The Effect of Drag Reducing Polymer to the Interfacial Tension of Oil-Water, Two Phase Mixture

By

Sarah Amirah Binti Kamaruddin

14860

Dissertation in partial fulfillment of the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

JANUARY 2015

Universiti Teknologi PETRONAS Bandar Seri Iskandar 32610 Tronoh Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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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.

SARAH AMIRAH KAMARUDDIN

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ABSTRACT

The use of polymeric drag reducing additives (PDRA) have been discovered in the early 20th century, where its first large-scale commercial utilization has been implemented in the Trans-Alaskan Pipeline System (TAPS) in 1979. The ability of polymer solution to modify the viscosity of the flowing medium translates into its assistance of altering the flow properties during the transportation of fluids. During the process, PDRA promoted the bubbly and dispersed flow into stratified regime, where oil-water is separated via a pronounced interfacial boundary. In this condition, the nature of the interfacial tension is unknown due to the changes caused by the dilution of PDRA into the flowing medium. This research presents the study on the rheological properties of the partially hydrolyzed polyacrylamide (PHPA) solution that acts as the PDRA its ability to affect the oil-water interfacial tension. The experimental work consists of viscometry and the pendant drop analyses, conducted for various concentration of PDRA at various temperatures. The study shows that the PDRA exhibit a shear thickening effect and is proven from the flow behavior index where the n > 1. The PHPA solution at 7 000 and 10 000 ppm gives higher viscosity and provides better reduction of the interfacial tension which are 10.96 mN/m and 8.31 mN/m at 25°C between the oil-water interphase. However, at elevated temperature the PHPA solutions do not demonstrate much difference in the behavior of the flow as well as its effect towards the interfacial tension of the oil-water interphase.

TABLE OF CONTENTS

CERTIFICATION OF APPROVAL	i
CERTIFICATION OF ORIGINALITY	ii
ACKNOWLEDGEMENT	iii
ABSTRACT	iv
LIST OF FIGURES	vii
LIST OF TABLES	ix
CHAPTER 1: INTRODUCTION	1
1.1 Background of study	1
1.2 Problem Statement	3
1.3 Objectives and Scope of Study	3
CHAPTER 2: LITERATURE REVIEW/THEORY	4
2.1 Polymeric Drag Reducing Agent	4
2.2 Stratified Flow	5
2.3 Viscosity and Shearing Effect	6
2.4 Interfacial Tension	7
2.5 Interfacial Surface Tension and Contact Angle of Oil-Water Phase	8
2.6 The Pendant Drop Method	11
CHAPTER 3: METHODOLOGY	15
3.1 Materials and Equipment	15
3.2 Parameters used in Experiment	16
3.3 Standard Operating Procedures	16
3.3.1 Preparation of PHPA solutions	16
3.3.2 Viscometry Study of the PHPA Solution	17
3.3.3 Determination of the Interfacial Tension of the Oil-Water Phase	17
CHAPTER 4: RESULTS AND DISCUSSION	20
4.1.1 Behavior of PHPA solution during mixing	

4.1.2 Physical Appearance	. 20
4.2.1 Density	. 21
4.2.2 Turbidity	. 22
4.2.3 pH Level	. 23
4.2.4 Rheological Properties	. 25
4.2.5 Interfacial Tension	. 31

CHAPTER 5: CONCLUSION AND RECOMMENDATION......43

5.1 Conclusion	43
5.2 Recommendation	44

REFERENCES

APPENDICES

LIST OF FIGURES

Figure 1:Velocity profiles of the turbulent flow of (a) a pure liquid and (b) a liquid with polymer
additive. (Nesyn et al., 2012)1
Figure 2: Polyacrylamide powder2
Figure 3: Illustration of pipeline turbulent flow regions, (Abubakar, 2014)4
Figure 4: Graph of viscosity vs time of oil water phase (Wang et al, 2011)7
Figure 5: a) Definition of the contact angle that a particle assumes at the oil-water interface b)
energetic configuration of a liquid drop on a glass surrounded by oil (Pichot et al, 2012)9
Figure 6: a) Interfacial elasticity in the presence of only pectins (HMP or SBP) at the oil-
solution interface. (Gülseren & Corredig, 2014)11
Figure 7: Theoretical configurations observed for axisymmetric fluid-fluid interfaces in a
gravitational field12
Figure 8: The pendant drop method14
Figure 9: a) Set up of goniometer for pendant drop test b) Drop of PHPA solution in kerosene
inside the liquid chamber
Figure 10: Schematic drawing of apparatus set-up18
Figure 11: PHPA solution at different concentrations20
Figure 12: Graph of density versus concentration of PHPA solution21
Figure 13: Graph of turbidity versus concentration of PHPA solution23
Figure 14: Graph of pH value versus concentration24
Figure 15: Graph of shear stress vs shear rate of 1 000 ppm PHPA solution at 25°C, 40°C and
50°C25
Figure 16: Graph of shear stress vs shear rate of 3 000 ppm PHPA solution at 25°C, 40°C and
50°C25
Figure 17: Graph of shear stress vs shear rate of 5 000 ppm PHPA solution at 25°C, 40°C and
50°C
Figure 18: Graph of shear stress vs shear rate of 7 000 ppm PHPA solution at 25°C, 40°C and
50°C26
Figure 19: Graph of shear stress vs shear rate of 10 000 ppm PHPA solution at 25°C, 40°C and
50°C

Figure 20: Dimensions and symbols used in the program of the goniometer	.31
Figure 21: Graph of interfacial tension of tap and distilled water at different temperatures	. 40
Figure 22: Graph of interfacial tension vs concentration of PHPA solution at different	
temperatures	.40
Figure 23: Graph of interfacial tension vs temperature of PHPA solution at different	
concentrations	.41

LIST OF TABLES

Table 1: Density of PHPA Solution	. 21
Table 2:Turbidity of the PHPA Solution	22
Table 3: pH level of the PHPA Solution	23
Table 4: Table of n values for PHPA solutions at different concentration	. 29
Table 5: Data from interfacial tension measurement experiment	. 33
Table 6: Rheological Properties of 1 000 ppm PHPA solution	. 51
Table 7: Rheological Properties of 3 000 ppm PHPA solution	. 52
Table 8: Rheological Properties of 5 000 ppm PHPA solution	. 53
Table 9: Rheological Properties of 7 000 ppm PHPA solution	. 54
Table 10: Rheological Properties of 10 000 ppm PHPA solution	55

CHAPTER 1: INTRODUCTION

1.1 Background of study

Ever since Toms' finding in late 1940s that suggested on the use of polymer additive to enhance the flow of crude oil in the pipeline, the research on drag-reducing additives (DRA) has increased ever since. After almost three decades, the first commercial use of a polymeric drag-reducing additive (PDRA) to increase the flow rate in a crude oil pipeline began in 1979 in the Trans-Alaska Pipeline System (TAPS). The ability of polymer solution to modify the viscosity of the medium translates into its assistance of altering the flow properties during the transportation of fluids. In a multiphase system consisting of immiscible liquids, PDRA could alter the interface between the phases, particularly during stratified flow. This change would affect the shape of the curvature experienced during the flow to be either flat, concave upwards or concave downwards, which further decodes to the modification of pressure drop during the flow.

PDRA has been widely used in the oil and gas industry especially in the pipeline system. It has shown great advantages whereby it could reduce up to 80% of drag force in the pipeline system, (Abubakar et al, 2014). Due to its practicability, the PDRA could reduce the usage of pumps and provide better efficiency in flow of liquid in pipelines. Where studies show that the polymeric DRA affects the spatial distribution of fluids in the pipe and the boundaries between different flow patterns (Oliver and Young, 1968; Greskovich abd Shrier, 1971; Virk, 1975).



Figure 1:Velocity profiles of the turbulent flow of (a) a pure liquid and (b) a liquid with polymer additive. (Nesyn et al., 2012)

There are many types of DRA; among the types are polymers, fibers, microbubbles, surfactant and compliant coating. For this particular study, partially hydrolyzed polyacrylamide (PHPA) is used. The PHPA has a variety of application in the oil and gas industry where it improves the production of oil, reduce friction, fluid loss control and lubrication. From a study in 1992, polyacrylamide was used as a PDRA and it has shown a tremendous effect where the drag effect was reduced by using 0.25 ppm of polyacrylamide (Wei and Willmarth, 1992). Al Sarkhi mentioned in 2010 that polymer helps in reducing the Reynolds shear stress and varying velocity.



