

**STUDY ON EMULSION STABILITY AND CHEMICAL DEMULSIFICATION
CHARACTERISTICS**

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**A thesis submitted in fulfillment
of the requirements for the award of the degree of
Bachelor of Chemical Engineering**

**Faculty of Chemical & Natural Resources Engineering
Universiti Malaysia Pahang**

May 2009

I declare that this thesis entitled “Study on Emulsion Stability and Chemical Demulsification Characteristics” is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.”

Signature :

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Date : May 2009

*Special Dedication to my family members,
my friends, my fellow colleague and all faculty members
For all your care, support and believe in me.*

ACKNOWLEDGEMENT

I would like to forward my appreciation to my thesis supervisor, Mr Abdurahman H. Nour and my panels Mr. Saiful Nizam Hasan and Mr. Mohamad Nor Man for their guidance and support. I am also thankful for Mr. Sulaiman for his advises and opinions given throughout this study.

I am very thankful to Universiti Malaysia Pahang (UMP) for providing good facilities in the campus. To all the staff in Faculty of Chemical & Natural Resources Engineering, a very big thanks you to all.

My sincere appreciation also extends to all my fellow colleagues and others who have provided assistance at various occasions. Their views and tips are useful indeed. Thank you for the time sacrificed to accompany me. And last but not least, I am grateful to all my family members.

ABSTRACT

Water in oil emulsion occurs at many stages in the production and treatment of crude oil. About two third of petroleum production of every oil field exists in the form of water in oil emulsion. The emulsion stability results from the presence of interfacial barrier preventing coalescence of the dispersed water droplets. This is due to the present of polar components such as asphaltenes, resins, wax and naphtenic acids in the crude oil. It has been reported that the combination of oil-soluble demulsifiers and water-soluble demulsifiers produced great result in water separation. From the screening process of single oil-soluble demulsifiers, the most effective chemicals as demulsifier are hexylamine and dioctylamine while butanoic acid, and formic acid are the most effective chemicals in water-soluble group. This new formulation was found to be effective for demulsification of water-in-oil emulsion of Dubai, Miri, and Masalah fields emulsion system. In order to obtain better understanding and results, optimizing on agitation and temperature conditions, the mechanism demulsification study are recommended for further study.

ABSTRAK

Emulsi air dalam minyak berlaku di banyak tahap pengeluaran dan perawatan minyak mentah. Sebanyak dua per tiga daripada pengeluaran petroleum di setiap lapangan wujud dalam bentuk emulsi air dalam minyak. Kestabilan system emulsi ini adalah disebabkan kehadiran halangan antaramuka yang menghalang pertautan titisan air. Ini adalah kerana dengan adanya komponen berkutub seperti asphaltin, resin, bahan berlipid dan asid naftenik di dalam minyak mentah. Didapati bahawa campuran bahan penyahmulsi larut-minyak dan bahan penyahemulsi larut-air menghasilkan keputusan yang lebih baik di dalam pemisahan air. Daripada proses pemilihan bahan penyahemulsi, yang menghasilkan pemisahan air yang terbaik ialah heksilamina dan dioktilamina untuk bahan penyahemulsi larut-minyak manakala metil metakrilat, butil akrilat dan asid akrilik untuk bahan penyahemulsi larut-air. Formulasi baru ini berkesan di dalam menyahemulsikan emulsi air dalam minyak dari lapangan Dubai, Miri dan Masalah sistem emulsi tunggal. Untuk memperolehi pemahaman dan keputusan yang lebih baik, pengoptimuman ke atas pengacauan dan suhu serta mekanisma penyahemulsi adalah disarankan untuk kajian masa akan datang.

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LIST OF ABRAVIATIONS

EPMI	- ESSO Production Malaysia Incorporated
BS&W	- Basic sediment and water
SARA	- Saturates (including waxes), aromatics, resin and asphaltene
O/W	- Oil-in-water emulsion
W/O	- Water-in-oil emulsion
O/W/O	- Oil-in-water-in-oil emulsion
MSDS	- Material Safety Data Sheets
SDDS	- Sodium dodecyl sulphate
Span 80	- Sorbitan monooleate

CHAPTER 1

RESEARCH BACKGROUND

1.1 Introduction

Malaysia is important to world energy markets because of its 75.0 trillion cubic feet of natural gas reserves and its net oil exports of over 260,000 barrels per day. Three oil fields (Dubai, Miri and Masilah) of PETRONAS Malaysian contract areas in East Cost of Malaysia are having severe emulsion problem. The emulsion is either normal or inverted emulsion and stable. This crude oil has basic sediment and water (BS&W) between 2 to 11%, which is higher than specified BS&W (less than 0.5%). As a result, they have to some extent to sell their crude oil in the form of emulsion at low price due to the high cost for treating the emulsions.

Water-in-oil emulsion are formed during the production of crude oil, which is often accompanied with water. The stability of the emulsion is ranging from a few minutes to years depending on the nature of the crude oil and to some extent the nature of water (Bhardwaj and Hartland, 1988). A recent report has suggested that an equivalent volume of water accompanied the daily production of some 60 million barrels of crude oil (Ivanov and Kralchevcky, 1996). Under the production conditions, a proportion of this water can become intimately dispersed throughout the crude oil as small droplets.

Crude oils consist of, in any case, a series of hydrocarbons such as alkanes,

naphtenes, and aromatic compounds as well as phenols, carboxylic acids, and metals. A major fraction of sulfur and nitrogen compounds may be present as well. The carbon numbers of all these components range from 1 (methane) through 50 or more (asphaltenes). Some of these components can form films at oil surfaces, and others are surface active. So, the tendency to form stable or unstable emulsions of different kinds varies greatly among different oils (Schramm, 1992).

