FORMATION AND STABILITY STUDY OF SOME MALAYSIAN CRUDE OIL EMULSIONS

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For my beloved mother, late-father, brother, sisters, sister in-law,
nephew "Rizal", and mas Ranto.

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ABSTRACT

The formation of water in crude oil emulsions is often undesirable since it causes problems in petroleum recovery and processing. Hence, the objective of this study is to investigate the crude oil emulsion characteristics and its stability using some selected Malaysian crude oil emulsion samples in order to obtain a better understanding on problems. Some crude oil emulsion samples provided by ESSO Production (M) Inc. as well as model systems consisting of pure oil, synthetic oil (toluene/decane), and crude oil components were used in the study. Some important properties of crude oils and oilfield brines, and the effect of some physical conditions on the crude oil emulsion stability were investigated. In addition, the effect of crude oil components on emulsion formation and stability was also studied. The stability was assessed by measuring the percentage of water separation. Some physical and chemical properties of crude oils have a correlation with each other. Analysis of crude oil components showed that hydrogen/carbon (H/C) ratio of wax is higher than asphaltene. Besides, Fourier Transform Infra Red (FTIR) analysis showed that asphaltene, resin, and oil contained substantial functional groups as polar carrier and aromatic contents, which have important roles in emulsion formation and stability. This study indicated that crude oils, which have higher asphaltene content, lower resin/asphaltene (R/A) ratio, and higher wax contents, would have a stable emulsion. At 28 °C, the 0.5% (w/w) of asphaltene content in crude oil was sufficient to form a stable crude oil emulsion. Asphaltene has a significant role to enhance emulsion stability, while resin would decrease the stability. Wax and solid particles could contribute to the emulsion stability but they do not effective as much as asphaltene. Analysis of factor controlling emulsion stability using factorial design provides the mathematical model, which indicates the role of crude oil components and their interactions terms on the crude oil emulsion formation and stability.

ABSTRAK

Pembentukan emulsi air di dalam minyak mentah tidak dikehendaki kerana ia menyebabkan masalah di dalam industri penghasilan dan pemprosesan petroleum. Oleh kerana itu, tujuan kajian ini adalah untuk mengkaji ciri-ciri emulsi minyak mentah dan kestabilan emulsi daripada beberapa minyak mentah di Malaysia. Minyak mentah yang diperolehi daripada syarikat ESSO Production (M) Inc. digunakan dalam kajian ini di samping menggunakan model emulsi yang mengandungi minyak tulen, minyak buatan (*toluene/decane*) dan komponen-komponen daripada minyak mentah. Kajian ini memeriksa beberapa sifat yang penting daripada minyak mentah dan air garam serta kesan-kesan beberapa keadaan fizik terhadap pembentukan dan kestabilan emulsi. Selain itu, kesan-kesan pelbagai komponen daripada minyak mentah terhadap pembentukan dan kestabilan emulsi juga dikaji. Kestabilan dinilai melalui peratus pemisahan air. Beberapa sifat fizik dan kimia daripada minyak mentah menunjukkan bahawa ada hubungan di antaranya. Analisis ke atas komponen-komponen minyak mentah menunjukkan bahawa nisbah H/C daripada lilin lebih tinggi dibandingkan asfaltin. Analisis FTIR pula menunjukkan bahawa asfaltin, resin, dan minyak tulen mengandungi kumpulan berfungsi sebagai pembawa sifat polar dan aromatik yang memiliki pengaruh penting terhadap pembentukan dan kestabilan emulsi. Penyelidikan ini menunjukkan bahawa minyak mentah yang mengandungi asfaltin dan lilin tinggi serta nisbah resin/asfaltin yang rendah akan membentuk emulsi yang stabil. Pada suhu suhu 28 ^{o}C, kepekatan asfaltin dalam minyak mentah sebesar 0.5% (w/w) dapat menghasilkan emulsi yang stabil. Asfaltin akan memberi kesan nyata terhadap peningkatan kestabilan emulsi, manakala resin akan mengurangkannya. Lilin dan pepejal dapat memberi kesan terhadap kestabilan emulsi, tetapi tak sebesar asfaltin. Analisis faktor yang mengawal kestabilan emulsi dengan menggunakan *factorial design* menghasilkan model matematik yang dapat menunjukkan peranan pelbagai komponen dari minyak mentah dan interaksi mereka terhadap pembentukan dan kestabilan emulsi.

