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JUDUL : ENHANCEMENT OF FLOW IN PIPELINE TRANSPORTATION FOR CRUDE OIL EMULSION

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ENHANCEMENT OF FLOW IN PIPELINE TRANSPORTATION

FOR CRUDE OIL EMULSION

KHOO SUE ANN

Report submitted in partial fulfilment of the requirements

for the award of the degree of the

Bachelor of Chemical Engineering (Gas Technology)

Faculty of Chemical & Natural Resources Engineering

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JANUARY 2012

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I hereby declare that the work in this thesis entitled "*Enhancement of flow in pipeline transportation for crude oil emulsion*" is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree

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ABSTRACT

This study presents the flow enhancement of crude oil in pipeline transportation using emulsion. High viscosity and low pour point of crude oil often hinder transportation from processing wells to the enhanced oil recovery reservoir. Therefore, a stable oil-in-water emulsion is desired, by comparing different types of surfactant. Demulsification process too is necessary to separate the oil in water. Emulsion was prepared using Span 80, Span 83, and Triton X-100 each respectively in a ratio of 70-30% o/w and 50-50% o/w. Parameters include varying mixing speed in emulsion preparation, temperature and rheological properties of the emulsion were studied by carrying out stability tests. Interfacial properties such as surface tension and interfacial tension of the emulsion were also measured. The effect of droplet diameter with surfactant concentration in the emulsion was also studied. The most stable emulsion was used for transportation in a 3meter pipeline. Rheological data on the emulsion was used to correlate to the laminar flow during transportation. Three demulsifiers: dioctylamine, cocoamine, hexylamine were used to compare for their effectiveness in demulsification. The study reveals that the stability of o/w emulsion increases when an anionic surfactant, Span 83, was used. By increasing the oil content, the speed and mixing temperature resulted in an increased emulsion stability, and a reduced droplet diameter. Dioctylamine proved to be the best demulsifier among cocoamine and hexylamine.

ABSTRAK

Kajian membentangkan peningkatan aliran minyak mentah dalam saluran pai pengangkutan menggunakan emulsi. Kelikatan yang tinggi minyak mentah sering menghindar pengangkutan dari pemprosesan telaga ke pumulihan takungan minyak. Oleh itu, emulsi minyak dalam air yang stabil adalah diingini. Emulsi disediakan dengan perbandingan antara tiga jenis 'surfactant'. Span 80, Span 83, dan Triton X-100 digunakan sebagai 'surfactant' dengan mengguna nisbah 70-30% minyak/air dan 50/50% minyak air. Parameter yang dikaji termasuk kelajuan semasa menghasil emulsi, suhu dan sifat reologi untuk menguji kestabilan emulsi. Ketegangan antara emulsi dan saiz titisan emulsi juga dikaji. Emulsi yang paling stabil digunakan untuk diangkut dalam paip berpanjangan 3meter. Data reologi emulsi digunakan untuk mendapat jenis pengaliran emulsi. Akhirnya, tiga demulsifier (dioctylamine, cocoamine dan hexylamine) digunakan untuk membanding keberkesanan dalam memisahkan emulsi. Kajian menunjukkan kestabilan minyak/air meningkat apabila 'surfactant' berionik, Span 83, digunakan. Dengan meningkatkan kandungan minyak, kelajuan dan suhu pencampuran akan memberikan emulsi yang lebih stabil. Emulsi jenis laminar ditunjukkan semasa pengangkutan melalui paip. Dioctylamine dibuktikan merupakan demulsifier yang terbaik antara cocoamine dan hexylamine.

TABLE OF CONTENTS

SUPERVISOR'S DECLARATION	ii
STUDENT'S DECLARATION	iii
ACKNOWLEDGEMENTS	iv
ABSTRACT	V
ABSTRAK	vi
TABLE OF CONTENTS	viii
LIST OF TABLES	xiii
LIST OF FIGURES	xiv
LIST OF SYMBOLS	xvi
LIST OF APPENDICES	xvii

CHAPTER 1 INTRODUCTION

1.1	Research Background	1
1.2	Problem Statement	3
1.3	Research Objective	3
1.4	Scope of Study	4
1.5	Significance of Study	4

CHAPTER 2 LITERATURE REVIEW

2.1	Physical properties of crude oil	5
2.2	Chemical properties of crude oil	7
2.3	Methods of transportation	8
	2.3.1 Dilution method	9

	2.3.2	Partial upgrading method	9
	2.3.3	Heating method	9
	2.3.4	Oil-in-water emulsion	10
	2.3.5	Core annular flow	10
2.4	Types	of emulsions	11
	2.4.1	Water-in-oil	12
	2.4.2	Oil-in-water	12
	2.4.3	Multiple emulsion	12
2.5	Emuls	ifying agents	13
	2.5.1	Surface-active agents	13
	2.5.2	Finely divided solids	14
2.6	Surfac	etant and its stability in O/W emulsion	14
2.7	Flow b	behaviour of the O/W emulsion	16
	2.7.1	Oil content of the emulsion	16
	2.7.2	Speed of mixing	16
	2.7.3	Surfactant concentration	17
	2.7.4	Effect of salt concentration	18
	2.7.5	Effect of temperature of homogenization	18
	2.7.6	Effect of resin/asphaltene ratios	18
	2.7.7	Effect of pH	19
	2.7.8	Slip flow effect	19
2.8	Factor	rs considered in transportation across pipeline	19
	2.8.1	Pressure drop	19

ix

	2.8.2 Energy expanded	20
2.9	Demulsification	20
2.10	Types of demulsifier	20
	2.10.1 Chemical demulsifier	20
	2.10.2 Microwave heating	23
	2.10.3 Thermal method	23

CHAPTER 3 METHODOLOGY

3.1	Introduction		24
3.2	2 Materials		
	3.2.1	Raw Materials	25
	3.2.2	Emulsifiers	25
	3.2.3	Demulsifiers	25
3.3	Equip	ment	25
3.4 Experimental procedure		imental procedure	26
	3.4.1	Surface tension determination	26
	3.4.2	Interfacial tension (IFT) determination	26
	3.4.3	Small-scale emulsification	27
	3.4.4	Measuring type of prepared emulsions	30
	3.4.5	Gravitational stability test	30
	3.4.6	Measuring droplet size distribution	30
	3.4.7	Brookfield test	31

3.4.8	Pilot-scale emulsification	31
3.4.9	Pipeline flow experiment	32
3.4.10	Demulsifiers screening	32

CHAPTER 4 RESULTS AND DISCUSSION

4.1	Introd	uction	34
4.2	Surfac	e tension and interfacial tension analysis	35
4.3	Emuls	ion stability screening process	36
4.4	Brookfield analysis		
	4.4.1	Effect of temperature and viscosity	37
	4.4.2	Effect of shear stress and shear rate	41
	4.4.3	Effect of viscosity and RPM	43
	4.4.4	Effect of viscosity and shear rate	44
4.5	Gravit	ation stability test	46
	4.5.1	Percent water separated and time	46
	4.5.2	Effect of percent water separated and surfactant	
		concentration	47
4.6	Transj	portation in pipeline	50
	4.6.1	Type of flow	50
4.7	Demu	lsification process	51
	4.7.1	Effectiveness of demulsifier	51

CHAPTER 5 CONCLUSION AND RECOMMENDATIONS

5.1	Conclusion		
	5.1.1	Emulsion stability	54
	5.1.2	Flow regime of emulsion	55
	5.1.3	Demulsification	55
5.2	Recor	nmendations	56
REF	ERENC	ES	57
APP	ENDICI	ES	60
A		Calculations	60
В		MSDS for emulsifier and demulsifier	61
С		Tabulated results	66
D		Sample image	72
E		Graphs	74

LIST OF TABLES

TABLE NO.	TITLE	PAGE	
2.1	Sample physical properties of Geisium crude oil		5
2.2	Physical properties of crude oil from OPEC		6
2.3	Composition of West Paydar crude oil		7
3.1	Summary of emulsifiers required to form emulsion samples		29
3.2	Summary of demulsifiers		33
4.1	IFT between crude oil and water		35
4.2	Surface tension of distilled water and air		35
4.3	Properties of emulsifiers		36
4.4	Values to calculate Reynold's number		50

LIST OF FIGURES

FIGURE	NO. TITLE	PAGE
2.1	Pipeline design allowing core flow of heavy oils	11
2.2	Emulsions found in petroleum transportation	12
2.3	Photomicrograph of a W/O/W emulsion	13
2.4	Scheme of a newly developed surfactant molecule	15
3.1	Du Nouy interfacial tensiometer	27
3.2	Overview for emulsion preparation and destabilization	28
3.3	Brookfield rotational digital viscometer	31
3.4	Process flow diagram of experimental pipeline	32
4.1	Viscosity versus temperature at 100rpm	37
4.2	Viscosity versus temperature at 150rpm	37
4.3	Viscosity versus temperature at 200rpm	38
4.4	Viscosity versus temperature at 100rpm	38
4.5	Viscosity versus temperature at 150rpm	39
4.6	Viscosity versus temperature at 200rpm	39
4.7	Shear Stress versus Shear Rate, spindle speed of 150rpm	40
4.8	Shear Stress versus Shear Rate, spindle speed of 150rpm	41
4.9	Viscosity versus RPM for 50:50 O/W emulsion	42
4.10	Viscosity versus RPM for 70:30 O/W emulsion	42
4.11	Viscosity versus Shear Rate for 50:50 O/W emulsion	44
4.12	Viscosity versus Shear Rate for 70:30 O/W emulsion	45
4.13	Water separation versus time at emulsion mixed at 1500rpr	n
	Surfactant concentration of 0.5 wt%	46

FIGURE NO	O. TITLE I	PAGE	
4.14	Water separation versus time at emulsion mixed at 1500rpm		
	Surfactant concentration of 1.0wt%	47	
4.15	Water separation versus surfactant concentration at 1500rpm	l	
	mixing speed	47	
4.16	Water separation versus surfactant concentration at 1000rpm	l	
	mixing speed	48	
4.17	Water separation versus surfactant concentration at 1500rpm	L	
	mixing speed	48	
4.18	Water separation versus surfactant concentration at 1000rpm	L	
	mixing speed	49	
4.19	Percent water separated versus time over a period of two day	vs 51	
4.20	Percent water separated versus time over a period of two day	vs 51	
4.21	Percent water separated versus time over a period of two day	vs 52	
4.22	Percent water separated versus time over a period of two day	vs 52	

LIST OF SYMBOLS

O/W	-	oil-in-water emulsion
W/O	-	water-in-oil emulsion
O/W/O	-	oil-in-water-in-oil emulsion
W/O/W	-	water-in-oil-in-water emulsion
Q	-	volumetric flow rate (m ³ /s)
Re	-	Reynolds number
Т	-	temperature (⁰ C)
μ	-	viscosity (N.s/m ²)
ρ	-	density (kg/m ³)
V	-	mean velocity
D	-	diameter of pipe (m)
MSDS	-	Material Safety Data Sheet

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

Oil transportation has always been a complex and highly technical operation. Since crude oil accounts a large fraction of the world's potentially recoverable oil reserves, thus puts them in the frontline of the energy resources. Proper scheduling of crude oil transportation presents vast economic potential. Therefore this thesis presents the art of transporting crude oil through a pipeline system which is designed to deliver quantities of crude oil from the production area to the refinery. The transportation of materials by pipeline can be substantially more economical than by means of shipping, which involves a relatively long distance of pipeline for transportation. Also, an extensive application of pipeline procedures can be applied through the movement of commercial crude oil to a distant market where it can be marketed and consumed.

Several alternative transportation methods for heavy crudes have been suggested and engaged, including preheating of the crude oil with continuous heating of the pipeline, dilution with lighter crude oils, and partial upgrading. (S.N.Ashrafizadeh & M.Kamran, 2010). These above-mentioned methods experience logistic, technical, or economic drawback.

Currently, we only consider one general approach in transporting the heavy oil, i.e. by viscosity reduction (Peter & Pilehvari, 1993). Reduction of oil's viscosity can be accomplished by many methods. Modern researchers constantly seek ways to apply emulsions to improve the transport of crude oil, as well as study methods of minimizing production problems caused by emulsions. Increasing offshore oil and gas exploration and production resulted in the transportation of well fluids in pipelines over relatively long distance.