Figure 2: Polyacrylamide powder

From previous studies, there are many topics on single-phase flow and only now the study on multiphase flow starts to emerge and expands. Most of the studies are about pressure drop, drag reduction and the efficiency of the PDRA; and not much considered the impact of PDRA towards the change of interfacial curvature of the flowing fluids in the pipe that may affect the overall pressure drop. As PDRA is added into the flowing medium and dissolved accordingly, the change of in-situ viscosity is predicted to influence the shape of the curvature due to the change of wettability towards the wall and two fluids interfaces. This study, therefore, will investigate the impact of the PHPA that is added into the liquid medium (solvent) by looking into the change of in-situ viscosity and its influence to the interfacial curvature in two-phase liquid system.

1.2 Problem Statement

The PDRA has been widely used in the pipeline system to help in drag reduction between oil and the pipeline in order to increase the flow rate of the oil. When PDRA is injected to a stratified flow of oil-water phase, the shape of the curvature of the multiphase changes accordingly. With the study on the viscosity of the PDRA, the reason behind the changes in the interfacial tension between the multiphases could be identified.

1.3 Objectives and Scope of Study

- 1. To investigate the rheological properties of diluted concentration of PHPA through shear analysis at various temperatures.
- 2. To determine the effect of dilute PHPA to the interfacial tension/contact angle in the oil-water, two-phase condition.

The PHPA acts as the polymeric drag-reducing agent (PDRA) in the pipeline system which transport oil. For this study, the viscosity and rheological properties of PHPA at different concentration will be analyzed by using viscometer and rheometer. The PHPA powder will be mixed with water to produce a solution at different concentration. The experiment consists of using PHPA at different concentration at a varying temperature. Since many studies has focused on how the DRP affect the pressure drop inside the pipeline, this study will be focused on the shear analysis and the effect of using PHPA to the interfacial surface tension in oil-water phase.

CHAPTER 2: LITERATURE REVIEW/THEORY

2.1 Polymeric Drag Reducing Agent

According to Katz (1992), Polymeric drag-reducing agent (PDRA) has been discovered since about forty years ago by Toms where it was observed that is could contribute 30 - 40% in drag reduction by adding 10 ppm by weight of polymethylmethacrylate to turbulent monochlorobeneze flowing down the pipe.

The evolvement of PDRA is from the problem that is caused by transporting the multiphase mixture from hundreds of kilometers to the separating tank. The pressure drop in the pipeline is very high and the usage of pump is not cost effective (Al-Sarkhi, 2010). The PDRA possess a lot of advantages where it saves a lot of cost, elevates production and reduce the pipeline pressure.

PDRA are long chain, with high molecular weight which are water and/or oil soluble and it gives better performance, (Abubakar et al., 2014). Usually at low velocity the flow of the multiphase liquid is stratified but as the velocity increases, the flow of the multiphase liquid changes to non-stratified and finally to dispersed flow. As mentioned by Al-Sarkhi (2010), the PDRA does not only help in the occurrence of pressure drop, it also contributes in the maintaining the stratified flow which would help in the separation of oil-water phase.



Figure 3: Illustration of pipeline turbulent flow regions, (Abubakar, 2014)

In order to overcome the difficulty in separation of the phases, the PDRA needs to be introduced as it could reduce the energy consumption and provides better efficiency in separating the multiphase liquid. Besides that, in 2006, Mowla and Naderi have done a study on different concentrations of PDRA where that findings prove that the optimum concentration that is needed to give the highest drag reduction is 18 ppm. However, the efficiency of the PDRA does not only depends on the concentration it also depends on the size and type of the pipe used as well.

From a study done by Al-Sarkhi and Hanratty (2012), they have found out that when drag reducing agent is being injected into a pipe with flowing air and water, the flow of the multiphase changes from annular to stratified flow and the PDRA cause a reduction in pressure drop inside the pipeline system. Meanwhile, a study on liquid hold up when using PDRA was done by Al-Yaari and Al-Sarkhi in 2012, where the velocity is remained but with varying volumetric flow rate of the water.

Polyacrylamide is commonly used polymers as a PDRA where it is a flexible molecule with a molecular weight of 5.0×10^6 g/mol. According to Pereira (2013), from the study that he made the result shows that the drag reduction increase as the concentration of polyacrylamide increases.

2.2 Stratified Flow

Stratified flow is a region with multiphase flow where it is consisting of different density fluid moving in vertical direction. Stratified flow makes it easier to separate the fluids into different layers whereby the lighter fluids will flow above the heavier fluid. When the multiphase fluid is flowed in a horizontal pipeline the fluids are then separated to different layers. Stratified type of flow is easier to occur when the flow rate is low especially at flat sections of the pipeline meanwhile, as the flow rate increases, the multiphase fluid tend to mixed and the flow becomes unbalanced and this flow is called wavy stratified flow.

2.3 Viscosity and Shearing Effect

Rheology is the science of flow and deformation of matter or more specifically it is the study of stress-deformation relationships where it relates to the study of rheological properties of the fluids.

$$\frac{stress}{strain} = modulus$$
$$\frac{stress}{shear rate} = viscosity$$

According to Hooke's Law, stress and strain are related through a proportionality constant which is known as modulus which then could be related to the fluids' viscosity, stress, strain and shear rate. Meanwhile, Newton Law explains that stress and strain are related through a proportionality constant which is viscosity. Both of these laws are linear laws where the stress is directly proportional to its strain.

Rheology helps in understanding more on how the fluids could be controlled and it is easier to predict the fluids' performance during handling, transportation, processing and application in the industry. However, rheology is focused more on the behavior of the fluids in complex field of flow. The rheological property greatly influences the movement of multiphase in a pipeline system. A study done by Meriaem-Benziane et al (2012), investigates on the rheological properties of crude oil in pipeline where they found out that the viscosity of the emulsion differs with different content of water. Both the crude oil and emulsion shows a different viscosity property where the emulsions shows the Herschel-Bulkley and Ostwald de Waele behavior meanwhile, crude oils shows Newtonian behavior with moderately constant viscosity, (Meriem-Benziane et al, 2012). As a whole the previous researches have shown that formation of emulsion in multiphase flow increases the flow in pipeline systems.

Previous research done by Wang et al (2011) on the flow characteristics of oilwater phase findings verifies that the flow pater and water content in a mixture affects the viscosity of the fluid. From the outcome of the study, at low water fractions the flow is fully dispersed; meanwhile, as the water fraction begins to increase the flow tends to change to annular and an increment in velocity was observed.



Figure 4: Graph of viscosity vs time of oil water phase (Wang et al, 2011)

The graph basically explains the effective viscosity over time of the flow at different velocity with different water fraction content. Increased in velocity increases the tendency of the water droplets to collide and coalesce with each other and the size of the water drops increases with increase in water fraction. Hence, the shear rate of the fluid flow increases and the fluid shows a behavior of shear thinning as the fluid velocity increases.

2.4 Interfacial Tension

Interfacial or surface tension exists when two phases are present. These phases can be gas-oil, oil-water, or gas-water. It is the force that holds the surface of a particular phase together and is usually measured in dynes/cm. The surface tension between gas and crude oil ranges from near zero to approximately 34 dynes/cm. Surface tension is a function of pressure, temperature, and the composition of each phase. The main forces involved in interfacial tension are adhesive forces between the liquid phases of one substance with either a solid, liquid or gas phase of another substance. The interaction occurs at the surfaces of the substances involved which is at its interface.

2.5 Interfacial Surface Tension and Contact Angle of Oil-Water Phase

According to Hyde et. al (2014), the liquid-liquid interfacial tension is one of the main physical parameter that affects the multiphase system in a wide range of processes which are separation and emulsification where these processes are widely used in the chemical industry especially in chemical processing. Cao and Li (2000) also mentioned that low interfacial tension is highly desirable in the chemical industry especially in chemical, enhance oil recovery and multiphase separation. The interfacial tension of oil-water phase could be reduced by using polymeric surfactants that combines the high viscosity of a polymer with the interfacial property of a conventional surfactant.

In the oil and gas industry, the two phase mixture system plays a huge role in how it is being processed. The dispersion of the oil-water phase is important in the production of petroleum as two immiscible liquids are mixed where one of the phase is dispersed into the other. Water is usually injected into the oil wells and other chemicals such as asphaltenes, resins and polymers which acts as surfactant which help in improving the oil recovery. These chemicals help in producing a stabilized multiphase as it helps in reducing the energy form when the mixture is sheared in a turbulent multiphase flow, (Wang et al, 2011). Guifeng et al (2007) also mentions that surfactants has widely being used due to its outstanding technology applications in emulsion stability, enhanced oil recovery and detergency where it could help to minimize the interfacial tension of the multiphase.

Interfacial tension is highly affected by the intermolecular forces between the molecules where tension is build up between the immiscible multiphase flows as the particles behave differently. According to Isehunwa and Olubukola (2012), temperature, impurities and pressure does not affect the interfacial tension of oil-brine flow system. The oil-water phase contains polar organic compounds and emulsions thus, when other compounds such as resins, asphaltenes and organic acids are present at the interfacial film it would affect the physical properties of the compounds that exist at the oil-water phase, (Shen et al, 2005).

