The spray used was a very fine sprayer which could help to break up the particle size of the diesel and water before mixing. This spraying method proven that it could enhance the stability of the micro emulsion produced. The time of mixing for this experiment had been increase from 30 minutes in the earlier experiment to 1 hour per sample of combination. This step was taken to ensure that the mixing process was done properly and evenly. Apart from that, the process of spraying diesel and water into the mixer take some time. All the steps taken was to ensure that the particle size of the emulsion produced would be small enough which could reach less than 10 microns.

The analyzing process has not been done yet due to the sample just got over the observation process. The analyzing process will cover on the viscosity, clarity, microns size, API gravity and emission after burning of the emulsion. This analyzing process will be perform in order to ensure the quality and the compatibility of the emulsion to be use in the engine, the improvement achieved from the emulsification process, and the ability to be commercialize in the market. The analyzing result will be report and discuss in the final report.

# **5.0 CONCLUSION**

The author had completed the first phase last semester where first phase was for collecting information and knowledge about water-diesel emulsion, emulsification process, and other related issues. The author had been reading and did some study through the journal posted in the website and books from the library regarding emulsion and emulsification process. The author had concluded all the reading and studies done in phase by drafting an experiment procedure for emulsification process to test the emulsification process and prolonging the stability of the water-diesel emulsion.

The author had run the experiment during the semester break. Although some of the equipments require for the experiment was not available at that time, but the author managed to find replacement equipments which does not meet the requirement but still be able to do the experiment. Due to improper equipment used, the emulsion sample produced via experiment turn out to be macro emulsion instead of micro emulsion. This happen because the mixer used during the experiment couldn't meet the rotating speed required. But the experiment was not a failure. The author managed to identify the most possible emulsion ratio that could produce stabile emulsion. With this, the author could avoid wasting on the materials and time use to identify the most stabile emulsion composition.

The author had done the experiment using the proper equipment as per requirement recently. The author had noticed a lot of improvement from the previous experiment by using proper equipment and did some modification on the emulsification method. The author had satisfied with the result of the recent experiment where micro emulsion of diesel had been able to be produce which is very stabile. Next, the author will produce more of the micro emulsion to be analyzed in order to ensure the quality of the emulsion produced. The analyzing will be done in three times which will mark the final process of completing this project.

# **6.0 REFERENCES**

- 1. http://en.wikipedia.org/
- 2. <u>http://pps.ms.northropgrumman.com/</u>
- 3. http://www.rmisonline.com/
- 4. http://www.lsbu.ac.uk/
- 5. http://www.visionlearning.com/
- 6. http://hypertextbook.com/
- 7. <u>http://www.patentstorm.us/</u>
- 8. <u>http://www.about.com/</u>
- 9. http://www.sciencedirect.com/

- 10. http://www.idealibrary.com/
- 11. http://www.ingentaconnect.com/
- 12. http://chestofbooks.com/
- 13. http://www.ice.org.in/
- 14. www.lmbe.seu.edu.cn/
- 15. www.aapspharmscitech.org/
- 16. <u>www.rsc.org/</u>
- 17. www.scielo.br/

# **APPENDICES**



Figure 29: Preparing the aparatus and chemical for the experiment



Figure 30: Preparing the emulsifier (Labsa) for the experiment



Figure 31: Observing the emulsification process



Figure 32: Close look on the mixing of the water and diesel



Figure 33: Initial condition of the emulsion sample (1)



Figure 34: Separated emulsion sample

24/08/09





Pure Diesel



Opaque Emulsified Diesel



Macro Emulsified Diesel



Micro Emulsified Diesel