A recent review by Rafael et.al (2010) states that O/W emulsions are deliberately produced to reduce the viscosity of highly viscous heavy crudes so they can be transported easily through the pipeline. This efficient way is achieved with the help of surfactant agents. The stability of crude oil is favored by the concentration of surfactants which contribute to decrease the interfacial tension between the crude oil and water. In this way, crude oil is transported in the form of fine crude oil droplets in a continuous phase comprising water as the main component. Water-in-oil emulsions can be made that contain high doses of oil. The viscosity of these emulsions is much lower than the viscosity of the crude oil and relatively uninfluenced by the oil type. "Oil-inwater emulsions with oil concentrations great enough to be of economic interest are possible, and the diluents (water) is usually cheap and easily disposed or recycled". (Peter & Pilehvari, 1993).

In order to transport the crude oil emulsion systems, the first 3 steps are conducted, which are, producing the oil-in-water emulsions, transportation of produced O/W emulsions to the desired destination and finally separation of oil and water phases. The paper focuses on the pipeline transportation that is particularly challenged by the high viscosity of heavy oils and low mobility. Since the viscosity of the crude oils is the major factor of obstructing pipeline transport, a cheap, environmentally acceptable method must be found to lower the viscosity (Peter & Pilehvari, 1993).

1.2 PROBLEM STATEMENT

Fluid extracted from the wells is difficult to handle through pipelines by normal pumping means. The major setback of transportation is due to the high viscosity and low pour point of the crude oil. This is especially discerning with an increase of offshore activity of oil exploration and production. Consequently, special heating units installed in the pumping stations along the route of the pipeline is being used. These oil heaters would burn night and day to maintain pumpable fluidity of the crude oil. However, this method is not favorable since it is not economical by having the need to increase energy consumption.

Also, present issues like instability of asphaltenes, paraffin precipitation and high viscosity that cause multiphase flow, clogging of pipes, high-pressure drops, and production stops, contributes to the problem of transporting using pipeline. The high concentrations of sulfur and several metals, particularly nickel and vanadium (Shadi W. Hasan, 2010) hinder the crude oil from being pumped through the pipeline.

Therefore it is crucial to determine a novel method to enhance the crude oil transportation in the pipeline. This is so as to increase the oil mobility of viscous oils, while reducing its viscosity (Yousef, George, Elgibaly, & Elkamel, 2004).

1.3 RESEARCH OBJECTIVE

The objective of this thesis is to improve crude oil transportation by using oil in water emulsion. Rheological properties and characteristics of its emulsion were investigated in order to improve flow. Accuracy and reproducibility in obtaining the data for design and analysis is aimed throughout the research of transporting oil through pipeline.

1.4 SCOPE OF STUDY

i. Characterization of O/W emulsions in terms of chemical and physical properties i.e. stability of emulsions, shear stress, shear rate, dynamic viscosity, rotations per minute(rpm), temperature, surface tension, interfacial tension(IFT),

ii. Facilitating the handling and transporting the crude oil emulsion system includes producing the oil-in-water emulsions and transportation of produced O/W emulsions in a simulated pipeline.

iii. The study also aims to determine a suitable demulsifier for separation of oil and water phases after the emulsion is transported.

v. To provide an improved method of handling and transporting the crude oil at low pumping costs and under reduced friction conditions.

1.5 RATIONALE AND SIGNIFICANCE

A simple and cost effective surfactant will be proposed in producing O/W emulsion in lab simulation. The characteristics and behavior of O/W crude studied will provide better understanding of emulsion in pipeline.

A generic solution for crude oil transportation will provide useful aid of transportation of crude using pipeline in the petroleum industry.

CHAPTER 2

LITERATURE REVIEW

This chapter gives justification on why O/W emulsions are selected to be studied over other methods of transportation. It also reviews about the stability and surfactants normally used in the emulsions.

2.1 PHYSICAL PROPERTIES OF CRUDE OIL

Knowledge on the physical properties or classification of crude oil compound is important. This is so as to optimize its performance in a refinery and to produce the correct range of products for a particular market.

Crude oil refers to conventional crude oil. It exists as a liquid mixture in natural underground reservoirs and at atmospheric pressures. Conventional crude usually ranges from 20 to 40 API density gravity.

Value
0.946g/cm ³
18
2000cP
4.3psi

Table 2.1Sample physical properties of Geisium crude oil((Zaki, 1996)

Crude oil	Country	API gravity(°)	% wt sulfur
Sahara Blend	Algeria	47	0.11
Minas	Indonesia	35	0.08
Iran Heavy	Iran	30	2.0
Basra Light	Iraq	30.2	2.6
Kuwait	Kuwait	31	2.63
Es Sider	Libya	36.6	0.42
Bonny Light	Nigeria	34.3	0.15
Qatar Marine	Qatar	35	1.6
Arab Light	Saudi Arabia	33.4	1.8
Murban	UAE	39	0.9
BCF 17	Venezuela	16.5	2.5

Table 2.2OPEC –Organization of the Petroleum Exporting Countries basket afterJune 2005 (Vassiliou, 2009)

i. Specific gravity

Sometimes referred to as "relative density" in modern scientific usage, it is the ratio of weight of crude oil at a given temperature and volume relative to the weight of the equal volume of water at the same temperature. (Oil & Gas Field Technical Terms Glossary, 2007-2010). The density of oils may vary depending on the field of origin produced, as oils tend to become lighter with depth due to the higher quantities of light paraffin.

ii. Viscosity

Heavy oil generally has a viscosity between 1,000 and 10,000 centipoise(cP), while conventional crudes' viscosities range between 10 and 100cP. (Vassiliou, 2009). Generally, viscosity and specific gravity of oils are related directly to each other and vary with the composition of oil. Oil having a higher average molecule weight will also have a higher specific gravity and viscosity.

Pour point is the temperature where the oil will not flow in a definite manner. It relates with an indication of property of oil at low temperatures and an estimation of the amount of paraffin wax. If no paraffin wax is present in the oil, its pour point would depend on the viscosity of the crude oil (Oil & Gas Field Technical Terms Glossary, 2007-2010).

2.2 CHEMICAL PROPERTIES OF CRUDE OIL

Petroleum contains 4 groups of hydrocarbons, i.e. alkane or paraffin, cycloalkanes or napthenes, aromatic and naphthenoaromatics or complex hydrocarbon. Crude oil contains between 15% to 20% of alkanes. It may rise to as high as 35% in very paraffinic crude oil or drop to 0 in heavy biodegraded oil (Kinghorn, 1983).

Characteristics	Value	Experimental method	
Saturated	34.22wt%	SARA	
Aromatics	38.82wt%	SARA	
Resins	19.96wt%	SARA	
Asphaltenes	6.58wt%	SARA	
Wax appearance and temperature	122°F	Viscosity	
Wax	3.56wt%	HV-237	

Table 2.3Composition of West Paydar crude oil (S.N.Ashrafizadeh & M.Kamran,2010)

Non-hydrocarbons in petroleum are sulfur compounds, oxygen compounds, nitrogen compounds, and metallic compounds.

Sulfur compounds make up the largest group of non-hydrocarbons in petroleum, such as H_2S , mercaptan, alkylsulfides like allylsulfide and thiobenzene. Generally, the quantity of sulfur increases as the density of the crude oil increases or API gravity decreases. They are commonly found in petroleum distillates or in distillation residue.

The sulfur compounds must be destroyed or removed as it can poison the metallic catalyst during the refining process (McCain, 1990).

As for oxygen compounds occurring in petroleum, its amount is usually less than 2%. In cases where oxygen content is reported to be higher than the usual, it may have been the oil has suffered prolonged exposure to the atmosphere either during or after production. It may also be that the increase of the boiling point of the fraction resulted in higher oxygen content (McCain, 1990).

Generally, nitrogen content in petroleum is low and falls within the range 0.1 to 2.0%. It is common to detect trace amounts of nitrogen, in higher asphaltenes in oil will have higher nitrogen content(Neumann, Lahme, & Severin, 1981).

Metallic compounds occur in very small concentration, therefore is called trace metals. They could be inorganic salts, metal soaps, organic metal-complex compounds. Their nature and their abundances in crude oil can provide information as to the origin, migration and maturation of petroleum while providing a basis for regional geochemical prospect. Its nature has now become the interest for refinery operator and environmentalist who are concerned with the emissions from oil-fired power plants. Nickel and vanadium are most common, but ferum, zinc, chromium, mangan, cobalt and others are almost always present (McCain, 1990).

2.3 METHODS OF TRANSPORTATION

According to (Sanier, Henaut, & Argilier, 2004), heavy crude oils cannot be transported with conventional pipelines due to their high viscosity. Additional treatments are required to reduce the viscosity or in lowering the friction in the pipe.

2.3.1 Dilution Method

Dilution of heavy crude oil by addition of lighter liquid hydrocarbons, usually condensates from natural gas production, or lighter crude oils are methods used since the 1930s to reduce the viscosity of heavy oils. According to Shadi W. Hasan(2010), at 25°C, the presence of 20% of light crude oil within the heavy crude oil phase causes 96% viscosity reduction using Canadian crude. However it may require considerable investments in pumping and pipelines due to the increase of the transport volume and the need to separate the solvent, process it and then returning it to the oil production site. Also, as high as 30% volume of diluents are used to meet the API gravity specification. Special attention must be paid to asphaltene and paraffins stability, since condensate or light oil addition would cause precipitation and pipeline clogging. From past experience, heavy oil dilution may reduce viscosity but other issues remain unsolved like asphaltene and paraffin deposition (Rafael, et al., 2010). Recycling of diluents might be solution but it requires large investment in installing an extra pipeline. (Sanier, et. al., 2004)

2.3.2 Partial Upgrading Method

The heavy crude is being upgraded into a lighter crude. (Sanier, Henaut, & Argilier, 2004). This method consists of altering the composition of heavy oils to make them less viscous. According to Saniere(2004), traditional hydrotreating process, deasphalting process Solvahl, thermal treatment Tervahl process and catalytic hydrotreatment Hyvahl processes can be used in this application.

2.3.3 Heating Method

Heating is common for ameliorating the flow properties of heavy crude oil. With increasing temperature, viscosity decreases swiftly (Sanier et. al.,2004). It is important to heat the oil to a point where the oil has a substantially reduced viscosity. Shadi W. Hasan (2010) found that heavy crude viscosity decreases significantly from 10.0 to 2.5 Pa s when the temperature changes from 25°C to 75°C. However, the design of a heated pipeline needs much effort as it involves consideration on expansion of the pipelines, number of pumping/heating stations, and heat loss. The principle drawbacks are the

high capital and operational cost of heating the pipeline over an extended distance (Shadi W. Hasan, 2010). A greater corrosion rate of the internal pipe will occur due to the temperature increase (Guevera, 1998). The method is not feasible to be applied in underwater pipeline transportation of heavy oil through a heated pipeline due to the cooling effect of the surrounding water (Shadi W. Hasan, 2010). In addition, his study showed that heating could induce changes in the colloidal structure of the crude oils and worsen their rheological properties. Considerable amounts of energy are used in the heating method and diluents prove to encounter logistic problems.

2.3.4 Oil-in-Water emulsion

In this method, with the help of suitable surfactants the oil phase becomes dispersed in the water phase and stable oil-in-water emulsions are produced. This consequently results in a significant reduction in the oil viscosity with a viscosity range of about 50-200cP. This method is useful in transporting crude oils with viscosities higher than 1000cP particularly in cold regions. According to Poynter(1970), another advantage would be, since water is the continuous phase, crude oil would have no contact with the pipe wall, thus significantly reduces pipe corrosion (for crudes with high sulfur content) and also preventing the formation of sediments in pipes (for crudes with high asphaltene content). Restarting of pipeline after emergency shutdown and reemulsification of oil may not pose major problems.

2.3.5 Core annular flow

This method of transportation is where a water film surrounds the oil core and acts as a lubricant. Water fractions of 10-30% are typically used. Addition of chemicals such as sodium hexametaphosphate to the water increases the water's ability to adhere to the pipe and displace the oil films without forming an emulsion (Rafael, et. al, 2010). Configuration of this method is stable but the oils tend to adhere to the wall, leading to restriction and an eventual blockage of the flow system. For normal pumping operation of crude oil, interruptions are expected in the process because of mechanical failure, power interruptions and ruptures in the pipeline or climate conditions. When annular flow is used as a form of transportation, interruptions in the operation even in short

periods of time can result in stratification of the two phases. The difficulty is even exacerbated during a shutdown operation allowing stratification of oil and water phases requiring a large restart pressure. (Sanier, Henaut, & Argilier, 2004) In attempt to restore the annular flow by pumping simultaneously, a multiphase system with different viscosities creates peaks in the discharge pressure of pumps or along the pipeline. This will then exceed the maximum allowable pressure because of large pressure peaks (Rafael, et al., 2010).



