THE EFFECT OF LOW SULPHUR WAX RESIDUE (LSWR) SURFACTANT IN STABILIZATION OF CRUDE OIL EMULSION

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ABSTRACT

The crude oil had found in the depth of the earth and pumped out on land or in the seabed. Before being used as fuel or as a raw material in the petrochemical industry, crude oil is refined into different fractions separated into light and heavy fractions, which are then, converted into various products, such as petrol, diesel oil, or jet fuel. Usually, in the crude oil had presence of water which may cause a lot of problems due to transporting, operational problems and equipment corrosion. Therefore, this motivated many researchers to study the stabilization of crude oil emulsion since few years. Thus, the main aim of this study is to prepare of model emulsion which water in oil by prepared the sample first with continuous phase (crude oil) and emulsifier before added the dispersed phase. Then, the characteristic of the water in oil emulsion had study the stabilization via difference surfactants and their concentration for 20%-80% and 50%-50% water and crude oil ratio samples. However, the 20%-80% showed most stable compared to 50%-50%. Moreover, LSWR also had found as most stable as span 83, span 80 and triton x-100. The stable crude oil emulsion also had undergoes mechanism for characterize the affected of viscosity at varied temperature, rpm and concentration for crude oil and the aqueous phase. In this mechanism applied, the characteristic of crude oil and aqueous phase had showed the rose of temperature, rpm or concentration, the decreasing of viscosity. Then, the stable crude oil emulsion had evaluated the performance of de-emulsification via difference chemicals surfactant and their concentration at normal gravitational settling. The approximately 75% of water had separated at 24 to 96 hours had showed optimum and the best separation via Hexylamine. Hence, this study affords an efficient stabilization and separation only by using chemicals surfactants and concentration with the normal gravitational settling.

Key words: Stabilization; De-emulsification; Water-in- oil emulsion; LSWR

ABSTRAK

Minyak mentah telah ditemui di dalam perut bumi dan dipam keluar ke darat atau di dasar laut. Sebelum digunakan sebagai bahan api atau sebagai bahan mentah dalam industri petrokimia , minyak mentah ditapis ke dalam pecahan yang berbeza dipisahkan kepada pecahan-pecahan ringan dan berat , yang kemudiannya , ditukar menjadi pelbagai produk, seperti petrol , minyak diesel, atau bahan api jet. Kebiasanya, dalam minyak mentah mempunyai kehadiran air yang boleh menyebabkan banyak masalah kepada pengangkutan , pemprosesan dan penghakisan terhadap alatan pemprosesan. Hal ini telah mendorong ramai penyelidik untuk mengkaji kestabilan emulsi minyak mentah sejak beberapa tahun. Maka, tujuan utama kajian ini adalah untuk menyediakan model emulsi jenis air di dalam minyak dengan menyediakan sampel pertama dengan bahan medium berterusan (iaitu minyak mentah) dan pengemulsi sebelum menambah bahan medium terserak. Kemudian , ciri air di dalam emulsi minyak telah mengkaji penstabilan melalui perbezaan surfaktan terhadap bahan kaji untuk jenis 20 % -80 % dan 50 % -50 % nisbah air dan minyak mentah. Walau bagaimanapun, 20% -80 % menunjukkan paling stabil berbanding dengan 50 % -50 %. Selain itu, LSWR juga didapati sebagai paling stabil berbanding Span 83, Span 80 dan Triton X-100. Emulsi minyak mentah yang stabil juga mempunyai mekanisme dan mengklasifikasikan kesan terhadap kelikatan pada suhu yang berbeza-beza , kesan rpm kepada kepekatan minyak mentah dan bahan mesium akueus. Mekanisme yang digunakan terhadap minyak mentah dan bahan medium akueus telah mengkaji terhadap peningkatan di dalam suhu, rpm atau kadar kelajuan pusingan, maka semakin berkurangan kelikatan emulsi minyak mentah. Kemudian , emulsi minyak mentah yang stabil telah mengkaji berkaitan penyah emulsi dari bahan kimia surfaktan yang berbeza. Proses ini berfokus pada pemendapan proses melalui graviti normal. Kira-kira 75% air telah dipisahkan di antara 24-96 jam. Hal ini telah menunjukkan agen optimum pengasingan terbaik adalah Hexylamine . Oleh itu, kajian ini membuktikan pengstabilitan emulsi dan pengasingan yang paling efisien boleh didapati melalui penggunaan bahan kimia surfaktan dan proses pemendapan pada tarikan graviti biasa.