The natural petroleum emulsion resulting from the secondary production consists of crude oil as dispersion medium and brine as dispersed phase, normally stabilized by natural chemicals such as asphaltenes, resins, solid such as clays and waxes (Bhardwaj and Hartland, 1988). For asphaltenes in particular, the presence of heteroatoms in the essentially aromatic structure imparts amphiphilic characteristics (Selvarajan et al., 2001).

Emulsions are undesirable because the volume of dispersed water occupies space in the processing equipment and pipelines, increased operating and capital costs. Moreover, the characteristics and physical properties of oil change significantly upon emulsification. The density of emulsion can increase from 800 kg/m³ for the original oil to 1030 kg/m³ for the emulsion. The most significant change is observed in viscosity, which typically increases from a few mPa·s or less to about 1000 mPa·s (Fingas et al., 1993).

In crude oil processing or refining, the desalting techniques comprise the intentional mixing of the incoming crude with a fresh “wash water” to extract the water soluble salts and hydrophilic solid that were form. However, the presence of water in crude oil can interfere with refining operations, provoke corrosions, increase heat capacity and reduce the handling capacity of refining equipments and pipelines (Selvarajan et al., 2001). Emulsion resolution is therefore an important element in handling the petroleum, from the time it is produced until it enters the refining process.

In order to minimize the production problems related with crude oil emulsions and environmental concerns, petroleum operators need to prevent their formation or to break them (Gafonova, 2000). In some cases when the formation of emulsions is a result of poor operation practices, it is possible to prevent emulsion formation. Nevertheless, in many instances emulsion formation is predictable. The exclusion of water during recovery from the oil wells and prevention of agitation is difficult to realize, and emulsions must be treated.

The treatment of water-in-crude oil emulsions involves the application of, thermal, electrical, chemical process or their combinations. Thermal method or heat treatment in emulsion breaking is usually based on the overall economic picture of a treating facility. Excess heat is not supplementary when it is more commercial to add chemical or set up electrostatic heat. Temperatures are not high enough to significantly rise up water solubility in a particular crude oil, and high temperatures do not cause large amounts of asphaltenes to become insoluble in the crude oil and form an interface pad (Grace, 1992).

Electrical methods disturb the surface tension of each droplet, possibly by causing polar molecules to reorient themselves (Grace, 1992). This reorientation weakens the film around each droplet because the polar molecules are no longer intense at the droplets surface. This process does not typically resolve emulsions completely by itself, although it is an efficient and often required addition of chemicals or heat.

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 equipments or modifications of the existing equipment.

There are anionic, cationic, nonionic and amphoteric surfactants that have been used as demulsifiers. Emulsion breakers are typically specific for site or crude oil type. Conventional emulsion breakers are most commonly formulated from the following type of chemistries; polyglycols and polyglycol esters, ethoxylated alcohols and amines, ethoxylated resin, ethoxylated phenol formaldehyde resins, ethoxylated nonylphenols, polyhydric alcohols, ethylene oxide, propylene oxide block copolymer fatty acids, fatty alcohols, fatty amine and quaternaries and sulfonic acid salts. Basically, commercial emulsion breakers may contain one type of active ingredient.

Polymeric demulsifiers are also the most common demulsifiers used to break water in oil emulsion. The polymeric demulsifiers are capable of adsorbing at the oil or water interface by displacing the interfacial film. Interfacial active fraction presence in the oil poses a sufficient numbers of functional groups that can penetrate into the oil or water interface, and form an interfacial layer which can be broken by demulsifiers (Zaki et al., 1996).

The film that encapsulating the water droplets is formed by adsorbed solid particles or surface-active materials. The rigidity and structure of this film determines the stability of the emulsion. Unfortunately, since crude oil is an extremely complex mixture of many thousand of compounds, it is difficult to identify the role of any of these compounds in the crude oil emulsion stabilization. Despite extensive research, even the composition of the interfacial film is poorly understood. Therefore, it is almost impossible to predict the performance of demulsifiers or other treatment methods (Gafonova, 2000).

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 a very 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

with the emulsion, adequately heat may be required to facilitate or fully resolve an emulsion, and sufficient residence time must be allowed in treating vessels to permit settling of demulsified water droplets.

In order to devise optimum treatment for water-in-oil emulsions by using chemical treatment method, it is vital to understand how they are stabilized and destabilized the emulsion. Therefore, screenings of demulsifiers are very important in deciding the most effective demulsifiers in breaking the emulsion system. This result will be lead to demulsifiers formulation for treating Malaysian crude oil emulsion.

1.2 Objectives and Scope

The objective of this study is to identify, screening the existing emulsifiers and demulsifiers for stability and demulsification of crude oil emulsion. Firstly, the study will be focused on single emulsifier and demulsifier in both water and oil-soluble also acid groups. This test will be carried out by using beaker test method at the fixed concentration and temperature for real emulsion systems.

Secondly, by using the best emulsifier and demulsifiers from three groups, the test will be proceeding by varying the concentration to know the flow pattern of emulsification and demulsification.

Finally, the effectiveness of this formulation will be tested by using single emulsion system and will be compared with other commercial demulsifiers formulation. The excellent result will be measured from the water separation level.

1.3 Report Outline

Respective chapter of this thesis can be generally identified with one of the objective of research described in section 1.2. The thesis contains five chapters which each chapter respectively containing its own introduction, descriptions of the relative topics and scopes to achieve the objectives of research and summary. Chapter I basically discussed about the entire project study, which contains research background, objectives and scopes of this study and thesis outline.