Figure 2.1 Pipeline design allowing core flow of heavy oils (Rafael, et al., 2010)

In short, O/W emulsion is a reliable option method chose to be studied because of the activation of natural surfactants occurring in heavy and extra heavy crudes (Rafael, et. al., 2010). Generally, non-ionic surfactants would be a good choice because they are not affected by the salinity of water, other than being relatively cheap and undesirable organic residues that may affect the oil properties are avoided.

2.4 TYPES OF EMULSION

In any oil and water phases, the type of emulsion formed relies on several factors. When the volume fraction of one phase is very small compared to the other, the phase that has the smaller fraction is the dispersed phase while the other is the continuous phase. If the volume-phase ratio is close to 1(50:50 ratio) then other factors shall determine the type of emulsion formed (Kokal, 1995).

2.4.1 Water-in-oil

Water-in-oil emulsions consist of water droplets in a continuous oil phase that is commonly found in the oil industry.

2.4.2 Oil-in-water

Oil-in-water emulsions are sometimes referred to as "reverse" emulsions (Kokal, 1995). Viscosity of O/W emulsions were found to increase as the oil content of the emulsion increased to 60% in sample crude oil. The oil content that increase beyond this value causes a sudden increase in the emulsion viscosity. At this point, phase inversion to W/O emulsions occur. Therefore, emulsions made with oil contents higher than 60% is not suitable to make O/W emulsions (Rafael, et al., 2010).



Figure 2.2 Emulsions found in petroleum transportation (Rafael, et al., 2010)

2.4.3 Multiple Emulsion

Multiple emulsions are more complex and consist of tiny droplets suspended in larger droplets that are suspended in a continuous phase. Taking the example of a waterin-oil-in-water emulsion, it consists of water droplets suspended in larger oil droplets that, again, are suspended in a continuous water phase (Kokal, 1995).



Figure 2.3 Photomicrograph of a W/O/W emulsion (Kokal, 1995)

Most of the emulsions are not thermodynamically stable. Practically, stable emulsions that resist demulsification treatments may be stable for years. Meta-stable emulsions contain oil, water and emulsifying agent(usually surfactant, macromolecule, or fine solids)

2.5 EMULSIFYING AGENT

2.5.1 Surface-active Agents

These surfactants are compounds that are partly soluble in both oil and water. It has a hydrophobic part that has an affinity for oil; a hydrophilic part that has an affinity for water. The molecular structure of the surfactants tend to concentrate at the oil/water interface, forming interfacial films. This affects the interfacial tension (IFT) and dispersion of the emulsified droplets. Natural emulsifiers such as asphaltenes and resins, organic acids and bases has higher boiling fractions (Kokal, 1995).

There are different classes of surfactants. One commonly used in applications are anionics, due to their ease and low cost of manufacture. They have a negatively charged head group such as carboxylates $(-CO_2^-)$, sulfate $(-OSO_3^-)$, and sulfonates $(-S)_3^-)$ groups. Its applications include use in detergent, personal care products, emulsifiers and soaps.

As for cationics, they are positively charged head groups and are mostly involved in applications on absorption at surfaces. Being negatively charged(metal, plastics, minerals, fibres, hairs and cell membranes), they can be modified during treatment with cationic surfactants. Commonly used as an anticorrosion and antistatic agents, flotation collectors, fabric softeners, hair conditioners and bactericides.

Non-ionic surfactants have a strong affinity for water due to their strong dipoledipole interactions from the hydrogen bonding(e.g. ethoxylates, $-(OCH_2CH_2)_mOH$) The length of both the hydrophilic and hydrophobic groups in the ionics can be varied to obtain highest efficiency in use. The hydrophilic group is usually a polyhydric alcohol or ethylene oxide; the lipophilic group is usually a fatty acid or fatty alcohol. Non-ionics' water solubility can be predicted by their HLB(Hydrophole Lipophile Balance). The lower the HLB value, the more lipophilic the surfactant(used in W/O emulsions) whilst the higher the HLB value the more water soluble the surfactant is(O/W emulsions).

Zwitterionics makes up the smallest surfactant class due to their high cost of manufacture. Having excellent dermatological properties and skin compatibility, they are commonly used in shampoos and cosmetics.

2.5.2 Finely Divided Solids

These mechanical stabilizers are much smaller than submicron emulsion droplets. The particles collect at the oil/water interface and are wetted by both oil and water. To stabilize the emulsions, these fine solids depend on particle size, interparticle interactions, and the wettability of the particles. It can be found in clay particles, sand, asphaltenes and waxes, corrosion products, mineral scales and drilling muds during oil production (Kokal, 1995).

2.6 SURFACTANTS AND ITS STABILITY IN O/W EMULSIONS

The use of surfactants and water to form stable O/W emulsions with crude oils are subjected to a series of patents (Zaki, 1996). Aqueous surfactant solutions convert viscous heavy crude oil into low viscosity O/W emulsions. The advantage of non-ionic surfactants is that they are not affected by the salinity of the water. According to Yousef al-Roomi, emulsion viscosity increases as volume concentrations of the dispersed phase increase. Triton X is commonly used as they are relatively cheap, emulsions are easily separated and do not produce any undesirable organic residue that can affect the oil properties. (Yousef et al., 2004).

In Yousef's newly developed surfactant, the structure of the designed molecule has two partial charges to provide a comprehensive adhesion effect in forming emulsions.

		$\partial(-)$		0		$H \vartheta(+)$
						1
CH_2	=	СН	-	С	-	NR

Figure 2.4 Scheme of a newly developed surfactant molecule (Yousef et al., 2004)

A common method of homogenization is used to form emulsification although new methods of emulsification by membranes and ultrasonic waves are being studied recently. Long term stability of emulsions is required for pipeline transporting. Emulsions flowing through porous media are bound to dilution by water and oil and subject to agents that can modify the interfacial tension of the emulsion (Peter & Pilehvari, 1993).

From the thermodynamic point of view, an emulsion is an unstable system as there is a natural tendency for a liquid-liquid system to separate and reduce its interfacial energy. Stabilizing agents suppress the mechanisms involved (sedimentation, aggregation or flocculation, coalescence, and phase inversion) that would break down an emulsion. Sedimentation occurs when the falling water droplets from an emulsion due to the density difference between the oil and water. Aggregation or flocculation is the grouping of water droplets in an emulsion without changing its surface area. Coalescence is the fusing the droplets in forming larger drops with a reduced total surface area (Kokal, 1995).

The literature on emulsion rheology is full of contradicting data under the impression of similar emulsions. According to Clark (1993), "rheology behavior of emulsions is highly dependent on the oil droplet size". Reducing its size can alter the behavior of the emulsion from Newtonian to a highly shear thinning fluid. Most

emulsions show highly shear thinning behavior at low shear rates (below 20s⁻¹); at high shear rates, the behavior becomes Newtonian.

The relationship between viscosity and dispersed phase vary with the variation in emulsion characteristics such as the type of surfactant, surfactant concentrations and temperature (Yousef, George, Elgibaly, & Elkamel, 2004). Oil/aqueous solution of surfactant and oil/surfactant emulsions exhibit a shear thinning behavior that fits the power-law model over wide range of shear rates. Even in low concentration of emulsions, Yousef's(2004) newly developed surfactant molecule can reduce the viscosity of heavy crude emulsions greatly. His emulsions based on a newly designed surfactant molecule have the benefits of low cost and lower mixing energy as compared to commercial surfactant.

The stability of O/W emulsions increase as the surfactant and salt concentration, speed, time of mixing of emulsion, and pH of aqueous phase and temperature of homogenization increase (S.N.Ashrafizadeh & M.Kamran, 2010). Lowest emulsifier concentration recorded by S.N. Ashrafizadeh was 2 wt %. As for high viscosity crude such as synthesis crude oil, homogenization vessel heating would provide more stable emulsions with lower viscosities.

2.7 FLOR BEHAVIOR OF O/W EMULSION

2.7.1 Oil Content of the Emulsion

The oil content of the emulsion affects the stability, pour point and dynamic shear viscosity of the crude oil. The results from Shadi W. Hasan et al.(2010) indicated that as the volume of the dispersed phase increases, the rate of coalescence increases owing to the increased entropy for effective collisions between the dispersed droplets. The influence of the oil content of the emulsion on its pour point is a very important parameter to study, in order to be sure that the pour point of the prepared O/W does not increase to cause transportation troubles in pipelines at low temperatures. For all the oil contents studied, the measured pour points were found to be lower than that of the crude oil, this means that the formation of an O/W emulsion for a particular crude oil

decreases its pour point value. Shadi W. Hasan et al.(2010) studies the most appropriate conditions for decreasing the effective viscosity of viscous crude oil via O/W emulsion formation. It is clear that, decreasing the oil content or conversely increasing the water content of the emulsion is accompanied with a decrease in its apparent viscosity. From the economic point of view, it is more profitable and cost-effective to reduce the viscosity of the crude oil using the minimum amount of water. Doing so, would result in an increased throughput of the pipeline and reducing the corrosion problems that would arise from the co-transportation of water with crude oil in the form of an O/W emulsion.

2.7.2 Speed of Mixing

Increasing the mixing speed results in increasing the viscosity of the emulsion. The dependence of the mean droplet size distribution of the emulsions on the speed of mixing decreases as the speed of mixing is increased. Increasing the mixing speed results in the decrease of the droplet size of the oil dispersed phase which increases the viscosity of the emulsion. Shadi W.Hasan et al.(2010) considered the effect of droplet size distribution on the stability and viscosity of the emulsion. They stated that: for a given volume fraction, the smaller droplet size dispersions are more stable and gave higher viscosity. This may be due to more particle–particle interactions because of the larger interfacial area. For emulsion systems having relatively large droplet size of the dispersed phase (diameter =10 mm), the hydrodynamic forces are dominant (hard-sphere interaction) and the relative viscosity is independent of the droplet size.

On the other contrary, for relatively small dispersed droplets the colloidal surface forces and Brownian motion are dominant, and the relative viscosity increases with the decrease in the droplet size of the dispersed phase at a given shear stress. The influence of the mixing speed on the stability of the emulsion was studied. This concludes that the stability of the O/W type of emulsion increases by increasing the mixing speed.

2.7.3 Surfactant Concentration

From the economic point of view, it would be more profitable to decrease as much surfactant concentration to stabilize the crude oil-in-water emulsion. The emulsion stability increases as the surfactant concentration is increased. Emulsion stability (100%) was observed for the surfactant concentrations ranging from 2.5% to 1.5% at a mixing speed of 700 rpm.(Shadi W.Hasan et al., 2010). This has lead to the formation of a more stable emulsion with an increase in viscosity from 78 to 177.5 cP. The emulsions remained stable by subsequent decrease in the surfactant concentration to 0.25% at constant mixing speed 1200 rpm. It is clear that increasing the surfactant concentration increases the emulsion stability .This observation is explained by the fact that increasing the surfactant concentration results in increasing the number of surfactant molecules adsorbed at the oil-water interface. The adsorbed surfactant molecules due to their non-ionic nature provide a steric barrier to coalescence of the dispersed oil droplets. The steric barrier is formed by the repulsive interactions occurring between the hydrated ethylene oxide units of the NPE molecules adsorbed at the surface of a dispersed oil droplet and those adsorbed at the surface of another droplet.

2.7.4 Effect of Salt Concentration

According to S.N. Ashrafizadeh, increasing salt concentration of sodium chloride in the water phase of the emulsion, increases the viscosity of the emulsions. On the other hand, the increased salt concentration reduces the amount of separated water. Similarly, when salt is added, the viscosity is increased in various aqueous surfactant systems. This is due to the salt ions acting as barriers among the oil droplets and water phase, thus the water and oil's interfacial tension is lowered at higher aqueous salinity. When salinity of the aqueous phase increases, the low interfacial tension results in smaller droplets of dispersed phased, the emulsions are more stabilized.

2.7.5 Effect of Temperature of Homogenization

The temperature of the homogenization process of oil-in-water can be very effective in its emulsion making performance. As illustrated by Ashrafizadeh et al. (2010), raising the temperature of homogenization has resulted in emulsions with lower viscosities and higher stabilities. It is notable that increasing the temperature of mixing would result in softening the bituminous particles and therefore, a monotonous dispersion of oil droplets in the water phase would occur.

2.7.6 Effect of Resin/Asphaltene Ratios

According to Abdurahman(2007), naturally occurring asphaltene and resin in crude oil can stabilize the emulsion. The asphaltene and resin act as an emulsifying agent reducing the interfacial tension and induces a repulsive force between the droplets. The resin/asphaltene ratio(R/A) is important to predict the emulsion stability. Solubility of asphaltene increase with presence of resin. A higher R/A ratio indicates easier separation of emulsions. High resin concentration stores more dissolved asphaltene in the oil phase.