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LIST OF ABBREVIATION

A	Asphaltene
A^o	Amstrong
AAS	Atomic Absorption Spectrophotometry
API	American Petroleum Institute
b.s.w	Bottom, sediment, and water
C	Concentration, mg/l
^oC	^{o} Celcius
Cal	Calorie
CMC	Critical Micelle Concentration
cm	centimeter
Cn	Carbon number (n = 1,2.3,4,.....)
cP	Centi Poise
EDAX	Energy Dispersive X-Ray
^oF	^{o}Farenheit
FTIR	Fourier Transform Infra Red
g	Gram
ICPMS	Inductive Coupled Plasma-Mass Spectroscopy
K	Kelvin
Kg	Kilogram
m	Meter
meq/l	Milliequivalent per liter
mg	Milligram
mg/L	Milligram per liter
mmN/m	Milli-Newton per meter
ng	nanogram
O/W	Oil-in-water emulsion

O/W/O	Oil-in-water-in-oil emulsion
ppm	Parts per million
R	Resin
rpm	Rotation per minutes
RSM	Response Surface Methodology
S	Solid particles
SARA	Saturates Aromatic Resin Asphaltene
UNITAR	United Nations Institute of Research
W	Wax
W	Weight
W/O	Water-in-oil emulsion
W/O/W	Water-in-oil-in-water emulsion
w/w	Weight per weight
WSp	Water separation

LIST OF NOMENCLATURE

A	Interfacial surface area of droplet, m^2
G	Intensive Gibbs Energy, kJ/mole
n	Constant
k	Richardson constant
R	Radius of sphere, cm
P_L	Laplace pressure, dyne
T	Temperature, °C or K
ΔS	Change in entropy, cal/mole

Greek Symbols

ϕ	Dispersed phase volume fraction
γ	Interfacial tension, mN/m
η	Intrinsic viscosity, cP
π	Interfacial pressure, mN/m
ρ	Liquid density, kg/m^3

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CHAPTER 1

INTRODUCTION

1.1 Background

Crude oil production in Malaysia has been stable in recent years, with monthly production rate from 1996 to the early of 2002, fluctuated between 650,000 to 730,000 barrels per day (bbl/d) [EIA, 2002]. Malaysia's domestic oil productions produced primarily from the offshore of Peninsula Malaysia, while some are produced in the fields of East Malaysia such as Kinabalu field.

Most of Malaysia's oil contains low sulphur and high quality crude with petroleum gravity in the range of 35 – 45 °API [Petronas, 2004]. However, the Malaysia petroleum industries are still having several emulsion problems in demulsifying the crude oil emulsion [Sim, 1999]. Particularly, the emulsion problems can be encountered at the early stages of the offshore production of crude oil. It raises two consequences; first, it leads to shut down of the oil wells to prevent the b.s.w (bottom, sediment, and water) level from going higher. Second, the crude oil has to be sold in the form of low price oil because of the difficulties and high cost of treating the emulsion [Sim, 1999].

Emulsions may be encountered in all stages in petroleum recovery and processing industry (drilling fluid, production, process plant, and transportation emulsions). Generally, the reservoir contains gas, oil, and water within a porous matrix and it is retained by a geological trap such as an impermeable anticline The

presence of water, which always be produced with crude oil, could be coming from the original reservoir saturation or due to a variety of circumstance such as well bored position, reservoir permeability, reservoir depleting or aging, injection of water or steam beneath the crude oil zone as mean of secondary oil recovery. Initially, water and oil phases present as independent phases. Shearing force in the well and across control valves cause intense mixing of the fluids and forming water-in-crude oil emulsion [McMahon, 1992]. The emulsion is undesirable since the volume of dispersed water occupies space in the processing equipments and increases the overall viscosity of the oil phase. Furthermore, because it is highly saline (in some cases it might be approaching saturation, which salinity is over than 35,000 ppm [Collins, 1975]), it variably leads to cause and extend corrosion problems. As was reported by Taylor [1992], an equivalent volume of water accompanied the daily productions of some 60 million barrels of crude oil. Presently, the numbers of crude oil field co-producing water with crude oil in emulsion form is steadily increasing [Taylor, 1992; Ooi *et al.*, 1997]..