The historical aspects of crude oil emulsion; characteristics of crude oil, theories of emulsions and demulsification, variability of applied chemicals, and limitation of present demulsifier techniques are presented will be described in Chapter II. This chapter reinforces the belief that a qualitative view of emulsion breaking is essential at this time for the petroleum industry.

All the materials and methods including the material that have been used in the experiments; either equipments or chemicals, experimental methods to break down the emulsion problems and a little bit of analytical methods to determine the physical and chemical properties of crude oil emulsion and demulsification are discussed in Chapter III. Besides, there are a lot of discussion about demulsifiers screening process and optimization by using two level factorial designs.

The discussions and elaborations of experimental results, which are based on the combination of the theories from the literature studies and the results obtained from the research, are noticed in Chapter IV. The conclusions of this thesis are based on demulsification formulation on treating Malaysian crude oil emulsion and remarks are discussed in Chapter V. Beside that, the recommendations for future study are also included to give the ideas in doing this study.

1.4 Summary

Emulsion problems in crude oil production and processing have gained serious consideration either from fundamental and practical aspects by oil companies as well as researchers for the last few decades. One of the focuses is on developing effective demulsifiers, which involves screening, formulation, testing and demulsification study for crude oil demulsification process. This study will address some of the fundamental and practical aspects of these areas of interest.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Crude oil is a complex fluid containing asphaltenes, resins and naphthenic acid. Asphaltenes is the heaviest and most polar fraction in the crude oil and responsible in rising up the variety of nuisances and stabilized the water in oil emulsion that occurred during crude oil production. It is widely known that deposition and flocculation of asphaltenes may be occurred when the thermodynamic equilibrium is disturbed (Auflem, 2002).

The potential of oil recovery will be reduced by the adsorption of asphaltenes on to the reservoirs mineral surfaces, whereby the wet ability of the reservoir is changed from water-wet to oil-wet. Furthermore, the asphaltenes may deposit on the steel walls and accumulate in the fluid processing units. Clean up of deposited asphaltenes caused reducing the oil production.

The water and oil phases are co-produced during oil production and transportation. The dispersion of water droplets in oil or oil droplets in water will be formed by sufficient mixing energy from the refinery. The interfacial active agents in the crude oil such as asphaltenes, resins and naphthenic acid may accumulate at the water-oil interface and hinder the droplets to separate. Among these components, asphaltenes are believed to be the major causes in stabilized the emulsion. This is because they tend to

adsorb at water-in-crude oil interfaces to form a rigid film surrounding the water droplets and protect the interfacial film from rupturing during droplet-droplet collisions (Sjöblom et al., 1992). Consequently, the formation of particularly stable water-in-crude oil emulsion is facilitated.

Emulsion problems in crude oil productions resulted in a demand for expensive emulsion separation equipment such as water treaters, separators and coalescers. Hence, chemical demulsification is the suitable method from both operational and economic point of view to break the crude oil emulsion. A chemical agent typically acts on the interfacial film by either reacting chemically with the polar crude oil components or by modifying the environment of the demulsification. Among chemical agents, interfacial-active demulsifiers, which weaken the stabilizing films to enhance droplets coalescence, are preferred due to lower additions rates needed.

Crude oil specificity has long been recognized and many demulsifier products are formulated as a mixture of agents in a carrier solvent to improve performance. There are four types of surfactants that have been used as demulsifiers; ionic, anionic, cationic and zwitterionic. The early demulsification relied on the reversal of the emulsion type demulsifier as hydrophilic ionic surfactants followed by oil compatible anionic surfactants.

The formulation of commercial demulsifiers is largely based on empirical approaches in an attempt to get the effective, which can work in shorter separation times and at smaller dosages (Selvarajan et al., 2001). Typically laboratory testing is followed by evaluation under more representative dynamic conditions in a pilot scale process unit and eventually in the field.

According to Grace (1992), emulsions of oil and water are one of many problems directly associated with the petroleum industry, in both oil-field production and refinery environments. Whether these emulsions are created inadvertently or are unavoidable, as

in the oil field production area, or are deliberately induced, as in refinery desalting operations, the economic necessity to eliminate emulsions or maximize oil-water separation is present. Furthermore, the economics of oil-water separation dictate the labor, resources and monies dedicated to this issue. Before we describe the methods and economics of emulsion breaking at commercial facilities, we will restate several key concepts concerning emulsions and petroleum industry.”

Therefore, considering many aspects that are related in petroleum processing, it is important to develop the demulsifier formulation to solve the emulsion problems. The aspects that are important to be studied are such as crude oil composition and characterization, emulsions and emulsion stability, stabilization of water-in-crude oil emulsions and destabilization of crude oil emulsions.

2.2 Crude Oil Emulsion Composition

2.2.1 Introduction

Crude oil contains complex mixture of organic composite. Its composition can vary due to its reservoir’s place of origin, depth and age (Speight, 1991). Crude oils mainly consists the mixture of hydrogen and carbons, with little amount of sulphur, nitrogen and oxygen as well as structures with incorporated metallic molecules such as nickel, vanadium, copper and iron (Speight, 1991). There is a broad variation in physical properties from the lighter oils to the bitumens. For this reason, several classification systems of petroleum were proposed based on different criteria: viscosity, density (specific gravity or API gravity), pH, surface tension and interfacial tension.