2.7.7 Effect of pH

No viscosity enhancement is observed with the increase of pH of the solution upon addition of hydrochloric acid and sodium hydroxide, whilst the emulsion stability is significantly increased (S.N.Ashrafizadeh & M.Kamran, 2010). At continuous phase of emulsions, increasing the pH from 6 to 9 increases the absolute value of zeta potential of the droplets resulting in formation of emulsions with higher stabilities (Sakka, 2002).Bai(2009) concluded that in neutral and weak acidic and basic conditions with pH from 4 to 10, the IFT reduces significantly with the addition of heavy oil and its polar components, showing stronger synergetic effect. This confirms that there is interaction beween heavy oil, its polar components and the emulsifier.
2.7.8 Slip Flow Effect

Slip-flow is the motion of the main body of fluid relative to an adjacent surface with shear taking place across a thin liquid film separating the bulk of fluid from the surface. Wall-slip depends on the flow curves for a fluid on tube diameter when a capillary tube viscometer is used or on gap width when a coaxial cylinder instrument is used. The power consistency index, K' experimented by Peter (1993) in small size tubes is nearly the same, but it is not feasible to be used in large pipelines in the field as it may result in large errors. Therefore, minimum of 3 pipe sizes should be collected in scale-up studies to correct any slip effects.

2.8 FACTORS CONSIDERED IN TRANSPORTATION ACROSS PIPELINE

2.8.1 Pressure Drop

Generally, as the dispersed phase concentration increased, pressure drop increased when comparing different emulsion oil concentrations velocities in the turbulent region. For emulsions with different dispersed phase concentrations, the differences between pressure drops increased with velocity. At equal flow rates, for 70.2 % emulsions in laminar flow, pressure drops were lower than pressure drops of turbulent flow for lower concentration emulsions. It is useful to compare pressure loss for different concentrations of o/w emulsions. (Sanchez & Zakin, 1994).

2.8.2 Energy Expanded

According to Sanchez, energy loss per kilogram of oil decreased as the concentration of oil increase at comparable oil mass flow rates. At turbulent flow, no maximum dispersed-phase volume fraction which minimises energy loss was present.

2.9 **DEMULSIFICATION**

Demulsification or emulsion breaking is necessary in many practical applications such as the petroleum industry, coating, painting, and waste water treatment in environmental technology. Demulsification has gained importance due to the use of steam and caustic injection or combustion process, for in-situ recovery of heavy crude oils, is complicated by the production of viscous emulsions of oil, water and clay. Therefore, the demulsification of crude oil emulsions forms an integral part of crude oil transportation.

2.10 TYPES OF DEMULSIFIER

After transformation of crude oil is carried out, different methods can be applied to separate the oil and water phases. Few important methods are thermal demulsification, electrodemulsification, chemical demulsification, microwave heating (Abdurahman, Anwaruddin, & Yunus, 2007)free-thaw method, and demulsification by membranes (S.N.Ashrafizadeh & M.Kamran, 2010). Other methods such as pH adjustment, filtration, membrane separation is also used in modern scientific research (Kim, 1995)

2.10.1 Chemical Demulsifier

Chemical demulsification is most widely used in treating water-in-oil and oil-inwater emulsions and involves the use of chemical additives to accelerate the emulsion breaking process (Kim, 1995).

Chemical demulsifier, alkyl phenol-formaldehyde ethoxylated-propoxylated in a 60ppm dose was added to demulsify a stable 90% Geisum crude O/W emulsion at 50°C to completely resolve the emulsion (Zaki, 1996). Whilst amine demulsifiers group suggested to be more effective in emulsion breaking than polyhydric and acid demulsifiers (Abdurahman, Rosli, & Zulkifly, 2007).

Demulsifying action consists of the combination at the interface of the added species with asphaltenes until an 'optimum formulation' is attained, at which the interfacial amphiphile mixture exhibits the same affinity for both phases. The more hydrophilic it is, the less amount is required to attain proper formulation at the interface. The best condition for breaking emulsion is observed when "there is compromise at using a not-too-hydrophillic demulsifier in a not-too-small concentration" (Miguel, Patrick, & Jean, 2006).

A common method in determining relative emulsion stability for lab-scale is the simple bottle test. The bottle test is an empirical test in which varying amounts of potential demulsifiers are added into a series of tubes containing subsample of an emulsion to be broken. After some specific time, the extent of phase separation and appearance of the interface separating the phases are noted.

Recommended by Kokal, the bottle tests should be conducted with fresh emulsions (within a few minutes of sampling) because sample aging has a significant effect on demulsifier dosages. During then, other factors should also be noted: clarity of the water, color and appearance of the emulsion, sediments in the water, presence of a rag layer, and loose solids hanging at the interface. Chemicals should be tested at various concentrations, operating temperatures and settling times and more importantly, the amount of water and salt remaining in the transported crude. The best demulsifier is the one that produces the speediest, cleanest separation at the lowest possible cost per unit barrel of crude.

For demulsifier to be effective, it must mix thoroughly with the emulsion and transfer to the film surrounding the water droplets. Ideally, the demulsifier should be injected in a continuous stream using inline mixers that are upstream so that the demulsifier has time to mix intimately with the emulsion. Demulsifier slugging creates localized high concentration areas and promotes re-emulsification, thus should be avoided. According to Kokal(1995), one method to enhance the mixing is to dilute the demulsifier with sufficient quantities of a diluents(usually solvent) and the diluted mixture is injected into the emulsion.

Besides, turbulence created during the injection enhances the diffusion and dispersion of demulsifier into the emulsion, increasing the probability of collisions

between water droplets. The turbulence must be continuous to allow the chemical to reach the interface between oil and water. Care should be taken that the intensity is not so severe to cause further tightening of the emulsion.

Gentle agitation is performed to mix the demulsifier into the bulk of the emulsion. It is necessary for the water droplets to collide, increasing the chances of coalescence. Excessive agitation should be avoided to lead to further emulsification. Simply, a moderate level of agitation is required, and excessive turbulence should be avoided. Plate packing or baffles inside the separators help distribute the emulsion evenly and cause gentle agitation. The surface of the plates also helps in drop coalescence.

After gentle agitation of the mixing demulsifier, a period of quiescent settlement to enhance coalescence should be followed using gravity settling. The dimensions of the vessel and retention time of the fluid in the separator is then taken into consideration (Kokal, 1995).

Success of the chemical demulsifying methods depends upon:

- i. The retention time of the emulsion in the equipment
- ii. Type of emulsion to be treated
- iii. Level of the water cut
- iv. Whether to heat the system or not
- v. If the feed is constant or changing in composition

2.10.2 Microwave Heating

Emulsion breaking could also be achieved by microwave heating. The separation is much faster with microwave heating rather than conventional heating separation. The microwave's radiation raises the temperature of emulsion, reduces its viscosity and finally results in the separation of water from oil (Abdurahman, Rosli, & Zulkifly, 2007)

2.10.3 Thermal Method

This is by the addition of heat to enhance emulsion breaking in both refinery and oil field. In the oil field, resolutions may occur with light oils in which paraffin forms the main emulsifying agents. Increasing the temperature well above the paraffin melting point ranging between 50-65°C may completely destabilize an emulsion. Therefore, the optimum operating temperature at refinery is 70°C. However, the application of heat alone is rarely sufficient in emulsion resolution (Grace, 1992).

CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

In this chapter, the materials and the equipments used for the research will be described and the experimental procedure will be elaborated. For transporting the crude oil emulsion systems, the first 3 steps are conducted, i.e, producing the oil-in-water emulsions, transportation of produced O/W emulsions to the desired destination and finally separation of oil and water phases. Experimental methods involve emulsion sample preparation, experimental set-up for equipments, and sample characterization. In the series of experiment, the influence of operating parameters including oil content of the emulsion, surfactant concentration, speed of mixing on the stability and viscosity of the emulsion is investigated. The process variables in the transportation through the pipeline is the Reynolds number and flow velocity.

3.2 MATERIALS

3.2.1 Raw Materials

- i. Blended crude oil
- ii. Distilled water

3.2.2 Emulsifiers

All chemicals used are industrial grade reagents.

- i. Triton X-100
- ii. Span 80(Sorbitan monooleate)
- iii. Span 83 (sorbitan sesquioleate)

3.2.3 Demulsifiers

Amine functional groups

- i. Dioctylamine
- ii. Cocoamine
- iii. Hexylamine

3.3 EQUIPMENT

- i Brookfield viscometer
- ii. Digital Tensiometer
- iii. Tank
- iv. Transparent PVC pipes
- v. Valves

3.4 EXPERIMENTAL PROCEDURES

3.4.1 Surface Tension Determination

The equipment used is Du Nouy Interfacial Tensiometer equipped with 6cm circumference platinum ring. The ring is attached to the lever arm. Distilled water is filled in the beaker and placed on the sample platform of the tensiometer. The sample platform assembly is raised by means of dial-adjusting screw until the ring is immersed approximately 5mm into the water. The ring should be centered in the test vessel. The torsion of wire will gradually increase while slowly lowering the table. These simultaneous adjustments are performed carefully proportioned, while the ring system remained constant at its zero position. Continue this step until the liquid film breaks and the ring breaks free. The scale reading at the breaking point of the liquid film is the force the pull exerted on the ring, which is the surface tension. The measurement is made in dynes/cm. The experiment is repeated and four measurements are recorded for accuracy.

3.4.2 Interfacial Tension (IFT) Determination

As oil is lighter than water, the aqueous solution (water) is first placed in the sample vessel. The ring was positioned under the surface of the water to completely wet it and while in this position the light phase is carefully pipetted onto the surface of the heavy phase. The interface should be allowed to reach equilibrium, therefore 5 minutes is allocated before pulling the ring through the light phase.

Two set of samples were recorded, which were 50:50 oil water ratio and also 70:30 oil water ratio with total volume of 50ml each respectively. The experiment is repeated and four measurements are recorded for accuracy.



Figure 3.1: Du Nouy Interfacial Tensiometer (Model: SEO- DST30M)

3.4.3 Small-Scale Emulsification

O/W emulsions preparation



Figure 3.2 Overview for emulsion preparation and destabilization

In each series of experiments, water-in-oil emulsions were prepared using various amounts of particular oil samples while other parameters were fixed at desirable values. Same amount of oil, water and mixing was used on different kinds of surfactants. Then, the maximum limit of oil content for each sample will be determined. Phase inversion would occur if limit is exceeded.

The oil-in-water emulsions are prepared at room temperature with a standard three-blade propeller at mixing speed of 1000rpm and 1500rpm respectively. 1wt % of Triton X-100 is added into 50ml jar of water (continuous phase). Crude oil(dispersed phase) is added slowly to the solution. The volume of crude oil added is calculated based on the ratio of oil to water of 70:30 and in another series of experiment of 50:50 oil to water ratio. The emulsion is homogenized for 10 minutes to reduce the average particle size to a few microns. Steps mentioned above were repeated using emulsifiers shown in Table 3.1. MSDS of all emulsifiers are given in Appendix B.

Mixing speed, rpm	Emulsifier	Concentration, wt%	
1000	Triton X-100	0.5	
		1.0	
	Span 80	0.5	
		1.0	
	Span 83	0.5	
		1.0	
1500	Triton X-100,	0.5	
		1.0	
	Span 80	0.5	
		1.0	
	Span 83	0.5	
		1.0	

Table 3.1Summary of emulsifiers required to form emulsion samples

3.4.4 Measuring type of prepared emulsions

The different prepared samples of O/W emulsions were tested for their stability. The prepared emulsions are checked for O/W or W/O emulsions by using filter paper test. For filter paper test, using a dropper, few drops of the emulsion is dropped on the filter paper. To confirm the emulsion is an O/W emulsion, the continuous phase (water) should spread out quickly on the filter paper, whilst the crude oil will be concentrated inside the water. If the emulsion is a W/O emulsion, the opposite will be observed.

3.4.5 Gravitational Stability Test

Emulsions prepared were each poured into a 50ml glass cylinder and tested for stability by means of gravitation. The emulsion will be covered tightly with parafilm. The separated water volume was registered every 10, 30, 60, 120, 360, 720, 1440 and 2880 minutes. Observation was recorded and percent water separated will be calculated based on the following:

% water separated = $\left(\frac{\text{volume of water separated,mL}}{\text{original volume of crude oil and water,mL}}\right) \times 100\%$

3.4.6 Measuring Droplet Size Distribution

A research microscope was used to observe the droplet size of each emulsion sample. The droplet size distribution was obtained by placing a small drop of the emulsion on a glass slide. Thereafter, several pictures of the emulsion drop were taken using Canon digital camera (Model: EOS 40D). Images of droplets were measured using AxioVision software tool. In order to get a credible impression of the droplet sizes for each emulsion, more than 50 droplets were counted in the distribution population. Average droplet mean size of the droplets were calculated.

