STUDY ON WAX DEPOSITION OF HEAVY CRUDE OIL IN PIPELINES

NADIA ELIZA NATRAH BINTI JAMALUDDIN

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering (Gas Technology)

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JANUARY 2014

ABSTRACT

This thesis presents wax deposition of heavy crude oil in pipelines study. Pipelines are widely used to transport crude oil. Wax deposition in a pipeline was caused by the high viscosity of the heavy crude oil, particularly if it is left untreated, may have severe consequences on the operational efficiency of a pipeline system. In order to overcome the wax deposition of the heavy crude oil, the crude oil is suggested to mix with water and emulsifier at certain conditions so that it will formed oil in water (O/W) emulsion. In this study, both chemical and physical properties of O/W emulsion that prepared by using three types of emulsifiers; Coca Amide DEA (non-ionic and biodegradable surfactant that synthesis from coconut oil plus diethanolamine), Sodium Dodecyl Sulfate (anionic and biodegradable surfactant that synthesis from coconut oil only) with one type of conventional chemical emulsifier (Span 80) were examined. O/W emulsions with two different ratios (50-50% and 70-30%) were prepared at 1500 rpm mixing speed with the concentrations (0.3 wt%, 0.5 wt%, 1.0 wt% and 1.5 wt %) for each emulsifier to test the stability conditions. Instead of stability; shear rate, shear stress and viscosity were determined by Brookfield Viscometer. On the other hand, the droplet size was carried out by using Digital Carl Zeiss Microscope. Result shows that Sodium Dodecyl Sulfate at 1.5 wt% mixed with 70-30% O/W obtained the most stable emulsion for transportation compared to the other two. Then, properties of heavy crude oil were tested via Fourier Transform Infrared (FTIR). The properties are important to know in order to predict the occurrence of wax deposition during transportation. Next, the determination of Wax Appearance Temperature (WAT) using Koehler Cloud and Pour Point Bath. As the temperature decreases, crystalline structure will start to appear. Cloud and pour point of o/w emulsion using Sodium Dodecyl Sulfate which act as emulsifier are -1°C and -19°C respectively. Demulsification is the process of separation of water from the heavy crude oil. Crude oil need to be separate quickly from the water. This is to ensure the crude oil value can be maximized and the operating cost can be minimized. Demulsifiers (Hexylamine and Dioctylamine) with different concentrations (0.2 wt% and 0.5 wt%,1.0 wt% and 1.5 wt%) were used for transportation. The relative rates of water separation were characterized via beaker test. Hexylamine promotes the best coalescene of droplets compared with the other demulsifier that used in this study which is Dioctylamine.

Keywords: wax, heavy crude oil, emulsion, separation, stabilization, WAT,
demulsification, destabilization

