STABILITY AND CHEMICAL DEMULSIFICATION OF WATER-IN-CRUDE OIL EMULSIONS (CHEMICAL METHOD)

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ABSTRACT

The formation of water-in-crude oil (W/O) emulsion can be encountered at many stages during drilling, producing, transporting and processing of crude oils. A good understanding of petroleum emulsions is necessary for the intention to control and enhance the processes in all these stages. In this study, both chemical and physicochemical properties of W/O emulsions that prepared by using cocamide DEA (non-ionic and biodegradable surfactant that synthesized from coconut oil) and three types of conventional chemical emulsifiers (span 83, SDDS, triton X-100) were investigated. 50-50% W/O emulsions were prepared at 800rpm (mixing speed) with three different concentrations of each emulsifier. These emulsions were tested for relative rates of water separation (stability test), viscosity, shear stress, and shear rate at varied temperature and stirring speed of Brookfield viscometer. Results shown that span 83 and cocamide DEA were both effective. For chemical demulsification, demulsifiers with different concentrations were used to treat 50-50 and 20-80% W/O emulsions prepared at varied mixing speed. The relative rates of water separation were characterized via beaker tests. Coco amine and palm-based oleyl amine (synthesized from coconut oil and palm oil) were concluded to promote the best coalescence of droplets in compared with others conventional demulsifiers: hexylamine, PEG 600, and propylene glycol.

Key words: Demulsification, w/o emulsion stabilization, biodegradable, cocamide DEA, coco amine

ABSTRAK

Emulsi air dalam minyak berlaku di banyak tahap pengeluran dan perawatan minyak mentah. Pemahaman tentang kestabilan emulsi yang kukuh adalah penting untuk proses pengawalan. Dalam kajian ini, sifat-sifat fizikal emulsi akan disiasat dengan Brookfield viscometer. Jenis bahan kimia yang digunakan adalah cocamide DEA, span 83, SDDS dan Triton X-100. Cocamide dibuat daripada minyak kelapa dan dianggap sebagai bahan kimia semula jadi yang selamat diguna.

Demulsifikasi adalah pemisahan air dari minyak mentah. Ini adalah penting untuk memaksimumkan kualiti minyak dan juga meminimumkan kos operasi. Jenis bahan kimia yang digunakan adalah coco amine, palm-based amine, hexylamine, PEG 600 dan propylene glycol. Coco amine yang dibuat daripada minyak kelapa dan palm-based oleyl amine yang dibuat daripada minyak kelapa sawit adalah bahan kimia semula jadi.

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O/W	Oil-in-Water emulsion
W/O	Water-in-Oil emulsion
O/W/O	Oil-in-Water-in-Oil emulsion
W/O/W	Water-in-Oil-in-Water emulsion
MSDS	Material Safety Data Sheets
Cocamide DEA	Cocamide diethanolamine
Span 83	Sodium dodecyl sulphates
SDDS	Sorbitan sesquioleate
Triton X-100	Octylphenolpoly (ethyleneglycolether)$_x$
PEG 600	Polyethylene glycol 600
PG	Propylene glycol

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The formation of water-in-crude oil (W/O) emulsion can be encountered at many stages during drilling, producing, transporting and processing of crude oils. Therefore, a good understanding of petroleum emulsions is necessary for the sake of controlling and enhancing processes at all these stages.

Emulsions behavior is mainly controlled by the properties of the adsorbed layers that stabilise the oil-water surfaces. The complexity of petroleum emulsions comes from the oil composition in terms of surface-active molecules contained in the crude, such as low molecular weight fatty acids, naphthenic acids and asphaltenes. These molecules cover a large range of chemical structures, molecular weights, and HLB (Hydrophilic-Lypophilic Balance) values and able to interact between themselves and/or reorganise at the water/oil interface (Langevin e*t al*., 2004).