3.4.7 Brookfield Test

Rheological properties of emulsion were determined by a viscometer with UL adapter using spindle No. 31. The Brookfield Viscometer is equipped with a water bath thermostat. Emulsion samples were tested at varied temperatures (25°C, 50°C, 70°C, 90°C) and at varied spindle speed (100rpm, 150rpm, 200rpm). Viscosity, shear rate and shear stress of emulsion samples were measured.



Figure 3.23 Brookfield Rotational Digital Viscometer (Model: LV/DV-III Ultra Rheometer)

3.4.8 Pilot-Scale Emulsification

One most stable emulsion (in terms of O/W ratio, surfactant concentration, and mixing speed) from the stability tests conducted above was used to prepare the emulsion in a pilot scale. Total volume of 1L of stable emulsion was prepared. Emulsion was prepared by placing the required amount of water in a 2L beaker, then the best emulsifier was added while stirring the water in the beaker with the mixer. Crude oil was gradually added under continuous intense mixing of the blend for five minutes. A simple scale-up procedure using approximately equal energy input per mass of emulsion is utilized to determine the batch mixer rotational speed and time of mixing.

3.4.9 Pipeline Flow Experiment

The prepared pilot scale emulsion was flowed through an open loop system of a 3m long horizontal pipe. A pump is used to pump the emulsion from tank A to tank B through the pipeline.



Figure 3.4 Process flow diagram of experimental pipeline

The flow behavior of oil-in-water emulsions in pipeline was studied. The volumetric flowrate was determined by the amount of emulsion collected at tank B from divided by the time taken to travel from tank A to tank B. The type of flow inside the pipeline can be determined from the Reynold's number.

$$\operatorname{Re} = \frac{\rho V_{avg} D}{\mu}$$

3.4.10 Demulsifiers Screening

One most stable emulsion (in terms of O/W ratio, surfactant concentration, and mixing speed) from the stability tests conducted above will be used to test for demulsification. Demulsifiers used were as summarized in Table 3.2. Demulsifier of the stated concentration was injected into a 50ml emulsion system. Preparation of emulsion was

discussed in Section 3.4.3. The system was stirred at the stated speed summarized in Table 3.2 for 1 minute to homogenize the demulsifier and emulsion.

Mixing speed, rpm	Demulsifier	Concentration, wt%	
1000	Dioctylamine	0.5	
		1.0	
	Cocoamine	0.5	
		1.0	
	Hexylamine	0.5	
		1.0	
1500	Dioctylamine	0.5	
		1.0	
	Cocoamine	0.5	
		1.0	
	Hexylamine	0.5	
		1.0	

Table 3.2 Summary of demulsifiers

Bottle test method was used in the demulsifiers screening in order to find out the most effective demulsifier. This was done by transferring the emulsion with demulsifier into a 50ml capacity glass cylinder graduated with 0.5ml graduations. Cylinders were tightly covered with parafilm. Separated water volume was registered every 10, 30, 60, 120, 360, 720, 1440 and 2880 minutes.

The water-dropout data was collected and analyzed to determine the best demulsifier, by being the one most separated.

% water separated =
$$\left(\frac{\text{volume of separated water,mL}}{\text{original volume of water in the emulsion,mL}}\right)$$
 100%

Note: Bottle tests should be conducted with fresh emulsions(within a few minutes of sampling), because sample aging has a significant effect on demulsifier dosages.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 INTRODUCTION

The chapter presents the experimental results using different types of emulsifier to investigate for emulsion stability before transporting through a 3m long pipe. Stability on two volumetric ratio of oil in water was discussed. Fluid properties, that were surface tension of crude oil and temperature effect on emulsion viscosity were discussed. Results on rheological properties: shear rate, and shear stress were shown. Fluid kinematics of emulsion was discussed using the Reynolds transport theorem. A brief discussion on efficiency of demulsifier used in breaking crude oil emulsion was also conducted.

4.2 SURFACE TENSION AND INTERFACIAL TENSION ANALYSIS

Surface tension is a measure of the force acting at a boundary between two phases. The attractive forces between two immiscible liquids, are referred to as interfacial tension. Interfacial tension of crude oil and water are important before introducing the presence and concentration of emulsifiers.

ComponentTension (dyne/cm)Max. Weight (g)Water69.1520.875

Table 4.1: Surface tension of distilled water and air

Distilled water was observed to have a high surface tension. This was due to its high polarity of having large intermolecular forces.

Oil-Water Ratio	Tension (dyne/cm)	Max. Weight (g)
50 : 50	1.109	0.017
70:30	2.913	0.044

Table 4.2: IFT between crude oil and water

From the test, it was observed that a decrease in O/W ratio increased the IFT between oil and water phase. Since crude oil is hydrophobic and non-polar, when come into contact with highly polar distilled water, the heavy and light phase will want to reject one another. When more oil is placed upon the water surface, the surface-tension forces will be spreaded out, thus increasing the IFT value.

The interfacial tension of water-oil is less than the surface tension of water-air because the mutual attraction was moderated by all the molecules involved. Therefore, adding surfactants to oil and water will ease the formation and stability of the oil in water emulsion. For an O/W emulsion, the surfactant acted as a modified interface between the oil and water, which resulted in a deposited film on the oil droplet. The effect of surfactant is to expand the interface which in turn must be balanced by the tendency for the interface to contract under normal interfacial tension forces.

4.3 EMULSION STABILITY SCREENING PROCESS

In this study, the rheological properties of 50-50% O/W emulsion and 70-30 % O/W emulsion at mixing speed of 1500rpm were discussed. Viscosity, shear stress, shear rate and magnitude of water separation were studied. The effectiveness of a surfactant was determined by carrying out various stability tests. A comparison between three chemical emulsifiers were made: Triton X-100, Span 80 and Span 83.

Emulsifier	Solubility in Water	Туре
Triton X-100	Yes	Non-ionic
Span 80	Yes	Non-ionic
Span 83	Yes	Non-ionic

 Table 4.3: Properties of emulsifiers

4.4 BROOKFIELD ANALYSIS

4.4.1 Effect of temperature and viscosity

At 50-50 ratio of O/W emulsion, 1.0 wt% emulsifier at 1500rpm:



Figure 4.1: Viscosity versus Temperature at 100 rpm spindle speed



Figure 4.2: Viscosity versus Temperature at 150 rpm spindle speed



Figure 4.3: Viscosity versus Temperature at 200 rpm spindle speed

Figure 4.1, 4.2 and 4.3 showed viscosity of 50:50 O/W emulsion as a function of temperature, using 1.0 wt % emulsifier at varied temperature and spindle speed. There is a difference of viscosity magnitude between emulsions when different surfactant is used. Temperature affects the emulsion stability due to the alteration of interfacial tension and viscosity of emulsion, thus decreasing their viscosity. (Anisa, Nour, & Nour, 2010).

For liquids, viscosity is approximated as

$$\mu = a10^{b/(T-c)}$$
(Equation 4.1)

where T is absolute temperature and a, b, and c are experimentally determined constants. When surfactants of Triton X-100 and Span 80 were used, the graph trend fits the general equation where viscosity of liquids decreases with temperature.

However, when Span 83 is used as emulsifier, an unusual observation was reported. There had been fluctuation of viscosity against temperature. When temperature increased from 25°C to 50°C, the viscosity increased, whereby the trend does not agree with Equation 4.1. This effect can be explained using the Brownian motion. Further increment of temperature reduced the repulsion between molecules and the van der Waals attractive forces take over leading to Brownian flocculation which was followed by an increase in viscosity. At temperature between 50°C to 70°C, the particle surface was covered, thereby reducing the attractive forces, which led to some

deflocculation and hence lowering of the viscosity. From 70°C to 90°C, Brownian forces take control on the viscosity of the emulsion again.

At 50-50 ratio of O/W emulsion, the emulsion using Span 83 as surfactant would have a tendency to undergo a phase inversion, which is termed as Phase-Inversion-Temperature (PIT). The phase inversion starts at 50° C and temporarily switches back and forth between O/W and W/O emulsion.

At 70-30 ratio of O/W emulsion, 1.0 wt% emulsifier:



Figure 4.4: Viscosity versus Temperature at 100 rpm spindle speed



Figure 4.5: Viscosity versus Temperature at 150 rpm spindle speed



Figure 4.6: Viscosity versus Temperature at 200 rpm spindle speed

The viscosity of the emulsion is observed to increase when the oil phase volume increases. Figure 4.4, 4.5, and 4.6 showed a decreased viscosity when temperature was increased at different spindle speed. Viscosity is caused by the cohesive forces between the molecules in liquids. Since the molecules of emulsion possessed more energy at higher temperatures, they opposed the large cohesive intermolecular forces strongly. Thus, resulting in the energized molecules of emulsion to move more freely, as shown in the decreased viscosity.

As for the different types of surfactant used, a change of temperature will result in a change to stability of the emulsion. An increase in temperature will change the solubility of emulsifiers and rupture the interfacial film on the surface of the dispersed droplets. Therefore, the classification of emulsifiers in terms of decreasing stability of emulsion was as followed: Span 83, Span 80 and Triton X-100. The high emulsion viscosity was attributed to the stronger attraction force between crude oil and water molecules. Hence, triton x-100 is the weakest emulsifier in terms of providing resistance to flow in relative comparison to the other emulsifiers. Overall, the general trend of the viscosity versus temperature graphs indicated that as the temperature of emulsion increases, its viscosity decreases. In the liquid, cohesive forces between the molecules preceeds the molecular momentum transfer between the molecules, because the molecules are closely packed (Haresh, 2008). When emulsion is heated, the cohesive forces between the molecules reduce, thus the forces of attraction between them reduce, thus reducing the viscosity of the emulsion.

On the other hand, for relatively small dispersed droplets, the colloidal surface forces and Brownian motion are dominant, and the relative viscosity increases with the decrease.

4.4.2 Effect of Shear Stress and Shear Rate



For 50:50 O/W emulsions, surfactant concentration of 1.0 wt%, 25^oC:

Figure 4.7: Shear Stress versus Shear Rate



For 70:30 O/W emulsions, surfactant concentration of 1.0 wt %, 25° C:

Figure 4.8: Shear Stress versus Shear Rate, spindle speed of 150rpm

Results from the Figure 4.7 and 4.8 showed plots of shear stress versus shear rate of emulsion. Shear force acting on a Newtonian fluid layer is expressed as

$$F = TA = \mu A \frac{du}{dy}$$
(Equation 4.2)

where T is shear stress, A is the contact area between the plate and emulsion, and $\frac{du}{dy}$ is rate of deformation (shear rate). The graph trend showed that the relationship was non-linear, indicating that the emulsion is categorized as a non-Newtonian fluid.

The flow property exhibited by the emulsion differs to that of a Newtonian fluid. In a Newtonian fluid, the shear stress and shear rate should be linear, passing through the origin. In this study, the relationship of S/R is not constant. Thus, a constant coefficient of viscosity cannot be defined.

The slightly outward curved line indicated that the non-Newtonian fluid experienced shear-thinning or pseudoplasticity behaviour.

4.4.3 Effect of Viscosity and RPM





Figure 4.9: Viscosity versus RPM for 50:50 O/W emulsion



Figure 4.10: Viscosity versus RPM for 70:30 O/W emulsion

Figure 4.9 and 4.10 showed the effect of spindle speed on the emulsion viscosity. The rheological study of the emulsions indicated that as the RPM increases, the viscosity decreases. The trend followed the equation of

$$T = \mu \frac{2\prod R^3 \dot{nL}}{l}$$
 (Equation 4.3)

where T is torque, L is the length of rheometer's cylinder, \dot{n} is the RPM (revolutions per minute), l is the fluid layer of thickness within a small gap between two concentric cylinders. As RPM is increased, internal resistance is increased. The increase of the drag, will lower the apparent viscosity of the emulsion. This confirmed the shear thinning nature of the fluid.

4.4.4 Effect of Viscosity and Shear Rate



For 50:50 O/W emulsions, surfactant concentration of 1.0wt%, 25⁰C:

Figure 4.11: Viscosity versus Shear Rate for 50:50 O/W emulsion

For 70:30 O/W emulsions, at 1500 rpm mixing speed, surfactant concentration of 1.0wt%, 25^{0} C:



Figure 4.12: Viscosity versus Shear Rate for 70:30 O/W emulsion

The emulsion displayed a decreasing viscosity with an increasing shear rate. Emulsion for which the apparent viscosity decreased with the rate of deformation (shear rate), exhibited pseudoplastic behaviour. The pseudoplastic fluid when sheared, the less viscous it become. When Span 83 is used as emulsifier, the viscosity is higher than using Span 80 and Triton X-100 at a constant shear rate.