Kata kunci: Penstabilan ; Penyah emulsi ; Emulsi jenis air di dalam minyak ; LSWR

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LIST OF ABBREVIATIONS

η	Viscosity
A_2	Constant of eq. (1)
A_3	Constant of eq. (2)
V	Volume
V_W	Volume of water
V_O	Volume of oil
V_E	Volume of emulsifier
V_D	Volume of de-emulsifier
C_2	Constant of eq. (1)
C_3	Constant of eq. (2)
ω	Emulsifier concentration
%	Percentage
T	Temperature
rpm	Revolution per minute
CMC	Critical Micelle Concentration
W/O	Water in oil emulsion
O/W	Oil in water emulsion

INTRODUCTION

1.1 Overview

The demands on crude oil is increasing due to the Paris- Based adviser to energy-consuming nation in the monthly market report said the Global consumption will increase by 1.1 million barrels a day, or 1.2%, to 92 million in 2014. Then, by 2015 the consumption will increase to 99 billion barrels per day. The expansion is 100,000 barrels a day less than July 2013, when the estimate for 2014 was first introduced. Then, Refinery operating rates will ease after a record surge in July. Then, this statement had means the oil price had rising daily due to the world demand of the crude oil and the limited of energy. Hence, the several of surfactant such as LSWR, Triton X-100, Span 80 and Span 83 had been used to determine the optimum stabilization of the heavy crude oil and the optimum separation of heavy crude oil from the de-emulsification from Hexylamine, Octylamine, Dioctylamine and Polyethelene Glycol 600.

The Crude Oil or Petroleum is known as simply unprocessed oil which found in deep beneath the earth's surface. The crude oil is defined as a mixture of hydrocarbons that exists as a liquid in natural underground reservoirs and remains liquid when brought to the surface. Petroleum products are produced from the processing of crude oil at petroleum refineries and the extraction of liquid hydrocarbons at natural gas processing plants. Petroleum is the broad category that includes both crude oil and petroleum products. The terms "oil" and "petroleum" are sometimes used interchangeably. Crude oil can come in many different weights and colours, and can differ greatly in its composition. As little as half of the composition of heavy oils can be made up of hydrocarbons, while the lightest oils can be up to 97% hydrocarbons.

The emulsion had defines as unstable thermodynamic system which contain two immiscible liquid phases. The water-in-oil (w/o) had defined by Chen and Tao, 2005 as the w/o is water dispersed and encapsulated within oil column. Cendejas et al., 2010 had defined the w/o as emulsion which had water drops that dispersed in a homogenous crude oil phase. Harpur et al., 1997 had reported that when two droplets approach each other, the interfaces are separated by a thin film of oil. The o/w emulsions are dispersion of oil droplets and encapsulated within the water column [Chen and Tao, 2005]. In US

pattern publication of Santana et.al, 2010, the complex emulsion is made up of tiny drops of a phase suspended inside larger drops of another phase. The type of emulsion play important role in order to continue in the emulsification process which need to be stabilize.

The crude oil emulsions have three types which are i) water in oil emulsion, (ii) oil in water emulsion, and (iii) complex emulsion. In this experimental work, the type of emulsion will be turn from the oil in water emulsion to water in oil emulsion. This is because the crude oil is transferred first from the pipeline to the refinery part for the separation process. Then, by transferred the type of oil in water emulsion into water in oil emulsion will be study for further process in the emulsification and de-emulsification process.

Then, de-emulsification is the breaking or destabilization crude oil emulsions in order to separate the w/o emulsion in two clear immiscible phase which oil and water phase. Fan et.al, 2009 had defined the de-emulsification is a breaking emulsion process which separate water from oil, where the one of the step in crude oil process. The separation rate of w/o emulsion usually function that had be considered for the use of de-emulsified, the emulsion stability, the temperature, the concentration, the process residence time and the mixing temperature [Sunil, 2004]. Via 4 principals methods which are mechanical, chemical, electrical and thermal. However, in this study, the principals method had choose chemicals as de-emulsification agents. Adam had thought de-emulsifier had decreasing the surface tension for liquids and then dissociate the large oil block.

Dalmanzonne and Noik said, in the offshore production usually had used classical separators that faced a problem that need residence time of separation. In the production process had use heating or electro coalescence which they also added chemical additive in order to enhanced the separation.

Hence, some of variable such as RPM (Revolution Per Minutes), temperature, water contents, processing times and type of chemical agent which refer to emulsification agent and de-emulsification agents. So, the RPM and temperature will be considering during apply Brook Field equipment in order to determine the gravity stability, processing time, viscosity, density, shear rate, shear stress, surface tension, interfacial

tension, flash point and cloud point. The chemical agents for emulsification and de-emulsification will apply in order to evaluate the most effectiveness in stabilization and destabilization of crude oil emulsion. The water content in the crude oil also had varied in order to determine the stabilization of crude oil emulsion.