ABSTRAK

Tesis ini membentangkan kajian mengenai lilin pemendapan minyak mentah berat dalam saluran paip. Saluran paip digunakan secara meluas untuk mengangkut minyak mentah. Lilin pemendapan di dalam talian paip disebabkan oleh kelikatan minyak mentah berat terutamanya,jika ia tidak dirawat, boleh membawa kesan yang teruk kepada kecekapan operasi sistem talian paip. Untuk mengatasi pemendapan lilin minyak mentah berat, minyak mentah adalah dicadangkan untuk bercampur dengan air dan pengemulsi pada keadaan tertentu supaya ia akan membentuk minyak dalam air (O / W) emulsi. Dalam kajian ini, kedua-dua ciri kimia dan fizikal O / W emulsi yang disediakan dengan menggunakan tiga jenis pengemulsi, Coca Amide DEA (surfaktan bukan ionik dan mesra alam yang disintesis dari minyak kelapa ditambah DEA), Sodium Dodecyl Sulfate (anionik dan surfactant terbiodegradasikan sintesis dari minyak kelapa sahaja) dengan satu jenis pengemulsi kimia konvensional (Span 80) telah diperiksa. O / W emulsi dengan dua nisbah yang berbeza (50-50% dan 70-30%) telah disediakan pada 1500 rpm kelajuan dengan kepekatan (0.3% berat, 0.5% berat, 1.0% dan 1.5% berat) bagi setiap pengemulsi untuk menguji syarat kestabilan. Untuk kestabilan; kadar ricih, tegasan ricih dan kelikatan ditentukan oleh Brookfield Viscometer. Sebaliknya, saiz titisan telah dijalankan dengan menggunakan Digital Carl Zeiss Microscope. Keputusan menunjukkan bahawa Sodium Dodecyl Sulfate pada 1.5% berat bercampur dengan 70-30% O / W terbentuk emulsi yang paling stabil untuk pengangkutan berbanding dengan dua yang lain. Kemudian, sifat-sifat minyak mentah berat telah diuji melalui Fourier Transform Infrared (FTIR). Ciri-ciri penting untuk meramalkan berlakunya pemendapan lilin semasa pengangkutan. Seterusnya, penentuan Lilin Rupa Suhu (WAT) menggunakan Koehler Awan dan Tuangkan Point Bath. Sebagai suhu berkurangan, struktur kristal akan mula muncul. Cloud dan Pour point o / w emulsi menggunakan Sodium Dodecyl Sulfate yang bertindak sebagai pengemulsi adalah -1 ° C dan -19 ° C. Demulsification adalah proses pengasingan air dari minyak mentah yang berat. Minyak mentah perlu berasingan dengan cepat dari air. Ini adalah untuk memastikan nilai minyak mentah boleh dimaksimumkan dan kos operasi dapat dikurangkan. Demulsifiers (Hexylamine dan Dioctylamine) dengan kepekatan yang berbeza (0.2% berat dan 0.5% berat, 1.0% dan 1.5% berat) telah digunakan untuk pengangkutan. Kadar relatif perpisahan air telah disifatkan melalui ujian bikar. Hexylamine menggalakkan coalescene terbaik titisan berbanding demulsifier yang lain yang digunakan dalam kajian ini iaitu Dioctylamine.

Kata kunci: lilin, minyak mentah berat, emulsi, perpisahan, penstabilan, WAT, demulsification, ketidakstabilan

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

Coca Amide DEA	Coca Amide diethanolamine
Span 80	Sorbitan Monooleate
SDS	Sodium Dodecyl Sulfate
O/W	Oil-in-Water emulsion
O/W/O	Oil-in-Water-in-Oil emulsion
W/O	Water-in-Oil emulsion
W/O/W	Water-in-Oil-in-Water emulsion
WAT	Wax Appearance Temperature
WPT	Wax Precipitation Temperature

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.0 INTRODUCTION

1.1 STUDY BACKGROUND

Pipelines are widely used to transport crude oil. Wax deposition in a pipeline, particularly if it is left untreated, may have severe consequences on the operational efficiency of a pipeline system. Crude oil is an organic mixture containing SARA; saturates (paraffin/waxes), aromatics, resins, asphaltenes (Lee, 2008). Deposition of the solid residues may occur in the production facilities at the well head, in pipelines during transportation to the refinery, or in storage tanks at the shipping terminal (Allen and Roberts, 1982). The presence of such solid waxes increases fluid viscosity and its accumulation on the walls reduces the flow line section, causing the blockage of filters, valves and even pipelines, increasing pumping costs, and reducing or even stopping oil production or transport. Their high efficiency makes their use every economic way and attractive to separate oil and water (Staiss et al., 1991).

The temperature gradient occurs between the fluids and flow line when the environment condition outside pipe wall changes. The decreasing of the temperature makes the pipe wall undergo the heat transfer process between itself and the environment to maintain the temperature. Low quality of the crude oil purity during the distillation process makes the contents in crude oil still have clay from the drilling process which help wax producing during the transportation process.