According to Bancroft (1913), the stability of any emulsion is largely due to the nature of the interfacial film that is formed. The stability of this film is strongly dependent upon the surfactant adsorption-desorption kinetics, solubility, and interfacial rheological properties such as elasticity, interfacial tension gradient, and interfacial viscosity.

Emulsion is undesirable due to the occupation of the dispersed water in the processing equipments and pipelines that increases the operating and capital cost. Furthermore, the chemical and physicochemical properties of oil change considerably upon emulsification. The density of the emulsion can increases from 800 kg/ m^3 for the original oil to 1030 kg/ m^3 for the emulsion. The drastic change of viscosity will be observed, which typically increases from a few mPa•s or less to about 1000 mPa•s (Fingas, *et al*., 1993).

Demulsification (emulsion breaking) is needed in many practical applications such as petroleum industry, environment technology, and waste-water treatment. Demulsification is the process of separation of water from crude oil. Crude oil need to be separated efficiently and quickly from the water to allow further treatment for example refinery so that the crude oil value can be maximised and the operating cost can be minimised.

Currently, water-crude oil emulsions are typically destabilized through the use of chemical demulsifiers. The chemical structure of these demulsifiers is usually based on alkylphenol formaldehyde ethoxylated resins. These chemical demulsifiers are effective, but, unfortunately, these chemicals are now believed to be endocrine disrupters, and thus it is likely that they may be banned by various national environmental protection agencies (Zaki, *et al*., 1996, 1997, 1998).

Other means of destabilizing asphaltene-stabilized W/O emulsions include thermal pressurization and rapid depressurization (Ohsol *et al*., 1999), electrostatic droplet shattering and coalescence. Both of these methods are established around efforts at “cracking” or “disrupting” the rigid, viscoelastic film of asphaltenes that forms around the water droplets. One problem with these methods is the reforming of stabilized water droplets due to readsorption of displaced or “disrupted” asphaltenic film fragments in shear fields under solvent conditions at which the asphaltenes are capable of reassembly (Hart, 1997; Mitchell, 1998).

This research is conducted to gain a better understanding of stabilization of emulsion by using not only conventional but biodegradable emulsifier that synthesized from coconut oil (natural resources): cocamide DEA. At the end of this research, a generic but efficient and sustainable W/O separation method is developed. In this regards, demulsifiers that extracted from natural resources were used to treat water-in-crude oil emulsion: coco amine from coconut oil and palm-based oleyl amine from palm oil.

1.2 Problem Statement

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

Since the viscosity of an emulsion is always larger than the viscosity of the continuous phase, emulsion with water as the continuous phase (oil-in-water (O/W) emulsion) is necessary for transporting of highly viscous heavy oil (Ahmed *et al.,* 1999). Therefore, the inversion of emulsion and the stability of the o/w emulsion are both essential for the transportation.

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

On the other hand, crude oil need to be separated efficiently and quickly from the water to allow further treatment for example refinery so that the crude oil value can be maximised and the operating cost can be minimised.

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Although, countless of studies have been carried out on oil-water emulsions in the past few decades, but the general theory for both the emulsification and demulsification is yet to be elucidated.

1.3 Objective

First part of this research is conducted to gain a better understanding of stabilization of emulsion by using not only conventional but biodegradable emulsifier that synthesized from coconut oil: cocamide DEA.

Second part of this research is to develop a generic but efficient and sustainable W/O separation method by using chemical demulsifiers that are less hazardous: coco amine synthesized from coconut oil and palm-based oleyl amine synthesized from palm oil.

Finally, the main aim of this study is to put an effort to achieve a “green technology” by using chemical emulsifiers and demulsifiers that are synthesized from natural resources, so it would be more environmental friendly.