As mentioned by Dardelle and Erni, (2014), complex coacervation occurs from formation of two liquid phases where the liquid-liquid phase are separated. The liquidliquid system consists of polymer and a dilute continuous solvent phase. When there is an existence of a third liquid phase in the liquid-liquid system the coacervate phase will tend to wet the oil-water interface.

Pichot and Spyropoulos (2012), had done a study using surfactant to study the interfacial surface tension of oil and water. They have mentioned the types of surfactant that is used did not really affect the contact angle of the oil-water phase but it is only affected by the usage of high concentration of surfactant. The displacement of particle between the liquid phases is correlated to the oil-water interfacial tension and contact angle. According to Rosen (1989), the contact angle that is produced after a liquid is dropped on the surface is one of the best ways to determine the wetting of a solid surface.



Figure 5: a) Definition of the contact angle that a particle assumes at the oil-water interface b) energetic configuration of a liquid drop on a glass surrounded by oil (Pichot et al, 2012)

The following formula is to determine the interfacial tension increment per unit fractional change in the interfacial area:

$$\varepsilon = \frac{d\gamma}{d\ln A} = |\varepsilon| \exp(i\theta)$$

- ϵ Dilatational modulus γ Interfacial tension
- θ Phase angle A Area of the interface

Interfacial tension of oil-water phase could be determined by the following equation:

$$\gamma = (\gamma_1 - \gamma_2) \exp(\alpha V^{0.7}) + \gamma_2$$

γ : Interfacial tension

- $\gamma_1 \gamma_2$: Interfacial tensions of pure oils/water where $\gamma_1 > \gamma_2$
- α : Exponential coefficient
- V: Volume fraction of the oil mixture

The equation was developed by Kim and Burgess in 2001. The equation used a nonlinear regression in order to get the interfacial tension between the miscible organic fluids over its composition range, (Kim & Burgess, 2001). Through experimentations using five types of oil mixtures, the authors conclude that the interfacial tension is affected by the volume fraction and the interfacial tension difference of the two pure oils. The equation that was developed is able to predict the interfacial tension of miscible multiphase mixtures.

In 2014, Gülseren and Corredig studied on the interactions between commercial pectins and polyglycerol polyricinoleate (PGPR) at the oil-water interface. High methoxyl pectin (HMP) and sugar beet pectin (SBP) were used as model polysaccharides because of their differences in interfacial activity. The usage of SBP has caused a declination in the interfacial tension synergistically with PGPR while HMP affects the interfacial activity where it causes a difference in the viscoelastic properties of the interface. However, the characteristic of the HMP is assumed to be a non-adsorbing polymer at the oil-water interface.



Figure 6: a) Interfacial elasticity in the presence of only pectins (HMP or SBP) at the oil-solution interface. (Gülseren & Corredig, 2014)

2.6 The Pendant Drop Method

There are many ways to measure interfacial tension. Chang and Franses (2011) have reviewed on a few methods that are only applicable for gas-liquid systems. The interfacial tension of liquid-liquid systems, on the other hand, could be measured by using optical analysis like the pendant drop, sessile drop and spinning drop techniques. The most applied method to analyze liquid-liquid systems is the pendant drop method uses the system of Axis Symmetric Drop Shape Analysis (ADSA) whereby it uses a software with high-resolution images to match experimental drop profiles with solutions to the Young–Laplace equation of capillarity, (Hyde et al, 2014). The pendant drop method uses the concept of axis symmetric fluid bodies which are analyzed in a vertical direction as it is affected by gravitational forces that affects the surface curvature. In 1980, Boucher has found eight ways to get the interfacial equation arrangement. The equations are further described by the Young–Laplace equation and is expressed by three ordinary differential equations:

1.
$$\frac{d\phi}{ds} + \frac{\sin\phi}{x} = 2\lambda(H - Y)$$

2. $\frac{dx}{ds} = \cos\phi$

3.
$$\frac{dY}{dS} = \sin \emptyset$$

4. $a = \sqrt{g\Delta\rho/\gamma}$
5. $Bo = \frac{\Delta\rho gR^2}{\gamma}$

- S: Distance along the drop surface and the meridian angle
- Ø: Angle from the horizontal plane
- λ : Type of drop
- H: Shape factor
- X: Radial coordinate
- Y: Vertical coordinate
- a: Capillary length to normalized the coordinates

Bo: Characterization of the deformation of the interfacial tension

- R: Characteristics of length in the system
- γ : Interfacial tension



Figure 7: Theoretical configurations observed for axisymmetric fluid-fluid interfaces in a gravitational field

Interfacial tension or surface tension could be measured in two ways which is through the pendant drop method or sessile drop method. The pendant drop method is the most widely used method to calculate the interfacial tension or surface tension measurement. According to Woodward, the pendant drop mode is more accurate than the sessile drop because it is easier to make assumptions on the axial symmetry. As mentioned by Saad (2011), the accuracy of the measurement of the interfacial tension decreases when the shape is more spherical than 'pear shaped'. In order to make this experiment successful, the pendant drop design must be fully optimized. A drop of liquid is suspended from the needle of a microsyringe either in liquid or gas chamber where the shape of the drop is caused by gravity and the interfacial tension. Then the interfacial tension is measured by using the drop shape analysis (DSA) which is from the shadow of the drop image.

Wordward also mentioned that the assumptions made on DSA is that the drop is symmetric of a vertical axis and it is only caused by gravity and interfacial tension and the viscosity of the liquid does not affect the shape as it is not in motion. On the other hand, the Young- Laplace equation of capillarity proves that the drop needs to be affected by the force of gravity because the gravity cause the pendant drop shape to be elongated meanwhile the surface tension causes to drop shape to be round. The drop also tends to be more spherical with increase in the surface or interfacial tension. Other than that, the pendant drop also relates to the density and pressure that is exerted to the drop which is proven from the Young Laplace equation:

$$\Delta p = \sigma \left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

p = pressure

 σ = interfacial tension

 $\mathbf{r} = \mathbf{radius}$ of curvature

The pendant drop method could be done in two ways which is by hanging down or dispensed up. When it is hanging down, the drop is always heavier when forming a liquid-liquid phase while dispensed down is when the tip of the needle is below the bubble and the drop is lighter than the other liquid media.



Figure 8: The pendant drop method

CHAPTER 3: METHODOLOGY

3.1 Materials and Equipment

The analytical equipment used to complete the study are:

- 1. Bohlin C-VOR Rheometer
- 2. Ramé-hart Model 260 (p/n 260-F4) Goniometer

The materials that are needed to complete the study are:

- 1. Partially Hydrolysed Polyacrylamide (PHPA) powder
- 2. Kerosene
- 3. Distilled water

Kerosene

The kerosene is obtained from a consumer-grade, purchased at local PETRON Malaysia petrol pump. The Petron Kerosene is a refined kerosene with clean and efficient burning qualities.

Application: fuel for stoves, lamps, kerosene-fueled engines, boilers and furnaces.

Type/Quality Level: Kerosene

Typical Characteristics:

Appearance: Clear and Bright

Total Sulfur, % wt.: 0.01

Final Boiling Point, °C: 233.7

Flash Point (ABEL), °C: 39.5

Density at 15°C, kg/m³: 788.5

3.2 Parameters used in Experiment

For this study, the parameters that are used are different concentration of the PHPA solution which consists of 1000 ppm, 3000 ppm, 5000 ppm, 7000 ppm and 10000 ppm. This PHPA solutions are tested through viscometry test at different temperature which are at 25°C, 40°C and 50°C. The same goes in determining the interfacial tension between the kerosene and PHPA solution. The PHPA solution at all the 5 different concentration will go through pendant drop method test immersed in kerosene.

3.3 Standard Operating Procedures

The experimental work in this project can be divided into four parts. The experimental works are as follows:

- 1. The preparation of PHPA solutions at different concentrations.
- The rheology analysis of dilute PHPA solutions at various temperatures using Bohlin C-VOR Rheometer
- The investigation of interfacial tension/contact angle using the Ramé-hart Model 260 (p/n 260-F4) Goniometer.

3.3.1 Preparation of PHPA solutions

The following explains the procedure to prepare the mixture of water and the drag reducing agent that will be used for the experiments:

- 1. Prepare a beaker with 100mL of distilled water. Determine the amount in parts per millions (ppm) of polyacrylamide powder to be used.
- 2. Calculate the amount of polyacrylamide powder in gram (g) to be mixed.
- 3. Measure the exact amount in gram (g) needed which are 0.1, 0.2, 0.3, 0.5, 0.7 and 1.0.
- Place a magnetic stirrer inside the beaker and turn on the stirrer and at a speed of 50 RPM. The solution is stirred for 2 hours.
- 5. Cover the beaker with a plastic sheet.