Crude oils consist of light hydrocarbon such as gasoline, asphaltenes, resins, waxes and naphthenic acid. The asphaltene content of petroleum is an important aspect of fluid process ability. The method of dividing crude oil into four major fractions:

saturates (including 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.

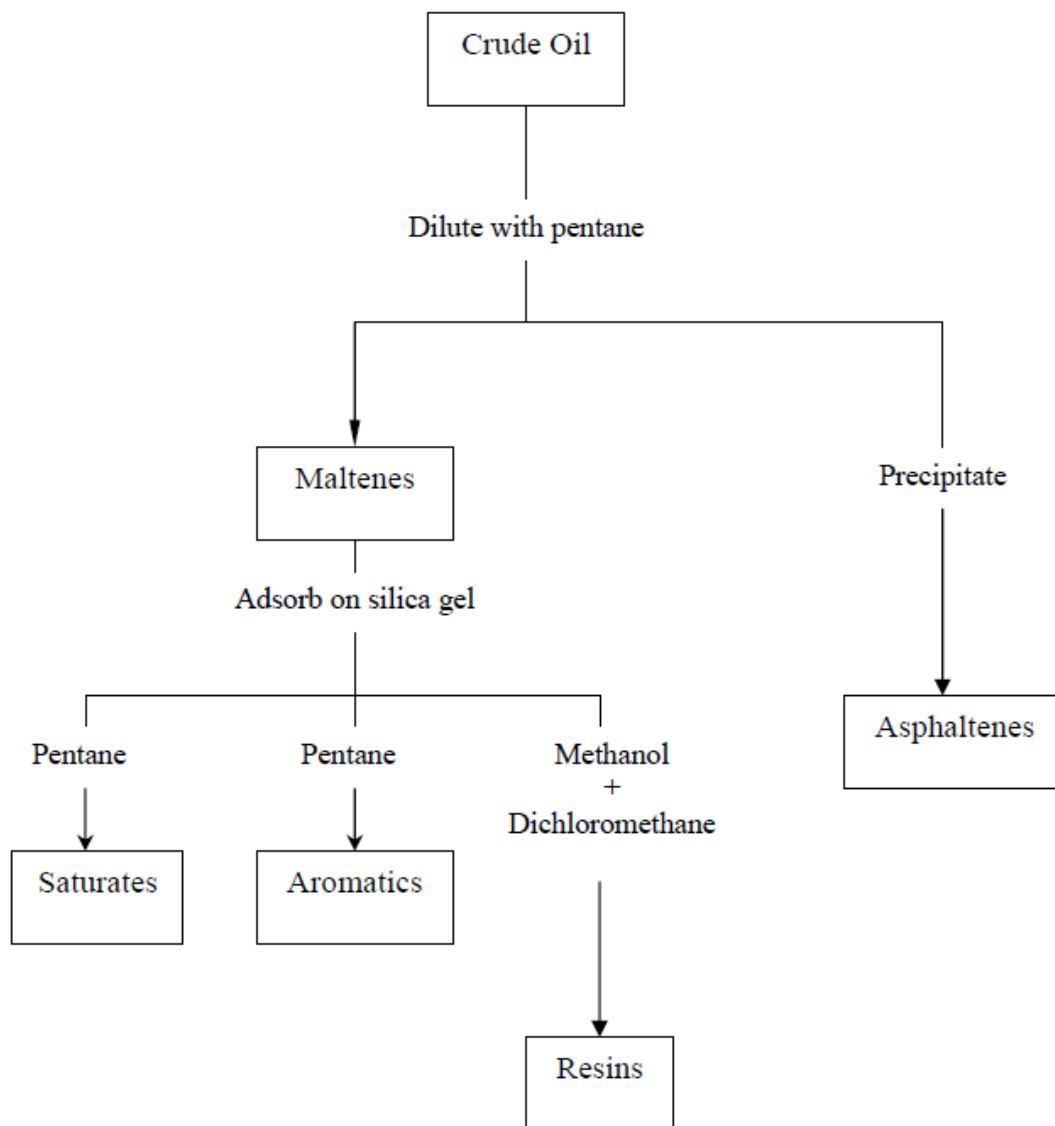


Figure 2.1: Schematic of SARA fractionation of crude oils (Auflem, 2002)

The fractions of crude oil that have been identified as contributing to the formation of water-in-oil emulsion includes asphaltenes, resins and waxes and can exist in both the dissolved and particulate form (Lee, 1999).

The basis method to remove asphaltenes is by precipitation in paraffinic solvent such as n-pentane. Chromatographic fractionation method is used to separate the deasphalted oil into saturates, aromatics and resins (Aske et al., 2001). From the four classes of compounds, only the saturated are easily discernible from the rest of the hydrocarbons in the mixture. This is because of the absence of π -bonds, which allows them to be readily differentiated from the aromatic components by asset of the difference in their polarity. The balance of the oil is contained aromatics and heteroatomic compounds of varying degree of functionalism, alkyl substitution and condensation.

The saturates or aliphatics are non-polar hydrocarbons, having branched alkanes and straight-chain but without double bonds, as well as cycloalkanes or naphthenes. Cycloalkanes contain one or more rings, which may have several alkyl side chains. The proportion of saturates in a crude oil normally decreases with increasing molecular weight fractions, thus the saturates generally are the lightest fraction of the crude oil. Wax is a sub-class of the saturates, consisting primarily of straight-chain alkanes, mainly ranging from C₂₀ to C₃₀. Wax precipitates as a particulate solid at low temperatures, and is known to effect emulsion stability properties of crude oil systems (Zaki et al., 2000).