Understanding of the chemistry involved in the stabilization of water-in-crude oil emulsion is important for both economic and environmental reasons. In economical aspect, the separation of the crude oil emulsion is necessary. The water presence is unwanted since it has high concentration of chloride salt, which causes some difficulties (i.e. refining difficulties) such as corrosion, coke deposition, forming, and poisoning of downstream refinery catalyst and transportation difficulties such as pipeline and tank corrosion, scaling, and fouling. Extra power consumption and additional equipments are needed because the undesirable water occupies space in the processing equipment, thus it causes increasing of viscosity of the processing fluid, volume of involving equipments, and expense pumping [Clark *et al.*; 1993, Li *et al.*, 1992; McMahon, 1992]. Therefore, a premium is placed for treated oil and then, increasing API-degree through elimination of water usually causes a higher price for the oil.

The environmental aspect of the problems is emulsion formation during oceanic oil spills. Mixing energies from the action of wind and wave induce turbulence and lead to emulsification of the oil spill in the seas. When emulsions are formed, the properties and characteristics of oil spills are changing significantly

[Fingas *et al*, 2002]. As for environmental reason, pollution after oil spillage could be reduced if effective clean-up technique was developed. Past incidents have shown that the water-in- oil emulsions are responsible to make the effective clean up of the oil spillage more difficult [Yan *et al.*, 1996; Li *et al.*, 1992].

Crude oil emulsion system under surfactant effect composes complicated associated phenomena that cannot be treated as a subsystem. Surfactant effects create impulsive colloid repulsion imposing an energy barrier, which delay the formation of flocks almost definitely, thereby leading to kinetic stability condition [Rosen, 1978, CPS, 2004]. On the other hand, this kinetically stable system due to the imposed effect from the surfactant is at unstable thermodynamic condition that is out of the role of surfactant. Entropy and internal energy in the system are in values, which cannot be assumed that this system is thermodynamically stable. Therefore, the emulsions are to be said thermodynamically unstable and are frequently kinetically stable. The emulsion will finally separate into two clear liquids if it is left for enough time. However, in some cases, emulsion break-up can take very long time (even years) [Schramm, 1992]. In these cases, the emulsion is called stable.

Stability is a desired property for some emulsions. In other case, stability is undesirable, for examples, emulsions of waste oil in wastewater, as well as, water in crude oil emulsions occurring during oil production. Thus, in crude oil production industry, demulsification or destabilization treatment is necessary to speed up the phase of separation process in order to obtain high purity of crude oil [Cavallo *et al.*, 1990]. In fact, a lot of fundamental questions concerning stability mechanism and destabilization process still need further study. Many studies have been extensively undertaken to solve those two questions [Johansen *et al.*, 1989; Clark and Pilehvari, 1993; Ese *et al.*, 1997; Khadim and Sarbar, 1999; Ali and Alqam, 2000; Gafonova, 2000; Aske, 2002; Gu *et al.*, 2002]. The previous studies have established that there are many factors that could affect formation of stable emulsion, such as salinity of formation water, concentration of paraffinic compound in the crude oil, wax of fine particle content, the effect of surface-active component (asphaltene and resin), the effect of solid particles, fine dispersed droplet size, and others. It was recognized that concentration of asphaltene of crude oil has very important role in emulsion stability. However, the exact reasons, which contribute mostly to the formation of

stable emulsion in those particular fields, are only fully understood. In order to solve the emulsion problems, the understanding of this emulsion system is important.

The formation and stability of emulsion have been an interesting study due to the emulsion problems encountered. Most previous study dealt with standard international of crude oils. Less attention has been paid to Malaysian crude oils and their characteristics involving emulsion. From this point of view, it is important to study Malaysian crude oil in order to have complete information on their properties and emulsion characteristics. Another important factor is the solid particles found in asphaltene. No literature of the authors has dealt with this issue lending to a lack of information regarding the effect of solid particles isolated from asphaltene on emulsion behaviour. This causes a delay in the progress of understanding of some aspects in crude oil emulsion. In addition, interaction between different components of crude oil holds a considerable role in understanding the emulsion mechanism. For engineering application, it is a matter of induce to deal with emulsion using mathematical models based on experimental data that can widen the usage and analysis of different systems. It is, however, required specifically for Malaysian crude oils since such mathematical representations are lack in literature. From those points, this study, therefore, tries to answer the following question: What are the characteristics of Malaysian crude oil emulsion that affect on emulsion formation and stability.