1.2 Background of study

The stabilization of crude oil emulsion is important role in order to prevent the problem that causing a lot of cost in the operation. Sometimes, the water in oil emulsion form after the oil spills and known as "chocolate mousse" or "mousse" by the oil spill workers, complicate the clean-up of oil spills [NAS, 2002]. The presence of water in the crude oil faced a lot of trouble in operation and economic. The water in the crude oil is not only damage the equipment but cause problem for the production such as rising in viscosity, higher cost of transport and storage, corrosion and salt deposit in refining equipment and poisoning of catalyst [J.E. Thomas, 2004]. Hence, some of chemical additives had used as surfactant and determine the effect towards the stabilization of light crude oil. The main surfactant had been used in this study was Low Sulphur Wax Residue (LSWR). The LSWR had been used in stabilization of light crude oil. Then, the study had determined the optimum temperature, concentration, agitation speed and salinity of water for optimum stabilization of crude oil. The LSWR, Sorbitan Monooleate (Span 80), Sorbitan Sesquioleate (Span83) and Triton X-100 had been use as additive for emulsifier process. The, emulsification process had determine by additive from amine group which are Hexylamine, Dioctylamine and Octylamine.

1.3 Problem statement

The emulsion had widely use in the daily life such as in the field of food industry, cosmetics, pulp and paper and painting. However, in the petroleum there not familiar but had similar in the widespread. However, the presence of water in the crude oil in the downstream had motivated many researchers to investigate the study of formation mechanism and the stabilization of crude oil. The water presence had diluted the sulphur contains in the heavy crude oil will effected to the pipeline and the refinery equipment via corrosion and salt deposit. It also effected to the higher cost of transport and storage and poisoning of catalyst [J.E. Thomas, 2004].Hence, the stabilization of crude oil emulsion in oil emulsion type by using emulsifier surfactants had been done in this

research in order to minimize the weaknesses and leaking from previous researched. Then, at the end of the production of crude oil the stable emulsion need to breaking with de-emulsification process in order to have pure crude oil. Therefore, in this study, the heavy crude oil from PETRONAS Refinery, at Malacca, Malaysia, Brookfield equipment, different concentration of emulsifier and de-emulsifier agents will be use and analyse the stabilization on the crude oil emulsion which considering the environmental friendly, economical and better operational.

1.4 Objectives

The following are the objectives of this research:

1. Preparation of model emulsions and their characteristics by study the stabilization using different type of surfactants.
2. To elucidate the mechanisms of characterization of oil and aqueous phases.
3. To evaluate the performance of chemical surfactants in de-emulsification of crude oil emulsions.

1.5 Scope of this research

The following are the scope of this research:

1. Characterization of emulsions in terms of physical and chemical parameters.
2. Overall performance of surfactants in stabilization of crude oil emulsions.
3. To evaluate the parameters affecting the stabilization of crude oil emulsions such as water emulsion, agitation speed, processing time, RPM, temperature, viscosity and shear rate.

1.6 Rationale and significant

The presence of water in crude oil might damage a lot of equipment and effect on the operational problems. Then, the highest demand of heavy crude oil had proposed a research towards reduced the cost and operational problems such as using the natural surfactant in the crude oil emulsion and de-emulsification process. Then, the problem had come out with research on stabilization of crude oil emulsion and optimum separation of water via de-emulsification method. Hence, this method will encounter the

entire problem such as repair the corrosion equipment, the salt deposit in the equipment and many more problems that will face in the refinery plants.

1.7 Motivation

The presence of water in the crude oil affected a lot of problems. Then, it will affect in the costing in repairing all the problem equipment. Then, the problems not only affected to the equipment but the operational and the production of the crude oil also will face the problem. Hence, the study on the stabilization of crude oil emulsion and de-emulsification process via different chemical agents can decreasing the costing and enhance the production of the light crude oil.

2 LITERATURE REVIEW

2.1 Crude oil

The crude oil found in the depth of the earth. The crude oil pumped out on land or in the seabed. The crude oil is a complex mixture which made up from thousands of different chemical components. The main chemical component is organic compounds hydrocarbons. It usually makes up about 95%of the crude oil and usually the hydrocarbon make up for low than 50%. The crude oil is a liquid found naturally in rock, containing mostly complex hydrocarbons, with some additional organic material. The Crude Oil or Petroleum, is known as simply unprocessed oil which found in deep beneath the earth's surface. However, Crude oil is defined as a mixture of hydrocarbons that exists as a liquid in natural underground reservoirs and remains liquid when brought to the surface. Petroleum products are produced from the processing of crude oil at petroleum refineries and the extraction of liquid hydrocarbons at natural gas processing plants. Petroleum is the broad category that includes both crude oil and petroleum products. The terms "oil" and "petroleum" are sometimes used interchangeably. Crude oil can come in many different weights and colours, and can differ greatly in its composition. As little as half of the composition of heavy oils can be made up of hydrocarbons, while the lightest oils can be up to 97% hydrocarbons.