Several methods (Bernadiner, 1993; Hunt, 1996) have been used to enhance the low temperature properties of crude oil. Pretreatment with pour point depressants (PDD) is an interesting solution for transportation of waxy crude oils through pipelines. Another favorable pipeline approach is the transport of viscous crudes as concentrated oil-in-water (O/W) emulsions (Gregoli et al., 2006; Lappin and Saur, 1989). The technical activity of this approach was showed in an Indonesia pipeline (Lamb and Simpson, 1963) and in a 20 km-long, 0.203 km-diameter pipeline in California. In this approach, with the aid of good surfactants, the oil phase evolved into dispersed in the water phase also stable oil-in-water emulsions are formed. Formation of an emulsion makes an important reduction in the emulsion viscosity. O/W emulsion also might reduce corrosion with a crude oil with large sulfur content; corrosion will appear with the use of an aqueous phase, together with the use of formation water, which is rich in salts. Due to the reduction in viscosity, the transport-assisted and transportation costs problems are shortened. Because of water is the continuous phase, crude oil did not affect pipe wall, which reduces the corrosion of pipe for crudes with high sulfur contents and inhibit the deposition of silts in pipes, as is familiar for crudes with high asphaltene contents (Poynter and Tigrina, 1970). Viability of injecting aqueous surfactant solution into a well bore to alter emulsification in the pump for the production of less viscous O/W emulsions will rise the productivity of a reservoir (Simon and Poynter, 1968; Steinborn and Flock, 1982).

1.2 PROBLEM STATEMENT

a. Wax appears thicker and thicker makes the flow area smaller with time going by persuade the transportation capacity and operation safety of the pipelines. It is because it can increase the pressure, blocking area and can cause leakage.

b. The low quality of crude oil purity during the distillation process makes the contents in crude oil still have clay from the drilling process which help wax producing during the transportation process.

c. The temperature gradient occurs between the fluids and the flow line when the environment condition outside pipe wall changes. The decreasing of the temperature makes the pipe wall undergo the heat transfer process between itself and the environment to maintain the temperature.

1.3 RESEARCH OBJECTIVES

a. To overcome the wax deposition of crude oil in pipelines transportation by using oil-in-water emulsion technique

b. Preparation of model emulsion and their characteristic by study the stability using different type of surfactant with different concentration, different volume ratio oil in water emulsion and its chemical demulsification.

1.4 SCOPE OF STUDY

I. Characterization of oil and aqueous phases: oil type, oil concentration, viscosity and temperature dependence.

II. Chemical parameters affecting the stability of O/W emulsions.

III. Preparation of model emulsions and their characterization: W/O and O/W emulsions will be prepared.

IV. Determination of pour and cloud point of emulsion.

V. Destabilization of emulsion

1.5 SIGNIFICANCE OF STUDY

a. Reduced the transportation costs of the crude oil through pipelines

b. Methods that have been used can be applied in the industry which related to the wax deposition problems.

c. Methods might be commercialized by having personal operation that the data used to maintain the wall from waxes production over long period of time.

CHAPTER 2

LITERATURE REVIEW

Crude oil is an organic mixture containing SARA; saturates (paraffin/waxes), aromatics, resins, aspaltenes and also naphtenes (Lee,2008). As the presence of high molecular weight of hydrocarbon which is above C35 in a crude oil, it may cause major economic problems if deposition of the hydrocarbon is allowed to occur during production or transportation. Deposition of the solid residues may occur in the production facilities at the well head, in pipelines during transportation to the refinery, or in storage tanks at the shipping terminal (Allen and Roberts, 1982). The presence of such solid waxes increases fluid viscosity and its accumulation on the walls reduces the flowline section, causing the blockage of filters, valves and even pipelines, increasing pumping costs, and reducing or even stopping oil production or transport.

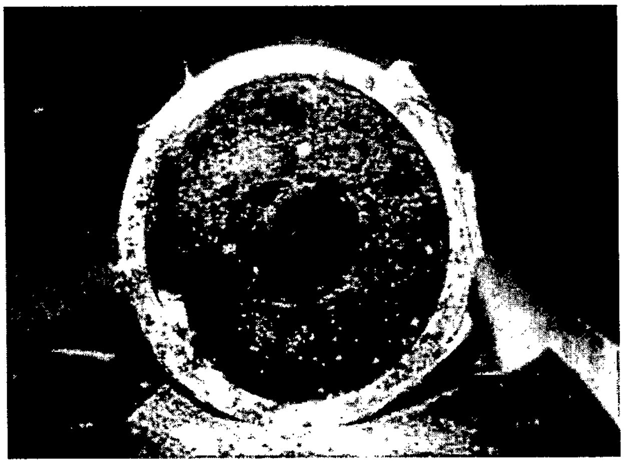

Figure 2.1: Wax deposition in a subsea pipeline (Banki et. Al)

