

CHARACTERIZATION, DEMULSIFICATION AND TRANSPORTATION OF  
HEAVY CRUDE OIL VIA OIL-IN-WATER (O/W) EMULSION

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## ABSTRACT

The production of heavy crude oil is limited due to its high viscosity. It is expected to increase in the future as low viscosity crudes are depleted. The high viscosity lead to increase of pump energy as it creates high pressure drop. In order to reduce the viscosity of the heavy crude, it is suggested to mix it with water and optimum emulsifiers to create a lower viscous fluid, oil-in-water (O/W) emulsions. In this study, both chemical and physical properties of O/W emulsion that prepared by using cocoamide DEA (non-ionic and biodegradable surfactant that synthesis from coconut oil) and two types of conventional chemical emulsifiers (Span 83 and Triton X-100) were investigated. O/W emulsions with two different ratios (50-50% and 65-35%) were prepared at three different mixing speed (500rpm, 1000rpm and 1500rpm) with the concentrations (0.2 wt%, 0.5 wt% and 1.0 wt%) of each emulsifier. These emulsions were tested for relative rates of water separation (stability test), viscosity, shear stress and shear rate at varied temperature and stirring speed of Brookfield viscometer. While the droplet size was carried out by using Carl Zeiss Research Microscope and its software. Results sho that Span 83 at 1.0 wt% mixed with 65-35% O/W with 1500rpm mixing speed obtained the most stable emulsion for transportation compared to the other two. Then, its chemical properties were tested via Fourier Transform Infrared (FTIR). These chemical properties are important in order to predict the occurrence of wax deposition during the transportation. The transportation of the emulsion then carried out by using the laboratory scale pipeline. Demulsification is the process of separation of water from crude oil. Crude oil need to be separate efficiently and quickly from the water to allow further treatment. This is to ensure the crude oil value can be maximized and the operating cost can be minimized. Demulsifiers (Hexylamine and Coco Amine) with different concentrations (0.2 wt% and 0.5 wt%) were used for transportation. The relative rates of water separation were characterized via beaker test. Coco amine that synthesized from coconut oil promotes the best coalescene of droplets compared with the conventional demulsifier that used in this study which is hexylamine.

**Key words:** Transportation, demulsification, o/w stabilization, biodegradable, coco amine.

## ABSTRAK

Pengeluaran minyak mentah adalah terhad disebabkan kelikatan yang tinggi. Ia dijangka meningkat pada masa akan datang kerana minyak mentah kelikatan rendah berkurangan. Kelikatan yang tinggi membawa kepada peningkatan tenaga pam kerana ia mewujudkan penurunan tekanan yang tinggi. Dalam usaha untuk mengurangkan kelikatan minyak mentah, ia dicadangkan untuk bergaul dengan air dan pengemulsi optimum untuk mewujudkan bendalir likat yang rendah, emulsi minyak dalam air (O / W). Dalam kajian ini, kedua-dua sifat-sifat kimia dan fizikal emulsi O / W yang disediakan dengan menggunakan Cocoamide DEA (bukan ionik dan surfaktan terbiodegradasi disebabkan ia disintesis dari minyak kelapa) dan dua jenis pengemulsi kimia konvensional (Span 83 dan Triton X-100) disiasat. Emulsi O / W (dengan dua nisbah berbeza (50-50% dan 65-35%)) telah disediakan di tiga kelajuan percampuran yang berbeza (500rpm, 1000rpm dan 1500rpm) dengan kepekatan (0.2%, 0.5% dan 1.0%) pengemulsi masing-masing. Emulsi ini telah diuji untuk kadar relatif pemisahan air (ujian kestabilan), kelikatan, tegasan ricih dan kadar ricih pada suhu yang pelbagai dan kelajuan kacau menggunakan Brookfield viscometer. Selain itu, pengukuran saiz titisan telah dijalankan dengan menggunakan Mikroskop Carl Zeiss dan perisian. Keputusan menunjukkan bahawa Span 83 pada 1.0% dicampur dengan 65-35% O / W dengan kelajuan 1500rpm percampuran memperoleh emulsi yang paling stabil untuk pengangkutan berbanding dengan yang dua lagi. Kemudian, sifat-sifat kimia telah diuji melalui Fourier Transform Infrared (FTIR). Sifat-sifat kimia ini adalah penting untuk meramal berlakunya pemendapan lilin semasa pengangkutan. Pengangkutan emulsi kemudian dijalankan dengan menggunakan saluran paip skala makmal. Demulsification adalah proses pengasingan air dari minyak mentah. Minyak mentah perlu berasingan dengan cekap dan cepat dari air untuk membolehkan rawatan lanjut. Ini adalah untuk memastikan nilai minyak mentah boleh dimaksimumkan dan kos operasi dapat dikurangkan. Demulsifiers (Hexylamine dan Coco Amine) dengan kepekatan yang berbeza (0.2% berat dan 0.5% berat) telah digunakan untuk pengangkutan. Kadar relatif pemisahan air dicirikan melalui ujian bikar. Coco Amine yang disintesis dari minyak kelapa menggalakkan coalescence antara titisan berbanding dengan demulsifier konvensional yang digunakan dalam kajian ini yang hexylamine.

Kata kunci: Pengangkutan, demulsification, o / w penstabilan, terbiodegradasi, Coco Amine

## **CHAPTER 1**

### **INTRODUCTION**

#### **1.0 INTRODUCTION**

#### **1.1 BACKGROUND OF STUDY**

Crude oil is a complex mixture of saturates (paraffins/ waxes), aromatics, naphthenes, asphaltenes and resins (Lee, 2008). In petroleum industry, the viscosity of crude oil is the crucial part to investigate. The viscosity of crude oil in industry is about flow properties of emulsion which involve two phase flows between water and crude oil. Emulsion is a system which dispersion of a liquid phase to another and exhibit unstable thermodynamically (Ilia Anisa and Nour, 2010). Water is normally present in crude oil reservoirs or is injected as stem to simulate oil production (Hannisdal, 2005; Fingas et al., 2004).