1.2 Objectives and Scopes of Works

The objectives of this research are:

a. To study the characteristics of some selected Malaysian crude oil emulsions in order to provide valuable information to solve the emulsion problems.
   This was achieving by analyzing some important properties of selected Malaysian crude oils and oilfield brines, such as ^{o}API, viscosity, pour point, wax appearance, chemical composition of crude oils, and chemical analysis

of crude oil components (functional groups and elemental analysis). These will lead to predict the degree of stability of crude oil emulsion samples.

b. To study the formation and stability of Malaysian crude oil emulsion samples, which includes to study:
    i. The effect of temperature, asphaltene content, pH, and salinity of aqueous phase on the formation and stability of crude oil emulsions;
    ii. The effect of crude oil components such as asphaltene, resin, wax, and solid particles on the formation and stability of water-in-oil emulsion as single component and mixed components;
    iii. Factors (fractions) controlling the emulsion stability using factorial design.

1.3 Thesis Outline

This thesis is organized into five chapters. Chapter 1 presents general information regarding the background, objectives, and scopes of this research.

Chapter 2 discusses a general topic on the subject of water-in-crude oil emulsion. The first section of this chapter deliberates about the basic emulsion principles with a main focus on controlling factors of the stability of emulsion. Then, it is followed by a section describing characterization of the asphaltenes, resins, waxes and solid particles as components of crude oil, with the main focus on the mechanism of their association and surface-active properties. The next section provides a description of the conducted research in the area of crude oil emulsion.

Material and experimental procedures, which are used to achieve the objectives of this research, are presented in Chapter 3. This includes separation of crude oil components such as asphalthenes, resins, waxes and solid particles; measurement of physical and chemical properties of crude oil, crude oil components and oilfield brine; preparation of model emulsion; and finally, emulsion stability test.

The main findings of this research are presented in Chapter 4, which summarizes the results obtained from the characterization of crude oil, components of crude oil (asphalthene, resin, waxes, and solid particles), and oilfield brine. The results from stability test for single component and mixture of varying concentration of asphalthenes, resins, waxes and solid particles are presented in this chapter. Comparative study of model emulsion and crude oil emulsion is presented as well. The effect of interaction between the components and the emulsion stability, which is analysed using Response Surface Methodology (RSM), is reported in this chapter.

Finally, Chapter 5 summarizes the findings of the study followed by recommendations for additional research required for further characterizing of stability mechanisms of water-in-crude oil emulsion.

1.4 Summary

Crude oil emulsions, which are encountered in the petroleum production industry, are undesirable as they cause several problems. Therefore, the study of factor(s), which affects the formation and stability crude oil emulsion and the effects of interfacially active fractions to the emulsion stability, serves as prerequisites results for solving the emulsion problems. After understanding the factors that cause certain oil fields have more stable emulsion compare to the other fields, specific designs or technique can be developed or selected to prevent or demulsify these stable crude oil emulsions. Furthermore, the data of physical and chemical properties of the reservoir can be used to develop correlation to predict the future of emulsion crude oil wells.

carbonyl and pyrolle, and aromaticity in crude oil and crude oil components, in order to give a clearer illustration of their effect on formation and stability of emulsion. In addition, analysis of acidic, basic and amphoteric contents of fractions is suggested to obtain a complete picture of crude oil components characterization.

ii. Molecular weight of crude oil and its components is recommended to be analyzed in sequence to obtain their correlation with the functional groups and aromaticity which then, can be used to study their effect on emulsion stability.

iii. Instead of using bottle test to asses the emulsion stability, more details study to include the water concentration profile (hold-up) and sedimenting and coalescing interface behaviour studies are suggested.

iv. To understand the role of each crude oil components on the emulsion formation and stability, it is proposed to measure the compositional of the interfacial film formed by the components (asphaltene, resin, wax and solid particles), followed by the determination of the surface active compounds per area of water-oil emulsion interface. These data may provide information in what form of asphaltene, resin, wax or solid particles adsorbed on the interface.

v. The comparison study of emulsion stability at different oil compositions is suggested since it is another good tool for understanding of each component role on emulsion stability.

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