6. Leave the mixture for 24 hours for hydration

3.3.2 Viscometry Study of the PHPA Solution

The following explains the procedure to prepare the PHPA solution to be tested for viscometry studies in order to study the viscosity of the solution:

- 1. Prepare the PHPA solution at 1000, 2000, 3000, 5000, 7000 and 10000 ppm.
- 2. Turn on the rheometer, heater and air compressor.
- 3. Determine the range of shear stress and strain data in the simulation.
- 4. Set the shear rate as a constant which starts from 0 to 10000 1/s.
- 5. Set the temperature to 25, 40 and 50°C for each tests.
- 6. Attached the 4/40 spindle with the rheometer and zero the equipment by adjusting the gap size.
- 7. Put the sample on the spindle and press start option.
- 8. Trim the sample from the spindle and press again start option to continue the test.
- 9. After test has completed, obtain the graph from the simulation which is on the computer screen.
- 10. Repeat each tests for 3 times.

3.3.3 Determination of the Interfacial Tension of the Oil-Water Phase

The pendant drop method using the goniometer equipment is chosen to determine the interfacial tension of the multiphase as mentioned in the literature review. The microsyringe assy which contains the PHPA solution helps in exerting pressure to produce the liquid drop at the needle tip is placed in the environmental chamber which contains kerosene oil. The scale of video image of the drop in greyscale mode is measured to get the actual dimension of the drop. The interfacial tension is then calculated using the following equation: $\gamma = \Delta \rho \ g \ R_0^2 / \beta$

 γ = interfacial tension

 $\Delta \rho$ = difference in mass density

g = gravity constant

 $\mathbf{R}_0 = \mathbf{is}$ the radius of curvature at the drop apex and

β = is the shape factor



Figure 9: a) Set up of goniometer for pendant drop test b) Drop of PHPA solution in kerosene inside the liquid chamber



Figure 10: Schematic drawing of apparatus set-up

The following explains the procedure to prepare the PHPA solution to be tested for the interfacial tension studies in order to study the viscosity of the solution:

- 1. Prepare the PHPA solution at 1000, 2000, 3000, 5000, 7000 and 10000 ppm.
- 2. Set up the apparatus.
- 3. Place the kerosene into the environmental chamber.
- 4. Then place the PHPA solution in the microsyringe assy then place the needle on the microsyringe assy.
- 5. Turn on the camera and then turn on the light with the light intensity ranges from 30-40.
- 6. Exert some pressure to the microsyringe assy to make the shape of the PHPA solution to be like a 'pear shape' of pendant drop.
- 7. Adjust the sharpness of the image to measure the interfacial tension of the kerosene and PHPA solution phase.
- 8. Set the temperature of the environmental chamber at 25°C, 40 and 50°C in order to heat the kerosene oil.
- 9. Take the measurement of the interfacial tension by placing the axisymmetric line on the drop image.
- 10. Wait for the calculation of the image and copy the data.
- 11. Repeat each test for 3 times for all three different temperatures at different PHPA solution concentration.

CHAPTER 4: RESULTS AND DISCUSSION

For this study, the results are analyzed qualitatively and quantitatively. For qualitative results, the physical properties of the PHPA solution are analyzed before and after it is mixed. Meanwhile, in the qualitative results the turbidity, pH value, viscosity and density of the PHPA solution are analyzed.

4.1 Qualitative Result

4.1.1 Behavior of PHPA solution during mixing

The behavior of the PHPA solution at different concentrations shows different characteristics. While mixing using the magnetic stirrer, as the concentration increases it is harder to mix the solution. When the rpm of the magnetic stirrer is increased, the magnetic stirrer bar could not continue stirring. As the concentration of the solution increases, the solution becomes clumpier and jelly like. Hence, more force is needed to agitate the solution at the same speed.

The magnetic stirrer is used to avoid the solution from over shearing as it could affect in determining the viscosity behavior of the solution.



4.1.2 Physical Appearance

Figure 11: PHPA solution at different concentrations

Figure 8 shows the solution at 1000, 3000, 5000, 7000 and 10000 ppm (from left to right). From the figure, it could be seen that as the concentration increases, the solution becomes cloudier. In addition, the solution becomes more jelly like and stickier.

4.2 Quantitative Result

4.2.1 Density

Concentration of PHPA Solution, ppm	Density, kg/m ³
1 000	983.38
3 000	972.79
5 000	974.17
7 000	958.27
10 000	962.14

Table 1: Density of PHPA Solution



Figure 12: Graph of density versus concentration of PHPA solution

The density of the concentration of the PHPA solutions does not show any constant trend in the density with increasing concentration. The reason behind this is still in study. This may be due to the difference in the size of the granular powder of the polyacrylamide, the nature of the polymer, presence of bubbles in the solution and how the solution was prepared. When preparing a polymer solution from an emulsion, there are two physical phenomena which are phase inversion and dissolution which take place and need some specific conditions to be made properly. The beads of hydrogel come in contact with water and dissolve. Polyacrylamides in solution are sensitive to free-radical chain degradation. Free radicals are formed in water by a number of oxidising and reducing agents. Mostly they are formed from dissolved oxygen and iron.

4.2.2 Turbidity

Turbidity is the measurement of the cloudiness of a fluid. The turbidity is caused by the presence of particles that are invisible to the naked eyes. The suspended particles reduce the amount of light that could enter the fluid.

Concentration of PHPA	Turbidity, NTU
Solution, ppm	
1 000	3.99
3 000	4.28
5 000	4.64
7 000	5.43
10 000	6.21

Table 2: Turbidity of the PHPA Solution



Figure 13: Graph of turbidity versus concentration of PHPA solution

From the table above, it shows the result of the turbidity of the PHPA solution. It shows that, as concentration of the PHPA powder increases, the turbidity also increases. This reflects back to the physical appearance of the polymer that was mentioned before in the qualitative findings. Higher turbidity shows that the polymer becomes cloudier.

4.2.3 pH Level

Concentration of PHPA	pH Level
Solution, ppm	
1 000	8.212
3 000	8.129
5 000	7.752
7 000	7.257
10 000	7.079



Figure 14: Graph of pH value versus concentration

According to table 3, the pH level of the PHPA solution decreases with increasing concentrations. This means that the solution is more alkaline as the concentration decreases.

The polyacrylamide contains acrylamide, sodium azide and water. Basically acrylate polymers use acrylate monomers in order to form. The acrylic acid consists of vinyl and carboxylic groups. The acrylate is an organic acid where it will form equilibrium with the H⁺ ions hence leaving the OH⁻ ions free in the solution causes it to become basis. As more PHPA powder is diluted into the water, it causes the concentration of the solution to increase. At this point, the interaction of the polymer molecules starts to become stable with the water molecules and it forms equilibrium again. The H⁺ and OH⁻ ions becomes stable and as it wants to reach equilibrium, it will form the water molecule again and becomes a neutral solution. The main reason for instability of the water polymer solution obtained from cationic emulsions is the hydrolysis of the ester function of the cationic pendant group. Hydrolysis means that part of the cationic groups are transformed into anionic acrylate groups, giving an amphoteric polymer, thus reducing the cationicity

4.2.4 Rheological Properties

For the viscometry test, all the different concentration of PHPA solutions are tested at 25°C, 40°C and 50°C at a constant shear rate from 0 to 10 000 using Bohlin C-VOR Rheometer with the usage of 40° spindle. The following plots are the results obtained from the viscometry test.



Figure 15: Graph of shear stress vs shear rate of 1 000 ppm PHPA solution at 25°C, 40°C and 50°C



Figure 16: Graph of shear stress vs shear rate of 3 000 ppm PHPA solution at 25°C, 40°C and 50°C



Figure 17: Graph of shear stress vs shear rate of 5 000 ppm PHPA solution at 25°C, 40°C and 50°C



Figure 18: Graph of shear stress vs shear rate of 7 000 ppm PHPA solution at 25°C, 40°C and 50°C



Figure 19: Graph of shear stress vs shear rate of 10 000 ppm PHPA solution at 25°C, 40°C and 50°C

From the results obtained, it shows that as the concentration of PHPA solution increases the shear stress increases as well. The effect on temperature does not show much difference in the shear stress reading. At 1000, 3000 and 5000 ppm of PHPA solution, the shear stress is higher at lower temperature as compared to when the solution is at 7000 and 10,000 ppm. The shear stress and viscosity of the solutions increases as the concentration increases is due to the amount of solute in the solution increases hence, the solutions become thicker. Polymer with higher concentration has a longer chain of polymer and more cross linked chained due to the hydration period. More solute in the solution causes the bond to be stronger as it is linked together.