Emulsions occur naturally 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 corrossions issues and are difficult to break in desalting and dehydrating units before refining (Rafael et al., 2010). Emulsions or dispersions of heavy or extra-heavy crude oil in water (O/W) or in brine might be an alternative to pipeline transportation of high viscosity crudes because of viscosity reduction (Pilehvari et al., 1988; Ashrafizadeh and

Kamran, 2010). An O/W emulsions is a mixture of two immiscible liquids where oil phase is dispersed into the water continuous phase. In some locations, hydrocarbon diluents or lighter crudes may be not available or limited while fresh water, sea water or even formation water maybe available for emulsification (Rafael et al., 2010). O/W emulsions are very rare deliberately produced to reduce the viscosity of highly viscous crude oils so that they can be transported easily through 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).

Demulsification is the process of breaking emulsions in order to separate water from oil, which is also one of the first steps in processing the crude oil after transportation from reservoir. The quality of the crude oil is highly dependent on the residual contents of water and water-soluble contaminants, which will be problematic for the water treatment part of the processes (Fan et. al, 2009). Chemical demulsification is the most widely used method to treat crude oil-in-water (O/W) and water-in-crude oil (W/O) emulsions.

## **1.2 PROBLEM STATEMENT**

Hydrocarbon resources are very important regarding the fact that they include about 65% of the world's overall energy resources (Langevin et al., 2004 as cited in Ashrafizadeh and Kamran, 2010). Nowadays, crude oil is the most important hydrocarbon resource of the world and heavy crudes account for a large fraction of the world's potentially recoverable oil reserves (Chilingar and Yen, 1980; Langevin et al, 2004; Ashrafizadeh and Kamran, 2010). However, the heavy crude oils have a little portion in the world's oil production due to their high viscosities which cause problems in their pipeline transportation. Production of heavy crudes is expected to increase significantly in the near future as low viscosity crudes are depleted (Plegue et al., 1989). The major barrier to utilization of heavy oil is the high pressure drop that occurs during pipe flows of these oils. These pressure drops are due to the high viscosity of the oil and

lead to increases in the pumping energy required, which makes the oil's transportation costs unattractive (Bannwart, 2001). Several alternative transportation methods for heavy crudes has been proposed and employed, including preheating of the crude oil with subsequent heating of the pipeline (Layrisse, 1998; Saniere et al., 2004), dilution with lighter crude oils (Iona, 1978), partial upgrading (MacWilliams and Eadie, 1993), and injection of water sheath around the viscous crude. However, all the methods above are not economically and experience logistic and technical disadvantages. Wide application of these technologies in the oilfield is unsuitable because light oils are becoming increasingly scarce and because diluents such as kerosene and naphtha are very expensive (Santos et al., 2010).

The transport of viscous crudes as oil-in-water (O/W) emulsions is one of the newest pipeline techniques (Lappin and Saur, 1989; Gregoli et al., 2006). The emulsion of heavy oil can reduce the fluid's viscosity to significantly lower value, thus making its transportation in pipelines quite feasible (Langevin et al., 2004). This technology is designed to disperse the crude oil as droplet within an aqueous phase that contains an emulsifying agent. Use of this configuration is based on experimental evidence that under shear flow, the less viscous fluid of two-phase dispersion systems migrates to the high shear region (i.e., near the wall) and lubricates the flow (Joseph, 1997). Since the water is the continuous phase, crude oil has no contact with the pipe wall and this reduces the pipe corrosion (e.g. in the crudes with high sulphur content) and prevent forming of sediments in pipes (e.g. in the crudes with high asphaltene content) (Poynter and Tigrina, 1970).

There are three steps involves in order to transport the crude oil using emulsion systems, including producing the oil-in-water emulsions, transportation of produced emulsions to the desired destination and finally separation of oil and water phase. Chemical demulsification is the most widely used method to treat crude oil-in-water (O/W) and water-in-crude oil (W/O) emulsions. The chemical structure of these demulsifiers is usually based on alkylphenol formaldehyde ethoxylated resin (Tam, 2010). These chemical demulsifiers are effective, but, unfortunately, these chemicals are now believed to be endocrine disrupters, and thus it is likely that they may be banned by various national environmental protection agencies (Zaki et al., 1996, 1998).

### 1.3 RESEARCH OBJECTIVES

The main aim of this research work is to develop a generic but sufficient and sustainable O/W transportation and separation method based on the application of environmental friendly chemicals that extracted from coconuts.

### 1.4 SCOPE OF STUDY

- i. Characterization of oil and aqueous phases:  
Model oil phases for the emulsions will be prepared and characterized with respect to (i) surfactant type (ii) surfactant concentration (iii) viscosity and temperature dependence, using viscometer and Brookfield.
- ii. The physico-chemical and chemical parameters affecting the stability of O/W emulsions:  
This aim will achieved by characterizing the crude oil samples, furthermore, a correlation between the crude oil characteristics and the crude oil emulsions stability is addressed to investigate effect of the parameters.
- iii. Preparation of model emulsions and their characterization:  
W/O (for crude oil application) and O/W emulsions (for industrial water applications) will be prepared.
- iv. Enhancing the understanding to the role of SARA on pipeline transportation system:  
By investigating how SARA alters the stability of oil/water emulsions at the pipeline transportation system via FTIR.
- v. Determination of mechanism of wax deposition:  
The relationship between the behavior of crude oil emulsion and Reynolds's number is studied. The relationship of the velocity of the emulsion and the rate of wax deposition is investigated.

## 1.5 SIGNIFICANCE OF STUDY

One of the major difficulties in transportation of heavy crude oil through pipelines is very high viscosity of such fluid. Furthermore, mobility of heavy oils in reservoirs is also so low that their production is not economically feasible. The viscosity of the viscous oil should be reduced in order to increase the oil mobility (Roomi et al., 2004). This can be done by heating, blending of heavy oils with lighter oils or hydrocarbon gases as well as oil-in-water emulsification (Crandall and Wise, 1984; Gillies and Shook, 1992; Hardy et al., 1982; Zakin et al., 1979). Heating often requires considerable amounts of energy and there are some logistic problems in using diluents. For field production to be transported by pipeline using a diluent, two pipelines would be required, i.e., one for the oil and one for the diluent. It would thus be desirable to develop an alternative method for transportation (Roomi et al., 2004).

This research is conducted to develop a generic but efficient and sustainable O/W transportation and separation method by using environmental friendly chemicals that are extracted from coconuts and soybean.