The term aromatics refer to benzene and its structural derivates. Aromatics are common to all petroleum, and by far the majority of the aromatics contain alkyl chains and cycloalkane rings, along with additional aromatic rings. Aromatics are often classified as mono-, di-, and tri-aromatics depending on the number of aromatic rings present in the molecule. Polar, higher molecular weight aromatics may fall in the resin or asphaltenes fraction (Aske, 2002). The term of asphaltenes and resin will be discussed in Sections 2.2.2 and 2.2.3, respectively.

2.2.2 Asphaltenes

Asphaltenes are dark brown to black amorphous powder and have a specific gravity just above unity, and molar masses of 1000 to 10,000 g/mol (Speight, 1994). Asphaltenes has no definite melting point but decomposes when the temperature exceeds 300-400° C. Many research shown that changing in pressure, temperature and oil composition can cause asphaltene precipitation.

Asphaltenes are the non-volatile and polar fraction of petroleum that is insoluble in n-alkanes such as n-pentane or n-heptane. So, asphaltenes represent of crude oil components, rather than a chemical class. The polarity, molecular weight and aromaticity of precipitated asphaltenes are rise linearly with carbon number of n-alkane precipitant. Figure 2.2 represents the range of heavy compounds precipitated by mixing crude oil with n-pentane and n-heptane.

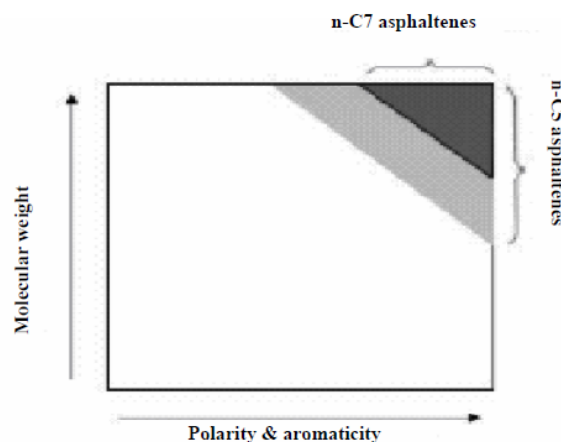


Figure 2.2: Hypothetical diagram representing the molecular characteristics of the asphaltenes precipitated from petroleum by n-alkane addition (Auflem, 2002)

The chemical compositions of crude oils, gained from for instance a SARA analysis, are not fully explaining the crude oil behaviour with regard to emulsion stability and asphaltene deposition. The information of the structure of the crude oil, which is a result of interactions between the continuums of chemical constituents in the

oil, is the most important. The interactions between the heavy end molecules, the asphaltenes and resins, play the most significant role in this sense.

The asphaltenes consist in part of polycyclic and cycloaliphatic naphthenic acids or of their oil-soluble calcium and magnesium salts, substituted phenols, and steroidcarboxylic acids. Most of the inorganic bonds of the crude are in the asphaltenes. Asphaltenes are interfacial active substance exist predominantly in the crude oil colloids. The interfacial active components of the asphaltenes are most active either directly before or during the start of flocculation (Schorling et al., 1998). Asphaltenes also contain metals including nickel, vanadium and iron.

The structure of asphaltenes is not well understood, but several possible structures have been proposed to explain the composition and properties of the asphaltene fraction. The structure for asphaltene is shown in Figure 2.3, which accounts for nitrogen, sulphur and oxygen in asphaltenes, excluding the organometallic. An organometallic complex is also shown which is assumed to complex other asphaltene compounds in the micelle. Such asphaltene sheets appear to be regularly stacked in lamellar and such structures, which are found in other surfactant systems, are known to enhance the emulsion stability (Lee, 1999).

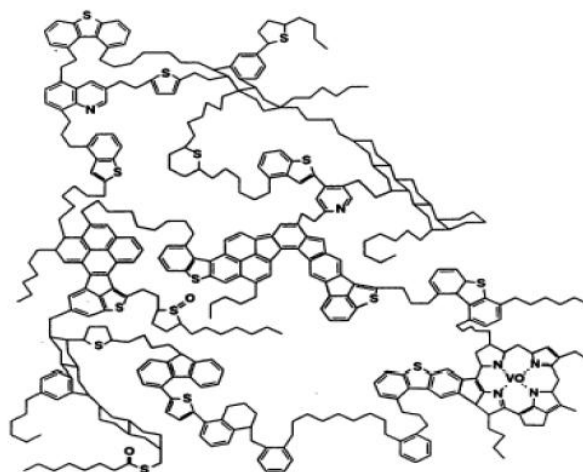


Figure 2.3: Hypothetical representation of an average asphaltene molecule (Gafonova, 2000)

Asphaltenes are believed to be suspending as a microcolloid in the crude oil, consisting of particles of about 3 nm. Each particle consists of one or more aromatic sheets of asphaltene monomers, with adsorbed resins acting as surfactants to stabilize the colloidal suspension. The molecules are believed to be holding together with π - bonds, hydrogen bonds, and electron donor-acceptor bonds (Aske, 2002).

2.2.3 Resin

Resins are black or dark brown semi solid, have a specific gravity near unity, molar mass ranging from 500 to 2000 g/mol and very adhesive materials (Gafonova, 2000). The content of resin in crude oils ranges from 2-40 wt%. From the Table 2.1, the content of resin in crude oil is higher compared to asphaltenes composition. Crude oil with a small amount or no asphaltenes has a lower concentration of resin than those with larger amount of asphaltenes. This is proved from data presented in the Table 2.2.