Commonly, the crude oil had divided into different solubility and polarity of chemical classes [Evdokimov, 2005]. This fraction also known as SARA families [Speight, 1998]. The SARA fractions are (i) saturated, (ii) aromatic, (iii) resin and (iv) asphaltenes. Certain fraction of crude oil had identified in cooperating in formation of crude oil emulsion. These chemical classes can act in both the dissolved and particulate form [Lee, 1999]. Before being used as fuel or as a raw material in the petrochemical industry, crude oil is refined into different fractions. At the refinery, crude oil is separated into light and heavy fractions, which are then, converted into various products, such as petrol, diesel oil, jet fuel. Kumar et.al, 2001 had reported which Most crude oil that contain asphaltenes and naphthenic acid tend to form stable w/o emulsion which are complex scattered systems. The crude oil had divided into two types which are sweet crude oil (light crude oil) and sour crude oil (heavy crude oil). The Crude oil

is a kind of complicated mixture which commonly contains large quantity of water and salt.

There are four main hydrocarbons found in crude oil, in varying amounts depending on the oil. The main hydrocarbons found in crude oil are Aliphatics, Alicyclics, and Polycyclic Aromatic Hydrocarbons (PAH). The Aliphatics and Alicyclics had some properties such as easily breaking down to natural process, the residence time in environment is less than a day, the structure of ring carbon and straight carbon are in weak bonds and also have low fluorescence characteristics. However, the polycyclic aromatic hydrocarbons (PAH) also have some properties which are prolonged breaking down to natural processes, can be carcinogenic to the plants and animals which most of them are toxic, most of abundant of the main hydrocarbons found in the crude oils, the hydrocarbon have strong bond for 6-sided carbon ring, highly fluorescence characteristic give highest potential in detection of PAH by using fluorescence technique and the PAH is difficult to separate with water via filtering technique which may causing hazard to human health retrieved via www.turnerdesigns.com

The PAH's aromatic can be form in the simplest structure as naphthalene and also can be through the complex structure such as asphaltenes. The aromatic compound is mainly factors for determining the fluorescence intensity which highly affect the properties of crude oil. Hence, figure below show the structure of naphthalene and asphaltenes.