As a result, the physico-chemical and chemical parameters of the emulsion and the effect of SARA to the wax deposition at different condition are studied. The type of flow and the Reynolds's number is determined. The chemicals that result in the least harmful to the environment are created to treat crude oil-water emulsion by blending these natural chemicals with the conventional synthesized chemicals under a suitable ratio.



## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.0 LITERATURE REVIEW**

#### **2.1 INTRODUCTION**

Emulsions are systems consisting of two or more liquid immiscible phases. Emulsion is a heterogeneous system, containing at least immiscible liquid intimately dispersed in another in the form of droplets with a diameter, in general, ranging between (0.1-20) microns and it is stabilized by an emulsifying agent, asphaltenes, resins and finely divided solids. The dispersed droplets are known as the internal phase. The liquid surrounding the dispersed droplets is the external or continuous phase. The emulsifying agent separates the dispersed droplets from the continuous phase (Lissant, 1988).

Crude oils, especially the heavy oils, contain large quantities of asphaltenes (high molecular weight polar components) that act as natural emulsifiers. Other crude oil components are also surface active: resins, fatty acids such as naphthenic acids, porphyrins, wax crystals, etc, but most of the time they cannot alone produce stable emulsion (Lee, 1999). However, they can associate to asphaltenes and affect emulsion stability. Resins solubilize asphaltenes in oil, and remove them from the interface,

therefore lowering emulsion stability. Waxes coadsorb at the interface and enhance the stability. Naphthenic and other naturally occurring fatty acids also do not seem able to stabilize emulsions alone. However, they are probably partly responsible for the important dependence of emulsion stability upon water pH. (Langevin et al., 2004).

Emulsions of crude oils are complex systems consisting of sophisticated mixtures of chemical structures. The constituent compounds affect emulsion stability and impact the level of interfacial tension reduction achieved between the phases. Droplets may also present a high density of charges, typically negative. These emulsions exhibit nearly shear-thinning rheological behaviour (Pal and Rhodes, 1989) resulting from the interplay of several phenomena including surface charge, salinity, disperse fraction volume and dispersed phase viscosity (Langevin et al., 2004; Salager et al., 2001). Several field tests have confirmed the viability of emulsion technology for transporting viscous crude oils. Oil-in-water emulsions have also been continuously pumped and stored for several days with no sign of degradation (Stockwell et al., 1988). Some reports have shown that emulsion technologies can enhance the oil recovery and can lead to an increase in the recovery factor of mature fields (Bertero et al., 1994).

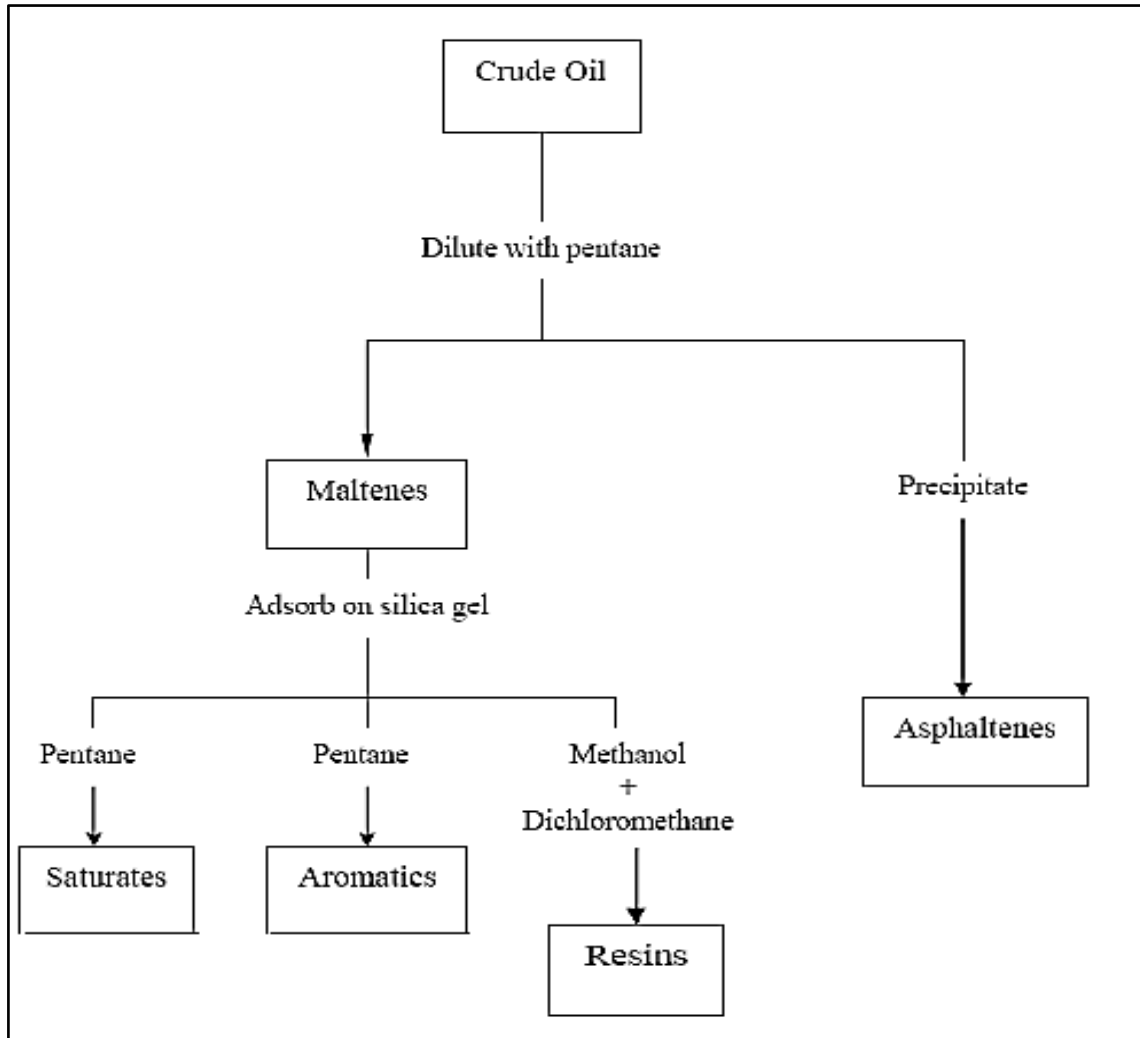
Despite several demonstrations of the O/W emulsions as a viable technology for transporting viscous oils, proposals to formulate and prepare heavy oil emulsions lack an understanding of the influence of many variables on emulsion properties. For transport technology, the most important properties of heavy oil-in-water emulsions are their stability and their viscosity. Continued examination of emulsification technologies should also enable prediction of component of reaching operational robustness (Santos et al., 2011).

