

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

There are three main methods for separation water-in-oil emulsion; electrical mechanical and chemical methods.

2.1 Electrical Method

Chih-Chieh and Yeong-Ching (2002) proposed that demulsification is an indispensable step in the application of emulsion liquid membrane (ELM) separation process. From their work, a novel microwave demulsification method is first applied in the ELM system to study the phenomenon of breaking water-in-oil (W/O) emulsion. The mechanism of microwave heating is essentially that of dielectric heating. After exposing the emulsion to the microwave electromagnetic (EM) field, molecular rotation, and ionic conduction due to the penetration of EM into the emulsion are responsible for the internal heating. So the application of microwave radiation results in the acceleration of separation emulsion. The effects of emulsion conditions and microwave operating conditions on the demulsification rate and the separation efficiency of W/O emulsion were systematically studied. The results showed that both demulsification rate and separation efficiency increased with increase in droplet size, concentrations of the carrier di(2-ethylhexyl)phosphoric acid (D2EHPA) and acid. However, they decreased with the increase in surfactant (Span 80) concentration and the oil phase-to-aqueous phase volume ratio (O/A). As for the effect of electrolyte concentration, it exhibited a peculiar maximum phenomenon. Both the demulsification rate and the separation efficiency were maximum when the concentration of electrolyte was about 0.5 M. The optimum microwave irradiation power and exposure time were suggested to be 420 W and 12 sec, respectively. Harpur *et al.* (1997) proposed the influence of a 50Hz sinusoidal electric field on flowing water-in-oil emulsions. A horizontal rectangular duct was used, with emulsion flowing through at flow rates up to 100 litre/min, giving Reynolds numbers (Re) in the range of 1000 to 12,000. Electrocoalescer performance was assessed by

measuring water droplet growth, using a specially developed technique with a laser diffraction particle sizer. Under conditions of high water-cut, electrocoalescence can be so efficient that free-water drop-out may occur, even in conditions of turbulent flow. This can lead to the formation of a layer of water co-flowing with the depleted emulsion in the duct. Study of the electrocoalescer behavior under these conditions has been carried out by image analysis using a Hamamatsu Image Processor.

2.2 Mechanical Method

Dezhi *et al.* (1999) using wetting coalescence materials to coagulated water droplets with each other together and become bigger droplets. Demulsification tests were carried out using conventional stirred- and packed-columns. From the four kinds of natural fibers and two kinds of inorganic materials tested, natural fiber A, selected from shaves of a wood showed the best performance in demulsification. The demulsification efficiency can exceed 97% when demulsification conditions are optimized. The packed-column showed much better performance both in terms of demulsification efficiency and repeated use of the recovered oil phase for extracting cadmium in simulated wastewater. Operating variables that govern the demulsification efficiency were investigated.

2.3 Chemical Method

The coexistence of crude oil and water results in emulsions. Emulsions are thermodynamically unstable. Natural surfactants are solids that stabilize such emulsions. Schorling *et al.* (1999) have studied the nature of these stabilizers. Asphaltene compound was found to be one of the main factors contributing to the stability of crude oil well emulsion. Some authors have also suggested that waxes (alkanes of high molecular weight) can enhance the stabilization in combination with asphaltenes. Asphaltenes are condensed aromatic rings containing saturated carbon chains and naphthenic rings as substituents, along with heteroatoms and metals. Asphaltenes are capable of crosslinking at the water-oil interface, preventing water droplet to coalesce. In other words, asphaltenes act as surface active agent. Although

these water-oil emulsions are thermodynamically unstable macroemulsion, they are nevertheless very resistant to coalescence and show a high dynamical stability sometimes over year.

Some authors suggested that there are four important actions required of a demulsifier; strong attraction to the oil-water interface, flocculation, coalescence, solid wetting.