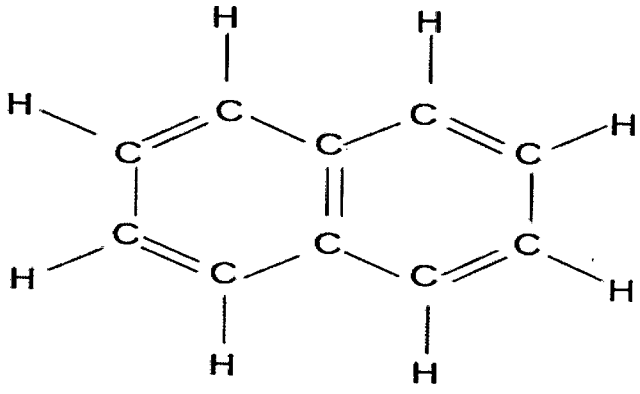

Figure 2.1.1 1:- structure of naphthalene

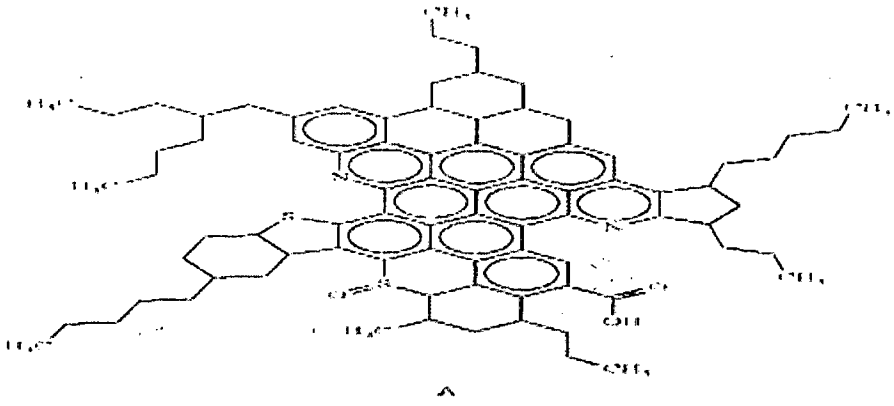

Figure 2.1.1 2:- Structure of asphaltene

The colour can range from pure black or dark brown to greenish or yellowish, depending on the composition. It also can be found as a liquid or solid. It is the major fuel used on the planet, and is used in the production of many synthetic materials like plastics as well. Overall properties of crude oils are dependent upon their chemical composition and structure. Crude oil is pumped and stored in barrels for future refinement. The refinement process may involve filtering, addition of additives, and specialized separation techniques to create specific crude oils and crude oil products. Generally all crude oils are made up of hydrocarbon compounds.

The crude oil also has advantages and disadvantages and it can be referred at the table 1.0.3 below as mention by V. Sandra

2.2 Type of crude oil

2.2.1 Heavy crude oil

The heavy crude oil is highly demand and too expensive due to the highly viscosities of it. The heavy term had referred to the viscosity and the density which are high for heavy crude oil. The heavy crude oil is less demands compared to the light crude oil [Chevron Pascagoula Refinery, 2013] This is because the heavy crude oil effected more the environmental with presence of carbon dioxide can be much as 3 times that light crude oil for the same quantity. Moreover, the environmental impact that causes by heavy crude are contaminated with sulphur and heavy metals which both of them must be removed. The heavy metals are often toxic and the removal of it from crude presents disposal issues. The sulphur content of heavy oil may be as high as 4.5% and if it are contributes to acid rain, combine with hydrogen, then, it produces hydrogen sulphide,

which can be deadly. Hence, sulphur also corrosive to the pipeline metal and refinery components [Petroleum.co.UK, 2013]. Via the hazard characterization document by U.S Environmental protection energy, the physical and chemical properties of petroleum had shown as in the Table 2.2.1.1, 2.2.1.2 and 2.2.1.3:-

Table 2.2.1.1: The physical and chemical properties of petroleum

Table 1. Physical-Chemical Properties of Petroleum[1]	
Property	Petroleum (Crude Oil)
CASRN	8002-05-9
Molecular Weight	Complex Mixture
Physical State	Light, mobile, straw-colored liquid to highly viscous, semi-solid, black substance
Melting Point	-30 to 30 °C (measured pour points)
Boiling Point	-1 to 565 °C (measured distillation range)
Vapor Pressure	142.5 mm Hg at 37 °C (measured Alaska North Slope crude oil); 165.8 mm Hg at 37 °C (measured Arabian medium crude oil); 337.5 mm Hg at 37 °C (measured Alif Temen crude oil); 202.5 mm Hg at 37 °C (measured Amna Libya crude oil); 97.5 mm Hg at 37 °C (measured Ashtart Tunisia crude oil); 45 mm Hg at 37 °C (measured Atkinson Canadian crude oil); 142.5 mm Hg at 37 °C (measured Alberta sweet mixed blend Canadian crude oil); 180 mm Hg at 37 °C (measured United Arab Emirate crude oil); 270 mm Hg at 37 °C (measured Beryl North Sea crude oil); 247.5 mm Hg at 37 °C (measured Bombay High Indiacrude oil);