As shown in figure 16 to 20, at certain point there seems to be fluctuation in the shear stress reading, the concentration of the polymer is not spread evenly throughout the bottle sample which is caused my certain parameters such as gravitational force. When

the polymer is left for hydration for one day, the gravity plays its role in pulling down the polymer down to the bottom of the sample bottle and while conducting the experiment, the sample is not taken at the exact location for every repetition of test. Other than that, the gel strength of the long chain polymer cause in the fluctuation of the reading as there is a possibility that the polymer in the sample bottler tends to gel up and form a long chain link with high strength. Where this phenomena has the ability to suspend the gravitational force and hold its position at any point of location in the sample bottle, hence resulting in the polymer to be concentrated at a certain point rather than throughout the sample bottle.

For accurate testing and analysis, it is very important that samples be taken correctly. After a long time of storage, as the emulsions have a tendency to settle, samples taken from the top of a tank may be too thin, due to excessive oil, and samples taken from the bottom can be too thick. It is imperative to take the necessary actions (mainly agitation) to homogenize the product before taking a sample. In order to check if the product is homogeneous, a sample must be taken from the top of the tank and a sample from the bottom. Then measure the viscosity of both samples and if they are the same, the product can be considered as homogeneous. If the viscosities are different, the product must be stirred again. When the viscosities are the same the value by itself is not particularly important; it may differ from the value given from the technical information - normally up to -/+ 50% is acceptable. These viscosities are called bulk viscosities. This bulk viscosity is a parameter which is related to the physical aspect and not related to the performance of the product. The value given on the technical information is an average. It is only used to estimate the characteristics of the pumps to move the product.

From the plots obtained, it shows that the PHPA solution shows a shear thickening effect as the viscosity increases as well as the shear stress. This can be proven from the equation of $\mu = k\gamma^{(n-1)}$ as the viscosity of a solution is the function of shear rate could be used from the Power Law equation.

 μ = viscosity (Pa.s)

k = consistency index (Pa.sⁿ)

n = flow behavior index

 γ = shear rate (1/s)

The values of k and n could be determined by changing the equation into log form which is as follows:

$$log\mu = \log k + (n-1)\log\gamma$$

Where $\log \mu$ is the y-axis of the plot and $\log \gamma$ is the x-axis of the plot, $\log k$ is the intercept point and (n-1) is the slope of the plot. The following table shows the calculated value of k and n by plotting the log μ versus log γ graph.

PHPA Solution	Temperature, °C	n
Concentration, ppm		
1 000	25	1.9335
	40	1.6337
	50	1.8418
3 000	25	2.4014
	40	2.7271
	50	2.9365
5 000	25	3.2846
	40	3.1027
	50	1.5282
7 000	25	2.3796
	40	2.2649
	50	2.2142
10 000	25	2.3153
	40	2.1819
	50	2.1955

Table 4: Table of n values for PHPA at different concentration

From the table above, it is proven that the PHPA solution at 1000, 3000, 5000, 7000 and 10000 ppm shows a shear thickening property. The n values do not equal to 1

which means that the fluid is a non-Newtonian fluid and when n>1 is shows that the fluid has a shear thickening behavior. The polymer is in the range of shear thickening however, at 1000, 3000 and 5000 ppm shows shear thickening properties as the n values decreases with increment of temperature but at 7000 and 10000 ppm the polymer show shear thickening properties as temperature increases.

4.2.5 Interfacial Tension

Interfacial tension exist when two phases are in contact with. It is the work that is done in order to change the size of the interface of two phases that do not mix with one another. The interfacial tension of the study is determined from the following equation:

$$\gamma = \Delta \rho \ g \ R_0^2 / \beta$$

 γ = interfacial tension

 $\Delta \rho =$ difference in mass density

g = gravity constant

 $\mathbf{R}_0 =$ is the radius of curvature at the drop apex and

 β = is the shape factor

The equations describing the drop profile are derived from the Young-Laplace equation and may be represented in dimensionless form:

$$d\theta/dS = 2 - \beta Y - \sin \theta / X$$
$$dX/dS = \cos \theta$$
$$dY/dS = \sin \theta$$

The co-ordinates x, y, s and θ are as illustrated below:



Figure 20: Dimensions and symbols used in the program of the goniometer

The parameter, s, is the distance along the drop profile from the drop apex. X, Y and S are dimensionless parameters made by dividing x, y, and s, respectively, by R₀. For pendant drops, β and the density difference, $\Delta \rho$, will be negative. A large number of theoretical dimensionless profiles were calculated for the whole possible β -range, from β = - 0.55 to 1020 by means of Kutta-Merson's numerical integration algorithm with automatic step length adjustment and each of the profile was measured mathematically by using cubic interpolation. In this way, curves correlating the parameters β and R₀ with measurable parameters as indicated in the figure were produced, and these curves were fitted with linear polynomials by the method of least squares. The parameters of the experiment are listed as below:

Gamma = Interfacial Tension (mN/m)

Beta = Shape Factor

 R_0 = Radius of Curvature at the Drop Apex (mm)

Area = Drop Surface Area (mm2)

Volume = The Drop Volume (mm3)

Theta = Contact Angle at the Drop Limit (horizontal) Hairline

Height = Total Measured Height from Hairline to Apex (mm)

Width = Maximum Width = the diameter if Theta > 90

	Temperature, °C	Gamma, mN/m	Beta	RO, mm	Area, mm	Volume, mm	Theta	Height, mm	Width
Tap Water in Kerosene	25	19.97	0.188	1.361	26.52	13.12	132.5	3.226	2.816
	40	22.12	0.172	1.368	26.28	13	136.54	3.159	2.82
	50	29.7	0.131	1.33	26.75	11.25	144.95	2.884	3.537
	•			•			·	·	<u>.</u>
Distilled Water in Kerosene	25	28.23	0.08	1.052	14.17	5.27	149.76	2.157	2.132
	40	25.05	0.208	1.603	38.27	22.17	113.64	4.118	3.329
	50	32.76	0.175	16.682	40.55	24.39	126.97	4.073	3.47

Table 5: Data from interfacial tension measurement experiment

PHPA 1000									
ppm	25	23.03	0.193	1.539	34.4	19.12	125.84	3.771	3.184
in kerosene									
	40	23.12	0.203	1.582	36.52	21.06	127.61	3.858	3.283
	50	23.23	0.201	1.575	36.34	20.74	123.76	3.902	3.265

PHPA 3000									
ppm	25	19.61	0.191	1.453	29.26	15.83	135.31	3.243	3.008
in kerosene									
	40	18.97	0.209	1.493	32.02	17.74	132.04	3.496	3.102
	50	18.77	0.21	1.492	32.77	17.93	126.61	3.658	3.104

PHPA 5000									
ppm	25	20.72	0.232	1.648	41.54	24.87	103.1	4.44	3.416
in kerosene									
	40	20.54	0.229	1.628	40.44	23.99	107.42	4.324	3.389
	50	19.83	0.236	1.625	40.78	24.1	98.34	4.445	3.375

PHPA 7000									
ppm in	25	10.96	0.295	1.409	32.59	17.3	100.87	4.007	2.946
kerosene									
	40	14.99	0.247	1.507	34.77	19.44	117.85	3.892	3.142
	50	15.76	0.235	1.507	34.33	19.08	119.75	3.843	3.139

PHPA 10000									
ppm in kerosene	25	8.31	0.328	1.278	28.01	13.59	89.39	3.906	2.63
	40	12.01	0.267	1.385	30.06	15.48	110.32	3.728	2.876
	50	13.91	0.241	1.417	30.61	15.97	116.01	3.682	2.944

Images of water and PHPA solution in kerosene using the Pendant Drop method Tap water in kerosene



25°C

40°C

50°C

Distilled water in kerosene



25°C

40°C

PHPA solution of 1 000 ppm in kerosene



25°C

40°C

50°C

PHPA solution of 3 000 ppm in kerosene



25°C

40°C

PHPA solution of 5 000 ppm in kerosene



25°C

40°C

50°C

PHPA solution of 7 000 ppm in kerosene



25°C

40°C

PHPA solution of 10 000 ppm in kerosene



25°C

40°C



Figure 21: Graph of interfacial tension of tap and distilled water at different temperatures



Figure 22: Graph of interfacial tension vs concentration of PHPA solution at different temperatures



Figure 23: Graph of interfacial tension vs temperature of PHPA solution at different concentrations

From the results obtained, the interfacial tension shows a trend where when the solution is at 1000, 3000 and 5000 ppm the interfacial tension shows a constant trend where it is almost similar with increasing temperature. Meanwhile, at higher concentration the interfacial tension increases with increase in temperature. When comparing in terms of the concentration, as the concentration of the PHPA solution increases the interfacial tension reduces. From the experiment, it also proves that by using the PHPA solution, the interfacial tension between the oil-water phase decreases from 28.3 mN/m at 25°C to 8.31 mN/m when using 10 000 ppm of PHPA solution at 25°C.