The resins are defined as the non volatile and polar fraction of crude oil that is soluble in n-pentane, n-heptane and aromatic solvents such as toluene but insoluble in methanol and propanol. The molecular species within the resin are same as to those in the aromatics. But, resins species have higher molar mass, greater polarity, higher heteroatom content and lower H/C ratio compared to aromatics.

The resin fraction consists of carbon, hydrogen, oxygen, nitrogen and naphthenic acids. The content of these elements in resin of various crude varies over a narrow range. The widest range is observed in sulfur content (Speight, 1991). Resins have a much higher H/C ratio compared to asphaltenes, indicating that they are less aromatic than asphaltenes. Asphaltenes are presumed to be maturation products of resin; in the maturation process the cyclic portion of resin molecules undergoes aromatization (Speight, 1991).

It is generally believed that resin molecules are composed of a highly polar end group, which may incorporate sulfur, oxygen or nitrogen, and a long non-polar end group. Nitrogen is present in resins in the form of pyrrole and indole groups. Infrared spectroscopic data indicated the presence of ester, ketone and acid functional groups. Sulfur is present in the form of cyclic sulfides (Gafonova, 2000).

However, structural studies of resin molecules have not been as intensive as they have been for asphaltenes. Resins were presented either as long paraffinic chain molecules with naphthenic rings in the center, or as condensed aromatic and naphthenic ring systems with heteroatoms scattered in different locations. The molecular structure of resin is shown in Figure 2.4 (Gafonova, 2000).

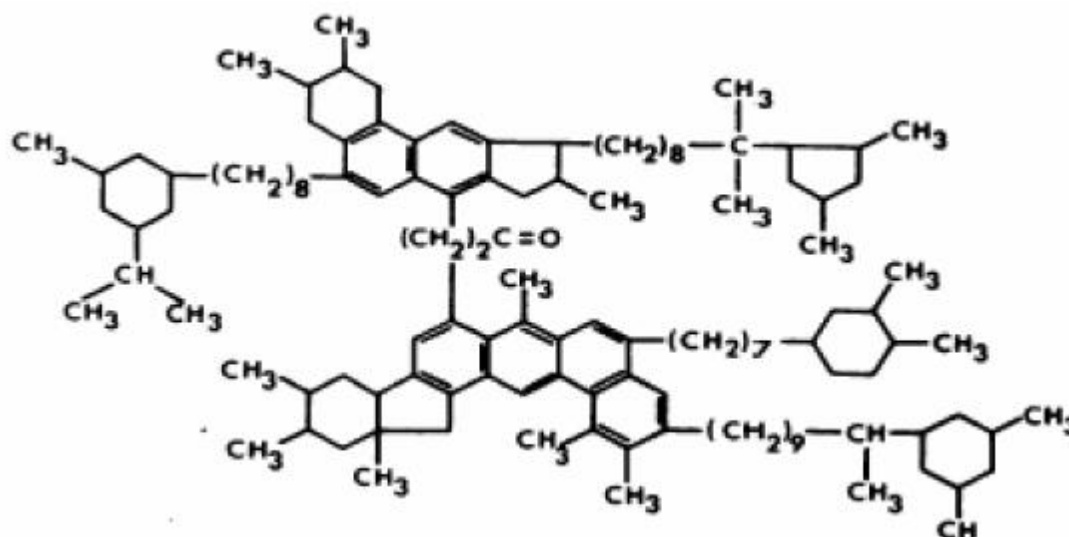


Figure 2.4: Hypothetical representation of an average resin molecule (Gafonova, 2000).

2.2.4 Waxes

Waxes are high molecular weight alkanes. A sensible description of wax is anything with a waxy feel and a melting point above body temperature and below the

boiling point of water. According to Becker (1997), waxes have been defined as esters of long-chain (C_{16} and above), monohydric (one hydroxyl group), or alcohols with long-chain (C_{16} and above) fatty acids. Actually, the natural waxes are mixtures of esters and frequently contain hydrocarbon as well.

Waxes form higher-order structures through solubility and inductive force, and the degree of structural complexity is a measure of their concentration and individual molecular weights. It is possible for multiple physical state (gas, liquid, and solid) to coexist under particular condition of pressure and temperature.

Majority of the waxes present in crude oil are in the form of monoxidized alkanes. This is because of the anaerobic (lack of oxygen) conditions under which biodegradation of organic matter takes place to form crude oils. These alkanes (C_nH_{2n+2}) may also exist as submatic, hetero-cyclic, and polymeric poly-sulfide parents (Becker, 1997).

Figure 2.5 shows the average structure of paraffin wax molecule system (Mussen, 1998). From the diagram, the wax molecules can combine with the fatty tails of the carboxylic acids stabilizing the interface. The crystal structure of waxes is the reason for the combination of wax in solids, asphaltenes and resins.

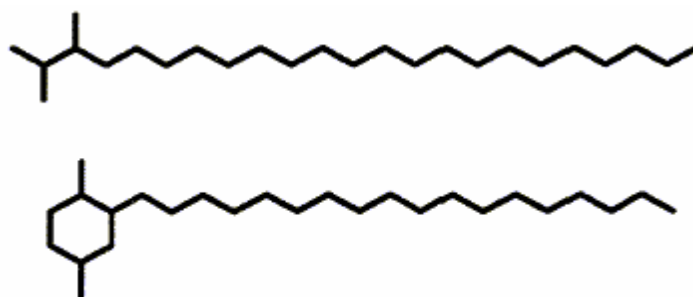


Figure 2.5: Average structure of paraffin wax molecule (Mussen, 1998)

2.2.5 Solids

Asphaltenes that precipitated from bitumen contain some other insoluble material referred as “solids”. This finely divided solids such as sand, wax crystals and clay particles can stabilize emulsions (Isaacs and Chow, 1992). The recent studies of Isaac and Chow (1992) demonstrated that solids prevent thinning of the thin film and the caused of the crude-oil film are so persistent.