Table 2.2.1.2:- Continuous of physical and chemical properties of petroleum

Table 1. Physical-Chemical Properties of Petroleum[1]	
	Aliphatic Fraction[2,3] 266 mm Hg (estimated >C5-C6); 47.9 mm Hg (estimated >C6-C8); 4.8 mm Hg (estimated >C8-C10); 0.48 mm Hg (estimated >C10-C12); 0.036 mm Hg (estimated >C12-C16); 8.3×10^{-4} mm Hg (estimated >C16-C21); Aromatic Fraction[2,3] 98.8 mm Hg (estimated >C5-C7); 28.9 mm Hg (estimated >C7-C8); 4.8 mm Hg (estimated >C8-C10); 0.48 mm Hg (estimated >C10-C12); 0.036 mm Hg (estimated >C12-C16); 8.3×10^{-4} mm Hg (estimated >C16-C21); 3.5×10^{-5} mm Hg (estimated >C21-C35)
Dissociation Constant (pKa)	Not applicable
Henry's Law Constant	Aliphatic Fraction[2,3] 0.74 atm-m^3/mol (estimated >C5-C6); 1.12 atm-m^3/mol (estimated >C6-C8); 1.79 atm-m^3/mol (estimated >C8-C10); 2.69 atm-m^3/mol (estimated >C10-C12); 11.7 atm-m^3/mol (estimated >C12-C16); 110 atm-m^3/mol (estimated >C16-C21); Aromatic Fraction[2,3] 0.0052 atm-m^3/mol (estimated >C5-C7); 0.0090 atm-m^3/mol (estimated >C7-C8); 0.011 atm-m^3/mol (estimated >C8-C10); 0.003 atm-m^3/mol (estimated >C10-C12); 0.001 atm-m^3/mol (estimated >C12-C16); 0.0029 atm-m^3/mol (estimated >C16-C21); 1.5×10^{-5} atm-m^3/mol (estimated >C21-C35)
Water Solubility	30 mg/L (measured at 5 °C; Norman Wells crude oil)[3,4]; 29-33 mg/L (measured at 20 °C; Norman Wells crude oil)[3,4]; 31.8-33.5 mg/L (measured at 22 °C; Norman Wells crude oil)[3,4]; 33 mg/L (measured at 20 °C; Norman Wells crude oil)[3,4]; 25.02 mg/L (measured at 22 °C; Alberta crude oil)[3,4]; 35.1 mg/L (measured at 22 °C; Swan Hills)[3,4]; 29.01 mg/L (measured at 22 °C; Prudhoe Bay crude oil)[3,4]; 23.6b-25.5 mg/L (measured at 22 °C; Lago Medio crude oil)[3,4]; 10.42 mg/L (measured at 22 °C; Kopanoar crude oil)[3,4]; 28.62 mg/L (measured at 22 °C; Murban crude oil)[3,4]; 29.6 mg/L (measured at 22 °C; Mobil A crude oil)[3,4];

Table 2.2.1.3:- Continuous of physical and chemical properties of petroleum

Table 1. Physical-Chemical Properties of Petroleum[1]	
	58 mg/L (measured at 22 °C; Mobil B crude oil) [1,4] Aliphatic Fraction[2,3] 36 mg/L (estimated >C5-C6); 5.4 mg/L (estimated >C6-C8); 0.43 mg/L (estimated >C8-C10); 0.034 mg/L (estimated >C10-C12); 7.6×10^{-4} mg/L (estimated >C12-C16); Aromatic Fraction[2,3] 1,800 mg/L (estimated >C5-C7); 520 mg/L (estimated >C7-C8); 65 mg/L (estimated >C8-C10); 25 mg/L (estimated >C10-C12); 5.8 mg/L (estimated >C12-C16); 0.65 mg/L (estimated >C16-C21); 6.6×10^{-3} mg/L (estimated >C21-C35)
$\text{Log } K_{ow}$	2 to > 6 (estimated)

[1] American Petroleum Institute Petroleum HPV Testing Group. Test Plan and Robust Summary for Crude Oil. November 15, 2003. Available online at http://www.epa.gov/oppt/chemrtk/pubs/summaries/crdoilc/c14858tc.htm as of December 7, 2010.
[2] Total Petroleum Hydrocarbon Criteria Working Group: Human Health Risk- Based Evaluation of Petroleum Release Sites: Implementing the Working Group Approach Volume 5. June 1999.
[3] The Total Petroleum Hydrocarbon Working Group subdivided aromatics and aliphatic hydrocarbons of crude oil into 13 aliphatic and aromatic fractions and provided representative physical-chemical properties for these fractions.
[4] Results based on the water soluble fraction of total benzene, toluene, ethyl benzene + xylenes (combined concentration) and naphthalenes. The lower molecular weight components may dissolve in water while other fractions may float and spread out on water where they may form emulsions.

Table 2.2.1.4:- The advantages and disadvantages of crude oil

Advantages	Disadvantages
Oil is one of the most abundant energy resources	Oil burning leads to carbon emissions
Liquid form of oil makes it easy to transport and use	Finite resources (some disagree)
Oil has high heating value	Oil recovery processes not efficient enough—technology needs to be developed to provide better yields
Relatively inexpensive	Oil drilling endangers the environment and ecosystem
No new technology needed to use	Oil transportation (by ship) can lead to spills, causing environmental and ecological damage (major oil spill near Spain in late Fall 2002)

2.2.2 Light crude oil

The light crude oil is low viscosity and density of crude oil. The wax content in the light crude oil is low. By the way, the light crude oil is highly demand in the world. The light crude oil produces higher percentage of kerosene, diesel fuel by oil refinery [Indexmundi]. Hence, the Table 2.1.2.1 is shown the comparison of heavy and light crude oil properties.

Table 2.2.2.1:- Comparison of light crude oil and heavy crude oil properties.