At higher volume of dispersed phase (70:30 O/W), emulsions showed characters of highly non-Newtonian fluid.

4.5 GRAVITATIONAL STABILITY TEST

4.5.1 Percent Water Separated and Time

At 25[°]C, for 50:50 O/W emulsions:



Figure 4.13: Water separation versus time at emulsion mixed at 1500rpm, surfactant concentration of 0.5wt %

At 25[°]C, for 70:30 O/W emulsions:



Figure 4.14: Water separation versus time at emulsion mixed at 1500rpm, surfactant concentration of 1.0wt %

For the experiment, physical stability of the emulsion was observed. A result of a one layer system was desired for use from an effective emulsifier. When Span 83 was used, it had the ability to resist changes in spatial distribution (coalescence) of water over time. It was also observed that a decrease in droplet size when higher mixing speed to emulsion forming is applied, it increases the overall stability of emulsion. Results from using Span 83 showed that when a lower ratio (70:30 O/W) continuous phase was used, only 5 percent of water was observed to separate, as compared to a 50 percent of water separated when 50:50 O/W emulsion was used.

Emulsions stabilized by Triton X-100 were the least stable. Even when 70:30 O/W emulsion was used, 40% of water still managed to separate. As higher as 80% of water was separated when 50:50 O/W emulsion was tested.

Overall, classification of emulsifiers in terms of decreasing stability of emulsion was therefore: span 83, span 80 and triton X-100.

4.5.2 Effect of Percent Water Separated and Surfactant Concentration

At 25°C, for 50:50 O/W emulsions:



Figure 4.15: Water separation versus surfactant concentration at 1000rpm mixing speed



Figure 4.16: Water separation versus surfactant concentration at 1500rpm mixing speed

At 25[°]C, for 70:30 O/W emulsions:



Figure 4.17: Water separation versus surfactant concentration at 1000rpm mixing speed



Figure 4.18: Water separation versus surfactant concentration at 1500rpm mixing speed

Figure 4.15, 4.16, 4.17 and 4.18 showed the percent of water separated from the emulsion versus surfactant concentration after an observation of 48 hours. The general trend showed that as surfactant concentration was increased, its effectiveness in stabilizing the emulsion was increased. This result was explained as when surfactant concentration increased, the surface energy of the film was increased, preventing the liquid to move the liquid molecules from the interior p to the surface against the attraction forces of other molecules.

Also, when a higher volumetric oil-water ratio (70:30) was used, results obtained were at its optimum. Meanwhile, it was observed that a higher mixing speed during emulsion formation would lead to an increased stability in the emulsion. When higher mixing speed was applied, droplet size would be decreased, thereby increasing the surface tension of the surfactant. This would lead to a higher performance surfactant.

Triton X-100 was concluded to be unstable as even when high concentration (1.0 wt%) was added to a higher volumetric oil-water ratio emulsion, 30% of water was still found to be separated.

When Span 83 was used as the surfactant, only 4.17% of water was found to be separated from the emulsion at 70:30 oil-in-water emulsion(1500rpm). Therefore this one emulsion is concluded to be the most stable among other emulsions. This type of emulsion was subsequently used in the transportation process and destabilization process.

4.6 TRANSPORTATION IN PIPELINE

4.6.1 Type of Flow

The most stable emulsion was used to flow through a 3m long horizontal pipe to determine the type of flow exhibited by the emulsion. 2 L of 70:30 oil-in-water emulsion was prepared. Emulsion was used to flow in a 3m long, 1 in. horizontal plastic pipeline using 1.0 wt% of Span 83 at 1500rpm mixing speed. The dynamic viscosity of emulsion was determined from earlier Brookfield test at 25° C, recorded at 0.1276 N.s/m². Time taken for emulsion to run through the 3m long pipe was 16 seconds, with 1.8L of emulsion collected at the end.

	Symbol	Unit	Value
Volumetric flowrate	Q	m3/s	1.125 x 10 ⁻⁴
Diameter of pipe	D	m	0.0254
Density	ρ	kg/m ³	794.7
Dynamic viscosity	μ	N.s/m ²	0.1276
Mean velocity	v	m/s	0.222

Table 4.4: Values to calculate Reynold's number

Calculations shown at Appendix A indicated that Reynold's number was 35.12

Under practical conditions, for

Laminar flow, $\text{Re} \leq 2300$

Turbulent flow, $\text{Re} \ge 4000$

Transitional flow, $2300 \le \text{Re} \le 4000$

Therefore, from calculations, type of flow of emulsion is laminar. In this case, the resistance to flow is independent to the pipe wall roughness, where pipe wall roughness can create local eddy currents within the emulsion adding resistance to its flow. By being a laminar flow, the emulsion fulfilled the characteristics of a low Reynolds number flow where viscous forces were dominant.

4.7 DEMULSIFICATION PROCESS

4.7.1 Effectiveness of Demulsifier

The most stable emulsion, which was 70:30 O/W ratio at mixing speed of 1500rpm using 1wt% Span 83 was used to be added to demulsifier for demulsification process.



At 25°C, 0.5 wt% demulsifier

Figure 4.19: Percent water separated versus time at 1000rpm mixing speed



Figure 4.20: Percent water separated versus time at 1500rpm mixing speed

At 25°C, 1.0 wt% demulsifier



Figure 4.21: Percent water separated versus time at 1000rpm mixing speed



Figure 4.22: Percent water separated versus time at 1500rpm mixing speed

Water separation is important in describing the potential and ability of formulation in demulsification process as compared to oil separation.

Therefore, figure 4.19, 4.20, 4.21, and 4.22 showed the percent water separated versus time, over an observation period of 48 hours, when different demulsifiers were used. The action of demulsifiers were mainly used to displace the stabilized emulsion.

Overall, Dioctylamine showed to be the most efficient demulsifier, followed by hexylamine, and cocoamine. The highest percentage of water separated was recorded at 83% when 1.0 wt% of dioctylamine was used as demulsifier, at 1500rpm mixing speed.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSION

In this study, we have examined the effect of several factors on enhancing the flow of crude oil through pipeline using emulsion. The flow regime of a stable emulsion was concluded. From the analysis of data obtained for the emulsions at different temperatures, dispersed phase volume fraction, surfactant concentration, and mixing speed, the following can be concluded:

5.1.1 Emulsion Stability

Viscosity decreased as temperature increased. A change in temperature affected the stability of emulsion. Increasing temperature decreased the stability of oil-in-water emulsion. At 50:50 ratio O/W emulsion, emulsion was unstable by showing a fluctuating temperature, indicating a phase inversion occurrence. As for 70:30 ratio oil/water emulsion, high temperature of up to 90^{0} C gives the highest viscosity of emulsion.

Increasing the dispersed phase volume gave an increase to the stability of emulsion. This also increased the viscosity of emulsion. A 70:30 ratio O/W emulsion is shown to be more stable than a 50:50 ratio of O/W emulsion.

Nature and concentration of emulsifying agents controlled the emulsion viscosity. As concentration increases, interfacial tension of water and oil were lowered, thus improving their stability and increases viscosity. When surfactant concentration

was 1.0wt %, emulsion was more stable by giving lesser separation of water, as compared to when surfactant concentration of 0.5 wt % was used.

Surfactant concentration gave an effect on the percentage of water separation. As concentration was increased, water separation was decreased. Least water separation indicated that emulsion was stable. Thus, a higher surfactant concentration of emulsion proved to produce a be more stable.

Study indicated that emulsion is a non-Newtonian pseudoplastic fluid. Shearthinning effect becomes stronger when droplet size is reduced.

The order of emulsifiers in decreasing stability were:

Span 83, Span 80, Triton X-100

5.1.2 Flow regime of emulsion

Stable emulsion displayed a laminar fluid flow, which was characterized by smooth streamlines and a highly ordered motion. Viscous forces exerted by emulsion were large enough to suppress rapid fluctuations of the emulsion. The emulsion was stable to produce a laminar flow throughout the pipeline, thus enhancing the flow of crude oil.

5.1.3 Demulsification

Order of demulsifier in terms of increasing stability on emulsion:

Dioctylamine, Hexylamine, Cocoamine

For 50-50 ratio and 70-30 ratio of o/w emulsion at mixing speed of 1000rpm, hexylamine showed the highest efficiency in water separation in both concentration of 0.5wt % and 1.0 wt %. At 1.0 wt%, 80% of water had been separated. No water was separated in emulsion when using cocoamine at 0.5wt% concentration.
5.2 **RECOMMENDATIONS**

Based on the results of this study, the following recommendations are suggested:

- 1. Analysis of the crude oil will provide more insight to the crude oil components.
- 2. More values should be obtained for graph of shear stress versus shear rate to further verify the behaviour of fluid.
- 3. Droplet size of crude oil in emulsion should be measured using a direct-screen capture microscope to provide higher accuracy measurement instead of capturing image of droplet with hand held digital camera.
- 4. Installation of a flow rate meter will greatly improve the accuracy of data while transporting emulsion through pipeline.

REFERENCES

- A., S., Henaut, I., & Argilier, J. (2004). Pipeline Transportation of Heavy Oils, a Strategic, Economic and Technological Challenge. *Oil & Gas Science & Technology*, 455-466.
- Abdurahman, H., Anwaruddin, H., & Yunus, R. M. (2007). Water-in-crude oil emulsions: its stabilization and demulsification. *Journal of Applied Sciences*.
- Abdurahman, H., Rosli, M. Y., & Zulkifly, J. (2007). Chemical Demulsification of Water-in-Crude Oil Emulsions. *Journal of Applied Sciences*.
- Anisa, A. I., Nour, A. H., & Nour, A. H. (2010, Oct 14). Catastrophic and Transitional Phase Inversion of Water-in-Oil Emulsion for Heavy and Light Crude Oil. Retrieved Dec 6, 2011, from Science Alert: http://scialert.net/fulltext/?doi=jas.2010.3076.3083&org=11
- Bai, J., Zhang, T., & Fan, W. (2009). The synergetic effect between heavy oil components and emulsifier in heavy oil-in-water emulsion. *Journal of petroleum science and engineering*, 189-192.
- Gillies, R. (1992). Emulsions for short distance transportation of heavy crude oil:pipe loop test results. *Journal of Canadian Petroleum Technology*, 41-47.
- Grace, R. (1992). Commercial Emulsion Breaking. In. In L. Schramm, Emulsions
- Guevera, E. G. (1998). Highly viscous oil transportation methods in the Venezuela oil industry. In *Proceedings of the 15th World Petroleum Congress* (pp. 495-501). London: John Wiley and Sons.
- Kim, Y.H. (1995). A study of dynamic interfacial mechanisms for demulsification of water-in-oil emulsions. *Illinois Institute of Technology: PhD Theses*.

- Kinghorn, R. (1983). An introduction of the physics and chemistry of petroleum. Chichester: John Wiley & Sons.
- Kokal, S. L. (1995). Chapter 12 Crude oil emulsions. In F. S. Manning, & R. E. Thompson, *Oilfield Processing*, Vol.2: Crude Oil (pp. 533-570). Los Angeles: Pennwell Books.
- McCain, W. (1990). *The Properties of Petroleum Fluids*(2nd ed.). Oklahoma,USA: Penn Well Books.
- Miguel, R., Patrick, B., & Jean, L. (2006). Breaking of Water-in-crude oil emulsions. 1.Physicochemical phenomenology of demulsifier action. *Energy & Fuels 2006*, 1600-1604.
- Neumann, H., Lahme, B., & Severin, D. (1981). Composition and Properties of Petroleum, Vol.5. Chichester: Wiley Ltd.
- Oil & Gas Field Technical Terms GlossaryRetrieved March 9, 2011, from http://oilgasglossary.com/relative-density.html
- Peter, E. C., & Pilehvari, A. (1993). Characterization of crude oil-in-water emulsions. Journal of Petroleum Science and Engineering, 165-181.

Poynter, G. T. (1970). Patent No. 3519006. US.

Rafael, M.P., Mosqueira, M. d., Zapata-Rendon, B., Mar-Juarez, E., Bernal-

S.N.Ashrafizadeh, & M.Kamran. (2010). Emulsification of heavy crude oil in water for pipeline transportation. *Journal of Petroleum Science and Engineering*.