A demulsifier should have strong attraction to the interface (good surfactant properties) and migrate rapidly through the continuous phase to reach the droplet interface. After concentrating at the oil/water interface, the demulsifier counteracts the emulsifying agent and promotes the formation of flocs or aggregates of the dispersed phase. In the flocculated system the emulsifier film is still continuous so the demulsifier must neutralize the emulsifier and facilitate the rupture of the droplet interface film, resulting in coalescence. Ideally this happens rapidly resulting in the separation of the oil and water phase. Additional of iron sulfides, clays, and drilling mud, they can be made water wet, causing emulsifier to leave the interface and be diffused into the water droplets or they can be made oil-wet so that they can be dispersed in the oil. Paraffins and asphaltenes can be dissolved by the demulsifier to make their films less viscous, or crystallization and precipitation can be prevented. It would be unusual if one chemical structure could produce all four desirable actions. A blend of compounds is therefore used to achieve the right balance of activity.

Since demulsification is a process for disrupting the oil/water emulsions, there are several techniques for improving the separation of crude oil emulsion, such as the addition of chemical demulsifier, pH adjustment, filtration, heat treatment and electrostatic demulsification, microemulsion, microwaves, and wetting coalescence materials. Among them, chemical demulsification using demulsifiers is in common use in oilfield. The demulsification ability of demulsifier is mainly controlled by two factors: one is the hydrophilic-hydrophobic ability, which has been studied by Jana *et al.* (2002) The hydrophile-lipophile balance (HLB) values were proposed for three commercial demulsifiers and found to change depending on the delivery medium, from HLB value 12.1 if the demulsifier was dissolved in naphtha to HLB value of 7.1 if the demulsifier was dissolved in water. This difference in apparent HLB may

arise from differences in interfacially active components in the diluent. It appears that demulsifier components delivered in naphtha and the water-soluble natural surfactants will seek to form O/W emulsions and, therefore, act to destabilize the W/O froth emulsions. Conversely, demulsifier components delivered in water and naturally occurring asphaltenes will act to stabilize the W/O froth emulsions; the other is the ability to destroy the interfacial film. Most demulsifiers is alkoxyate polymers that are mainly ethoxylated and propoxylated and sometimes both. They are macromolecules held in chains, industrial synthesized from petroleum chemicals. Commercial products are obtained by reaction of ethylene oxide with hydroprobe having an active hydrogen group in the presence of suitable catalyst. The polymers most employed in the demulsification industry are surfactants that exhibit both hydrophilic and hydrophobic groups. Commercial polymer formulations are diluted in solvents. The actions of solvents that are dissolved with the polymer do not induce a chemical change in the polymer. Aromatics such as benzene, toluene or xylene can help breaking emulsion by dissolving resin/asphaltenes to the oil phase. The emulsion breakers are typically specific for site or crude-oil type, which implies that a certain emulsion breakers that, has worked for oil A does not necessarily mean that it will equally work for crude B type. For instance, Alejandro *et al.* (2005) studied the effect of systematic changes in the structure of chemicals commonly used in demulsification operations (alkylphenol polyalkoxylated resins and polyurethane) on the stability and properties of brine-in-crude oil emulsions was assessed experimentally. Optimum performance was obtained with resins exhibiting intermediate hydrophilicity in a manner consistent with the condition of least emulsion stability for conventional oil-water-surfactant systems. In contrast, polyurethane promoted flocculation but only slow coalescence. The performance of polyurethane improved with increase of molecular weight. Phenolic resins and polyurethane acted synergistically when added simultaneously, rendering water separation rates significantly higher than those observed when they were used individually. Polyurethane aided sedimentation of water at moderate concentrations by "bridging" nearby droplets, but they retarded coalescence when added at significantly higher concentrations, even when phenolic resins were present.