Crude oils are mixture of light and heavy hydrocarbons. The components in crude oils can be classified into paraffin, naphthene and aromatic components. Though the non-n-alkane components in crude oils are minor, it is essential to consider the influence of non-alkane components in the model since their properties, such as fusion temperature and fusion enthalpy, are much different from paraffin. The solubility of each component of crude oils depends on the temperature and composition of the system(Chen and Zhao,2006).The applications of these chemicals as demulsifiers for treating crude oil are specially tailored to act at the oil/water interface. Their high efficiency makes their use avery economic way and attractive to separate oil and water (Staiss et al., 1991). Success of chemical demulsifying methods is dependent upon the adequate quantity of a properly selected chemical must be added into the emulsion, thorough mixing of the chemical.In order to handle the deposition problem, it is important to know wherewax will form, how much wax that will form, how fast the wax will form and how wax deposition can be prevented. To accomplish this, wax deposition models are used. These models predict the wax deposition profile along the pipeline, defines potential wax problems and estimates the pigging frequency before production starts up. However, for an operating pipe, the pigging frequency can be determined by Pressure Pulse profiling of deposits combined with tracer injection, and this way the location and extent of the deposit is measured. Usually these data will be correlated upto field data. Chemical methods are the most common method of emulsion resolution in both oil field and refinery. The combination of heat and application of chemicals designed to neutralize the effects of emulsifying agents have great advantages of being able to break an interfacial film effectively; without the addition of new equipment or modifications of the existing equipment.

Several factors such as shear rate, temperature and light oil concentration on the viscosity behavior have been studied. This study shows that the blending of the heavy crude oil with a limited amount of lighter crude oil provided better performance than the other alternatives(Shadi, Mamdouh and Nabil,2010).Crude oils produced from the formations are transported and processed at low temperatures where solid wax particles may precipitate. These solid particles cause additional pressure drop in production tubing, pipeline, and processing equipment and eventually cause plugging. Great saving in the cost of operating such equipment can be achieved from accurate modeling of wax appearance temperature (WAT) and the amount of wax formed at given conditions (Elsharkawy, Al-Sahhafand Fahim,1999).

Emulsions have long been of great practical interest due to their widespread occurrence in everyday life. They may be found in important areas such as food, cosmetics, pulp and paper, pharmaceutical and agricultural industry.Emulsions maybe encountered at all stages in the petroleum recovery and processing industry (drilling fluid, production, process plant, and transportation emulsions)(G.W. Mushrush, J.G. Speight,1995)(L.L. Schramm,1992).

Component of SARA (Saturates, Aromatics, Resins and Asphaltenes) can be separated by using technique of SARA analysis(Manar,2012). Particles that contain in the compounds are naturally hydrophilic. Due to the long term of exposure to the crude oil, the particles can become hydrophobic(oil-wet).Emulsions with particles and asphaltenes combined can be much more stable than those stabilized by asphaltenes alone, provided that enough asphaltenes are present: all the adsorption sites on the particle surface need to be saturated by asphaltenes (J. Sjoblom et al,2003),(T.H Plegue, S.G Frank, D.H., Fruman and J.L. Zakin,1989).

Crude oil, shale oil, and sand oil are sources of petroleum and contain hundreds of compounds, which can be grouped into four main classes: (i) saturates (alkanes and cycloparaffins), (ii) aromatics (mono-, di-, and polynuclear aromatic hydrocarbons (PAHs) with alkyl side chains), (iii) resins (aggregates with a multitude of building blocks such as sulfoxides, amides, thiophenes, pyridines, quinolines and carbazoles), and (iv) asphaltenes (aggregates of extended polyaromatics, naphthenic acids, sulfides, polyhydric phenols and fatty acids), (R. Vale, Silva, C.F Damin, Sanches Filho, & Welz, 2007).

The resins are high-molecular-weight polar hydrocarbons, which are known to stabilize asphaltenes in petroleum fluids. Resin fractions are easily obtained during high-performance liquid chromatography (HPLC) separation by polar solvent extractionThe saturates (or aliphatics) are the nonpolar compounds containing no double bonds and include both the alkanes and the cycloalkanes. Wax is a sub-class of the saturates. The aromatic consist of all compound with one or more benzene rings. These ring systems may be linked up with naphthene rings and/or aliphatic side chains (Friedemann, 2006).