The quality of the crude oil is highly dependent on the residual contents of water and water-soluble contaminants, which will be problematic for the water treatment part of the processes. The crude oil market demands that water in crudes must be removed to

a level of less than 0.5% BSW (bottom, solids, water) (Angle, 2001). Therefore, different methods, including both physical and chemical treatment, have been used to separate water from oil (Djuve et al., 2001; Less et al., 2008). Chemical demulsification consists of the addition of small amount of demulsifiers (usually 1-1000ppm) to enhance phase separation, usually using surfactants, polymers, pure solvents, or their mixture (Sjöblom et al., 2001). Non-ionic surfactants have been widely used for demulsification study as model systems, such as fatty esters, alkyl phenol ethers, polyoxypropylene glycol ethers, and fatty amides (Angle, 2001). It is very important to fully understand the mechanism of destabilization from studying the interaction or synergism of these surface-active components at the interface that directly relates to their amphiphilicity (Fan, et al., 2009)

## **2.2 INDIGENOUS STABILIZING COMPONENTS IN CRUDE OIL**

Crude oil consists of light hydrocarbons such as gasoline, asphaltenes, resins, waxes and naphthenic acid. The asphaltenes content of crude oil is an important aspect of fluid process ability. The method of dividing crude oil into four major fractions: saturates (include waxes), aromatics, resins and asphaltenes is called SARA fractionation, based on their polarity and solubility in the solvent. The method of dividing crude oil into these four fractions is illustrated in Figure 2.1.



**Figure 2.1:** Schematic of SARA fractionation of crude oils

Source: Auflem (2002)

### 2.2.1 Saturates and Aromatics

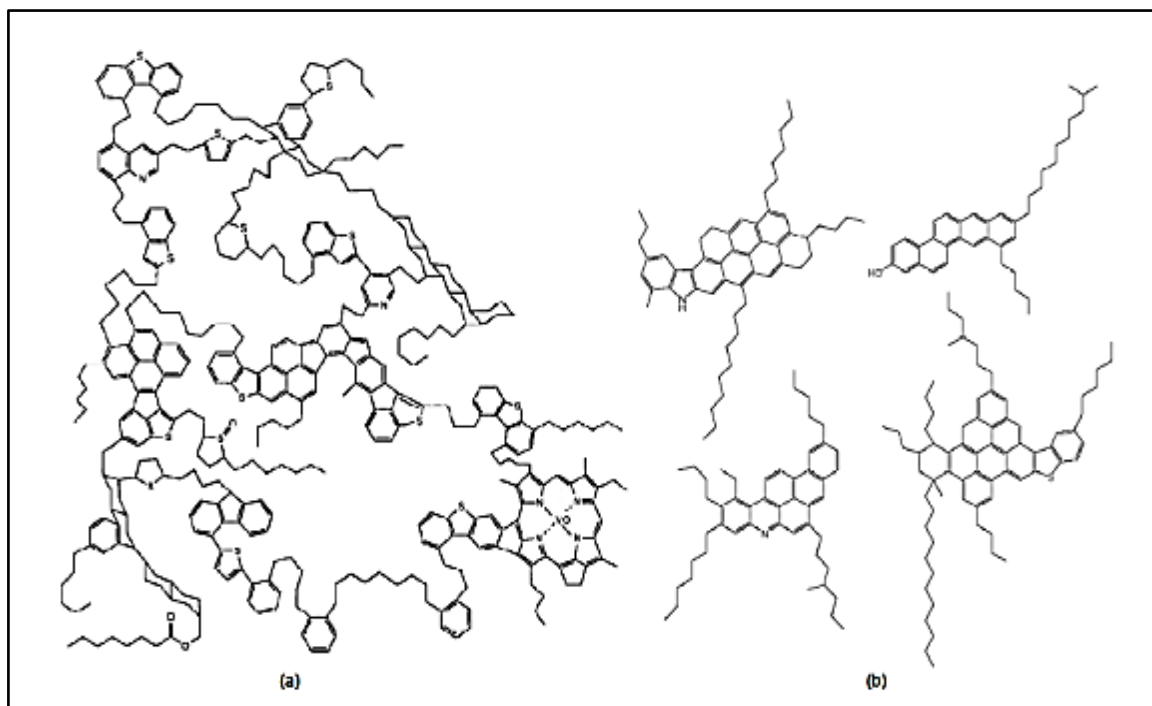
The saturates (or aliphatics) are the nonpolar compounds containing no double bonds and include both the alkanes and the cycloalkanes. Wax is a sub-class of the saturates. The aromatic consist of all compound with one or more benzene rings. These ring systems may be linked up with naphthene rings and/or aliphatic side chains (Friedemann, 2006).

### **2.2.2 Resins**

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.

### **2.2.3 Asphaltenes**

Asphaltenes are polar molecules that can be regarded as similar to the resins, but with higher molecular weight, typically 500 to 1500 g/mole. The asphaltene fraction, like the resins, is defined as a solubility class, namely the fraction of the crude oil precipitating in light alkanes such as pentane, hexane or heptane. The precipitate is soluble in aromatic solvents such as toluene and benzene. The asphaltene fraction contains the largest percentage of heteroatoms (O, S, and N) and organometallic constituents (Ni, V, Fe) in the crude oil. The structure of asphaltene molecules is believed to consist of polycyclic aromatic clusters, substituted with varying alkyl side chains. The molecular weight of asphaltene molecules has been difficult to measure due to the tendency of asphaltenes to self-aggregate, but molecular weight in the range 500 to 2000 g/mole are believed to be reasonable (Friedemann, 2006).