1.4 Scope of Research

Characterization of oil and aqueous phases:

a. Model oil phases for the emulsions will be prepared and characterized with respect to (i) hydrogen chain distribution (ii) surfactant type and concentration (iii) viscosity and temperature dependence, using viscometer and Brookfield.

b. The physicochemical and chemical parameters affecting the stability of W/O emulsions:
This aim will achieved by characterizing the crude oil samples, furthermore, a correlation between the crude oil characteristics and the crude oil emulsions stability is addressed to investigate effect of the parameters.

c. Preparation of model emulsions and their characterization:
W/O (for crude oil application) will be prepared.

d. Determination of mechanism of demulsification:
Initially this will be carried out by using the existing intensive demulsifiers, concentration of the surfactants.

1.5 Rationale and Significance

Currently, water-crude-oil emulsions are typically destabilized through the use of chemical demulsifiers. The chemical structure of these demulsifiers is usually based on alkylphenol formaldehyde ethoxylated resins. These chemical demulsifiers are effective, but, unfortunately, these chemicals are now believed to be endocrine disrupters, and thus it is likely that they may be banned by various national environmental protection agencies (Zaki *et al*., 1996, 1997, 1998).

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CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The formation of water-in-crude oil emulsion can be encountered at many stages during drilling, producing, transporting and processing of crude oils. Water and oil can mix while rising through the well and when passing through valves and pumps to form in most cases relatively stable dispersions of water droplets in crude oil, which are usually referred to as oil field emulsions (Abdurahman *et al.,* 2007). Therefore, a good understanding of petroleum emulsions is necessary for the sake of controlling and enhancing processes at all these stages.

Demulsification (emulsion breaking) is needed in many practical applications such as petroleum industry, environment technology, and waste-water treatment. Demulsification is the process of separation of water from crude oil. Crude oil need to be separated efficiently and quickly from the water to allow further treatment for example refinery so that the crude oil value can be maximised and the operating cost can be minimised.

Chemical demulsification is the most widely used method currently and in the past few decades. The chemical structure of these demulsifiers is usually based on alkylphenol formaldehyde ethoxylated resins. These chemical demulsifiers are effective, but, unfortunately, these chemicals are now believed to be endocrine disrupters, and thus it is likely that they may be banned by various national environmental protection agencies (Zaki *et al*., 1996, 1997, 1998).

2.2 Emulsion

Emulsions are oil-water mixtures stabilised by surfactant, consisting of either oil droplets dispersed in water (oil-in-water or O/W) or water droplets dispersed in oil (water-in-oil or W/O). Emulsions are metastable, so that the average droplet size in an emulsion tends to increase with time (Lissant, 1974).

Besides, there are also exist double emulsions such as oil-in-water-in-oil (O/W/O) and water-in-oil-in-water (W/O/W). For example, O/W/O denotes a double emulsion, containing oil droplets dispersed in aqueous droplets that are in turn dispersed in a continuous oil phase. The double emulsion droplets can be quite large (tens of μm) and can contain many tens of droplets of the ultimate internal phase (Laurier, 2005).

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

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

2.2.1 Macroemulsions

Macroemulsions are defined as that, at least one immiscible liquid dispersed in another as drops whose diameters generally exceed 100 nm. The stability is improved by the addition of surfactants and/or finely divided solids. It is considered only kinetically stable.

2.2.2 Miniemulsions

Miniemulsions are emulsions that the diameters of droplets are between 100 and 1000 nm and reportedly thermodynamically stable.

2.2.3 Microemulsions

Microemulsion is a transparent solution of micelles swollen with solubilizate and is thermodynamically stable. Microemulsions usually require the presence of both a surfactant and a cosurfactant which is short chain alcohol.