The reduction in the interfacial tension is caused by the interaction between the molecules of the polymer chain and the kerosene oil. The main reason of the reduction is due to the decline of adhesive forces between the molecules of the oil-water interface as the polymer is being introduced to the interface. The polymer molecules tend to be more cohesive towards each other thus reducing the interfacial tension simultaneously making

the condition to be more stable. Meanwhile, when comparing the interfacial tension with varying temperature, the temperature does not affect the interfacial tension that much for PHPA solution of 1000, 3000 and 5000 ppm. The proves that the polymeric chain of the PHPA solution is still strong and is not degraded even at high temperature but when compared to the PHPA solution at 7000 and 10000 ppm the interfacial tension at higher temperature increases this is due to the degradation of the polymer chain where the bond between the molecules tend to break hence the ability of the polymer to stabilize the condition reduces.

From the image of pendant drop shape of the oil-water phase before the polymer was used and after is used show a major difference where when the polymer is introduced the shape of the drop is more relax and less spherical as compared to before the polymer was introduced. Other than that, as the concentration increases, the shape is more stable and elongated as compared to without the polymer. The gravity plays an important role in the shape of the drop. Since the gravity is constant, the shape shows that the roundness of the drop is caused by the cohesive forces between the polymer molecule and the adhesive force between the interphase of the oil and water. For the image drop at 10000 ppm, it shows that the drop is elongated at 25°C and round at 40°C and 50°C, this is due to the cohesive and adhesive force and it could be translated by the reading of the interfacial tension where it is increased as temperature increases. Hence, this proves that as the interfacial tension decreases the shape is more relax and elongated. The PHPA solution is proven to help in the reduction of the interfacial tension of the oil-water phase.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This study consists of five parameter that is tested in the experimental work namely concentration, temperature, interfacial tension, shear stress and shear rate. The experiment consists of five different concentration of PHPA solution which is tested at elevated temperature in order to study its rheological properties as well as the interfacial tension of the oil-water phase.

The findings show that the PHPA solutions give a shear thickening effect and this is proven from the calculated flow behavior index, n value where it gives a value of more than 1. Moreover, the when the concentration of the PHPA solution increases, at constant shear rate, the shear stress and viscosity increases as well. This is because of the strong linkage of the polymer chain due to the increment in the number of solute of the polymer. However, the shear stress and viscosity do not show much difference at elevated temperature.

The interfacial tension of the oil-water phase is reduced when the PDRA is introduce into the oil-water interphase. From the findings, it show that as the concentration of PHPA solution increases the interfacial tension decreases. This is due to the reduction of adhesive forces between the molecules of the oil-water interface. Meanwhile, the effect of elevated temperature did not show much difference for PHPA solution at 1000, 3000 and 5000 ppm but at 7000 and 10000 ppm the PHPA solution starts to degrade as the temperature increases. The study is proven that with the introduction of PDRA, the interfacial tension between the oil-water phases is reduced and becomes more stable.

5.2 Recommendation

The rheological properties of the PHPA as a PDRA could be used for further study and developed to improve its proficiency in the industry. Further research should be carried out in order to investigate the shape of the stratified flow of the oil-water phase after the PDRA is injected into the pipeline system. This could be done by using a pipe with oil and water flowing inside it and adding probe around the pipe to calculate the actual height of the oil and water phase. Other than that, different types of PDRA and oil should be studies in order to study the different behaviors of other PDRA to the oil-water interphase.

REFERENCES

- Abubakar, A., et al. (2014). "Roles of drag reducing polymers in single- and multi-phase flows." Chemical Engineering Research and Design.
- Al-Sarkhi, A. (2010). "Drag reduction with polymers in gas-liquid/liquid-liquid flows in pipes: A literature review." Journal of Natural Gas Science and Engineering 2(1): 41-48.
- A. S. Pereira, R. M. Andrade, and E. J. Soares. (2013). "Drag reduction induced by flexible and rigid molecules in a turbulent flow into a rotating cylindrical double gap device: Comparison between Poly (ethylene oxide), Polyacrylamide, and Xanthan Gum," Journal of Non-Newtonian Fluid Mechanics 202(12): 72-87.
- Al-Wahaibi, T., et al. (2014). "Experimental investigation on flow patterns and pressure gradient through two pipe diameters in horizontal oil–water flows." Journal of Petroleum Science and Engineering.
- Al-Yaari, M., et al. (2012). "Effect of drag reducing polymers on water holdup in an oilwater horizontal flow." International Journal of Multiphase Flow **44**: 29-33.
- Al-Yaari, M., et al. (2013). "Effect of drag reducing polymers on surfactant-stabilized water–oil emulsions flow." Experimental Thermal and Fluid Science **51**: 319-331.
- Al-Yaari, M., et al. (2014). "Flow characteristics of surfactant stabilized water-in-oil emulsions." Chemical Engineering Research and Design **92**(3): 405-412.

- Atta, A. M., et al. (2014). "Dewatering of petroleum crude oil emulsions using modified Schiff base polymeric surfactants." Journal of Petroleum Science and Engineering 122: 719-728.(Pei, Zhang, Ge, Zhang, & Wang, 2014)
- Bardhan, S., et al. (2013). Interfacial composition and characterization of a quarternary water in oil mixed surfactant (cationic of different alkyl chain lengths + polyoxyethylene type nonionic) microemulsions in absence and presence of inorganic salt. Colloids and Surfaces: Physiochemical and Engineering Aspects.
 433: 219-229.
- Cao, Y. * Li, H. (2001). Interfacial activity of a novel family of polymeric surfactants. European Polymer Journal **28**: 1457-1463.
- da Silva, R. C. R., et al. (2006). "Wettability alteration of internal surfaces of pipelines for use in the transportation of heavy oil via core-flow." Journal of Petroleum Science and Engineering **51**(1-2): 17-25.
- Dardelle, G., & Erni, P. (2014). Three-phase interactions and interfacial transport phenomena in coacervate/oil/water systems. Adv Colloid Interface Sci, 206, 79-91. doi: 10.1016/j.cis.2013.10.001
- Gülseren, İ., & Corredig, M. (2014). Interactions between polyglycerol polyricinoleate (PGPR) and pectins at the oil–water interface and their influence on the stability of water-in-oil emulsions. *Food Hydrocolloids*, 34, 154-160. doi: 10.1016/j.foodhyd.2012.11.015
- Hyde, A., Phan, C., & Ingram, G. (2014). Determining liquid–liquid interfacial tension from a submerged meniscus. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 459, 267-273. doi: 10.1016/j.colsurfa.2014.07.016

J. Katz, "Drag Reduction by Polymer Additives," JSR, vol. 89, p. 720, 1992.

- Kalin, M. and M. Polajnar (2013). "The correlation between the surface energy, the contact angle and the spreading parameter, and their relevance for the wetting behaviour of DLC with lubricating oils." Tribology International **66**: 225-233.
- Kim, H. and D. J. Burgess (2001). "Prediction of Interfacial Tension between Oil Mixtures and Water." Journal of Colloid and Interface Science 241(2): 509-513.
- Meriem-Benziane, M., Abdul-Wahab, S. A., Benaicha, M., & Belhadri, M. (2012).
 Investigating the rheological properties of light crude oil and the characteristics of its emulsions in order to improve pipeline flow. *Fuel*, 95, 97-107. doi: 10.1016/j.fuel.2011.10.007
- Moradi, B., et al. (2014). "Effects of alcohols on interfacial tension between carbon dioxide and crude oil at elevated pressures and temperature." Journal of Petroleum Science and Engineering **121**: 103-109.
- Mowla, D. and A. Naderi (2006). "Experimental study of drag reduction by a polymeric additive in slug two-phase flow of crude oil and air in horizontal pipes." Chemical Engineering Science **61**(5): 1549-1554.
- Nedjhioui, M., et al. (2005). "Combined effects of polymer/surfactant/oil/alkali on physical chemical properties." Desalination **185**(1-3): 543-550.
- Pei, H., et al. (2014). "Effect of polymer on the interaction of alkali with heavy oil and its use in improving oil recovery." Colloids and Surfaces A: Physicochemical and Engineering Aspects 446: 57-64.