**Figure 2.2:** (a) A hypothetical asphaltene molecule ('Archipelago model'). (b) Four hypothetical asphaltene molecules

Source: Strausz (1992), Mullins (2005)

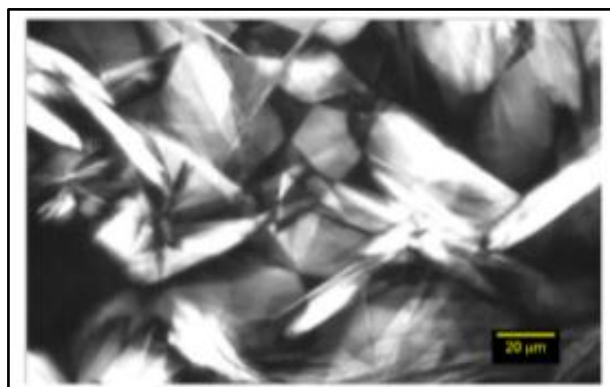
### 2.3 WAX

Petroleum wax is of two general types, the paraffin waxes in petroleum distillates and the microcrystalline waxes in petroleum residue. The melting point of wax is not directly related to its boiling point, because waxes contain hydrocarbons of different chemical nature. Nevertheless, waxes are graded according to their melting point (ASTM D-87, IP55) and oil content (ASTM D-721, IP 158; Speight, 2002).

Chemically, paraffin wax is a mixture of saturated aliphatic hydrocarbons (with the general formula  $C_nH_{2n+2}$ ). Wax is the residue extracted when lubricant oils are

dewaxed and it has a crystalline structure with a carbon number greater than 12. The main characteristics of wax are absence of color, absence of odor, translucence and a melting point above 45 °C (113 °F) (Speight, 2002).

The characteristics of wax-oil gels depend on the crystal morphology and structures of the crystal networks, which are strong functions of both thermal and shear histories (Singh et al., 2000). The crystallization of wax molecules below the cloud point temperature incurs formation of gels with a complex morphology. As shown in Figure 2.3, the structure of the wax-oil gel is an interlocking of various wax forms such as needles, plates and orthorhombic wax crystals, dependent on the cooling rate (thermal history), wax concentration and shear history (Dirand et al., 1998; Singh et al., 2000).



**Figure 2.3:** Cross-polarized microscope photo of wax-oil gel

Source: Lee et al. (2007)

During the refining of waxy crude oils, the wax becomes concentrated in the higher-boiling fractions used primarily for making lubricating oils. Refining of lubricating oil fractions to obtain a desirable low pour point usually requires the removal of most of the waxy components. The dewaxing step is generally performed by the chilling and filter pressing method, by centrifuge dewaxing, or by filtering a chilled solution of waxy lubricating oil in a specific solvent (Speight, 2002).

Wax provides improved strength, moisture proofing, appearance, and low cost for the food packaging industry, the largest consumers of waxes today. The coating of

corrugated board with hot melts is of increasing importance to the wax industry. Other uses include the coating of fruit and cheese, the lining of cans and barrels, and the manufacture of anti-corrosives. Because of its thermoplastic nature, wax lends itself to modeling and the making of replicas; blends of waxes are used by dentists when making dentures and by engineers when mass-producing precision castings such as those used for gas turbine blades. The high gloss characteristic of some petroleum waxes makes them suitable ingredients for polishes, particularly for the “paste” type that is commonly used on floors, furniture, cars, and foot wears. The highly refined waxes have excellent electrical properties and so find application in the insulation of low-voltage cables, small transformers, coils, capacitors and similar electronic components (Speight, 2002).

### **2.3.1 Causes and Effects of Wax Deposition**

Crystallization of solid paraffin is actually an example of liquid-solid phase equilibrium. It is explained in term of established principles of thermodynamics of solution. The solution of higher molecular weight hydrocarbons (HMWH) in lower molecular weight hydrocarbons usually act as a solvent. Generally, high molecular weight solids precipitate whenever the carrying capacity of the fluid solvent decreases. Temperature was the main parameter that controls the fluid solvent saturation. Solubility of higher molecular weight hydrocarbons depends on temperature and the flow velocity in low pressure environment. In high-pressure situation such as in the production tubing, liberation of lighter hydrocarbons as gases due to pressure change reduces the solvent fraction of reservoir fluid during transit from bottom hole to the surface. If larger pressure drops is allowed in the tubing liquid may contain large quantity of gases and the liquid flow rate decreased. HMWH may be exposed to longer heat loss and have greater tendency to crystallize and precipitate as wax (Abdul Aziz et al., 1999).

Usually, wax components drop out of the solution and crystallize at temperatures below the wax appearance temperature (WAT). Wax deposition in production tubing and pipelines is a common problem in cases where the fluid temperature is less than the WAT. Wax deposition along the inner walls of the pipeline increase the pressure drop, decreases the flow rate, and causes operational problems.



According to Lee (2008), wax deposition during the flow of waxy crude oils through subsea pipelines occurs as a result of the precipitation of wax molecules adjacent to the cold pipe wall. Thus, wax deposition can only occur when the inner pipe wall temperature is below the cloud point temperature. The precipitated wax molecules near the pipe wall start to form an incipient gel at the cold surface. The incipient gel formed at the pipe wall is a 3-D network structure of waxy crystals and contains a significant amount of oil trapped in it. The incipient gel grows as time progresses while there are radial thermal and mass transfer gradient as a result of heat losses to the surrounding as shown in Figure 2.4. To prevent blockage of pipelines, wax deposits should be removed periodically. Different mechanical, thermal and chemical techniques can be used for wax removal (Shock et al., 1955; Jorda, 1966; Narvaez et al., 1991; Svetgoff, 1984; Eastund et al., 1989). There is considerable interest in predicting the deposition rate, wax thickness and wax content as this helps to its prevention and use of various methods for its removal. (Hoteit et al., 2008).