LIGHT CRUDE OIL	HEAVY CRUDE OIL
Low density	High density
Flow freely	Not flow easily
Low specific gravity	High specific gravity
API gravity more than 10	API gravity less than 10
Low wax content	High wax content

2.3 Components of crude oil

Asphaltenes is most elements that contain in the crude oil. Asphaltene is a solid material that precipitating after the reaction of crude oil with low boiling liquid hydrocarbon such as heptane or pentane. Asphaltenes have higher molecular weight compare to the resin [Lee, 1999]. Ebeltoft et. al, 1992 said that how important of asphaltenes in the crude oil which removed the asphaltene via silicon column produced oil that did not form water-in- oil emulsion. The properties of asphaltene are soluble in aromatic solvents, e.g. xylene, insoluble in alkane solvents and the structural of asphaltenes itself. The carbon to hydrogen in asphaltenes, other elements found like nitrogen, oxygen sulfur and metal (basically are vanadium and nickel). Then, the asphaltenes concepts are to enhance the emulsion stability [Johansen et.al, 1989]. In order to determine the size of asphaltene particles, the alkane/aromatic ratio in oil play main role for it. The highest ratio of alkane/aromatic will show the asphaltenes particles form in the oil, then the size of practices had determined from the ratio [Richard f. lee et. al, 1999]. The oil data based that analyse had shown the amount of asphaltenes is the most significant for all variables [Evdokimov, 2005]. Bobra et. al (1992) and Griffith and Siegmund (1985) had described the behaviour of asphaltene solubility through the Hildebrand-Scatchard

equation. By assuming the oil will be composed of a solute (asphaltenes) and solvent (compounds in oil other than asphaltenes). Then, the solvent from lighter weight aromatic e.g. toluene, xylene had been used for the heavier asphaltenes. Hence, with the heaviest and most polar fraction in the crude oil and play a leading role in causing the variety of inconvenience like stabilization of the water-in-oil emulsion that occurs during crude oil production [Auflem, 2002]. By Sjoblom, et. al (1990) said it tend to absorb at water –in-crude oil interface in order to form the rigid film surrounding the water droplets and protect the interfacial film form rupturing during droplet-droplet collisions, giving rise to the formation of particularly stable water-in crude oil emulsion. Figure 2.2.0.1 below show the structure of asphaltene.

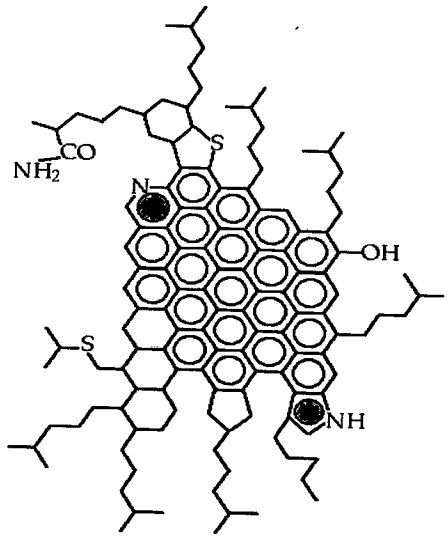

Figure 2.3.1.1:- Structure of asphaltene

2.4 Emulsion

2.4.1 Overview

The emulsion is unstable thermodynamic systems which have two immiscible liquid phases [Adam et.al]. Lan et. al, 2011 had mention emulsification as a process in the formation of water. Emulsion is a system that contains two immiscible liquid phases that one of them dispersed as globule/droplets on the other. The dispersed phase known as internal phase and the continuous phase as external phase [Ariyani, 2004].There have

three types of emulsion based on Santana et.al, (2010) which are (i) water in oil emulsion, (ii) oil in water emulsion, and (iii) complex emulsion. But, by Chen and Tao, 2005 mention there have two basic form of emulsion which are oil in water (o/w) and water in oil (w/o) emulsion. The o/w emulsions are dispersion of oil droplets and encapsulated within the water column. Then, the w/o is water dispersed and encapsulated within oil column. There have variety of emulsification method that reported by Lengevin et. al, 2004 which are simple shaking, mixing with rotor stator systems, liquid injection through porous membranes or high pressure devices (homogenizers, liquid jets). During the processing of the crude oil and during oil spills over the water the formation of emulsion had occurred [Efeovokhan et. al, 2010]. The presence of emulsion will causes a lot of problems to the corrosive equipment or may affect the quality and properties of oil [Adam et. al 2011]. Figure below show the type of emulsion in illustration.

