STUDY OF WATER-IN-DIESEL EMULSION STABILIZED

BY SURFACTANT

by

AHMAD NIZAR BIN YUNUS

Dissertation submitted in partial fulfilment of

the requirements for the

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(CHEMICAL ENGINEERING)

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Universiti Teknologi PETRONAS

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

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Approved by,

(Associate Professor Dr. Isa B Md. Tan)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2011

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 reference and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

AHMAD NIZAR B YUNUS

ABSTRACT

Emulsification of water in diesel to be used in internal combustion engine could be used as an alternative fuels as the natural hydrocarbon resources are depleting .The emulsified fuel is generally describe as an emulsion of water in standard diesel with special additives ,surfactants to stabilize the system. The main driving forces to emulsification fuel alternative are fuel efficiency and environmental impact. A detailed methodology is presented to document the steps taken in the experiment. This methodology is designed to study the factors that influence emulsion stability. The factors that are studied in this project are water/diesel ratio, emulsifier concentration, stirring time, stirring speed and temperature. Two surfactants are compared; Methyl Ester Sulfonate (MES) and PETROSTEPS .Based on the experiments done, PETROSTEPS shows better stability compared to MES. One of the criteria for stable emulsion is only one phase present .Most of the samples using PETROSTEPS as stabilizer have less than 50% of water separated after 24 hours of observation meanwhile samples using MES as stabilizers have more than 50% water separated after 24 hours .Particle size analysis has been done to determine the size of the sample. Samples using PETROSEPS has smaller range of particle size (6µm - 30µm) and sample using MES has a range of 90µm-600µm for the same fixed variable (W/D: 5/95, 2000RPM, Stirring Time: 15 minutes and temperature 30°C). The result shows the optimum process conditions for producing stable emulsion using PETROSTEPS are: water/diesel ratio, 5/95; emulsifier dosage, 0.5%; stirring time, 15 minutes; stirring speed, 2000rpm and mixing temperature of 30°C.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

Water-in-oil emulsions have been in the world of science since the dawn of petrochemical industry emerges. But now the attention towards the emulsified fuel has grabbed the attention of researchers around the world to study the feasibility of the emulsified fuel. During Second World War, researchers worked without success to improve fuel performance and stretch supplies by doping petrol with water .In 1994, American physicist Rudolph Gunnerman made headlines by claiming that his cream colored blend of water, naphtha and petrol cut pollution and boosted fuel efficiency by more than 40 percent ^[1]. Diesel engines are used widely as power plant for heavy machinery, vehicles and even power plant due to its fuel efficiency .The drawback of the diesel engine is the exhaust emissions .The main concern of the emissions are Nitrogen Oxides (NO_X) and Particulate Matter (PM) .Both of the substances are harmful towards the environment .A number of researches has been done on how to reduce both the substances. One of it is through emulsion of water-in-diesel. Several researchers have shown that introducing water into diesel fuel to produce emulsified diesel can significantly lower the pollution level of particulate matter and NO_X^[2]. However this might be an answer towards diesel engines emission, but stability of emulsified fuel has been questioned as the presence of water have affects to diesel engine.

1.2 Problem Statement

There is a need to study the stability of the emulsion between oil and water emulsion. The stability of the emulsification is significant in storing stage as several breakdown processes might happen before application. The greater the stability, the greater the emulsion of the oil.

The process variables that are important in this study are the effect of the water/diesel ratio, stirring intensity, stirring time, surfactant's dosage, and temperature.

1.3 Significance of the Project

The proper mixing and proportioning of the water, oil and surfactant creates a very stable emulsion that is ready to used as fuel .The emulsification of the diesel could be use for commercial usage for engine as it could provide stable and green fuel. This finding will change the world most consume fuel ^[3] and reduce the environmental effect. This experiment can develop a basis for extensive studies with hydrocarbons, including the control of interfacial behavior between oil and water.

The research can continue on the extensive study of the deformation rate of emulsified water-diesel and its effect on combustion (micro-explosions).

1.4 Objective

The project aims to study the emulsification diesel with water using surfactant, observe the stability of emulsification, percentage of mixing, and using variable parameters.

The main objectives are as follows

- i. To study the stability of the water-diesel emulsification
- ii. To investigate parameters that contribute to emulsion stability.

CHAPTER 2

LITERATURE REVIEW

2.1 Water in Diesel Emulsions

French oil company Elf Aquitaine which has begun to market "Aquazole", a milky looking blend of diesel fuel ,surfactants and about 13 percent water .The "Aquazole" has been verified to provide emissions reductions of 16 percent of NOx and 60 percent of PM. This verification was issued by the California Air Resources Board (ARB) .However the blend of Aquazole always is a secret kept by the organization. To find the right parameters that produce a stable emulsified fuel need an extensive study.



Figure 1 Aquazole sample produced by Elf

In another instance, Rudolf Gunnerman has pioneered in blending water and ethanol to produce fuel for internal combustion engines ^[4].He also tested petroleum and water, binding the elements together with a unique combination of additives .Gunnerman explained the water is within the oil as inside the engine,

the water turns to steam and explodes the carbon particles out (called atomization). The drops ejected are smaller and there is faster combustion

Both Gunnerman's and Aquazole are emulsions in which the water is dispersed in the fuel as small droplets. Water molecules are polar, possessing a tiny electrical charge that leaves them ready to bond with other charged molecules but unwilling to link to electrically neutral ones like those in petrol or diesel fuel .To overcome this repulsion, chemists use surfactants with polar groups at one end and non-polar groups at the other .These behave like molecular peacekeepers stabilizing the mixture by locking the water inside small surfactant bags called micelles^[5].

The micelles in these fuels are micrometers across ,so large that they scatter light and two fuels appear white .The size of the micelles also makes them unstable .With time ,the non-polar and polar components separate into distinct layers and the mixture become useless.

When the combustion process of Water-in-diesel emulsion takes place, it is atomized into numerous liquid droplets through a nozzle. As the boiling point of water is lower than diesel, the water envelope layer explodes through the outer layer of diesel molecules ^{[6].}This lead to micro-explosion behavior which emulsion drops are further atomized into finer droplets.

2.2 Mechanism of Emulsification

Water – in –diesel emulsification needs diesel, water, surfactant and energy. The energy required to expand the interface, $\Delta A\gamma$ (where ΔA is the increase in interfacial area when the bulk oil with area A₁ produces numerous droplets with areas A₂; A₂ >> A₁, γ is the interfacial tension). Since γ is postive, the energy required to expand the interface is large and positive ^[7].

This prove that the emulsification process is non-spontaneous and energy is required to produce the droplets .The formation of of large droplets (few μ m)as this case macro-emulsions is quite easy hence the high speed homogenizer provide enough energy to create the emulsion. For micro-emulsion and nano-

emulsion to happen ,it is quite difficult to produce as is needs a large amount of surfactant (can be costly) and energy. The high energy required to produce nanoemulsions can be understood from a consideration of the Laplace pressure p (Δp between inside and outside the droplet)^[1].

$$\Delta p = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \tag{1}$$

Equation 1 Laplace Pressure

Where R_1 and R_2 are the pricipal radii of curvature of the drop .

For a spherical drop $R_1 = R_2 = R$

$$\Delta p = \frac{\gamma}{2R} \tag{2}$$

Equation 2 Simplified Laplace pressure

Surfactants play a major role in the formation of emulsions ; by lowering the interfacial tension , p is reduced and hence the stress needed to break up a drop is reduce .