## **2.4 PIPELINE TRANSPORTATION**

Some emulsions are made to reduce viscosity so that oil can be made to flow. For example, the concentrated oil-in-water emulsions that are made from heavy oils and intended for economic pipeline transportation over large distances (Acevedo et al., 2001; Rimmer et al., 1992; Plegue et al., 1989). Another example will be the oil produced at off-shore drill sites in the form of oil-in-water emulsions (containing reservoir water) which may have to be transported to an on-shore processing centre, at which the oil may be re-emulsified (using fresh water) for other applications. Advantages include avoiding the use of diluents or heat which would otherwise be needed to reduce the oil viscosity sufficiently for pumping through the pipeline. Here the emulsions have to be surfactant-stabilized so that they will be stable during transport (but not too stable as they will have to be broken at the end of the pipeline). Both synthetic (Nunez et al., 1995; Rimmer, 1992) and natural surfactant (Acevedo et al., 2001) have been used. The emulsions also need to be stable under static conditions as well as flowing conditions so that, should a pipeline be shut-down for a period of time, the emulsion will not completely break, with consequent phase separation and increased pressure drop.

A number of kinds of emulsions, foams, and suspensions may be made to flow in tubes or pipes, at scales ranging from the laboratory (e.g., capillary viscometer) to full scale industry (e.g., transportation pipelines). The pressure drop and pumping requirements are functions of the type of flow and the rheological properties of the dispersion. If the flow rate in pipeline falls below the critical deposit velocity then particles or emulsion droplets will either sediment or cream to form a layer on the bottom or top wall, respectively, of the pipe. Some correlations that have been developed for the prediction of critical deposit velocity are discussed by Nasr-El-Din (1996) and Shook et al., (2002).

The converse to using a tube or pipe as a means of measuring viscosity is to use Poiseuille equation to predict the pressure drop needed to force fluid through the tube or pipe. This pressure difference  $\Delta P$  along the length of tube or pipe,  $L$ , is given by the following rearrangement of Poiseuille equation:

$$\Delta P = 8QL\eta/(\pi r^2) \quad (1)$$

where  $Q$  is the volumetric flow rate and  $\eta$  is the Newtonian viscosity.

For Newtonian fluids flowing in smooth pipes, the friction losses can be estimated for laminar flow ( $Re \leq 2100$ ) using the Fanning friction factor,  $f$ . The Reynolds number,  $Re$ , is given by:

$$Re = (\rho UD)/\eta \quad (2)$$

where  $\rho$  is the fluid density,  $U$  is the bulk fluid (linear) velocity (m/s), and  $D$  is the pipe inner diameter. The Hagen-Poiseuille equation yields:

$$f = 16/Re \quad (3)$$

And the Fanning friction factor is:

$$f = (2\tau_w)/(\rho U^2) \quad (4)$$

where  $\tau_w$  is the shear stress at the wall of the pipe.  $\tau_w$  is given in terms of pressure drop,  $\Delta P$  along a length,  $L$ , of the pipe as:

$$\tau_w = D\Delta P/(4L) \quad (5)$$

The shear rate at the wall of the pipe,

$$\gamma_w = 8U/D \quad (6)$$

Combining equations (4) and (5) gives,

$$f = \{D|(2\rho U^2)\}(\frac{\Delta P}{L}) \quad (7)$$

(Laurier, 2005)

## 2.5 EMULSION

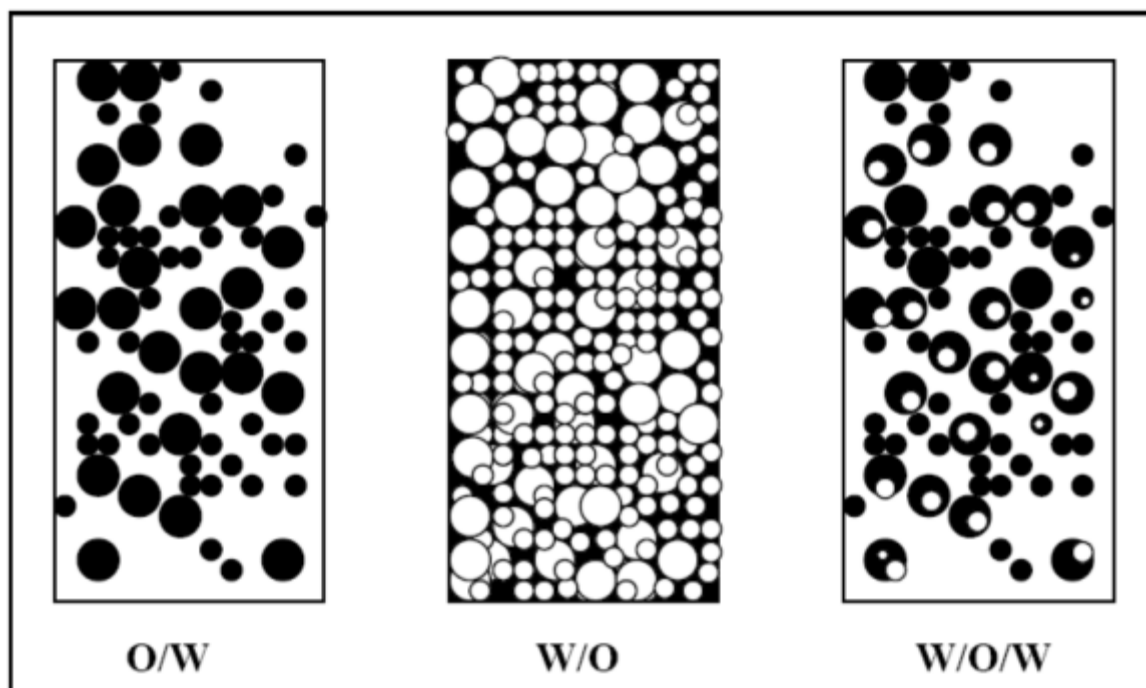
An emulsion is usually defined as a system in which one liquid is relatively distributed or dispersed, in the form of droplets, in other substantially immiscible liquids. In petroleum industry, water-in-oil (W/O) or oil-in-water (O/W) emulsions can lead to enormous financial losses if not treated correctly. 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).

Besides, there are also exist double emulsions such as oil-in-water-in-oil (O/W/O) and water-in-oil-in-water (W/O/W). For example, O/W/O denotes a double emulsion, containing oil droplets dispersed in aqueous droplets that are in turn dispersed

in a continuous oil phase. The double emulsion droplets can be quite large (tens of  $\mu\text{m}$ ) and can contain many tens of droplets of the ultimate internal phase (Laurier, 2005).