According to Pal et al. (1992), the role, which solids played in stabilizing emulsions is affected by the size of the solids. Smaller solids tend to give a higher yield stress, whereas larger solids tend to induce more pronounced shear thickening behaviour. When the emulsion-solids mixtures are of shear-thinning nature, smaller solids yield a higher viscosity compared to larger solids. However, when shear thickening occurs, the effect of solids size on the viscosity of the mixtures seems negligible.

When the oil droplets in an emulsion are sufficiently smaller than solids, the emulsion is the continuous phase for the solids. The solids cannot be treated as oil droplets even if the size and size distribution of the solids are similar to the oil droplets. The addition of solids to an emulsion generally give a higher viscosity than the pure emulsion at the same total concentration.

2.2.6 Hydrocarbons

Hydrocarbons exist in the liquid, solid or gaseous state, generally depending on the number and arrangement of the carbon atoms in their molecules. At normal temperature and pressure, those hydrocarbon molecules with up to four carbons are gaseous, those with twenty or more carbons are solid and those in between are liquid such as crude oils. Crude oils are mixture of hydrocarbon usually with a small portion of nonhydrocarbon such as oxygen, sulphur and nitrogen.

The simplest hydrocarbon is methane, it is comprises of one carbon atom surrounded by four hydrogen atoms. Two or more carbon atoms joined to one another as well as to hydrogen atoms. The carbon atoms may link together in a straight chain, a branched chain or a ring. The simpler hydrocarbons found in crude oils are paraffins (saturated hydrocarbon) in which each carbon atom is linked with the maximum possible number of hydrogen atoms with the generic formula of $C_n H_{2n+2}$. Hydrocarbons with straight or branched carbon atom chains and contains less than the maximum of hydrogen atoms per carbon atom are called "unsaturated" or "olefinic" and have the generic formula of $C_n H_{2n}$. Petroleum crude oils contain hundreds of different hydrocarbons, some of which are as complex as $C_{85}H_{60}$ (Rhee et al., 1989).

2.2.7 Oilfield brine

Binks (1993) studied that o/w droplets increase in size solubilizing more oil with increasing salt concentration while w/o droplets decrease in size. At low and high salt concentrations, the monolayer constrained to lie at the flat interface has a preferred tendency to curve and increase the tension. At intermediate concentrations, the tension is least because the flat monolayer has no tendency to curve.

Tambe and Sharma (1993) studied the effect of inorganic salts such as sodium chloride and calcium chloride on emulsion stability for some pH values. Seems that the presence of salt has an adverse effect on emulsion stability and decrease as pH increase. They concluded that the stability of oil-in-water emulsion decrease in favour of relatively more stable water-in-oil emulsion as pH increased.

2.3 Crude Oil Emulsion Formation and Stability

2.3.1 Classification of emulsion

Emulsion 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. Petroleum emulsions may not be as familiar but have a similar long-standing, widespread, and important occurrence in industry, where they are typically undesirable and can result in high pumping costs, pipeline corrosions, reduced throughput and special handling equipment. Emulsions may be encountered at all stages in the petroleum recovery and processing industry (drilling fluid, production, process plant, and transportation emulsions).

An emulsion is usually defined as a system in which one liquid is relatively distributed or dispersed, in the form of droplets, in another substantially immiscible liquid. The emulsion formation is a result of the co-production of water from the oil reservoir. During processing, pressure gradients over chokes and valves introduce sufficiently high mechanical energy input (shear forces) to disperse water as droplets in the oil phase (Aske, 2002).

Emulsions are a special kind of colloidal dispersions, which have at least one dimension between about 1 and 1000 nm. The dispersed phase is sometimes referred to as the internal phase, and the continuous as the external phase. Emulsions also form a rather special kind of colloidal system in that the droplets often exceed the 1000 nm limited size (Schramm, 1992).

In the petroleum industry the usual emulsions encountered are water droplets dispersed in the oil phase and termed as water-in-oil emulsion (W/O), conversely, if the

oil is the dispersed phase, it is termed oil-in-water (O/W) emulsion. Figure 2.6 shows the two simplest kinds of this emulsion.

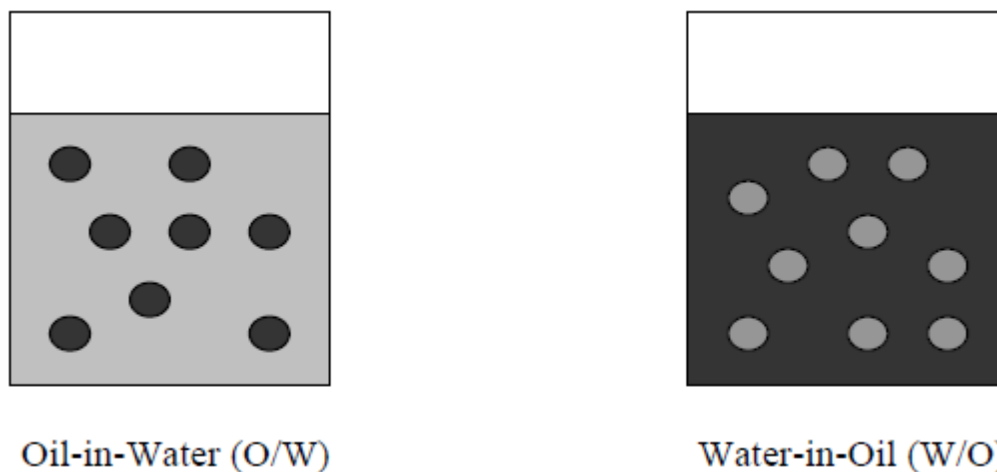


Figure 2.6: The schematic representation of two types of emulsion (Modified from Schramm, 1992)

In addition to the usual emulsion types, multiple emulsions for instance, oil droplets dispersed in water droplets that are in turn dispersed in a continuous oil phase (O/W/O) can occur.