Figure 2 Schematic diagram of the various processes occurring during the emulsion formation⁻

In the Figure 2 above, it illustrates the various process occuring during emulsification which consits of break up of droplets , adsorption of surfactants and droplet collision .Each of the process occurs numerous times during emulsification process. The time scale of each process os very short , typically in microsecond .This proves that emulsification process is a dynamic process , and that events occuring in the microsecond could be very important.

2 - 20 µm	Macro emulsion Milky White
0.1 - 0.3 µm	P.I.T. emulsion Bluish White P.I.T-=Phase Inversion Temperatu
< 0.1 µm	Micro emulsion Translucent
0.01 µm	Micellar emulsion Transparent
0.001µm	Molecular emulsion Transparent

Figure 3 Droplet size and the appearance of emulsions

2.3 Methods for Emulsification

There a few methods for emulsion preparations.Below is the list of some of the methods that may be applied to preapre an emulsion .

- 1) Simple pipe flow (low agitating energy)
- 2) Static mixers and general stirrers (low to medium energy, L-M).
- 3) High speed stirrer ,colloid mills and high pressure homogenizers .
- 4) Ultra sound generators.

There are also different routes that could be applied for the above methods such as batch or continous.In all methods ,there is liquid flow :both unbounded and strongly confined flow.In the unbounded flow the droplets are surrounded by a large amount of flowing liquid (the confining walls of the apparatus are far away from most of the droplets) .The forces can be frictional (mostly viscous) or inertial .Viscous forces cause shear stresses to act on the interface between the droplets and the continuous phase .The shear stress can be generated by laminar flow (LV) or turbulent turbulent flow (TV) which depends on the Reynolds number.

Equation 3 Reynolds Number

Where v =linear liquid velocity

- P = liquid density
- $\eta =$ liquid viscosity
- *l* = characteristic length given by the diameter of flow through a cylindircal tube.

For Laminar flow $R_e <\sim 1000$ whereas for turbulent flow $R_e >\sim 2000$. The most important regimes are laminar/viscous (LV), turbulent/viscous (TV) and turbulent/inertial (TI).

For water as the continous phase ,the regime is alwaydsTI .For higher viscosities of the continous phase ,the regime is TV.For still higher viscosities or small apparatus (small l),the regime is LV.for very small apparatus (laboratory homogenizers),the regime is nearly always LV^[1].

The viscosity of the continuous phase η plays an important role in some regimes. For the turbulent inertial regime, η has no effect on droplet size. For the turbulent viscous regime, larger η leads to smaller droplets. For laminar viscous, the effect is even stronger.

2.4 Stability of emulsion

The main criterion for a stable emulsion is the presence of only one phase .If more than one layer is found; it must be considered to be an unstable emulsion.



Figure 4 Stability of emulsion based on type of emulsion

Several breakdown processes may occur that depend on the particle size distribution and the density of difference between droplets and the medium. The magnitude of the attractive versus repulsive forces determines flocculation tendency. The solubility of the disperse liquids and the particle size distribution determines the Ostwald ripening.

Ostwald ripening is an observed phenomenon solid or liquid solutions which describes the change of an inhomogeneous structure over time. The stability of the liquid film between the droplets determines coalescence: phase inversion ^[1]. The various breakdown processes are shown in the figure below.



Figure 5 Schematic of the emulsion breakdown processes .

The physical phenomena involved in each breakdown process are not simply described, require analysis of the various surfaces forces involved. The above processes may take place simultaneously rather than consecutively which will complicate the analysis.

The viscosity of the oil is important in the break-up of droplets-the higher the viscosity ,the longer it takes to deform a drop .The deformation time denote by τ_{def} is given by the ratio of oil viscosity to the external stress acting on the drop.



From the equation 4, the time taken for an emulsion to deform can be predicted thus determine its storage stability condition could be done. The stability of the emulsion is significant as it will affect the combustion if not carefully investigated.

2.4.1 Parameters for emulsion stability

For a stable emulsion to take place, there are a few parameters that contribute to emulsion stability .This can be divided into surfactant dosage, oil/water ratio, stirring intensity, mixing temperature and mixing time.

2.4.1.1. Effect of surfactant dosage

Investigations have demonstrated that emulsifier concentration has a significant impact on emulsion stability .When the dosage of surfactant increase, the emulsion stability increase but only towards a certain point. When the dosage is too high the stability decreased due to a rapid coalescence and too low of surfactant dosage also destabilize the emulsion due to agglomeration of the oil droplets.

2.4.1.2. Effect of Oil/Water Ratio

Emulsion type is dependent on the relative phase volume ^[4]. Phase volume above ϕ >0.74 will result in either inversion or breaking . The emulsion would be packed more densely. It is crucial to determine the best water/oil ratio to make sure the emulsion is stable.

2.4.1.3. Effect of stirring intensity

Emulsification needs energy to disperse one immiscible liquid towards other liquid. Firstly, the interface of the two phases is deformed to such an extent that large droplets are formed .The large droplets will be broken up into smaller ones .During emulsification, the interfacial area between two liquids increases .It is the properties of the liquids which tend to minimize the surface area, hence there is a need for mechanical energy for emulsification process to take place. Increasing local dissipation of energy in breaking zone due to the rise of circulation consumption through mixer zone is found to be most effective way for diameter decrease. The main objective of stirring is to form a stable emulsion; basically breaking large liquids drops into smaller drops. High intensity does not necessarily mean better emulsion; too intense stirring will lead to the emulsifier to break away from oil-water interface.

2.4.1.4. Effect of temperature

The temperature is one of the significant factors in producing stable emulsion. The surface tension of most liquids decreases with increasing temperature .This is caused by increased kinetic energy imparted to the surface molecules at high temperature will tend to overcome the net attractive force of the bulk liquid .As the temperature increase towards critical value, the cohesive force between molecules approaches zero. Normally with increase temperature, it will be easier for emulsification to take place but if too high, there will be a chance that it will coagulate the particles which cause the deterioration of the emulsions. The interfacial adsorption of the emulsifier is adversely affected to some extent by increasing temperature. Affect will also be on the surfactant which is loosely adsorbed on the oil-water interface and will separate out from the emulsion. This will increase in collision and coalescence, thus destabilize the emulsion.

2.4.1.5. Effect of mixing time

Mixing time plays an important role in making a stable emulsion .Mixing will decrease the radii of droplets in the emulsion with increasing

emulsifying time .Emulsifier becomes more effective with increased mixing time. Nevertheless, too long of mixing will decrease the emulsifier effectiveness as it will cause the emulsifier to drop out from oil-water interface

CHAPTER 3

METHODOLOGY

Researches on few experiments will be conducted to identify the best stability regarding to the emulsification parameters (e.g. stirring intensity, mixture ratio, temperature, pressure etc.).Chemicals and apparatus are proposed to develop the experiments that will be conducted. Below are some of the experimental methods for assessing the stability of emulsion.

3.1 Experimental Methods for Assessing Emulsion Stability

There are a few methods basically to assess the emulsion stability. The methods are listed below:

3.1.1 Assessment of Creaming or sedimentation

Several methods may be applied to assess the creaming or sedimentation of emulsion:

- Measurement of the rate by direct observation of emulsion separation using measuring cylinders that are placed at constant temperature. This method allows one to obtain the rate as well as the equilibrium cream or sediment volume.
- Turbidity measurements as a function of height at various times, using, for example, the Turboscan (which measures turbidity from the back scattering of near IR light).
- Ultrasonic velocity and absorption at various heights in the cream or sedimentation tubes.