There is a very simple and reliable method of determining the type of emulsion. Upon addition of an emulsion of O/W to water, it will disperse. Similarly, W/O emulsion will mix with oil. In short, an emulsion will freely mix or dilute with more of its external phase, but not with more of its internal phase (Tam, 2010).

According to Becher (2001), emulsion is a heterogeneous system consisting of one liquid dispersed as tiny droplets in another liquid. Emulsion can be described into three different types, which are Macroemulsions, Miniemulsions, and Microemulsions.



**Figure 2.4:** Common Type of Crude Oil Emulsions: Oil-in-Water (O/W), Water-in-Oil (W/O), and less common: Water-in-Oil-in-Water (W/O/W)

Source: Paul, 2001

Oil-in-water (O/W) emulsions, consisting of oil droplets dispersed in water. By means of optimizing the efficiency of the transporting process and minimizing the

operating cost, emulsion with water as the continuous phase which is O/W emulsion is necessary for the transporting of highly viscous heavy oil. This is also because the viscosity of an emulsion is always larger than the viscosity of the continuous phase (Ahmed *et al.*, 1999).

Water-in-oil (W/O) emulsions, consisting of water droplets dispersed in oil. The formation of w/o emulsion is a natural problem that can be happen during the recovery, treatment, and transportation. Water and oil can mix while rising through the well and when passing through valves and pumps to form in most cases relatively stable dispersions of water droplets in crude oil, which are usually referred to as oil field emulsions (Abdurahman *et al.*, 2007).

## 2.6 EMULSIFICATION

Emulsification is a process to create emulsion. About 100 years ago, Bancroft proposed that when oil, water and surfactant are mixed, the continuous phase of the emulsion that forms is the phase where the surfactant is more soluble to (Tam, 2010). There are three main criteria that necessary for the formation of crude oil emulsions which is two immiscible liquids must be brought in contact, surface active component must be present as an emulsifying agent and have sufficient mixing or agitating effect in order to disperse one liquid into another as droplets (Fingas, 2004).

The pressure gradient or velocity gradient required for emulsion formation is mostly supplied by agitation. The large excess of energy required to produce emulsion of small droplets can only be supplied by very intense agitation, which needs much energy. A suitable surface active component can be added to the system in order to reduce the agitation energy needed to produce a certain droplet size. The formation of surfactant film around the droplet facilitates the process of emulsification and a reduction in agitation energy by factor of 10 or more can be achieved (Becker, 2005).

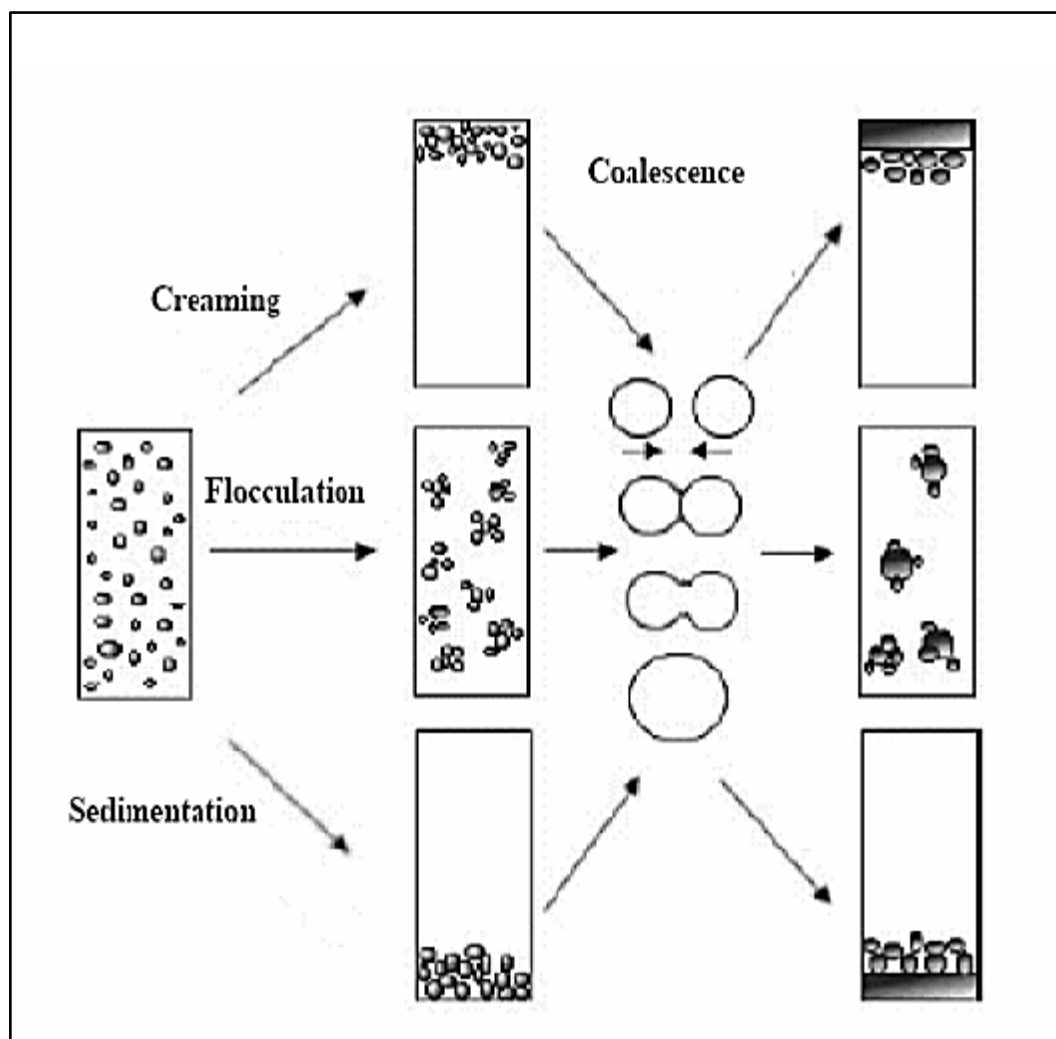
When particles are used to stabilised emulsions, the Bancroft rule translates into a condition for the contact angle  $\theta$  between the particle and the oil-water interface. If  $\theta >$

90°, the emulsion formed is W/O, if  $\theta < 90^\circ$ , O/W emulsion will be formed. The contact angle should not be too far from 90°, otherwise the energy required to remove the particles from the interface is small, and the emulsions are very unstable (Strassner, 1986). For particles with  $\theta \sim 90^\circ$ , both O/W and W/O emulsions can be made stable for long periods. Inversion occurs without hysteresis, by increasing or decreasing water volume fraction. This is in contrast to surfactant systems, where emulsions either do not invert (and form gel emulsions instead) or invert with a considerable hysteresis (as much as 0.3 in volume fraction). In addition, pickering emulsions are most stable near inversion, unlike surfactant emulsions which become notoriously unstable.