- Pichot, R., et al. (2012). "Competitive adsorption of surfactants and hydrophilic silica particles at the oil-water interface: interfacial tension and contact angle studies." J Colloid Interface Sci **377**(1): 396-405.
- Rodriguez, O. M. H. and L. S. Baldani (2012). "Prediction of pressure gradient and holdup in wavy stratified liquid–liquid inclined pipe flow." <u>Journal of Petroleum Science and</u> <u>Engineering</u> 96-97: 140-151.
- Saad, S. M. I., et al. (2011). "Design and accuracy of pendant drop methods for surface tension measurement." <u>Colloids and Surfaces A: Physicochemical and Engineering</u> <u>Aspects</u> 384(1-3): 442-452.
- Vashisth, S. and K. D. P. Nigam (2009). "Prediction of flow profiles and interfacial phenomena for two-phase flow in coiled tubes." <u>Chemical Engineering and</u> <u>Processing: Process Intensification</u> 48(1): 452-463.
- Wang, Y. Y., et al. (2004). "The interfacial dilational properties of hydrophobically modified associating polyacrylamide studied by the interfacial tension relaxation method at an oil-water interface." J Colloid Interface Sci 280(1): 76-82.
- Wang, W., Gong, J., & Angeli, P. (2011). Investigation on heavy crude-water two phase flow and related flow characteristics. *International Journal of Multiphase Flow*, 37(9), 1156-1164. doi: 10.1016/j.ijmultiphaseflow.2011.05.011
- Weldge, I. & Wolf, B.A. (2000). Reduction of interfacial tension between immiscible polymers to which phase one should add a compatibilizer. Polymer **42**: 3467-3473.
- Woodward, R. P. Surface tension measurements using the drop shape method. Portsmouth.

- Wu, S., et al. (2014). Nonlinear rheological behavior of a novel oil displacing agent. Joutnal of Applied Polymer Science.
- Xu, J., et al. (2013). Effect of surfactant headgroups on the oil/water interface: An interfacial tension measurement and simulation study. Journal of Molecular Structure.
 1052: 50-56.
- Zeinolabedini Hezave, A., et al. (2013). "Effect of different families (imidazolium and pyridinium) of ionic liquids-based surfactants on interfacial tension of water/crude oil system." Fluid Phase Equilibria **360**: 139-145.

APPENDICES

Appendix I: Key Milestone



Appendix II: Gantt Chart

		Semester							FY	۲ ۱											FYF	2					
		Week	1	2	3	4	5	6	7	8	9 1	10 1	1 12	13	14	1	2 3	4	5	6	7	8	9 1	10 1:	1 12	13	14
Â	ng Bu	Literature Review																									
Stu	Jen	Drag Reducing Polymer																									
Ie	att	Uses of Drag Reducing Polymer in Pipeline																									
atr	a	Partially Hydrolyzed Polyacrylamide																									
iter	Da	Interfacial Surface Tension and Contact Angle																									
		Rheological Effect of Using DRP in Two-Phase Mixture																									
		Experiment Planning																									
		Develop method and procedure																									
		Anticipate need for equipment & consumables																									
		Equipment and Consumable Research																									
tior		Purchase additional equipment																									
scu		Test experiment																									
ă		Simulation of method and process																									
ect		Anticipate experiment time frame																									
lo		Conduct Experiment																									
<u> </u>		Preparation of Drag Reducing Polymer Solution																									
		Rheology test using Viscometer																									
		Rheology test using Rheometer (varying Temperature)																									
		Determine Interfacial Surface Tension and Contact Angle																									
		Report writing																									
		Extended proposal																									
LIOC		Interim report																									
Re		Progress Report																									
		Dissertation																									
		Technical Paper																									
		Selection of Project Topic																									
		Preliminary Research Work																									
	P1	Submission of Extended Proposal																									
	Ľ.	Proposal Defence											_								$ \rightarrow $					\perp	
		Submission of Interim Draft Report																									
one		Submission of Interim Report											_									$ \rightarrow $				\perp	
est		Progress Report submission																									
Μ		Pre SEDEX																									
	5	Draft Report submission																									
	۲.	Dissertation Report submission (Soft Bound)																				\square					
	-	Technical Paper submission															_				$ \rightarrow $	$ \perp$					
		VIVA																				\square			\perp		
		Dissertation Report submission (Hard Bound)																									

Appendix III: Kerosene Product Data Sheet

	Product Data Sheet	
	PETRON Kerosene	
PETRON		
	DECODIDITION	
	DESCRIPTION	APPLICATION
	Petron Kerosene is a refined kerosene with clean and efficient burning qualities.	 Fuel for stoves, lamps, kerosene-fueled engines, boilers and furnaces
		TYPE/QUALITY LEVEL
		Kerosene
		AVAILABLE PACKAGES
		• Bulk
	TYPICAL CHARACTERISTICS	
	Appearance	Clear and Bright
	Total Sulfur, % wt.	0.01
	Distillation	222.7
	Final Boiling Point, °C	233.7
	Density at 15°C, kg/m ³	788.5
	Smoke Point, mm	24
	Copper Corrosion, 2hrs at 100°C	1
	Saybolt Color	+30 Accontable
	Odor	Acceptable
	Petron Malaysia Refining & Marketing Bhd (3927-V) Menara 1&P (Tower 1), Level 12A No. 46, Jalan Dungun Damansara Heights 50490 Kuala Lumpur	PDS Petron Kerosene 010413 rev0

Appendix III: Data from Viscometry Test

Sh	ear Rate	1/s	v	Viscosity Pa	s	Sł	near Stress	Pa
25	40	50	25	40	50	25	40	50
0.04991	188.5	0.05258	2.065	0.001786	3.133	0.1031	0.3366	0.1647
189.2	567.2	188.6	0.01624	0.001428	0.03053	3.073	0.8102	5.759
1323	756.3	567.2	0.01116	0.008963	0.01797	12.66	6.779	10.19
1512	1134	1134	0.02463	0.01203	0.01066	32.59	13.65	12.09
1890	2269	1323	0.0246	0.007962	0.01333	37.2	18.06	17.64
2457	2458	1701	0.02832	0.0116	0.01761	58.9	28.52	29.97
2836	3025	2080	0.02829	0.01169	0.01635	69.52	35.35	34.01
3214	3403	2269	0.02573	0.01105	0.02464	72.95	37.59	55.91
3403	3592	2836	0.02788	0.01807	0.02416	89.61	64.9	68.51
3592	4350	3025	0.03358	0.05815	0.02383	114.3	252.9	72.09
4159	4539	3403	0.04877	0.05969	0.02865	175.2	270.9	97.49
4539	4727	3970	0.06624	0.09497	0.03323	288.1	449	131.9
4728	4917	4159	0.0759	0.1052	0.05273	344.5	517.2	219.3
4917	5484	4350	0.1041	0.07944	0.06957	492.1	435.7	302.6
5673	5673	4539	0.103	0.08333	0.07941	506.3	472.7	360.4
6241	5862	5673	0.0937	0.0829	0.08776	549.3	501.7	497.9
6430	6052	6241	0.091	0.0836	0.09179	567.9	521.7	572.8
6619	6241	6430	0.09536	0.08687	0.09374	613.1	558.6	602.7
6808	6430	6808	0.0964	0.09028	0.09414	638.1	597.5	640.9
6997	6619	6997	0.09777	0.09311	0.09872	684.1	633.9	690.7
7186	6808	7186	0.1059	0.09457	0.09882	760.9	661.7	710.1
7375	6997	7375	0.1072	0.1025	0.1067	790.3	736.3	786.7
7564	7186	7564	0.1184	0.1089	0.112	917.8	823.9	847.1
7943	7564	7753	0.1243	0.1137	0.1147	986.9	881.7	889.6
8132	8132	7943	0.133	0.123	0.1227	1081	977.1	974.3
8321	8321	8321	0.144	0.1449	0.1401	1198	1206	1166
8510	8510	8510	0.1703	0.1712	0.1716	1449	1457	1460

Table 6: Rheological Properties of 1 000 ppm PHPA solution

S	hear Rate 1	/s	1	Viscosity Pa	S	Sł	near Stress	Pa
25	40	50	25	40	50	25	40	50
0.04968	0.04978	0.05016	8.526	10.58	17.99	0.4236	0.1693	0.9026
189.5	188.5	189.3	0.07982	0.06789	0.05059	15.13	7.932	9.578
378.7	376.1	378.2	0.08022	0.06594	0.07043	30.38	27.454	26.64
567.2	567.2	567.2	0.06849	0.05969	0.04949	38.85	32.445	28.07
756.3	756.3	756.3	0.08045	0.04969	0.04423	60.85	39.637	33.45
1134	1134	1134	0.07539	0.042325	0.04842	85.52	52.38	54.92
1323	1323	1323	0.07131	0.2063	0.05491	94.37	68.72	72.67
1701	1702	1701	0.06529	0.1721	0.04689	111.1	86.64	79.78
2457	2458	2458	0.06225	0.1404	0.0443	153	124.89	108.9
2647	2647	2647	0.06286	0.1348	0.03573	166.4	145.38	94.55
2836	2836	2836	0.06942	0.1373	0.0423	196.9	162.79	119.9
3214	3214	3214	0.07113	0.09288	0.04237	228.6	188.88	136.2
3592	3592	3592	0.07946	0.09877	0.06377	285.4	255.33	229
3781	3781	3781	0.08759	0.09979	0.06912	331.2	286.28	261.4
3970	3970	3970	0.08972	0.09164	0.07193	356.2	305.67	285.5
4159	4159	4159	0.1114	0.1054	0.08875	463.1	418.89	369.1
4349	4350	4350	0.1464	0.1102	0.1276	636.8	560.65	555.1
4539	4539	4539	0.1751	0.09584	0.1237	794.8	598.74	561.3
4728	4727	4728	0.1718	0.08688	0.1314	812.2	647.68	621.4
5295	5295	5295	0.2216	0.07018	0.1444	1165	742.15	764.7
5863	5862	5862	0.199	0.07921	0.1278	1173	786.02	749
6430	6430	6430	0.1729	0.07566	0.1188	1112	801.35	763.9
6997	6997	6997	0.1609	0.06525	0.1205	1055	869.67	843
7943	7943	7943	0.1269	0.06456	0.1226	1075	1002	974.1
8132	8132	8132	0.1333	0.07015	0.1336	1084	1084	1086
8321	8321	8321	0.1454	0.0629	0.1478	1210	1215	1230
8510	8510	8510	0.17	0.06757	0.1692	1447	1443	1440