Centrifugation may be applied to accelerate the rate of creaming or sedimentation, but one should be careful in the amount of g force that may be applied (g should not exceed the critical g force that causes deformation of the emulsion droplets and oil separation).

3.1.2 Assessment of Emulsion Flocculation

For dilute emulsions (which may be obtained by carefully diluting the concentrate in the supernatant liquid), the rate of flocculation can be determined by measuring turbidity, t, as a function of time

 $\tau = An_0 V_1^2 (1 + n_0 kt)$ (5)

Equation 5 Turbidity

Where A is an optical constant, n_0 is the number of droplets at time $t \frac{1}{4}$ zero, VI is the volume of the droplets and k is the rate constant of flocculation. Thus, a plot of t versus t gives a straight line, in the initial time of flocculation, and k can be calculated from the slope of the line. Flocculation of emulsions can also be assessed by direct droplet counting using optical microscopy (with image analysis), using the Photo sedimentation methods.

3.1.3 Assessment of Ostwald Ripening

The best procedure to follow Ostwald ripening is to plot R3 versus time; following Eq. 3.2 This gives a straight line, from which the rate of Ostwald ripening can be calculated. In this way one can assess the effects of the various additives that may reduce Ostwald ripening, e.g. addition of highly insoluble oil and/or an oil-soluble polymeric surfactant.

$$r^{3} = \frac{8}{9} \left[\frac{S(\infty) \gamma V_{\rm m} D}{\rho RT} \right] t \qquad (6)$$

Equation $6 r^3$ vs. time

3.1.4 Assessment of Coalescence

The rate of coalescence is measured by following the droplet number n or average droplet size d (diameter) as a function of time. Plots of log (droplet number) or average diameter versus time give straight lines (at least in the initial stages of coalescence), from which the rate of coalescence k can be estimated using Eq. (6.73). In this way, one can compare the stabilizers, e.g. mixed surfactant films, liquid crystalline phase and macromolecular surfactants.

3.1.5 Assessment of Phase Inversion

The most common procedure to assess phase inversion is to measure the conductivity or the viscosity of the emulsion as a function of f, increase of temperature and/or addition of electrolyte. For example, for an O/W emulsion phase, inversion to W/O is accompanied by a rapid decrease in conductivity and viscosity

3.2 Chemicals and Apparatus

3.2.1 Chemicals:

- a) Commercial Diesel
- b) Surfactants (Methyl Ester Sulfonate (MES) C₁₆- C₁₈ and PETROSTEPS)
- c) Distilled Water

3.2.2 Apparatus and Equipments Used:

- a) Beakers
- b) Measurement cylinders
- c) Glass rod
- d) Mechanical Stirrer.



Brand : Heidolph Model:RZR1 Range RPM : 280-2000/min

- e) Retort Stand
- f) Heater
- g) Thermometer
- h) Graduated cone cylinder

3.2.3 Safety Precaution Apparel:

- a) Laboratory Coat
- b) Rubber Gloves
- c) Safety goggles
- d) Face Mask

3.3 Experimental setup.

3.3.1: Experiment 1: Effect of emulsifier dosage on emulsion stability

Distilled water will be used in this experiment. Using 4 beakers, the volume of water will be constant (5% of total volume)

Prepared diesel in the beaker by measuring 275 mL of diesel using volumetric cylinder and pour it into the beakers. The ratio of water/diesel for each beaker is different based on water-diesel ratio

- 1) Prepare the surfactant by 0.2% wt of diesel. The surfactant that will be used is
- 2) Add the water, diesel and surfactant into each beaker.
- Place the beaker under the mechanical stirrer and set the speed to 2000rpm for 15 minutes.
- 4) Pour the solution to the volumetric cylinder and measure the relative volume.
- 5) Repeat step 1-4 with different emulsifier dosage (0.4% wt, 0.5 % wt, 1% wt%)
- Observe the percentage of separated water using graduated cone cylinder every 30 minutes for 2.5 hours.
- 7) Calculate percentage of water separated for each 30 minutes.
- 8) Repeat the experiment using another type of surfactant.

3.3.2 Experiment 2 Effect of Water -oil ratio effects on emulsion stability.

Distilled water will be used in this experiment. Using 4 beakers, the volume of water will be constant (5% of total volume)

Prepared diesel in the beaker by measuring 275 mL of diesel using volumetric cylinder and pour it into the beakers.

- Prepare the surfactant by 0.2% wt of diesel. The surfactant that will be used is Methyl Ester Sulfonate (MES) C₁₆- C₁₈
- 2) Add the water, diesel and surfactant into each beaker.
- Place the beaker under the mechanical stirrer and set the speed to 2000rpm for 15 minutes

- 4) Pour the solution to the volumetric cylinder and measure percentage of water separated using graduated cone cylinder.
- 5) Repeat step 1-4 with different water-diesel ratio (10%, 15%, and 20%)
- 6) Observe the percentage of separated water every 30 minutes for 2.5 hours.
- 7) Calculate percentage of water separated for each 30 minutes.
- 9) Repeat the experiment using another type of surfactant.



Figure 6 Example of phase separation

3.3.3: Experiment 3 Effect of stirring time on emulsion stability

Distilled water will be used in this experiment. Using 4 beakers, the volume of water will be constant (5% of total volume)

Prepared diesel in the beaker by measuring 275 mL of diesel using volumetric cylinder and pour it into the beakers.

- 1) Prepare the surfactant by 0.2% wt of diesel. The surfactant that will be used is Methyl Ester Sulfonate (MES) C_{16} C_{18}
- 2) Add the water, diesel and surfactant into each beaker.
- 3) Place the beaker under the mechanical stirrer and set the speed to 2000rpm with initial stirring time of 5 minutes.
- Pour the solution to the volumetric cylinder and measure percentage of water separated using graduated cone cylinder.
- 5) Repeat step 1-4 with different stirring time (10 minutes, 15 minutes, 20 minutes and 30 minutes)
- 6) Observe the percentage of separated water every 30 minutes for 2.5 hours.
- 7) Calculate percentage of water separated for each 30 minutes.
- 8) Complete the table below
- 9) Repeat the experiment using another type of surfactant.

3.3.4: Experiment 4: Effect of stirring speed on emulsion stability

Distilled water will be used in this experiment. Using 4 beakers, the volume of water will be constant (5% of total volume)

Prepared diesel in the beaker by measuring 275 mL of diesel using volumetric cylinder and pour it into the beakers.

- Prepare the surfactant by 0.2% wt of diesel. The surfactant that will be used is Methyl Ester Sulfonate (MES) C₁₆- C₁₈
- 2) Add the water, diesel and surfactant into each beaker.
- Place the beaker under the mechanical stirrer and set the initial speed to 500RPM with stirring time of 15 minutes.
- Pour the solution to the volumetric cylinder and measure percentage of water separated using graduated cone cylinder.
- 5) Repeat step 1-4 with different stirring speed (1000RPM, 1500 RPM, and 2000RPM)
- 6) Observe the percentage of separated water every 30 minutes for 2.5 hours .
- 7) Calculate percentage of water separated for each 30 minutes.
- 8) Complete the table below
- 9) Repeat the experiment using another type of surfactant.