There is largely variety of emulsification methods such as simple shaking, mixing with rotor-stator systems, liquid injection through porous membranes, or high pressure devices (homogenizer, liquid jets), etc. (Walstra, 1993). When the emulsion is formed, the interfaces are stretched rapidly and ruptured in different flow conditions according to the method used: laminar with low shear mixers, extensional with jets and porous membranes, turbulent with mixers having toothed rotors and high pressure homogenizers (Tam, 2010).

## **2.7 EMULSION STABILITY**

Stability is a consequence of the small droplet size and the presence of an interfacial film on the droplets in emulsions, which make stable dispersions. That is the suspended droplets do not settle out or float rapidly, and the droplets do not coalesce quickly (Luma, 2002). The definition of emulsion stability, it is considered against three different processes which is creaming (sedimentation), aggregation and coalescence as shown in figure 2.7 (Schramm, 2007).



**Figure 2.5:** Processes taking place in an emulsion leading to Emulsion Breakdown and Separation

Source: Auflem, 2002

Emulsion can be categorized into stable, unstable and meso-stable emulsions according to stability (NRT Science & Technology Committee, 1997):

- i. Stable emulsions will persist for days, weeks and longer. In addition, stable emulsion will increase with viscosity over time. Increasing alignment of asphaltenes at the oil-water interface may cause increase of viscosity.

- ii. Unstable emulsions usually persist for only a few hours after mixing stops. These emulsions are ready to separate into oil and water due to insufficient water particle interactions. However, the oil may retain small amounts of water, especially if the oil is viscous.
- iii. Meso-stable emulsions are probably the most common emulsion that was formed in the fields. These emulsions can be red or black in appearance. This emulsion has the properties between stable and unstable emulsions. It is suspected that these emulsions contain either insufficient asphaltenes to render them completely stable or contain too many destabilizing materials such as smaller aromatics. The viscosity of the oil may be high enough to stabilize some water droplets for a period of time. Particles, which are water-wet, tend to stabilize (O/W) emulsions while those oil-wet tend to stabilize (W/O) emulsions.

(Auflem, 2002)

According to Kim, 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 behavior is mainly controlled by the properties of the adsorbed layers that stabilise the oil-water surfaces. The complexity of petroleum emulsions comes from the oil composition in terms of surface-active molecules contained in the crude, such as low molecular weight fatty acids, naphthenic acids and asphaltenes. These molecules cover a large range of chemical structures, molecular weights, and HLB (Hydrophilic-



Lypophilic Balance) values and able to interact between themselves and/or reorganise at the water/oil interface (Langevin *et al.*, 2004).

Bancroft (1913) proposed that, the stability of any emulsion is largely due to the nature of the interfacial film that is formed. The stability of this film is strongly dependent upon the surfactant adsorption-desorption kinetics, solubility, and interfacial rheological properties such as elasticity, interfacial tension gradient, and interfacial viscosity. A stable emulsion is composed of an aqueous phase, an oil phase, and an emulsifying agent. Particles and surfactants found in crude oil can act as emulsifying agents and thus can promote and stabilize water-in-oil emulsions (Bobra, 1990, 1991).

Most of the emulsions are thermodynamically unstable and will eventually phase separate, but as a practical matter, quite stable emulsions can occur that resist demulsification treatments and may be stable for weeks/months/years. Most meta-stable emulsions that will be encountered in practice contain oil, water, and an emulsifying agent (or stabiliser) which is usually a surfactant, a macromolecule, finely divided solids, or gas. The emulsifier may be needed to make the emulsion easier to form, or it may form a protective film, that helps keep the emulsion from breaking (Laurier, 2005).

Crude oils especially the heavy oils contain large amount of asphaltenes (high molecular weight polar components) that act as natural emulsifier. Other crude oil components are also surface active: resins, fatty acids such as naphthenic acids, wax crystal, etc, but most of the time they cannot create stable emulsions alone. However, they can associate to asphaltenes and affect emulsion stability (Langevin *et al.*, 2004; Lee, 1999).

Particles such as silica, clay, iron oxides, etc, can be present in crude oils. These particles are naturally hydrophilic, but can become oil-wet (hydrophobic) due to long-term exposure to the crude in the absence of water. A decrease in the size of oil-wet

particle results in an increase in W/O emulsion stability. Pickering emulsion which is a kind of emulsion that involved with particles and asphaltenes combined can be much more stable than those stabilised by asphaltenes alone, provided that enough asphaltenes are present: all the adsorption sites on the particle surface need to be saturated by asphaltenes (Tam, 2010).

Emulsification has the advantage of lower cost compared with heating and offers the possibility of testing different surfactants or designing new ones based on indigenous constituents of the oil and specific transportation challenges (Clark *et al.*, 1993; Schubert *et al.*, 1992).

## **2.8 DEMULSIFICATION**

Demulsification or emulsion breaking is carried out by using either four methods such as mechanical, thermal, chemical and electrical (Gafonova, 2000). The knowledge of the properties and characteristics of the emulsion and the mechanism that are taking place during coalescence of water droplets are required for fast separation (Ese *et al.*, 2006).

There are many kinds of mechanical separation tools that are typical equipment used in destabilization the crude oil emulsion such as cyclones, gravity settling tanks, centrifugal separators and many materials had been suggested to be used as porous coalescers such as fiberglass, glass, Teflon. Other materials such as clay, magnesium silicate, or silica gel had been used as a filter aid in conventional filter press (Auflem, 2002).

Thermal method is carried out by the addition of heat to enhance emulsion breaking in oil field. An increase in temperature above the paraffin melting point ranging between 50-65 °C may completely destabilize an emulsion. So, the optimum