

CHAPTER II

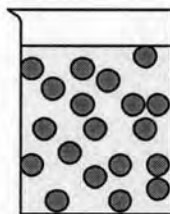
LITERATURE REVIEW



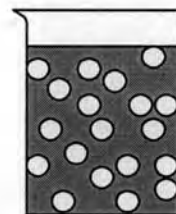
2.1 Definition and Classification of Emulsions

An emulsion is a dispersion of one liquid in another with which it is immiscible. The dispersed phase is sometimes referred to as the internal (disperse) phase and the continuous phase as the external phase. The particle sizes of the dispersed phase lie between a few hundred nanometers and a few tens of micrometers. Majority of emulsions, one of the liquids is aqueous and another is hydrocarbon and referred to as oil. Two types of emulsion are readily distinguished in principle, depending upon which kind of liquid forms the continuous phase. Figure 2.1 shows the various typed of emulsions.

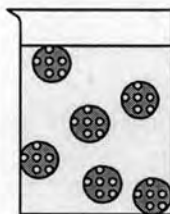
- Water – in – oil (W/O) emulsions. The W/O emulsions consist of water droplets in a continuous oil phase.
- Oil – in – Water (O/W) emulsions. The O/W emulsions consist of oil droplets in a continuous water phase.



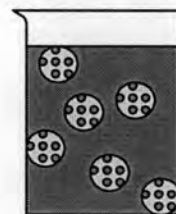
Oil-in-Water (O/W)



Water-in-Oil (W/O)



Water-in-Oil-in-Water
(W/O/W)



Oil-in-water-in-Oil
(O/W/O)

Figures 2.1 shows the various typed of emulsions: (Upper) the two simplest kinds of emulsions, oil-in-water (O/W) and water-in-oil (W/O). (Lower) the next level of complexity, water-in-oil-in-water (W/O/W) and oil-in-water-in-oil (O/W/O). The droplet sizes have been greatly exaggerated. (Schramm, 2005)

Practical situations are not always so simple and one may encounter double emulsions, that is, emulsions that are 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, continuous oil droplets dispersed in aqueous droplets that are in turn dispersed in a continuous oil phase.

Type of emulsion that is formed depends upon a number of factors. If the ratio of phase volumes is very small, it is frequently the dispersed phase. Most emulsions are not thermodynamically stable, but as a practical matter, quite stable emulsions can occur that resist demulsification treatments and may be stable for weeks/months/years. Most meta – stable emulsions that will be encountered in practice contain oil, water and an emulsifying agent (or stabilizer) which is usually a surfactant, a macromolecule, or finely divided solids. 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.

Emulsions may contain not just oil, water, and emulsifier (usually a surfactant), but also solid particles, and even gas. In the large Canadian oil sands mining and processing operations bitumen is separated from the sand matrix, in large tumbler slurry by a flotation process. The product of the flotation process is bituminous froth, an emulsion that may be either water (and air) dispersed in the oil (primary flotation). In either case, the emulsions must be broken and the water removed before the bitumen can be up graded to synthetic crude oil, but the presence of solid particles and film – forming components from the bitumen can make this very difficult.

2.1.1 Stability of Emulsions

Not all emulsions are equal in stability. There are several factors that contribute to the stability of an emulsion. Produced oilfield emulsions are classified on the basis of their degree of kinetic stability as follows.

- Loose emulsions. Those separated in a few minutes. The separated water is sometimes referred to as free water.
- Medium emulsions. Will separated in ten minutes or more.
- Tight emulsions. Will separated (sometimes only partially) in a matter of hours or even days.

Emulsions are considered special liquid – in – liquid colloidal dispersions. Their kinetic stability is a consequence of a small droplet size and the presence of an interfacial film around the water droplets. Emulsion kinetic stability is attained by stabilizing agents (or emulsifiers) that could be naturally occurring in the crude oil (asphaltenes, for example). These stabilizers suppress the mechanisms involved in emulsion breakdown.

1. Interfacial Films. As mentioned previously, produced oilfield emulsions are stabilized by films that form around the water droplets at the oil/water interface. These films are believed to result from the adsorption of high – molecular weight polar molecules that are interfacially active. These films enhance the stability of emulsion by (a) reducing interfacial tension (IFT) and (b) increasing the interfacial viscosity. Highly viscous interfacial films retard the rate of oil – film drainage during the coagulation of the water droplets by providing a mechanical barrier to coalescence. This can lead to a reduction in the rate of emulsion breakdown.