3.3.5: Experiment 5 Effect of temperature on emulsion stability

Distilled water will be used in this experiment. Using 4 beakers, the volume of water will be constant (5% of total volume)

Prepared diesel in the beaker by measuring 275 mL of diesel using volumetric cylinder and pour it into the beakers.

- Prepare the surfactant by 0.2% wt of diesel. The surfactant that will be used is Methyl Ester Sulfonate (MES) C₁₆- C₁₈
- 2) Add the water, diesel and surfactant into each beaker.
- 3) Place the beaker on the hot plate and set the initial temperature to 30°C .Wait till the temperature reach the set point value and start the homogenizer once the temperature reached the desired value.

- 4) Pour the solution to the volumetric cylinder and measure percentage of water separated using graduated cone cylinder.
- 5) Repeat step 1-4 with different temperature (40°C, 50°C, 70°C)
- 6) Observe the percentage of separated water every 30 minutes for 2.5 hours.
- 7) Calculate percentage of water separated for each 30 minutes.
- 8) Complete the table below
- 9) Repeat the experiment using another type of surfactant.

3.3.6: Experiment 6 Particle Size Analysis

For this experiment, we will be used Malvern MASTERIZER 2000 to assess particle size of the emulsion.

Using certain parameters selected from previous experiment (water-oil ratio and emulsifier dosage), we will investigate the particle size and discuss its effect on emulsion stability and performance.

- Prepare sample from previous experiment by using 2 samples from first experiment (MES as surfactant) and 2 samples from second experiment (PETROSTEPS as surfactant).
- 2) Put the sample under in the optical image analyzer and observe the particle size for the emulsion.
- Relate the stability result from previous experiment with the droplet size distribution and discuss it.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Result and Discussion for experiment 1 –Effect of Water-Diesel Ratio in Emulsion Stability for MES and PETROSTEPS as surfactant

Experiment 1 tries to determine which of the Water-Diesel is the best combination for emulsion stabilize by conventional surfactant, Methyl Ethyl Sulfonate (MES) C_{16} - C_{18} . To assess the stability, the volume of water separated will be determine by observation of 30 ml of the emulsion sample using graduated cone. The volume of the water separated will be taken for every 30 minutes for 2.5 hours and will be left for 24 hours. To ease the observation activity, only 30ml of the sample will taken out for observation which 30mL.Out of 30mL, 1.5mL should be the water phase as the emulsion is being put into graduated cone right after mixing ceased.

Sample	Water/	Volume of	Volume of	Volume of	Volume of	Volume of
	Diesel	water	water	water	water	water
	Ratio	separated	separated after	separated	separated	separated after
		after 30 mins	60 mins(mL)	after 90	after 120	150mins(mL)
		(mL)		mins(mL)	mins(mL)	
1	5/95	0.1(6.67%)	0.4(26.67%)	0.7(46.67%)	0.8(53.33%)	0.8(53.33%)
2	10/90	0.15 (5%)	0.5(16.7%)	1.4(46.67%)	1.8(60%)	2.2(73%)
3	15/85	1.2(26.67%)	1.5(33.33%)	1.8(40%)	2.2(48.9%)	2.8(62.2%)
4	20/80	2.2(36.67%)	2.8(46.67%)	3.2(53.33%)	4.5(75%)	5.0(83.3%)

Table 1 Percentage of water separated in water/diesel ratio effect experiment using MES as surfactant



Figure 7 Comparison for effects of water oil ratio on emulsion stability using MES as surfactant

The figures 7 above showed the result for each sample in the experiment of water/ diesel ratio effect on stability of the emulsion. For water/diesel ratio of 5/95, the water started to separate towards 2.5 hours period of observation. It starts from 6.67% up to 55% and stable for period of 2.5 hours until 24 hours of observation which the water phase totally phase out .During the first 2 hours of observation, sample 1 shows that the emulsion consists of 3 layers of phase which is diesel, emulsion and water phase .After 2 hours the water phase was clearly seen even the presence of water is in small amount.

For emulsion with W/D ratio of 10/90, the emulsion is showing it is an unstable emulsion. Starting from 30 minutes from mixing ceased, 5% of water already separated and the emulsion started to have 3 phases which are clean diesel phase, emulsion and water phase. The percentage again increasing steadily for the period of 2.5 hours of observation to 73% of separated water .Emulsion with water/diesel ratio of15/85, showed the same characteristics with Sample 2 in terms of percentage of water separation .Only the difference that sample 3 started to phase out early which at 30 minutes of observation, 26.7% of the water in emulsion separated out thus signifies the instability of the emulsion.

Sample 4 of W/D ratio of 20/80 which represents ratio of water in diesel .The emulsion was highly unstable due to higher ratio of water. The effect of ratios has also affected the energy required to disperse the water droplet into diesel molecules. Higher energy requires higher speed mixing as the ratio of water to diesel increase.

Based on the Figure 7 above, all four samples are being compared in terms of percentage water separated over time. All four samples show characteristics of meta-stable emulsion which is macro-emulsion which only stable for few hours. This may be due to unsuitable surfactant, temperature, mixing speed, type of homogenizer and more. But the main concern is the effect of the water/oil ratio towards the emulsion stability .Based on the Figure above, the most stable out of all four samples is sample 1 which ratio of water/diesel is 5/95 .Overall all the samples shows instability for period of 2.5 hours and after 24 hours, the phase separation was clearly visible.

Sample	Water/Diesel	Volume of				
	Ratio	water	water	water	water	water
		separated	separated	separated	separated	separated
		after 30	after 60	after 90	after 120	after
		mins (mL)	mins(mL)	mins(mL)	mins(mL)	150mins(mL)
1	5/95	0.0 (0%)	0.1(6.67%)	0.1(6.67%)	0.2(13.3%)	0.2(13.3%)
2	10/90	0.2(6.7%)	0.2(6.7%)	0.5(16.7%)	0.5(16.7)	0.6(20%)
3	15/85	0.4(8.9%)	0.7(15.5%)	0.8(17.8%)	1.2(26.7%)	1.5(33.3%)
4	20/80	0.8(13.3%)	1.4(23.3%)	1.8(30%)	2.1(35%)	2.4(40%)

Table 2 Percentage of water separated in water/diesel ratio effect experiment using PETROSTEPS as surfactant.



Figure 8 Effects of water/diesel ratio towards emulsion stability stabilized by PETROSTEPS

Table 2 and figure 8 shows the second experiment in effect of water/diesel ratio towards emulsion stability stabilized by PETROSTEPS. From the graph, we could see clearly that the emulsion stabilized by this surfactant is much stable when compared to the emulsion stabilized by MES. The most stable is the sample with water/diesel ratio of 5/95 .When compared to the same sample stabilized by MES the difference is more than 60% .Thus it has significant increment in emulsion stability .The potential of this surfactant may be developed .Nevertheless, the emulsion stability may be more stable when compared to emulsion stabilize by MES, this sample shows that after 24 hours, more than half of the water already separated out from the emulsion. For this experiment the most unstable is the sample 4 which has water/diesel ratio of 20/80.