The way to test the appropriate demulsifier for water-in-oil emulsion is carried out through the well known "bottle test" technique. Alexandre and Maurice (2000) suggested that a comprehensive approach based on earlier work on the rate of separation of surfactant-water-hydrocarbon mixtures, where it was found that "optimum" type III system in Windsor's nomenclature, exhibits the fastest separation rate. It is shown that the rules developed for microemulsion optimization can apply to the selection of demulsifier. They allow one to take into account the variation of salinity, temperature, and oil type and provide an explanation for the demulsifier concentration effect. Interfacial tension measurements have been carried out. The kinetic of demulsifier adsorption at the water-crude oil interface is found to correlate to phase separation rate: the higher the kinetics, the faster the separation rate.

Young and Darsh (1996) studied the factors affecting the demulsification and interfacial behavior of water-in-oil emulsions in the presence of oil-soluble demulsifiers. His experimental results were compared and related with the demulsifier performance. There is a one-to-one correlation between the performance of demulsifier and the interfacial activity of the partitioned demulsifier; the partitioned demulsifier components exhibit an increase in static and dynamic interfacial activity, low dynamic interfacial and film tension, and a low film dilational modulus with a high adsorption rate-low interfacial tension gradient (Marangoni-Gibbs stabilizing effect) and have excellent demulsification performance.

Jiangying *et al.* (2005) studied the effect of ethylene oxide (EO) and propylene oxide (PO) positions in nonionic surfactants on surfactant properties and demulsification performance. The properties and the performance of 20 blocked copolymers from four surfactant families were investigated and three pair isomeric compounds were compared. The results show that different positions of the ethylene oxide and propylene oxide in block copolymers lead to different HLB of surfactant. The sequential block copolymer is more hydrophilic than the reverse-sequential one with similar chemical composition. The greater the molecular weight, the greater the difference between the HLB of the two surfactant types. Generally, the demulsification performance of sequential copolymers is better than that of reverse-sequential copolymers. Position isomerism of the surfactant affects demulsification

performance by changing the HLB, interfacial properties, and steric characteristics at the interface.

Abdel-Azim *et al.* (2002) studied the effect of temperature, NaCl concentration (salinity), pH-value, and solvents on the demulsification efficiency of poly (ethylene terephthalate) waste in breaking synthetic water-in-benzene emulsions stabilized by petroleum asphaltenes. The demulsification efficiency increased when temperature was increased and the salinity of the liquid phase was decreased. The neutral pH-value of the liquid phase gives the optimum value so that it means the maximum demulsification efficiency. Water and 1, 2 propylene glycol were found to be the best solvents for the prepared demulsifiers. Demulsifiers provide an important means of breaking water-in-oil emulsions that occur in industrial processes. Kokal (2005) also concluded the method to tackle crude oil emulsions. The author revealed that emulsion are destabilized by increasing temperature and residence time, removal of solids, and controlling demulsifiers condition. The optimum pH for demulsification is approximately 10 without demulsifier. An addition of demulsifiers enhances the crude-oil/brine system in term of water separation. The optimum pH was change from approximately 10 for distill water to between 6 and 7 in the brine solution. The studied suggested that for mostcrude-oil/brine systems, there exist an optimum pH range for which the interfacial film exhibited minimum emulsion stabilizing or maximum emulsion breaking properties.

Mason *et al.* (1995) studied the drop size and concentration profile determination in petroleum emulsion separation by using a polymeric surfactant demulsifier to destabilize stable emulsions of brine in crude oil and studied while they were mixing and settling. After emulsion preparation and aging, demulsifier was added and the drop growth was measured using photomicroscope. Phase separation was monitored using gamma-ray absorption. Aged emulsions exhibited less drop growth during mixing and slow separation: however, the age of an emulsion could not always be controlled. Increased demulsifier concentration and longer mixing time after demulsifier addition both lead to a larger final drop size and faster separation. Optimizing the mixing conditions under which demulsifier is added to an emulsion could reduce the separation time, although these conditions would be system-

specific. The drop size after demulsifier addition was an important indicator of subsequent emulsion separation behavior.