2. Rigid or Solid Films. These are like an insoluble skin on water droplets and are characterized by very – high interfacial viscosity. There is considerable evidence that these films are formed by polar fractions of the oil and other emulsifiers and may be further stabilized by fine solids. These films play a significant role in hampering the droplets – coalescence process. They provide a structural barrier to droplet coalescence and increase emulsion stability. These films also have viscoelastic properties.

3. Mobile or Liquid films. These films, as the name implies, are mobile and characterized by low interfacial viscosities. These are formed, for example, when a demulsifier is added to an emulsion. They are inherently less stable. Coalescence of water droplets is enhanced.

Stability of emulsions has been correlated with the mobility of interfacial films. Surfactants that modify the rigidity of the film can considerably speed up the demulsification process. This will be discussed further under the section “Demulsification of Emulsions”

2.1.2 Factors Affecting Stability

The important factors that effect emulsion stability include the following.

1. Heavy fraction in crude oil. It is now well recognized that the naturally occurring emulsifiers (or stabilizers) are concentrated in the higher – boiling point, polar fraction of the crude oil. These include asphaltenes, resins, and oil soluble organic acids and bases. These compounds are the main constituents of the interfacial films surrounding the water droplets that give the emulsions their stability.

While it is well established that the heavy asphaltenic material stabilizes oil – continuous emulsions, there is considerable debate on the precise mechanism of stabilization. The asphaltenes reside at the oil/water interface because of their surface – active properties. The accumulation of asphaltenes at the interface results in the formation of a rigid film. When such a film is formed, it acts as a barrier to droplet coalescence. For two drops to coalesce together, the film has to be drained and ruptured. The presence of the asphaltenes can naturally retard the drainage of the film.

The state of asphaltenes in the crude oil also has an effect on its emulsion – stabilizing properties. While asphaltenes will stabilize emulsions when they are present in a colloidal state (not yet flocculated), there is strong evidence that their emulsion – stabilizing properties are significantly enhanced when they are precipitated from the crude oil and are present in the solid phase.

2. Solids. Fine-solid particles present in the crude oil are capable of effectively stabilizing emulsions. The effectiveness of these solids in stabilizing emulsion depends on such factors as the particle size, interparticle interactions, and the wettability of the solids. Solid particles stabilize emulsions by diffusing to the oil/water interface where they form rigid structures (films) that can sterically inhibit the coalescence of emulsion droplets. Furthermore, solid particles at the interface may be charged, which may also enhance the stability of the emulsion. Particles must be much smaller than the size of the emulsion droplets to act as emulsion stabilizers. These particles typically range from smaller than 1 μm to several μm in size, and they are suspended colloidal in the liquids.

The wettability of solid particles plays an important role in the emulsion – stabilizing process. If the solid remains entirely in the oil or water phase, it will not be an emulsion stabilizer. It must be present at the interface and must be

wetted by both the oil and water phases for it to act as an emulsion stabilizer. The solid were preferentially oil – wet (more of the solid in the oil phase), then a W/O emulsion will result. Oil – wet particles will preferentially partition into the oil phase and will prevent the coalescence of water droplets by steric hindrance. Similarly, water-wet solids will stabilize a water – continuous or an O/W emulsion. Examples of oil – wet solids are asphaltenes and waxes.

When solids are wetted by both the oil and water (intermediate wettability), they agglomerate at the interface and retard droplet/droplet coalescence. The ease of formation and stability of emulsions has been linked to asphaltene content of the crude oil, and to the pH of the water phase.

On the basis of the experiments performed, it was shown that the effectiveness of colloidal particles in stabilizing emulsions depends largely on the formation of a “densely packed” layer of solid particles (film) at the oil/water interface. This film provides steric hindrance also changes the rheological properties of the interface that exhibits viscoelastic behavior. This affects the rate of film drainage between droplets and also affects the displacement of particles at the interface.

3. Temperature. Temperature can affect emulsion stability significantly. Temperature affects the physical properties of oil, water, interfacial films, and surfactant solubility in the oil and water phases. These, in turn, affect the stability of emulsion. Perhaps the most important effect of temperature is on the viscosity of emulsions, it decreases with increasing temperatures. This decrease is mainly caused by a decrease in the oil viscosity. When waxes are present (crude below its cloud point) and are the source of emulsion problems, application of heat can eliminate the emulsion problem completely by redissolving the waxes into the crude oil temperature increases the thermal energy of the droplets and hence, increases the frequency of droplet collisions. It also reduces the interfacial viscosity and results in a faster film – drainage rate and enhanced droplet coalescence.