4.2 Result and Discussion for experiment 2 –Effect of emulsifier concentration in emulsion stability for MES and PETROSTEPS as surfactant

Surfactant lowers the interfacial tension, γ and causes a reduction in droplet size. It is important to analyze the effect surfactant dosage in emulsion stability. In this experiment, the objective is to find the best surfactant dosage for stable emulsion for this type of surfactant .Based on previous result, Sample 1 which water/diesel ratio of 5/95 will be the chosen as fixed parameters as also the stirring intensity of 2000 RPM and stirring time of 15 minutes. Below is the result for different type of emulsifier concentration .The emulsifier that will be used is Methyl Ethyl Sulfate (MES). To ease the observation activity , only 30ml of the sample will taken out for observation which 30mL.Out of 30mL ,1.5mL should be the water phase as the emulsion is being put into graduated cone right after mixing ceased .

Sample	Surfactant	Volume of	Volume of	Volume of	Volume of	Volume of
	Concentration	water	water	water	water	water
	(%wt)	separated	separated	separated	separated	separated
		after 30	after 60	after 90	after 120	after
		mins (mL)	mins(mL)	mins(mL)	mins(mL)	150mins(mL)
1	0.2	0.1(6.67%)	0.3(20%)	0.6(40%)	0.6(40%%)	0.7(46.67%)
2	0.4	0.3(20%)	0.6(40%)	0.7(46.7%)	0.9(60%)	1.0(66.7%)
3	0.5	0.3(20%)	0.7(46.7%)	0.7(46.7%)	1.0(66.7%)	1.1(73.3%)
4	1.0	0.6(40%)	0.8(53.3%)	1.0(66.7%)	1.3(86.67%)	1.4(93.3%)

Table 3 Percentage of water separated in emulsifier dosage effect experiment using MES as surfactant.



Figure 9 Comparison of percentage water separated

The figure 9 above shown result of the emulsion stability assessed by percentage of water separated for effect of emulsifier concentration on emulsion stability. For sample 1 shows emulsion of water-in-diesel stabilized by MES in concentration 0.2 wt%. The emulsion is unstable as it starts to break down into 3 phases at first hour and continue to phase out for 24 hours period .Same goes to other sample with increasing surfactant concentration. In theory, with increase of surfactant until the ideal point of concentration, the stability shall increase and but then decline if more surfactant is added towards the emulsion. The surface excess (number of moles adsorbed per unit area of the interface) increases with increasing surfactant concentration and will eventually, reaches a plateau value (saturation adsorption) .At this point, the emulsifiers will no longer keep the emulsion stabilize for long period of time. From the experiment done, it could be seen that the higher the concentration, the phase separation process occurs in shorter time. Adding more surfactant will change its behavior and negatively affect the emulsion stability due to the polydispersity effect of surfactant micelles formed at the water-diesel interfaces .Even though all samples are not stable as predicted, but the pattern was shown to prove that higher surfactant concentration will decrease the stability of the emulsion in general but given type of surfactant and other parameters the surfactant concentration does contribute a lot in the overall emulsion stability.

The figure 9 shown the comparison of the emulsion concentration effects for every samples done ranging from 0.2wt% to 1.0wt%.From this, it could be seen that, the lowest dosage of 0.2wt% has the best stability when compare with other concentration of surfactant. This shows that for MES and diesel emulsification, the best dosage for the emulsion to stabilize is 0.2wt% .Water separated increase significantly when surfactant concentration increasing. In this case, the MES might not be suitable to be used for water-in-diesel emulsion as the stability for the emulsion is unstable.

Sample	Surfactant	Volume of				
	Concentration	water	water	water	water	water
	(%wt)	separated	separated	separated	separated	separated
		after 30	after 60	after 90	after 120	after
		mins (mL)	mins(mL)	mins(mL)	mins(mL)	150mins(mL)
1	0.2	0.0(0%)	0.1(6.67%)	0.1(6.67%)	0.2(13.3%)	0.2(13.3%)
2	0.4	0.2(13.3%)	0.2(13.3%)	0.2(13.3%)	0.5(33.3%)	0.5(33.3%)
3	0.5	0.0(0%)	0.0(0%)	0.0(0%)	0.0(0%)	0.1(6.67%)
4	1.0	0.4(26.7%)	0.5(33.3%)	0.6(40%)	0.6(40%)	1(66.67%)

Table 4 Percentage of water separated in emulsifier dosage effect experiment using PETROSTEPS as surfactant.



Figure 10 Effects of emulsifier dosage towards emulsion stability stabilized by PETROSTEPS

Table 4 and Figure 10 show the result for the second experiment for effects of emulsifier dosage towards emulsifier stability. All the samples are stabilized by PETROSTEPS. There is significant increase in the stability of the emulsion. This could be seen in the graph when the surfactant dosage of 0.5wt% shows the greater stability as percentage of water separated over 2.5 hours of observation time is less than 10% .When compared to the emulsion stabilized by MES ,this samples shows the better stability . After 24 hours of observation, percentage of the water separated is less than 50 % (46.7%). Even though the sample shows great stability for few hours after mixing, overall it is not stable as the water continuously separated .The volume may not as much as previous experiment, but the emulsion still unstable to be used commercially as it will has a bad impact on the diesel engine. The most unstable emulsifier concentration for the experiment is sample 4 which shows in less than 2.5 hours the % water separated already reached more than 60% .With this, it is determine for the rest of the experiments using PETROSTEPS as surfactant the concentration will be 0.5%.

4.3 Result and Discussion for experiment 3 –Effect of Stirring Time in Emulsion Stability for MES and PETROSTEPS as surfactant

For emulsification process, mixing time plays an important role in determine the stability of the emulsion .The radii of the droplets in the emulsion decreased with increasing stirring speed and emulsifying time .But if the mixing time is too long, it will cause the emulsifier to drop out from the oil-water interface .From the experiment using MES as surfactant, the optimal time will be 20 minutes based on results shown below for each sample below:

Sample	Strring time	Volume of	Volume of	Volume of	Volume of	Volume of
		water	water	water	water	water
		separated after	separated	separated	separated after	separated after
		30 mins (mL)	after 60	after 90	120 mins(mL)	150mins(mL)
			mins(mL)	mins(mL)		
1	5 min	0.2(13.3%)	0.7(46.7%)	0.7(46.7%)	0.9(60%)	1.1(73.3%)
2	10 min	0.2(13.3%)	0.2(13.3%)	0.5(33.3%)	0.6(40%)	0.7(46.7%)
3	15 min	0.1(6.67%)	0.4(26.67%)	0.7(46.67%)	0.8(53.33%)	0.8(53.33%)
4	20 min	0.1(6.67%)	0.1(6.67%)	0.4(26.7%)	0.5(33.3%)	0.5(33.3%)
5	30 min	0.5(33.3%)	0.6(40%)	0.9(60%)	1.1(73.3%)	1.2(80%)

Table 5 Percentage of water separated stirring time effect experiment using MES as surfactant.



Figure 11 Effects of Stirring time towards emulsion stability using MES as surfactant.

Based on figure 11 above, the emulsion used MES as surfactant. For stirring time of 5 minutes shows the highest percentage of water separated over time. For only 2.5 hours ,>80% of water content separated out form the emulsion .That shows the emulsion was unstable due to short time of stirring .The most stable stirring time was 20 minutes . Time selection on emulsion stability has great impact as it will help the emulsification process. Short time may indicates the surfactant micelles has not been given enough time to be absorbed to form surface layer between water and diesel interface for this particular speed (2000 RPM). Stirring time may be shortened if there is higher speed of homogenizer is available .But the result may be uncertain due to there is no general standard for how long the emulsion should be mixed. Based on above figure, 20 minutes shows the most stable emulsion meanwhile for 30 minutes it shows great instability as the surfactant might drop out from the water/diesel interface and degree of emulsification is reduce.