Table 7: Rheological Properties of 3 000 ppm PHPA solution

S	hear Rate 1	/s		Viscosity Pa	S	She	ear Stress I	Pa
25	40	50	25	40	50	25	40	50
189.3	189.1	189.7	0.03543	0.029741	0.27925	8.1677	5.0424	4.9851
378.1	378.1	378.1	0.03615	0.03428	0.03401	24.2196	20.16	19.85
756.3	756.3	756.3	0.04417	0.03994	0.03755	45.31	26.35	22.08
945.3	945.3	945.3	0.05147	0.04782	0.04492	49.76	31.95	28.33
1134	1134	1134	0.05612	0.05014	0.05148	55.04	37.62	34.17
1701	1701	1701	0.06185	0.05773	0.05527	86.92	52.74	49.91
2082	2080	2080	0.06793	0.06149	0.06113	93.72	75.34	61.08
2458	2458	2458	0.07014	0.06381	0.06422	117.85	96.33	94.28
3214	3214	3214	0.07259	0.07122	0.07214	162.51	104.87	100.45
3592	3592	3592	0.07721	0.07427	0.0751	221.48	132.22	137.92
3781	3781	3781	0.07949	0.07527	0.07428	244.14	165.4	162.21
3970	3970	3970	0.08296	0.07622	0.07714	261.7	187.6	183.4
4159	4159	4159	0.08961	0.08506	0.08325	359.3	251.5	237.1
4728	4727	4727	0.09314	0.08924	0.8846	615.4	473.9	468
5106	5106	5106	0.09571	0.09332	0.0942	617.7	477.6	469.2
5484	5484	5484	0.0969	0.09373	0.09281	724.5	561.3	553.7
5862	5862	5862	0.09714	0.09492	0.09298	772.6	604.6	599.4
6430	6430	6430	0.09792	0.09514	0.09338	820.3	754.2	736.7
6619	6619	6619	0.09984	0.09715	0.09426	854.5	772.4	754.9
6997	6997	6997	0.1049	0.09989	0.09975	872.2	781.3	742.1
7186	7186	7186	0.1052	0.1017	0.09993	894.7	803.1	796.5
7754	7754	7754	0.1172	0.1167	0.1151	915.2	904.5	907.2
8132	8132	8132	0.1331	0.1333	0.1331	1190	1113	1115
8321	8321	8321	0.142	0.14	0.1492	1321	1305	1311
8509	8510	8509	0.17	0.1741	0.1714	1446	1455	1453

Table 8: Rheological Properties of 5 000 ppm PHPA solution

S	hear Rate 1	/s	Viscosity Pas Shear Stress Pa			Pa		
25	40	50	25	40	50	25	40	50
0.04993	0.05018	0.04845	40.65	33.51	15.68	2.03	1.681	0.76
189.7	189.4	189.1	0.1159	0.07856	0.05917	22	14.88	11.19
378.1	378.8	378.9	0.1065	0.07611	0.07117	40.25	28.83	26.96
567.2	567.3	567.2	0.08079	0.0749	0.05819	45.83	42.49	33.01
1134	1134	1134	0.06704	0.05451	0.06234	76.05	61.83	70.72
1891	1701	1890	0.06282	0.05372	0.0526	118.8	91.4	99.45
2080	1890	2080	0.07154	0.04889	0.0516	148.8	92.42	107.3
2458	2269	2457	0.06373	0.0561	0.05264	156.6	127.3	129.4
2647	2458	2647	0.06849	0.05271	0.04999	181.3	129.6	132.3
3214	2836	2836	0.05904	0.05308	0.04938	189.8	150.5	140
3403	3025	3025	0.06548	0.05652	0.05103	222.8	171	154.3
4159	3781	3970	0.1015	0.07089	0.07487	422.1	268	297.3
4539	4350	4539	0.1411	0.1341	0.133	640.4	583.4	603.6
4917	4539	4727	0.1476	0.1433	0.1476	725.9	650.2	698
5295	4728	4917	0.1766	0.1736	0.1526	935.1	820.7	750.5
5484	5295	5295	0.1896	0.1668	0.1623	1040	883.4	859.2
5863	6241	5484	0.1858	0.1823	0.1675	1089	1138	918.6
6241	6430	5862	0.1719	0.168	0.1667	1073	1080	977.2
6808	6808	6241	0.1845	0.1749	0.1589	1256	1191	991.9
6997	6997	6619	0.175	0.1851	0.1618	1225	1295	1071
7186	7186	6997	0.1841	0.1916	0.17	1323	1377	1190
7375	7375	7186	0.2032	0.1965	0.1779	1499	1449	1278
7564	7564	7564	0.2166	0.2023	0.1858	1639	1530	1405
7754	7753	7753	0.2362	0.2241	0.2057	1832	1738	1595
7943	7943	7943	0.261	0.2502	0.2294	2073	1987	1822
8132	8132	8132	0.2842	0.2937	0.2721	2311	2388	2212
8321	8321	8321	0.2959	0.3347	0.3136	2462	2785	2609

Table 9: Rheological Properties of 7 000 ppm PHPA solution

S	hear Rate 1	/s	V	viscosity Pa	ıs	She	Shear Stress Pa		
25	40	50	25	40	50	25	40	50	
0.05031	0.05016	0.05012	40.65	33.51	15.68	0.9468	4.476	1.017	
189.1	189.1	189.7	0.1159	0.07856	0.05917	32.45	27.82	18.28	
378.1	378.1	378.1	0.1065	0.07611	0.07117	41.27	37.9	37.53	
567.3	567.2	567.3	0.08079	0.0749	0.05819	49.92	50.38	48.06	
756.3	756.3	756.3	0.06704	0.05451	0.06234	73.16	67.42	61.97	
945.3	945.3	945.3	0.06282	0.05372	0.0526	94.54	79.2	81.72	
1323	1512	1323	0.07154	0.04889	0.0516	109.5	95.3	104.7	
1701	2080	1701	0.06373	0.0561	0.05264	143.9	153.3	112.2	
2080	2647	2080	0.06849	0.05271	0.04999	176.3	179.5	136.8	
2647	2836	2647	0.05904	0.05308	0.04938	180	206.5	174.1	
2836	3025	2836	0.06548	0.05652	0.05103	220.1	251.7	182	
3592	3592	3592	0.1015	0.07089	0.07487	297.2	321.3	295.9	
3970	3970	3970	0.1411	0.1341	0.133	362.1	366.1	381.5	
4159	4159	4159	0.1476	0.1433	0.1476	467.2	407.1	416.2	
4350	4350	4350	0.1766	0.1736	0.1526	656.2	698.2	662.3	
4539	4539	4539	0.1896	0.1668	0.1623	763.8	823.7	785.9	
5295	5484	5295	0.1858	0.1823	0.1675	1099	1077	1118	
6241	6241	6241	0.1719	0.168	0.1667	1274	1172	1181	
6619	6619	6619	0.1845	0.1749	0.1589	1388	1243	1189	
7186	7186	6997	0.175	0.1851	0.1618	1540	1410	1291	
7375	7375	7186	0.1841	0.1916	0.17	1735	1623	1451	
7564	7564	7375	0.2032	0.1965	0.1779	1901	1711	1544	
7754	7754	7564	0.2166	0.2023	0.1858	2022	1927	1666	
7943	7943	7754	0.2362	0.2241	0.2057	2328	2037	1755	
8132	8132	7943	0.261	0.2502	0.2294	2615	2419	2015	
8321	8321	8132	0.2842	0.2937	0.2721	3043	2785	2313	
8510	8509	8321	0.2959	0.3347	0.3136	4345	3600	2736	

Table 10: Rheological Properties of 10 000 ppm PHPA solution