2.2.4 O/W Emulsion

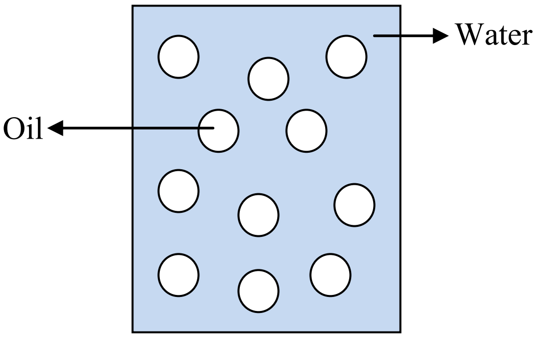

Figure 2. 1: Oil-in-Water (O/W)

The simplest kinds of emulsions, consisting of oil droplets dispersed in water. By means of optimising the efficiency of the transporting process and minimising the operating cost, emulsion with water as the continuous phase which is O/W emulsion is necessary for the transporting of highly viscous heavy oil. This is also because the viscosity of an emulsion is always larger than the viscosity of the continuous phase (Ahmed *et al.,* 1999).

2.2.5 W/O Emulsion

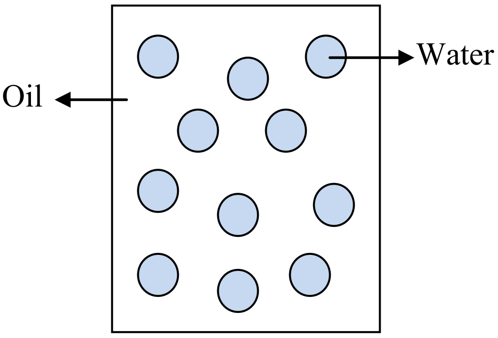

Figure 2. 2: Water-in-Oil (W/O)

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

2.3 Emulsification

Emulsification is a process to create emulsion. About 100 years ago, Bancroft proposed that when oil, water and surfactant are mixed, the continuous phase of the emulsion that forms is the phase where the surfactant is more soluble to.

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

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

2.4 Stability of the Emulsion

Emulsions behavior is mainly controlled by the properties of the adsorbed layers that stabilise the oil-water surfaces. The complexity of petroleum emulsions comes from the oil composition in terms of surface-active molecules contained in the crude, such as low molecular weight fatty acids, naphthenic acids and asphaltenes. These molecules cover a large range of chemical structures, molecular weights, and HLB (Hydrophilic-Lypophilic Balance) values and able to interact between themselves and/or reorganise at the water/oil interface (Langevin *et al*., 2004).

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

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

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

Resins solubilise asphaltenes in crude oil, and remove them from the interface, therefore lowering the stability. Waxes coadsorb at the interface and enhance the stability. Naphthenic and other naturally occurring fatty acids also do not seem able to stabilise emulsions alone. However, they are probably partly responsible for the important dependence of emulsion stability upon water pH.

Particles such as silica, clay, iron oxides, etc, can be present in crude oils. These particles are naturally hydrophilic, but can become oil-wet (hydrophobic) due to long-term exposure to the crude in the absence of water. A decrease in the size of oil-wet particle results in an increase in W/O emulsion stability. Pickering emulsion which is a kind of emulsion that involved with particles and asphaltenes combined can be much more stable that those stabilised by asphaltenes alone, provided that enough asphaltenes are present: all the adsorption sites on the particle surface need to be saturated by asphaltenes.

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

2.5 Demulsification (breaking emulsion)

Demulsification is a process to break the emulsion or in other words, it is a process to destabilise the emulsion formed. Methods presently available for demulsification can be generally classified as chemical, mechanical and electrical.

Before discuss in detailed about the methods of demulsifications, one must know that emulsions are thermodynamically unstable and will eventually phase separate. This occurs via a combination of physical mechanisms; the droplets will eventually coalesce, they can group together without coalescing (flocculate) as a result of attractive forces between the droplets, smaller droplets will preferentially dissolve and larger droplets will grow in a process known as Ostwald ripening and they will sediment if there is an appreciable difference in density between the two constituent phases (Johns * *et al.*, 2007).

Langevin *et al.* (2004) classified the mechanisms that leading to emulsion destabilisation as Ostwald Ripening, Sendimentation or Creaming, Coalescence (spontaneous), and Coalescence under stress.