Sample	Strring time	Volume of	Volume of	Volume of	Volume of	Volume of
		water	water	water	water	water
		separated	separated	separated	separated	separated
		after 30 mins	after 60	after 90	after 120	after
		(mL)	mins(mL)	mins(mL)	mins(mL)	150mins(mL)
1	5 min	0.1(6.67%)	0.2(13.3%)	0.4(26.67%)	0.7(46.67%)	0.7(46.67%)
2	10 min	0.0(0%)	0.1(6.67%)	0.3(20%)	0.5(33.3%)	0.5(33.3%)
3	15 min	0.0(0%)	0.0(0%)	0.1(6.67%)	0.1(6.67%)	0.2(13.3%)
4	20 min	0.1(6.67%)	0.1(6.67%)	0.2(13.3%)	0.2(13.3%)	0.5(33.3%)
5	30 min	0.2(13.3%)	0.2(13.3%)	0.4(26.7%)	0.5(33.3%)	0.6(40%)

Table 6 Effects Percentage of water separated in stirring time effect experiment using PETROSTEPS as surfactant.



Figure 12 Effects of stirring time towards emulsion stability stabilized by PETROSTEPS

Table 6 and figure 12 show the results for experiment effects of stirring time towards emulsion stability stabilized by PETROSTEPS. Form the graph the most stable is sample 3 which the variable parameter is stirring time of 15 minutes. Water start to phase out from the emulsion after 90 minutes mixing ceased. When compared with the samples using MES as surfactant, this definitely shows greater stability .After 24 hours, the total water separated out is less than 30% .The most unstable emulsion for this experiment is sample 1 with stirring time of 5 minutes. Within 2.5 hours almost 50% of the water separated .This is due to short time for the surfactant micelles to be transported to the interface of water/diesel. Thus, the best mixing time for PETROSTEPS surfactant is 15 minutes with homogenizer speed of 2000 RPM for this particular experiment.

4.4 Result and Discussion for experiment 4 –Effect of Stirring Speed in Emulsion Stability for MES and PETROSTEPS as surfactant

Stirring speed has a great effect on the emulsion stability. Stirring intensity provides the shear to elongate the drop before breaking and also to provide inertia to gather drops and help them coalescence. Increase in stirring speed would mainly increase the rupture mechanism, resulting decrease in drop size. It is also said that, with the increase of stirring intensity, the energy will increase thus aiding the emulsion formation .To break the droplet into smaller size a large amount of energy is needed .Low energy device will often not form stable emulsions and as energy increase, the emulsions become increasingly stable. The intensity however, if too much might cause the emulsifier to break away from the oil-water interface. For the surfactant to be effective, it must be transported to the water/diesel interface where absorption process occurred and surface layer formed. This was accelerated by the intensity stirring .Based on the graphs below, the pattern of the emulsion stability could be seen as when intensity increase the stability of the emulsion also increase .Both of the experiment shows that, with increasing revolution per minute (RPM), the percentage of water separated decrease .As the homogenizer only limited to 2000RPM further studies towards higher RPM could not been done . From the first experiment using Methyl Ester Sulfonate (MES) $C_{16} - C_{18}$ it shows that the highest RPM shows the highest stability among the entire sample.

Sample	Strring	Volume of	Volume of	Volume of	Volume of	Volume of
	speed	water	water	water	water	water
	(RPM)	separated	separated	separated	separated	separated
		after 30 mins	after 60	after 90	after 120	after
		(mL)	mins(mL)	mins(mL)	mins(mL)	150mins(mL)
1	500	0.4(26.7%)	0.5(33.3%)	0.9(60%)	0.9(60%)	1(66.7%)
2	1000	0.2(13.3%)	0.6(40%)	0.7(46.67%)	0.9(60%)	0.9(60%)
3	1500	0.3(20%)	0.5(33.3%)	0.8(53.33%)	0.8(53.33%)	0.9(60%)
4	2000	0.1(6.67%)	0.4(26.67%)	0.7(46.67%)	0.8(53.33%)	0.8(53.33%)

Table 7 Percentage of water separated in stirring speed effect experiment using MES as surfactant.



Figure 13 Comparison for all sample for effect of stirring Speed to emulsion stability using MES

For table and figure shown above, we could see that overall the stability of emulsion for all samples are unstable. Nevertheless the pattern we could see that the higher the RPM the stable emulsion .Thus this proved the hypothesis of the higher the RPM the stable the emulsion will be. Further studies on higher RPM could not be done as the homogenizer maximum speed is 2000 RPM.

Sample	Strring	Volume of	Volume of	Volume of	Volume of	Volume of
	speed	water	water	water	water	water
	(RPM)	separated	separated	separated	separated	separated
		after 30 mins	after 60	after 90	after 120	after
		(mL)	mins(mL)	mins(mL)	mins(mL)	150mins(mL)
1	500	0.2(13.3%)	0.5(33.3%)	0.6(40%)	0.8(53.33%)	0.8(53.33%)
2	1000	0.2(13.3%)	0.2(13.3%)	0.5(33.3%)	0.5(33.3%)	0.6(40%)
3	1500	0.1(6.67%)	0.1(6.67%)	0.3(20%)	0.4(26.67%)	0.4(26.67%)
4	2000	0.0 (0%)	0.1(6.67%)	0.1(6.67%)	0.2(13.3%)	0.2(13.3%)

 Table 8 Percentage of water separated in stirring speed effect experiment using PETROSTEPS as surfactant.



Figure 14 Effects of stirring speed towards emulsion stability stabilized by PETROSTEPS

From the table and graph shown above, Sample 4 shows most stable emulsion when mix with PETROSTEPS. The RPM for sample 4 is the maximum speed of the homogenizer which 2000RPM .With this surfactant, it shows better stability when compared with the sample using MES as surfactant. After 2.4 hours of observation, the amount of water separated is less than 20% .This shows increment in stability of the emulsion. Greater stability might be achieved if more powerful homogenizer available to conduct the experiment. The most unstable sample was sample 1 with 500 RPM .This proves that energy is needed to form an emulsion. With intense agitation, stable emulsion could be achieved.

4.5 Result and Discussion for experiment 5 –Effect of Temperature Ratio in Emulsion Stability for MES and PETROSTEPS as surfactant

For this experiment, the variable parameter that will be assessed is the temperature of the mixture when emulsification process took place. Generally interfacial tension will be reduce when temperature increase .The increased kinetic energy imparted to the surface molecules at higher temperature will tend to overcome the net attractive force of the bulk liquid (diesel) and as the temperature of the liquid approaches the critical value , the cohesive force between the molecules approaches zero . Higher temperature will yield better result for emulsion and it is generally true as the surface tension will vanish at the critical temperature. However, a sudden increase of the temperature will caused the particles to coagulate which will then cause the emulsion to deteriorate The surfactant interfacial adsorption is affected to some extent by increasing temperature .Thus, it will increase the probability of collision and coalesce and resulting in destabilizing the water in oil emulsions .