- Sakka, S. (2002). Sol-gel science and technology topics in fundamental research and applications. In Sol-Gel Prepared Ferroelectrics and Related Materials (pp. 33-35). New York: Kluwer academic publisher.
- Sanchez, L. E., & Zakin, J. L. (1994). Transport of viscous crudes as concentrated oilin-water emulsions. *Ind. Eng. Chem. Res.*, 3256-3261.
- Shadi W. Hasan, M. T. (2010). Heavy crude oil viscosity reduction and rheology for pipeline transportation. *Science Direct*, 1095-1100.
- Vassiliou, M. (2009). *Historical Dictionary of the Petroleum Industry*. Lanham, Md Scarecrow Press.
- Yousef, A.-R., George, R., Elgibaly, A., & Elkamel, A. (2004). Use of a novel surfactant for improving the transportability/transportation of heavy/viscous crude oil. *Journal of Petroleum Science & Engineering*, 235-243.
- Zaki, N. N. (1996). Surfactant stabilized crude oil-in-water emulsions for pipeline transportation of viscous crude oils. *Colloids and surfaces*, 582-594.

APPENDICES

APPENDIX A

(1)Calculation of volume of surfactant required based on weight percent concentration.

(a) 0.5 wt % of surfactant = $50ml \ge 0.5\% = 0.25 ml$

(b) 1.0 wt % of surfactant = 50 ml x 1.0 wt % = 0.50 ml

(2) Calculation for Reynold's number

Pipe diameter =
$$\frac{1'' \quad 0.0254m}{1''} = 0.0254m$$

 $\frac{1.8L \quad 1m^3}{1000L} = 0.0018m^3$

Volumetric flowrate, $Q = \frac{0.0018m^3}{16s} = 1.125 \text{ x } 10^{-4} \text{ m}^3/\text{s}$

For liquid flow, the Reynolds number was calculated by:

v
$$= \frac{4Q}{\Pi D^2} = \frac{4x \, 1.125 \, x \, 10^{-4}}{\Pi x \, 0.0254^2} = 0.222 \, \text{m/s}$$

N_{Re}
$$= \frac{\rho v D}{\mu} = \frac{794.7 \times 0.0247 \times 0.0254}{0.1276} = 35.12$$

APPENDIX B

MSDS FOR EMULSIFIER & DEMULSIFIER

1) MSDS for Triton X-100

General

Synonyms: polyethylene glycol P-1,1,3,3-tetramethylbutylphenyl ether, octyl phenol ethoxylate, 4-octylphenol polyethoxylate Molecular formula: $C_{14}H_{22}O(C_2H_4O)_n$ where the average number of ethylene oxide units per molecule is around 9 or 10

Physical data Appearance: viscous colourless liquid Melting point: 6 C Boiling point: > 200 C Vapour density: >1 Vapour pressure: <1 mm Hg at 20 C Density (g cm⁻³): 1.07 Flash point: 251 C

Stability

Stable. Incompatible with strong oxidizing agents. Viscosity increases as temperature falls and handling becomes difficult at temperatures below 20 C

Toxicology

Harmful if swallowed. Causes severe eye irritation. May be harmful if inhaled or in contact with skin. Toxicology not fully investigated. The product may contain traces of ethylene oxide or dioxane, which are probable human carcinogens.

Environmental information

Toxic to aquatic organisms - may cause long-term damage in the environment.

2) MSDS for Span 80

General

Synonym: SPAN 80, Arlacel 80, Sorbitan O; Sorbitan oleate; Sorbitan monooleic acid ester

Molecular Formula: C₂₄H₄₄O₆

Physical data

Physical state and appearance: Liquid.
Boiling Point: >100°C (212°F)
Specific Gravity: 1 (Water = 1)
Dispersion Properties: Dispersed in cold water.
Solubility:
Very slightly soluble in diethyl ether. Insoluble in cold water, acetone.
Conditions of Instability: Heat, incompatible materials

Toxicology

Slightly hazardous in case of skin contact (irritant), of ingestion, of inhalation.

Environmental information

Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.

3) MSDS for Span 83

General

Synonyms: Sorbitan sesquioleate Molecular formula: C₆₆H₁₂₆O₁₆

Physical data

Density : 0.989 g/mL at 25° C Vapor pressure : 0.81 psi (20° C) Refractive index : n20/D 1.478(lit.) Flash point : 113°C

Toxicology

Hazardous in case of skin contact (irritant), of ingestion, of inhalation. Slightly hazardous in case of skin contact (permeator)

Environmental information

Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise. The products of degradation are more toxic.

4) MSDS for Dioctylamine

General

Synonyms: di(2-ethylhexyl)amine, 2,2'-diethylhexylamine, 2-ethyl-N-(2-ethylhexyl)-1-hexanamine Molecular formula: C16H35N

Physical data

Appearance: colourless liquid Boiling point: 281 C Vapour density: 8.35 (air = 1) Density (g cm-3): 0.81 Flash point: 132 C Water solubility: negligible

Stability:

Stable. Combustible. Incompatible with oxidizing agents.

Toxicology:

Harmful if swallowed, inhaled or absorbed through the skin. Skin, eye and respiratory irritant.

5) MSDS for Cocoamine

General

Synonyms: ethoxylated cocoamine Molecular formula: C16H35N

Physical data

Boiling point (mm/Hg_ : >425^oF @ 760 Specific gravity : $1.03 @ 80^{o}F$ Physical form : Liquid @ $80^{o}F$ Solubility in water : Soluble.

Toxicology

Over exposure may cause gastrointestinal irritation, diarrhea, nausea and vomiting.

6) MSDS for Hexylamine

General

Synonyms: Aminohexane; 1-Hexanamine; Mono-n-hexylamine Molecular formula: C16H15N

Physical data

Physical state and appearance: Liquid. Color: Colorless Boiling Point: 130°C (266°F) - 132 C Melting Point: -23°C (-9.4°F) Specific Gravity: 0.766 (Water = 1) Vapor Density: 3.5 (Air = 1)

Stability

Stable. Combustible. Incompatible with oxidizing agents.

Toxicology

Acute Potential Health Effects: Skin: Causes severe skin irritation with possible burns depending on severity and length of exposure. Harmful if absorbed through skin. Eyes: Causes severe eye irritation with possible burns. Eye contact may result in permanent damage and complete vision loss. Inhalation: Destructive to the tissue of the mucous membranes and upper respiratory tract.

Environmental information

Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.

APPENDIX C

Table C.2: Tabulated data obtained from Rheometer

Emulsifi	ier				Triton X-	100		Span 80			Span 83		
		Mixing	Spindle			Shear	Shear		Shear	Shear		Shear	Shear
O/W	Conc.	speed	speed	Temp.	Viscosity	Stress	rate	Viscosity	Stress	rate	Viscosity	Stress	rate
ratio	(wt%)	(rpm)	(rpm)	(°C)	(cP)	(D/cm2)	(1/sec)	(cP)	(D/cm2)	(1/sec)	(cP)	(D/cm2)	(1/sec)
50-50	0.5	1000	100	25	10.9	3.98	34.0	11.4	6.32	34.0	22.2	8.06	34.0
				50	8.5	4.18	34.0	7.4	3.67	34.0	39.3	17.60	34.0
				70	8.4	3.37	34.0	6.2	3.16	34.0	17.1	7.75	34.0
				90	4.4	1.84	34.0	6.0	3.67	34.0	25.8	13.40	34.0
			150	25	11.4	5.81	51.0	12.8	7.95	51.0	22.6	11.40	51.0
				50	12.2	6.22	51.0	7.4	5.10	51.0	43.8	22.30	51.0
				70	8.8	4.49	51.0	6.4	4.39	51.0	18.4	9.48	51.0
				90	4.6	2.35	51.0	7.4	4.28	51.0	32.2	16.30	51.0
			200	25	11.7	7.44	68.0	15.3	15.60	68.0	23.4	15.10	68.0
				50	12.0	7.65	68.0	9.7	3.96	68.0	52.2	26.50	68.0
				70	9.9	6.02	68.0	8.7	2.56	68.0	22.5	11.60	68.0
				90	5.1	3.06	68.0	10.5	3.06	68.0	39.3	17.30	68.0
50-50	0.5	1500	100	25	16.9	6.93	34.0	44.1	19.20	34.0	30.1	10.10	34.0
				50	12.4	4.79	34.0	38.8	18.20	34.0	42.6	28.90	34.0
				70	10.0	3.98	34.0	34.6	15.90	34.0	41.1	27.80	34.0
				90	5.0	1.73	34.0	29.4	14.80	34.0	29.5	20.00	34.0
			150	25	17.2	8.67	51.0	48.6	25.10	51.0	34.8	17.70	51.0
				50	13.0	6.63	51.0	44.0	23.30	51.0	50.6	25.80	51.0
				70	11.2	5.71	51.0	39.8	20.60	51.0	47.4	24.20	51.0
				90	5.0	2.65	51.0	34.6	18.20	51.0	35.2	17.80	51.0
			200	25	20.4	11.50	68.0	56.7	29.70	68.0	42.0	28.60	68.0
				50	14.4	8.26	68.0	54.6	19.20	68.0	59.1	20.10	68.0
				70	12.9	6.63	68.0	47.7	23.40	68.0	52.0	18.40	68.0
				90	5.1	2.65	68.0	43.5	19.40	68.0	42.3	14.40	68.0

Emulsifi	er				Triton X-100			Span 80			Span 83		
		Mixing	Spindle			Shear	Shear		Shear	Shear		Shear	Shear
O/W	Conc.	speed	speed	Temp.	Viscosity	Stress	rate	Viscosity	Stress	rate	Viscosity	Stress	rate
ratio	(wt%)	(rpm)	(rpm)	(°C)	(cP)	(D/cm2)	(1/sec)	(cP)	(D/cm2)	(1/sec)	(cP)	(D/cm2)	(1/sec)
50-50	1.0	1000	100	25	15.0	5.91	34.0	62.2	26.40	34.0	32.4	11.00	34.0
				50	12.3	5.61	34.0	43.2	18.90	34.0	36.0	12.30	34.0
				70	10.2	4.89	34.0	34.5	14.80	34.0	24.6	8.46	34.0
				90	8.1	3.98	34.0	24.6	10.20	34.0	15.6	5.40	34.0
			150	25	15.8	7.95	51.0	68.0	34.50	51.0	29.8	15.10	51.0
				50	13.8	7.14	51.0	48.4	24.80	51.0	35.6	18.20	51.0
				70	11.4	5.91	51.0	37.8	19.50	51.0	24.6	8.46	51.0
				90	9.2	4.59	51.0	26.4	13.70	51.0	16.0	8.26	51.0
			200	25	16.5	10.40	68.0	78.3	42.80	68.0	28.8	19.50	68.0
				50	16.2	8.26	68.0	56.4	29.40	68.0	30.7	20.90	68.0
				70	14.1	6.83	68.0	43.5	23.40	68.0	20.2	13.70	68.0
				90	11.7	5.30	68.0	30.3	16.80	68.0	15.1	10.20	68.0
50-50	1.0	1500	100	25	24.6	10.30	34.0	49.9	23.00	34.0	58.5	19.60	34.0
				50	17.4	7.65	34.0	42.3	20.20	34.0	53.4	18.20	34.0
				70	15.0	6.83	34.0	31.5	14.30	34.0	42.3	14.40	34.0
				90	13.0	6.90	34.0	25.8	11.60	34.0	30.0	10.10	34.0
			150	25	26.2	10.30	51.0	56.8	28.70	51.0	44.6	22.70	51.0
				50	19.6	11.80	51.0	50.6	25.20	51.0	44.2	22.40	51.0
				70	16.8	8.46	51.0	36.8	18.50	51.0	34.8	17.60	51.0
				90	15.8	8.67	51.0	14.7	29.20	51.0	24.2	12.30	51.0
			200	25	30.3	13.30	68.0	68.7	34.60	68.0	37.3	25.30	68.0
				50	23.1	10.10	68.0	62.1	29.60	68.0	38.4	26.00	68.0
				70	20.7	8.57	68.0	43.2	22.20	68.0	28.6	19.70	68.0
				90	20.7	8.26	68.0	34.2	17.40	68.0	22.2	15.00	68.0