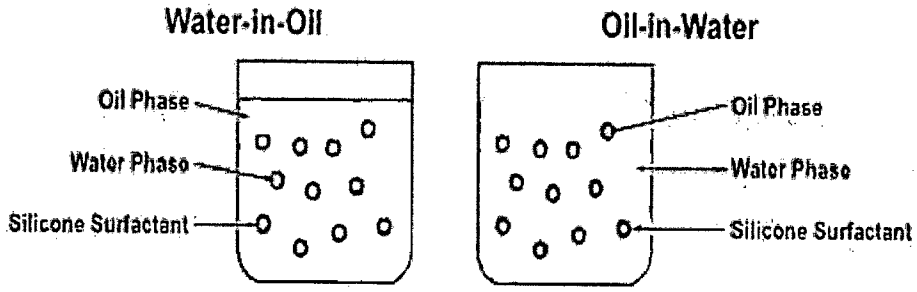

Figure 2.4.1: Illustration of water-in-oil

2.4.2 Type of emulsion

The w/o had defined by Chen and Tao, 2005 as the w/o is water dispersed and encapsulated within oil column. Cendejas et.al, 2010 had defined the w/o as emulsion which had water drops that dispersed in a homogenous crude oil phase. Harpur et. al, 1997 had reported that when two droplets approach each other, the interfaces are separated by a thin film of oil. The o/w emulsion is dispersion of oil droplets and encapsulated within the water column [Chen and Tao, 2005]. In US pattern publication of Santana et.al,2010, the complex emulsion is made up of tiny drops of a phase suspended inside larger drops of another phase. The type of emulsion play important role in order to continue in the emulsification process which need to be stabilize. Figure below show the illustration of phase of dispersion and continuous.

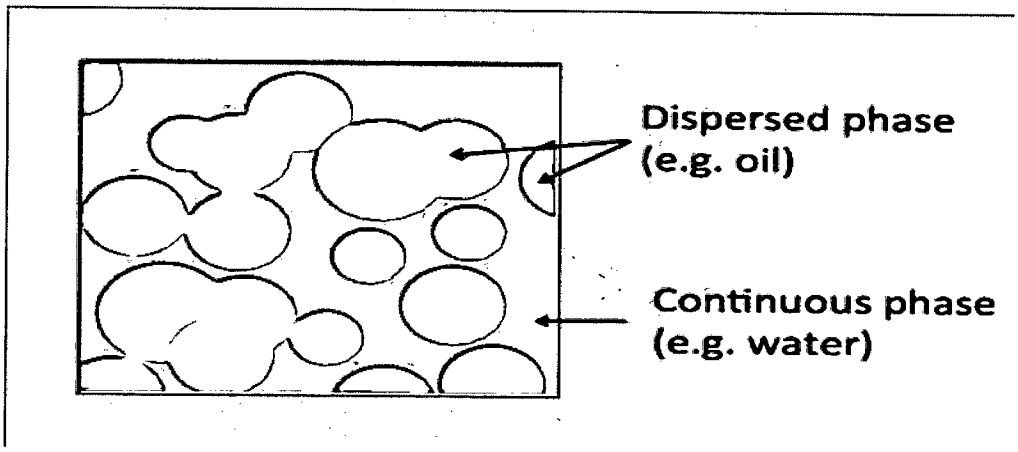

Figure 2.5.1: illustration of dispersed

2.5 De-emulsification

The crude oil emulsion need to separate the water in oil completely as Hayder et.al said to prevent the highest cost from corrosion in equipment during transporting and refining process. Then, Selvarajan et. al, 2011 had said de-emulsification is the breaking or destabilization crude oil emulsions in order to separate the w/o emulsion in two clear immiscible phase which oil and water phase. Fan et.al, 2009 had defined the de-emulsification is a breaking emulsion process which separate water from oil, where the one of the step in crude oil process. De-emulsifier is interfacial-active agent which weaken the stabilizing film to enhance droplet coalescence. The separation rate of w/o emulsion usually function that had be considered for the use of de-emulsified, the emulsion stability, the temperature, the concentration, the process residence time and the mixing temperature [Sunil, 2004]. Via 4 principals methods which are mechanical, chemical, electrical and thermal. The de-emulsification had added into to the emulsion mixture with suitable method had broken the crude oil emulsions from operational and economic point [Efeovbokhan et.al, 2010]. De-emulsifier had been used in petroleum industry in the different de-emulsification agents group [Santana et.al, 2010]. There have chemical product from amine, alcohol and polyhydric alcohol group [Abdurahman, 2010]. Adam had thought de-emulsifier had decreasing the surface tension for liquids and then dissociate the large oil block. Then, it also increases the interfacial action, which had been control by surface active material, molecular weight and length of the molecular chain.