The type of emulsion that is formed depends upon a number of factors. If the ratio of phase volumes is very large or very small, then the phase having the smaller volume is frequently the dispersed phase. If the ratio is closer to 1, the other factors determine the type of emulsion formed. Table 2.3 shows some simple examples of petroleum emulsion type.

Table 2.1: Examples of emulsion in the petroleum industry (Schramm, 1992)

Occurrence	Usual Type ^a
Undesirable Emulsions	
Well-head emulsions	W/O
Fuel oil emulsions (marine)	W/O
Oil sand flotation process, froth	W/O or O/W
Oil sand flotation process, diluted froth	O/W/O
Oil spill mousse emulsions	W/O
Tanker bilge emulsions	O/W
Desirable Emulsions	
Heavy oil pipeline emulsion	O/W
Oil sand flotation process slurry	O/W
Emulsion drilling fluid, oil-emulsion mud	O/W
Emulsion drilling fluid, oil-base mud	W/O
Asphalt emulsion	O/W
Enhance oil recovery in situ emulsions	O/W

^a W/O means water-in-oil; O/W means oil-in-water.

2.3.2 Emulsion Formation

According to Schubert and Armbruster (1992), there are three main criteria that are necessary for formation of crude oil emulsion:

1. Two immiscible liquids must be brought in contact;
2. Surface active component must present as the emulsifying agent;
3. Sufficient mixing or agitating effect must be provided in order to disperse one liquid into another as droplets.

During emulsion formation, the deformation of droplet is opposed by the pressure gradient between the external (convex) and the internal (concave) side of an interface. 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 or surfactant 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 (Becher, 1955).

A method requiring much less mechanical energy uses phase inversion. For example, if ultimately a W/O emulsion is desired, then a coarse O/W emulsion is first prepared by the addition of mechanical energy, and the oil content is progressively increased. At some volume fraction above 60-70%, the emulsion will suddenly invert and produce a W/O emulsion of much smaller water droplet sizes than were the oil droplets in the original O/W emulsions (Schramm, 1992).

2.3.3 Emulsion Stability

Stability is widely used to refer to the persistence of an emulsion in the environment, and has been identified as an important characteristic of water-in-oil emulsions. Some emulsions quickly decompose into separate oil and water phases once removed from the sea surface, while more stable emulsions can persist for days to years. Recent work indicates that the viscosity of an emulsion is correlated with its stability (NRT Science & Technology Committee, 1997).

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.

According to Schramm (1992), “colloidal species can come together in very different ways. In the definition of emulsion stability, it is considered against three different processes; creaming (sedimentation), aggregation and coalescence” as shown in Figure 2.7.

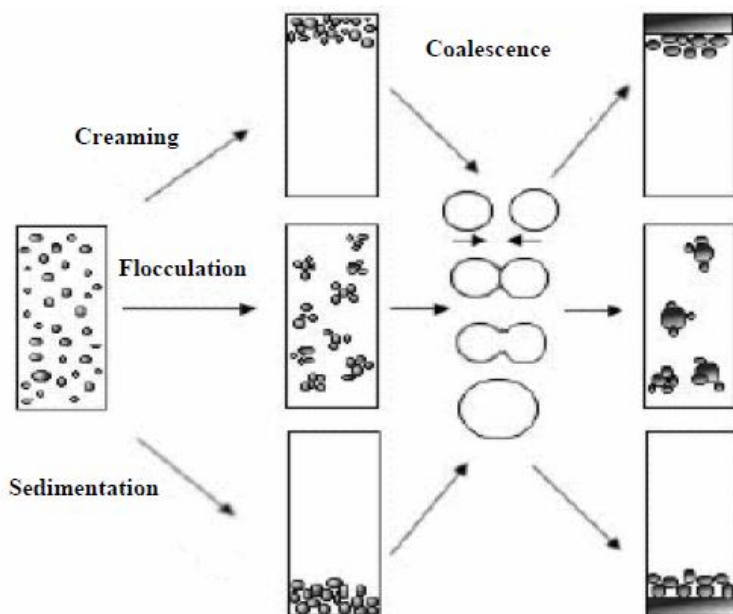


Figure 2.7: Processes taking place in an emulsion leading to emulsion breakdown and separation (Auflem, 2002)

Creaming is the opposite of sedimentation and results from a density different between the two liquid phases and creates a droplet concentration gradient, which result in a close packing of droplets. In aggregation, two or more droplets clump together, touching only at certain points, and with virtually no change in total surface area. So, aggregation of droplets may be said to occur when they stay very close to each other for a far longer time than if there were no attractive forces acting between them. The species retain their identity but lose their kinetic independence because the aggregation moves in single unit. Aggregation of droplets may lead to coalescence and the formation of larger droplets until the phase becomes separated.

In coalescence, two or more droplets fuse together to form a single larger unit with a reduced total surface area. The mechanism of coalescence occurs in two stages;