Emulsifier					Triton X-100			Span 80			Span 83		
O/W	Conc.	Mixing speed	Spindle speed	Temp.	Viscosity	Shear Stress	Shear rate	Viscosity	Shear Stress	Shear rate	Viscosity	Shear Stress	Shear rate
ratio	(wt%)	(rpm)	(rpm)	(°C)	(cP)	(D/cm2)	(1/sec)	(cP)	(D/cm2)	(1/sec)	(cP)	(D/cm2)	(1/sec)
70-30	0.5	1000	100	50	47.4	23.50	34.0	15.0	11.30	34.0	60.0	24.90	34.0
				70	36.4	18.20	34.0	13.2	4.69	34.0	42.4	16.80	34.0
				90	30.0	9.89	34.0	8.4	2.75	34.0	15.4	6.22	34.0
			150	25	80.0	40.70	51.0	31.4	17.40	51.0	101.6	51.80	51.0
				50	56.8	29.00	51.0	16.2	8.36	51.0	65.2	33.30	51.0
				70	43.6	22.00	51.0	13.4	6.93	51.0	44.6	22.70	51.0
				90	24.8	13.20	51.0	6.8	3.57	51.0	16.8	8.57	51.0
			200	25	92.4	47.30	68.0	32.7	21.30	68.0	117.2	62.90	68.0
				50	69.6	31.90	68.0	16.6	5.10	68.0	73.5	40.80	68.0
				70	54.0	25.10	68.0	14.0	8.97	68.0	48.0	28.80	68.0
				90	29.7	20.20	68.0	8.4	2.75	68.0	18.3	10.40	68.0
70-30	0.5	1500	100	25	71.7	32.50	34.0	127.6	45.10	34.0	85.6	18.20	34.0
				50	46.9	23.00	34.0	49.5	17.90	34.0	60.7	41.30	34.0
				70	34.0	16.60	34.0	32.1	33.70	34.0	54.4	37.00	34.0
				90	21.0	9.70	34.0	27.3	11.70	34.0	25.2	16.90	34.0
			150	25	81.8	41.30	51.0	129.6	66.20	51.0	95.4	39.40	51.0
				50	55.2	28.00	51.0	50.8	25.90	51.0	66.2	26.30	51.0
				70	40.0	20.50	51.0	33.4	17.40	51.0	58.6	21.80	51.0
				90	24.8	12.50	51.0	30.4	15.50	51.0	28.4	15.90	51.0
			200	25	96.3	48.50	68.0	132.6	86.90	68.0	116.4	48.50	68.0
				50	68.1	31.80	68.0	52.2	33.70	68.0	77.7	33.80	68.0
				70	48.3	7.67	68.0	36.9	21.70	68.0	64.2	29.90	68.0
				90	28.8	14.20	68.0	34.5	18.60	68.0	47.7	14.40	68.0

Emulsifier					Triton X-100			Span 80			Span 83		
O/W	Conc.	Mixing speed	Spindle speed	Temp.	Viscosity	Shear Stress	Shear rate	Viscosity	Shear Stress	Shear rate	Viscosity	Shear Stress	Shear rate
ratio	(wt%)	(rpm)	(rpm)	(°C)	(cP)	(D/cm2)	(1/sec)	(cP)	(D/cm2)	(1/sec)	(cP)	(D/cm2)	(1/sec)
70-30	1.0	1000	100	25	72.1	31.40	34.0	71.7	32.50	34.0	110.5	51.00	34.0
				50	50.1	23.50	34.0	46.9	23.00	34.0	81.6	36.90	34.0
				70	38.4	18.20	34.0	34.0	16.60	34.0	80.4	35.70	34.0
				90	21.7	9.89	34.0	21.0	9.79	34.0	70.2	35.30	34.0
			150	25	80.0	40.70	51.0	81.8	41.30	51.0	124.6	63.50	51.0
				50	56.8	29.00	51.0	55.2	28.00	51.0	91.0	46.40	51.0
				70	43.6	22.00	51.0	40.0	20.50	51.0	89.4	45.60	51.0
				90	24.8	13.20	51.0	24.8	12.50	51.0	86.2	44.10	51.0
			200	25	92.4	48.90	68.0	96.3	48.50	68.0	150.3	75.30	68.0
				50	69.6	33.90	68.0	68.1	31.80	68.0	108.3	55.50	68.0
				70	54.0	25.90	68.0	48.3	23.30	68.0	105.0	54.70	68.0
				90	29.7	14.90	68.0	28.8	14.20	68.0	104.1	48.30	68.0
70-30	1.0	1500	100	25	132.6	45.10	34.0	71.4	32.60	34.0	78.9	34.60	34.0
				50	52.2	17.90	34.0	46.3	22.90	34.0	54.4	21.30	34.0
				70	36.9	12.30	34.0	34.2	16.70	34.0	45.4	19.70	34.0
				90	34.5	11.70	34.0	20.8	9.89	34.0	32.4	13.10	34.0
			150	25	129.6	66.20	51.0	81.6	41.50	51.0	87.0	44.50	51.0
				50	50.8	25.90	51.0	55.0	27.90	51.0	55.6	28.50	51.0
				70	33.4	17.40	51.0	40.2	20.30	51.0	50.2	25.50	51.0
				90	30.4	15.50	51.0	25.0	12.40	51.0	35.0	17.90	51.0
			200	25	127.6	86.90	68.0	96.0	48.40	68.0	101.7	53.60	68.0
				50	49.5	33.70	68.0	67.8	31.70	68.0	62.4	36.90	68.0
				70	32.1	21.70	68.0	47.7	23.40	68.0	58.2	30.90	68.0
				90	27.3	18.60	68.0	28.5	14.30	68.0	38.4	21.90	68.0

					% water separation (v/v)										
		Conc.		Sample	10	30	60								
Emulsifier	Ratio	(wt %)	RPM	name	min	min	min	120min	180min	720min	1440min	2160min	2880min		
Triton X-	50-50	0.50	1000	Set 1	48.00	64.00	72.00	76.00	80.00	84.00	88.00	88.00	96.00		
100			1500	Set 2	48.00	56.00	60.00	60.00	64.00	76.00	80.00	84.00	84.00		
		1.00	1000	Set 3	16.00	24.00	28.00	36.00	56.00	72.00	72.00	72.00	80.00		
			1500	Set 4	16.00	20.00	24.00	36.00	40.00	72.00	76.00	80.00	80.00		
Triton X-	70-30	0.50	1000	Set 5	0.00	0.00	0.00	6.67	6.67	33.33	40.00	40.00	46.67		
100			1500	Set 6	0.00	0.00	0.00	6.67	6.67	26.67	33.33	33.33	40.00		
		1.00	1000	Set 7	0.00	0.00	0.00	0.00	0.00	20.00	26.67	26.67	33.33		
			1500	Set 8	0.00	0.00	0.00	0.00	0.00	13.33	26.67	26.67	40.00		
Span 80	50-50	0.50	1000	S01	12.00	28.00	36.00	48.00	48.00	60.00	64.00	64.00	72.00		
			1500	S02	1.60	4.00	28.00	32.00	36.00	62.40	65.60	68.00	68.00		
		1.00	1000	S03	24.00	52.00	52.00	52.00	56.00	68.00	68.00	68.00	72.00		
			1500	S04	0.00	4.00	16.00	36.00	40.00	62.40	65.60	65.60	68.00		
Span 80	70-30	0.50	1000	S05	0.00	0.00	0.00	2.67	6.67	40.00	46.67	46.67	53.33		
			1500	S06	0.00	0.00	0.00	0.00	0.00	26.67	36.67	40.00	46.67		
		1.00	1000	S07	0.00	0.00	0.00	0.00	0.00	26.67	33.33	33.33	40.00		
			1500	S08	0.00	0.00	0.00	0.00	0.00	2.67	26.67	26.67	33.33		
Span 83	50-50	0.50	1000	S31	4.26	8.51	42.55	46.81	51.06	55.32	55.32	59.57	63.83		
			1500	S 32	7.14	10.71	25.00	35.71	39.29	57.14	57.14	60.71	60.71		
		1.00	1000	S 33	1.67	16.67	45.83	54.17	58.33	66.67	69.17	69.17	70.83		
			1500	S 34	0.00	3.33	26.67	26.67	30.00	46.67	53.33	53.33	54.67		
Span 83	70-30	0.50	1000	S35	0.00	0.00	0.00	1.31	2.61	13.07	26.14	26.14	28.76		
			1500	S36	0.00	0.00	0.00	0.00	1.33	6.67	13.33	20.00	20.00		
		1.00	1000	S37	0.00	0.00	1.33	2.67	6.67	6.67	20.00	20.00	20.00		
			1500	S38	0.00	0.00	0.00	0.00	0.00	0.00	1.67	4.17	4.17		

Table C.3: Percent of water separated in gravitational stability test for emulsification

Demulsifier		Dioct	ylamine			Coco	amine		Hexylamine			
Concentration												
(wt%)	0.5		1.0		0.5		1.0		0.5		1.0	
Sample Name	1A	1 B	1C	1D	2A	2B	2C	2D	3A	3B	3 C	3D
RPM												
Time (min)	1000	1500	1000	1500	1000	1500	1000	1500	1000	1500	1000	1500
10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
60	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
120	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
180	6.67	13.33	8.33	50.00	0.00	0.00	0.00	0.00	8.33	16.67	8.33	16.67
720	33.33	40.00	50.00	66.67	0.00	0.00	0.00	0.00	33.33	33.33	41.67	33.33
1440	40.00	46.67	53.33	75.00	0.00	0.00	7.94	16.67	41.67	33.33	46.67	37.50
2160	46.67	46.67	53.33	75.00	0.00	7.94	15.87	16.67	41.67	41.67	46.67	41.67
2880	50.67	53.33	61.67	83.33	0.00	7.94	15.87	33.33	41.67	41.67	50.00	54.17

 Table C.4: Percent of water separated in bottle test for demulsification

APPENDIX D



(a) Set 1, Set 2, Set 3, Set 4



(c) S01, S02, S03, S04



(e) S31, S32, S33, S34



(b) Set 5, Set 6, Set 7, Set 8



(d) S05, S06, S07, S08



- (f) S35, S36, S37, S38
- Figure D.1: Gravitational stability test for emulsification process Name of sample from left to right Specification on sample name as in Appendix C, Table C.3



(a) 1A, 1B, 1C, 1D (b) 2A, 2B, 2C, 2D (c) 3A, 3B, 3C, 3D

Figure D.2:Bottle test on demulsification processName of sample from left to rightSpecifications on sample name as in Appendix C, Table C.4

APPENDIX E

Figure E.1: Viscosity versus temperature at 150rpm spindle speed

(a) At 50-50 ratio of O/W emulsion, 0.5 wt% emulsifier (1000rpm mixing speed):



(b) At 50-50 ratio of O/W emulsion, 0.5 wt% emulsifier (1500rpm mixing speed):



(c) At 50-50 ratio of O/W emulsion, 1.0 wt% emulsifier(1000rpm mixing speed):



(d) At 50-50 ratio of O/W emulsion, 1.0 wt% emulsifier(1500rpm mixing speed):





(e) At 70-30 ratio of O/W emulsion, 0.5 wt% emulsifier(1000rpm mixing speed):

(f) At 70-30 ratio of O/W emulsion, 0.5 wt% emulsifier (1500rpm mixing speed):





(g) At 70-30 ratio of O/W emulsion, 1.0 wt% emulsifier (1000rpm mixing speed):

(h) At 70-30 ratio of O/W emulsion, 1.0 wt% emulsifier(1500rpm mixing speed):



Figure E.2: Shear stress versus shear rate at 25°C

(a) At 50-50 ratio of O/W emulsion, 0.5 wt% emulsifier(1000rpm mixing speed):



(b) At 50-50 ratio of O/W emulsion, 0.5 wt% emulsifier(1500rpm mixing speed):



(c) At 50-50 ratio of O/W emulsion, 1.0 wt% emulsifier(1000rpm mixing speed):



(d) At 50-50 ratio of O/W emulsion, 1.0 wt% emulsifier(1500rpm mixing speed):



(e) At 70-30 ratio of O/W emulsion, 0.5 wt% emulsifier(1000rpm mixing speed):



(f) At 70-30 ratio of O/W emulsion, 0.5 wt% emulsifier(1500rpm mixing speed):



(g) At 70-30 ratio of O/W emulsion, 1.0 wt% emulsifier(1000rpm mixing speed):



(h) At 70-30 ratio of O/W emulsion, 1.0 wt% emulsifier(1500rpm mixing speed):



Figure E.3: Viscosity versus RPM

(a) At 50-50 ratio of O/W emulsion, 0.5 wt% emulsifier(1000rpm mixing speed):



(b) At 50-50 ratio of O/W emulsion, 0.5 wt% emulsifier(1500rpm mixing speed):



(c) At 50-50 ratio of O/W emulsion, 1.0 wt% emulsifier(1000rpm mixing speed):



(d) At 50-50 ratio of O/W emulsion, 1.0 wt% emulsifier(1500rpm mixing speed):



(e) At 70-30 ratio of O/W emulsion, 0.5 wt% emulsifier(1000rpm mixing speed):



(f) At 70-30 ratio of O/W emulsion, 0.5 wt% emulsifier(1500rpm mixing speed):



(g) At 70-30 ratio of O/W emulsion, 1.0 wt% emulsifier(1000rpm mixing speed):



(h) At 70-30 ratio of O/W emulsion, 1.0 wt% emulsifier(1500rpm mixing speed):