Sample	Temperature	Volume of	Volume of	Volume of	Volume of	Volume of	
	(°C)	water	water	water	water	water	
		separated	separated	separated	separated	separated	
		after 30	after 60	after 90	after 120	after	
		mins (mL)	mins(mL)	mins(mL)	mins(mL)	150mins(mL)	
1	30	0.1(6.67%)	0.5(33.3%)	0.5(33.3%)	0.6(40%)	0.7(46.67%)	
2	40	0.3(20%)	0.4(26.67%)	0.6(40%)	0.7(46.67%)	0.7(46.67%)	
3	50	0.5(33.3%)	0.5(33.3%)	0.7(46.67%)	0.8(53.33%)	1.1(73.3%)	
4	70	0.5(33.3%)	0.7(46.67%)	0.9(60%)	1.2(80%)	1.3(86.7%)	

Table 9 Percentage of water separated in temperature effect experiment using MES as surfactant.



Figure 15 Effects of temperature on Emulsion Stability using MES as surfactant

Table 9 and figure 15 shown the result for the experiment of the effect of the temperature on emulsion stability using MES as surfactant .From the figure 15, it could be conclude that the most stable temperature for this particular surfactant is 30° C and the most unstable is 70° C. At first increased temperature of 10° C form 30° C to 40° C, shows decrease in percentage of water separated but after an hour, 40° C shows greater instability when compared to 30° C. For 50° C, the water separated increasing steadily when compared to previous sample .Thus this shows that this particular surfactant is unstable when temperature increases. This might be the surfactant is sensitive towards temperature increase. The highest temperature for this experiment is 70° C and it is unstable. Almost 90% of water content is separated out from the emulsion within 2.5 hours. This may be adverse form the hypothesis that interfacial tension reduces when temperature increase thus aiding in the emulsion stability but the increase of temperature may affected the surfactant absorption ability thus deteriorated the emulsion.

Sample	Temperature	Volume of	Volume of	Volume of	Volume of	Volume of	
	(°C)	water	water	water	water	water	
		separated	separated	separated	separated	separated	
		after 30	after 60	after 90	after 120	after	
		mins (mL)	mins(mL)	mins(mL)	mins(mL)	150mins(mL)	
1	30	0.0 (0%)	0.1(6.67%)	0.1(6.67%)	0.2(13.3%)	0.2(13.3%)	
2	50	0.2(13.3%)	0.3(20%)	0.5(33.3%)	0.6(40%)	1.1(73.3%)	
3	70	0.3(20%)	0.5(33.3%)	0.7(46.67%)	0.8(53.3%)	0.9(60%)	

Table 10 Percentage of water separated in temperature effect experiment using MES as surfactant.



Figure 16 Effects of temperature towards emulsion stability stabilized by PETROSTEPS

Both figure 16 and table 10 shows the result for the effect of temperature towards emulsion stability stabilized by PETROSTEPS .Sample 1 which represents temperature of 30^oC shows the most stable emulsion with less than 20% of water content separated out form the emulsion .The most unstable was sample 2 which the temperature is 50^oC .Meanwhile it is different from samples from previous example which used MES as surfactant that at temperature of 70^oC shows the most unstable. For this sample which the temperature is 70^oC shows better stability when compared with sample using MES as surfactant.

4.6 Emulsion Droplet Size

This experiment using a Particle Size Analyzer (PSA) by Malvern Instrument model MASTERIZER[®] 2000. The objective of this experiment is to determine the size of the particle size for each emulsion prepared. Sample testing was done right after mixing ceased. The focused narrowed down towards the experiment of effects of water/oil ratio towards emulsion stability. The droplet size is an indicator towards instability of the emulsion .The larger the droplet size of the emulsion the unstable it will be. Water/diesel ratio and type of surfactant are the variable parameters where else surfactant concentration, mixing speed, mixing time and temperature remain constant.

Sample	Water/Diesel Ratio	Surfactant	Range of Droplet Size
	(vol %)		
1	5/95	Mehtyl Ester	90μm - 600 μm
		Sulfonate (MES)	(Max:200 µm)
2	10/90	Mehtyl Ester	100μm - 1800 μm
		Sulfonate (MES)	(Max:400 µm)
3	15/85	Mehtyl Ester	1000μm - 3000 μm
		Sulfonate (MES)	(Max:1800 µm)
4	20/80	Mehtyl Ester	1200μm - 2000 μm
		Sulfonate (MES)	(Max:2000 µm)
5	5/95	PETROSTPES	6μт -30 μт
			(Max:12 µm)
6	10/90	PETROSTPES	19μm - 30 μm
			(Max:25 µm)
7	15/85	PETROSTPES	20μm - 100 μm
			(Max:130 µm)
8	20/80	PETROSTPES	70μm - 180 μm
			(Max:50 µm)

Table 11 Result for emulsion droplet size

Table 11 shows the result for emulsion using different surfactant and water/diesel ratio experiment .From the tables 11, most of the samples using MES as surfactant have a large range of particle size increasing with the increase ratio of water/diesel. Maximum shown in the bracket indicates the largest volume of the sample has the particle size as stated .For sample using PETROSTEPS, a significant decrement in the droplet size .This shows the surfactant used is more stable when compared to

the sample using MES as surfactant. The range of the droplet size is not evenly distributed (refer **APPENDIX B**). This may caused by other parameters such as surfactant's concentration ,mixing speed ,mixing time and temperature is not at the optimum level to produce a stable emulsion As the concentration of water increase in the emulsion , the droplet size increase. As water concentration increase, the intensity of stirring and/or surfactant concentration should be increased to obtain a stable emulsion.

Sample using PETROSTEPS shows smaller range of particle size .This indicates, under same fixed variable, type of surfactant plays an important role towards emulsion droplet size .Emulsified fuels particle size should be small enough to be use in diesel engine fuel injection system .If it large, the molecule might pass the jet nozzle of fuel injector of the engine. Thus, it is important to analyze the particle size not only to study the relation with emulsion stability but also to assess the suitability of the emulsified fuel to be use in the conventional engine.



Figure 17 Sample of particle size analysis using Malvern MASTERIZER 2000 (refer APPENDIX B)

CHAPTER 5

CONCLUSION & RECOMMENDATIONS

5.1 Conclusion

Throughout the experiment, the parameters that contribute towards stability are studied which includes the effect of water/diesel ratio, type of emulsifier, emulsifier dosage, stirring speed, stirring time and temperature .It is proven that this parameters have a great affect towards emulsion stability and each of the emulsion need to be tailor made with optimal parameters to produce a stable emulsion.

Based on the experiment done, water/diesel ratio has significant affect towards emulsion stability .The emulsion stability increased with decreasing water to diesel ratio. This happened for both experiment which used MES and PETROSTEPS as surfactant. It is also showed that, the emulsion stability decreased with increasing concentration of surfactant. It applies to both surfactant that are used in the experiment .The optimum dosage for MES and PETROSTPES are 0.2 % and 0.5% respectively. Optimum mixing time for sample using MES as surfactant was 20 minutes and for PETROSTEPS is 15 minutes. Longer mixing time might cause emulsion stability to decrease due to drop-out of emulsifier from diesel-water interface .Higher stirring speed shows greater stability for both samples using MES and PETROSTEPS. The optimum speed was 2000 rpm .Further increment in speed could not be done as the homogenizer used was limited to 2000rpm.Higher temperature reduced emulsion stability .Thus, the optimal temperature for MES and PETROSTEPS samples are 30°C and 40°C respectively.