According to Friedemann (2006), this fraction is comprised of polar molecules often containing heteroatoms such as nitrogen, oxygen or sulfur. This fraction is operationally defined, and one common definition of resins is as the fraction soluble in light alkanes such as pentane and heptane, but insoluble in liquid propane. Naphthenic acids are a part of this fraction.

Asphaltenes comprise the most polar fraction of crude oil and consist of polyaromatic condensed rings with short aliphatic chains and heteroatoms such as nitrogen, oxygen, sulfur and various metals . Asphaltenes can cause a series of problems along the whole production chain from the reservoir to the refinery (Kaminski, T.J; Fogler, H.S; Wolf, N.; Wattana, P.; Mairal, A.;, 2000). Asphaltenes are black or brownish polar compounds formed by macromolecules with multiple condensed aromatic rings with relatively high contents of hetero-atoms and contaminant metals (Pujro, Richard; Falco, Marisa; Devard, Alejandra; Sendran, Ulises;, 2014). Asphaltenes are usually defined as that fraction of petroleum, which is soluble in toluene and insoluble in n-pentane or n-heptane at a dilution ratio of 40 volumes of solvent per volume of the petroleum sample. Asphaltenes are present in crude oils as colloidally suspended solid particles. Precipitation of asphaltene occurs when the oil loses its capacity to keep those particles dispersed (Qian, K.; Edwards, K.E.; Siskin, M.; Olmstead, W.N.; Mennito, A.S.; Dechert et al., G.J.;, 2007)

Emulsions naturally occur in petroleum production and pipelining, mainly those of water-in-oil (W/O) and more complex like oil-in-water-in-oil (O/W/O) emulsions . Such emulsions are detrimental for oil production since oil's viscosity raises, increment corrosion issues and are difficult to break in desalting and dehydrating units before refining. Nevertheless, emulsions or dispersions of heavy extra-heavy crude oil in water (O/W) or in brine may be an alternative to pipeline transportation of high-viscosity crudes because viscosity reduction (Pilehvari et al., 1988; Ashrafizadeh and Kamran, 2010). An O/W emulsion is a mixture of two immiscible liquids where oil phase is dispersed into the water continuous phase Fig. 2). In some locations, hydrocarbon diluents or lighter crudes may not available or limited while fresh water, sea water or even formation water may be available for emulsification. Very often O/W emulsions are deliberately produced to reduce the viscosity of highly viscous crude oils so that they can be transported easily through the pipeline (Zaki, 1997). The O/W emulsion reduces the viscosity of heavy crude oils and bitumens and may provide an alternative to the use of diluents or heat to reduce viscosity in pipelines (Langevin et al., 2004). Also, restarting a pipeline after an emergency shutdown and reemulsification of oil may not pose major problems (Simon and Poynter, 1970).

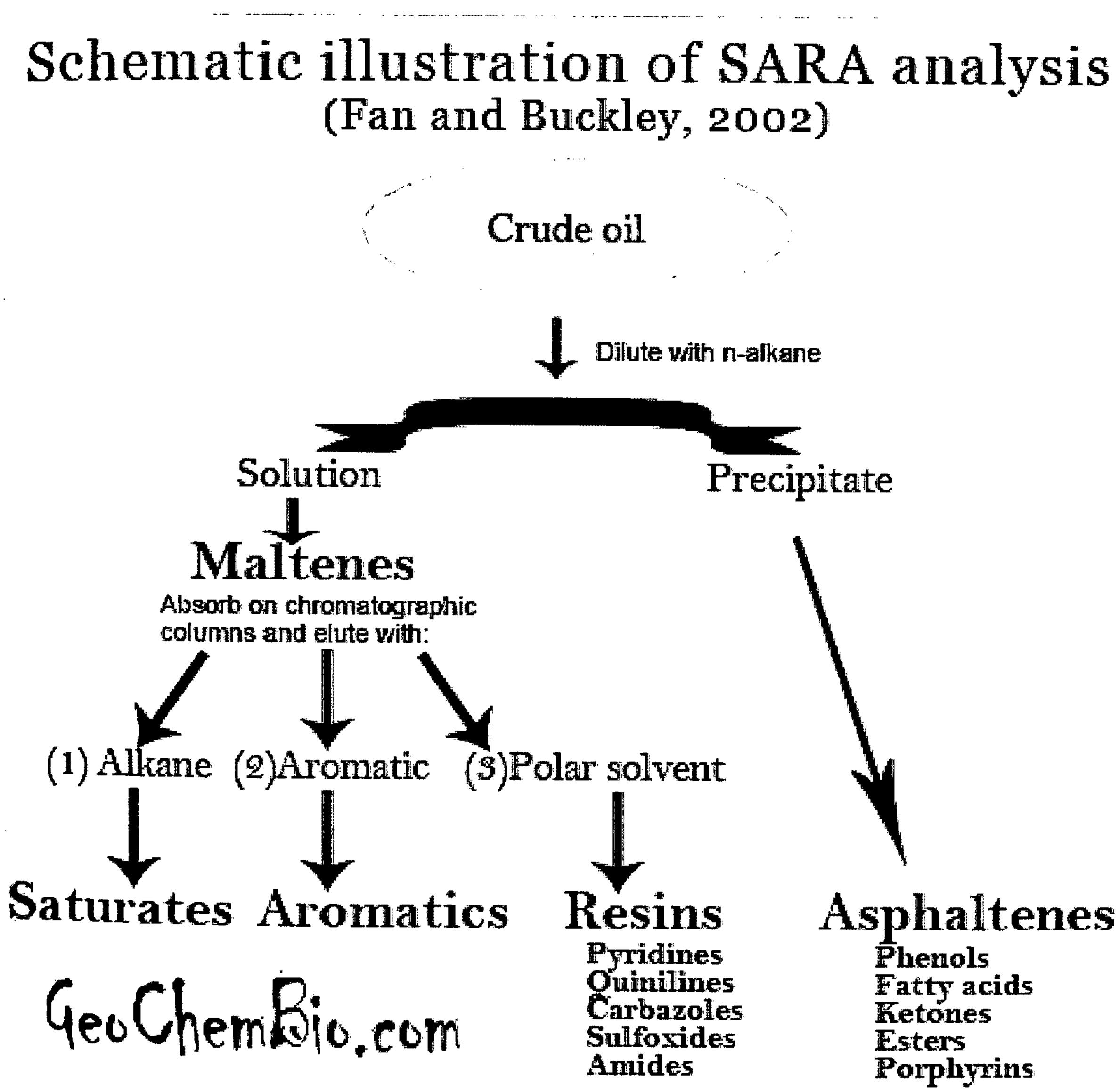

Figure 2.2 : Compounds in Crude Oil

Many problems related to wax, asphaltene, hydrates which may lead to deposition causing pressure drop, reducing production and risk of pipes plugging. Hence, slugging also one of the problems occurs as elevated viscosity and gelatin at low temperature operating system represent this potential rheological problem. High content of wax could be disadvantageous in crude oil as well as bitumens. In crude oil transportation, wax may crystallize at low temperature and precipitate as a solid material causing problems in pipelines and in production and processing equipment purport that paraffin deposition down hole and in surface equipment is one of the most serious problems in oil production operation, there will makes changes in physico-chemical equilibrium according to decreasing in temperature below paraffin melting pointcause crystallization, losses in component solubility and sequence of accumulation.

Moreover, precipitation of wax increase significantly due to temperature decrease, this transition typically occurs about 10-15°C below the Wax Appearance Temperature (WAT). WAT is the temperature at which visible crystallization occur, it is depending on the molecular weight and the concentration of the waxes and the chemical nature of non-waxy part of crude oil in term of hydrocarbon. The lowest temperature of crude oilcan flow under static condition is known as pour point temperature (PPT): KPPT as the temperature falls, crystal continuous and simultaneously the amount waxes precipitated increases. Pour point usuallydetermined by using the ASTM D97-87 procedure.

There are two basic types of emulsion in the oil field; they are water-(w/o) and oil-in-water (o/w). More than 95% of emulsion crude oil field are w/o type.Emulsion is the colloidal dispersion of two immiscible liquid phases. Which means aliquid is dispersed in a continuous liquid phase, dispersed phase is referred to an internal phase and continuous phase is referred to an external phase. Moreover, in this case, Oil in water emulsion is for oil droplets dispersed in water as continuous phase and water in oil emulsion is the water droplets dispersed in oil as continuous phases.