In droplet size experiment, it is shown that sample using PETROSTEPS has the smallest range of particle size of $6\mu m$ -30 μm (Max:12 μm). This could be considered as macro emulsion and the most stable of the samples observed .To

achieve micro –emulsion required an extensive set of experimental apparatus to achieve micro-emulsion. Particle size analyzing was also used to assess the suitability of the emulsion to be used in the fuel injection system .Unfortunately due to time constraint, experiment using a diesel engine to assess its performance and ability to reduce hazardous emissions could not be done.

5.2 Recommendations

For this experiment, both of the surfactant is conventional surfactant. Thus, for the next experiment, Gemini surfactant could be used as numerous studies shows that Gemini surfactant has better effect towards emulsion stability. Next recommendation would be the experimental apparatus such high speed homogenizer. The homogenizer available only has maximum rotation of 2000 Rpm. Thus, to study the effect of stirring towards emulsion stability, a higher range of speed should be use as the effect of the stirring speed could be fully studied.

Diesel engine should also be done to test the performance of the emulsified duel to diesel engine. Exhaust emission assessment could also be done to study the effect assess the amount of Nitrogen Oxides (NO_x) and Particulate Matter (PM) reduce as an effect of using emulsified fuels .

5.3 Way forward

Upon the completion of this project, it is hope it will benefit the petrochemical industry in developing a stable emulsified fuel to be use in the conventional diesel engine. It is hope more experiments and testing will be conducted to improve the emulsion stability to be used in conventional diesel engine.

CHAPTER 6

REFERENCES

- Gonglun Chen, Daniel Tao, An experimental study of stability of oilwateremulsion, Fuel Processing Technology, Volume 86, Issue 5, 25 February 2005, Pages 499-508.
- [2] Muzio,L and Quartucy, G.Implementing NO_x Control:Research to application.*Prog.Energy Combustion Sci.* 23:233-266,1997
- [3] Pischinger FF, Compression –ignition engines, In: Sher E, editor .Handbook of Pollution from internal combustion engines, London UK, Academic 1998 .p.261-2
- [4] R.Gunnerman, Water Fuel Emulsion, Business Week, 1994.
- [5] W.Ostwald ,Kolloid –Zeitschriff ,1910,p7
- [6] N. Zaki, P.C. Schorling and I. Rahimian, Petroleum Science and Technology 18 (2000) (7), pp. 945–963.
- [7] M.F. Fingas, B. Fieldhouse, L. Bier, D. Conrod and E. Tennyson, Author Affiliation: Environmental Technology Cent Source: ASTM Special Technical Publication, 1252, ASTM, Philadelphia, PA, USA (1994 (Oct 10– 11)), pp. 41–54
- [8] J.R. Campanelli and D.G. Cooper, *Canadian Journal of Chemical Engineering* 67 (1989) (5), pp. 851–855.
- [9] M.T.Ghannam, M.Y.E. Selim , Stability Behavior of Water-in-Diesel Fuel Emulsion , Petroleum Science Technology ,27 :396-411 ,2009 .
- [10] Klaus Tauer, MPI Colloids and Interfaces, Max-Planck-Institute fur Kolloid –und Grenflachenforschung,
- [11] Wang ,C., and Law ,C. ,Microexplosions of droplets under high pressure .Combust .Flame 59:53-62. 1983

- [12] M.Nadeem , C.Rangkuti , K.Anuar ,M.R.U. Haq ,I.B. Tan, S.S Shah, Diesel engine performance and emissions evaluation using emulsified fuels stabilized by conventional and Gemini surfactants .Fuel.2006:86:2111-2119.
- [13] Tharwat F. Tadros, Applied Surfactants: Principle and Applications .John Wiley & Sons, 2005
- [14] "Gunnerman Fuel', <u>www.rbbi.com/folders/fuel/a-21.html</u>
- [15] Rosen, Milton J, Surfactants and interfacial phenomena -3rd .John Wiley& Sons, 2004.
- [16] S.V. Verbich, S.S. Dukhin, A. Tarovski, O. Holt, O. Saether and J. Sjoblom, *Colloids and Surfaces. A, Physicochemical and Engineering Aspects* 123– 124 (1997), pp. 209–223.
- [17] A.Lif ,Krister Holmberg , Water –in-diesel emulsions and related systems , Advances in Colloid and Interface Science, Volumes 123-126, 16 November 2006, Pages 231-239.
- [18] Fingas, M., B. Fieldhouse, "Studies of water-in-oil emulsions: Stability studies", Spill Science & Technology Bulletin, Volume 3, Issue 4, Spill Science and Technology Bulletin, 1996, Pages 189-190
- [19] Laura-Isabel Tolosa ,Ana Forgiarini ,Paul Moreno ,Jean-Louis Salager , "Combined Effects of formulation and stirring on Emulsion drop size in the vicinity of three-phase behavior of Surfactant-Oil Water Systems", Ind. Eng. Chem. Res., 2006.
- [20] Fingas, M., B. Fieldhouse, M.Bobra and E. Tennyson "The Physics and Chemistry of Emulsions", in proceedings of the Workshop on Emulsions, Marine Spill Response Corporation, Washington, D.C., 7 P .1993b.
- [21] R.P. James , R.P. Charles , *Petroleum Spills* (1985), p.3.

APPENDICES

APPENDIX A

1) Example of emulsion after mixing - Experiment effects of water/diesel ratio (5/95) stabilized by MES



After mixing ceased



24 hours after mixing

2) Example of emulsion after mixing -Experiment effects of water/diesel ratio (20/80) stabilized by MES



After mixing



24 hours after mixing (clear view of phase separation)

3) Effects of stirring time towards emulsion stability



Difference of the emulsion stability for stirring time effect experiment

4) Emulsion before mixing and after mixing .Before mixing clear view of clean diesel with water phase at the bottom. After mixing shows the emulsion produced .



5) Example of data collection and observation of phase separation of the emulsion using graduated cone cylinder with (0.1 mL -200mL)



APPENDIX B

Particle Size Analyzer (PSA) by Malvern ®MASTERIZER 2000

All experiments are done with fixed parameters as below:

- Surfactant concentration 0.2%
- Stirring time : 15 minutes
- Stirring speed : 2000 RPM
- Temperature : Room Temperature (27°C 30°C)

Experiment 1 using Methyl Eshter Sulfonate (MES) and Experiment 2 using PETROSTEPS as surfactant.



1) Experiment 1 - Sample 1 (W/D 5/95)

2) Experiment 1 –Sample 2 (W/D 10/90)



3) Experiment 2 – Sample 3 (W/D 15/85)



4) Experiment 4 – Sample 4 (W/D 20/80)



5) Experiment 2 – Sample 1 (W/D 5/95)



⁶⁾ Experiment 2 – Sample 2 (W/D 10/90)



7) Experiment 2- Sample 3 (W/D 15/85)



8) Experiment 2 – Sample 4 (W/D 20/80)



Gantt Chart

No.	Detail/ Week	1	2	3	4	5	б	7		8	9	10	11	12	13	14	15
1	Project Work Continues																
2	Submission of Progress Report									•							
3	Project Work Continues																
									¥								
4	Pre-EDX								rea				0				
									B								
5	Submission of Draft Report								ter					•			
									les								
б	Submission of Dissertation (soft bound)								en						0		
									$\overline{\mathbf{N}}$								
7	Submission of Technical Paper								Iid						0		
									4								
8	Oral Presentation															•	
9	Submission of Project Dissertation (Hard Bound)																•