Crude oil exploration and production has continued into deep-waters and extreme environments where its cold temperature would cause wax deposition problems almost unavoidable during crude production. Wax deposition had exhibit a significant concern in the probe to increase oil recovery from producing reservoirs. The significance effects of wax deposition has the ability to disrupt the efficient crude oil production, yet leading to decline of the internal diameter of the pipe and results in prolific bad impacts. Conventional healing approaches have not show the best alternative to high production losses and profit uncertainty in the petroleum industry. Petroleum production can be significantly affected by deposition of paraffin wax during crude production, with devastating economic consequences. Hence, predicting wax problems within the production tubing and flow lines that could decrease or halt production is essential in optimizing production and operating efficiency.

An emulsion is usually defined as a system in which one liquid is relatively distributed or dispersed, in the form of droplets, in other substantially immiscible liquids. In petroleum industry, water-in-oil (W/O) or oil-in-water (O/W) emulsions can lead to enormous financial loses if not treated correctly. The emulsion formation is a result of the co-production of water from the oil reservoir. During processing, pressure gradients introduce sufficiently high mechanical energy input (shear forces) to disperse water as droplets in the oil phase. The dispersed phase is sometimes referred to as the internal phase, and the continuous as the external phase (Aske, 2002). Emulsions are oil-water mixtures stabilised by surfactant, consisting of either oil droplets dispersed in water (oil-in-water or O/W) or water droplets dispersed in oil (water-in-oil or W/O). Emulsions are metastable, so that the average droplet size in an emulsion tends to increase with time (Lissant, 1974).

There are two factors that affect the emulsion stability, which is viscosity and density difference. The application of heat and the addition of demulsifiers can reduce the viscosity. As the results, the rate of water droplets settlement and the mobility of water are increased and lead to collisions, coalescence and further increase in the rate of separation. Heat application to the emulsion also will decrease the density of the oil at a greater rate than that of water and thus allows more rapid settling of the water. This is due to the difference in densities of the two liquid phases may be increased. Dehydration of heavier oil is typically more difficult compared with light oil as its density is closer to that of water.

Emulsions are thermodynamically unstable and will eventually phase separate. This occurs via a combination of physical mechanisms; the droplets will eventually coalesce, they can group together without coalescing (flocculate) as a result of attractive forces between the droplets, smaller droplets will preferentially dissolve and larger droplets will grow in a process known as Ostwald ripening and they will sediment if there is an appreciable difference in density between the two constituent phases.

CHAPTER 3

MATERIALS AND METHODS

3.0 METHODS

3.1 INTRODUCTION

In order to solve the problems of this study, methods, materials and equipments were discussed. In this chapter, the study was carried out stage by stage in order to accomplish the objectives of this study.

Firstly is for the formation of emulsion and stability testing. By using Span 80, Sodium Dodecyl Sulfate (SDS) and Coco amide DEA that act as emulsifying agents, emulsion were formed. The emulsifiers are then added into the crude oil continuously with the tap water. To check the O/W formation, Filter Paper Test is conducted. After that, Brookfield Rotational Digital Rheometer LV/DV-III, Carl Zeiss Research Microscope and FTIR are used to check the stability of the emulsion. The most stable emulsion will be selected for modeling pipeline by checking its chemical and physical properties.

The most stable emulsion that is selected was used in the transportation for this stage. The dimensions of the modeling pipeline which is the diameter and pipe size is determined. Next, Reynolds number is calculated based on the parameters obtained and the type of the flow is identified.

Emulsion destabilization (demulsification process) which is the final stage of this study, is carried out. Demulsifiers dioctylamine and hexylamine were added into the emulsion at different concentration. The separation rate of the emulsion is studied and compared in order to determine the efficiency of the emulsion.

3.2 MATERIAL

3.2.1 Raw Material

The crude oil used is collected from **Petronas Refinery at Malacca** and the tap water used is taken from the Engineering laboratory of Faculty of Chemical Engineering and Chemical Resources in Universiti Malaysia Pahang.

Table 3.1: Type of crude oil used

Types of Crude Oil	Ratios of W/O	Ratios of O/W emulsion
Tapis	50% - 50%	50% - 50%
		70% - 30%

Figure 3.1: Heavy Crude Oil