4. Droplet Size. As mentioned previously, emulsion droplet sizes range from less than 1 μm to more than 50 μm . Generally, emulsions have a droplet size distribution rather than a fixed-droplet size. Generally, emulsions that have smaller – sized droplets will be more stable. For water separation, droplets have to coalesce, and the smaller the droplets, the longer it will take to separate. The droplet

size distribution affects emulsion viscosity-it is higher when droplets are smaller. Emulsion viscosity will also be higher when the droplet-size distribution is narrow.

5. pH. Water – phase pH has a strong influence on emulsion stability. The stabilizing, rigid – emulsion film contains organic acids and bases, asphaltenes with ionizable groups, and solids. Adding inorganic acids and bases strongly influence their ionization in the interfacial films and radically change the physical properties of the films. The pH of the water affects the rigidity of the interfacial films. PH also influences the type of emulsion formed. Low pH (acidic) generally produces W/O emulsions (corresponding to oil – wetting solid films), whereas, high pH (basic) produces O/W emulsion (corresponding to water – wetting mobile soap films). Optimum pH for demulsification is approximately 10, without demulsifier. An addition of a demulsifier enhances demulsification after one hour, and almost complete water separation is achieved after 24 hours, over a wide range of pH.

2.2 Mechanisms Involved in Demulsification

The emulsions are composed primarily of immiscible liquids. Separation should be the natural tendency of these liquid, providing a density differential between the liquid exists. How ever, the emulsion is stable with a given environment or emulsifying agent so, demulsification will occur when the given environments or emulsifying agent is neutralized. The rate of gravitational settling or rising is dependent on the surface tension of droplets that form the internal phase of the emulsion. Larger droplets have less surface tension as function of mass, so that increasing droplet size will increase the rate of separation.

Creaming

Due to the density differences between most edible oils and water, there is a tendency of the oil phase to concentrate at the top of the food emulsion. The rate of creaming can be lowered by reducing the droplet size, lowering the density difference between oil and the aqueous phase, and increasing the viscosity of the medium. In addition, the creaming rate is dependent on the volume fraction of the dispersed phase.



Inversion

Inversion refers to the process in which an emulsion suddenly changes form, from O/W to W/O or vice versa. The exact mechanism of inversion remains unclear, although obviously some processes of coalescence and dispersion are involved. In the region of the inversion point multiple emulsions may be encountered. The process is also not always exactly reversible. That is, hysteresis may occur if the inversion point is approached from different sides of the composition scale.

Flocculation

Flocculation is defined as a process by which two or more droplets aggregate without losing their individual identity. Bridging flocculation occurs in the presence of macromolecular emulsifying agents in an emulsion. Emulsion droplets flocculate through interaction of the adsorbed macromolecules between droplets. Bridging flocculation is a very complex phenomena and greatly depends on the size, type, amount of the macromolecules used in the system. In addition, rate of flocculation can be affected by the pH and ionic strength of the aqueous environment. Interactions among protein, polysaccharide, and water soluble surfactants can also affect the stability of the emulsion.

Coalescence

Coalescence is the process when two or more droplets collide to each other and results in the formation of one larger droplet. Coalescence involves breaking the interfacial film and is irreversible. At extreme, a planar interface exists between the homogeneous lipid phase and the homogeneous aqueous phase. Various factors, such as solubility of the emulsifier, pH, salts, emulsifier concentration, phase – volume ratio, temperature, and properties of the film, affect coalescence stability of emulsion.

In the destabilization, such a two-phase emulsion (Fig. 2.2) goes through several consecutive and parallel steps before the final stage of separated layers is reached.

As a first step, the droplets move due to diffusion of stirring, and if the repulsion potential is too weak, they become aggregated to each other; flocculation has taken place. The single droplets are now replaced by twins (or multiples) separated by a thin film. This step is important because the destabilizations process now passes from the realm of particles in random motion in a medium to describe the

phenomena in a thin liquid film of colloidal dimensions. Then thickness of the thin film is reduced due to the van der Waals attraction, and when a critical value of its dimension is reached, the film bursts and the two droplets unite to a single droplet. Coalescence has occurred.

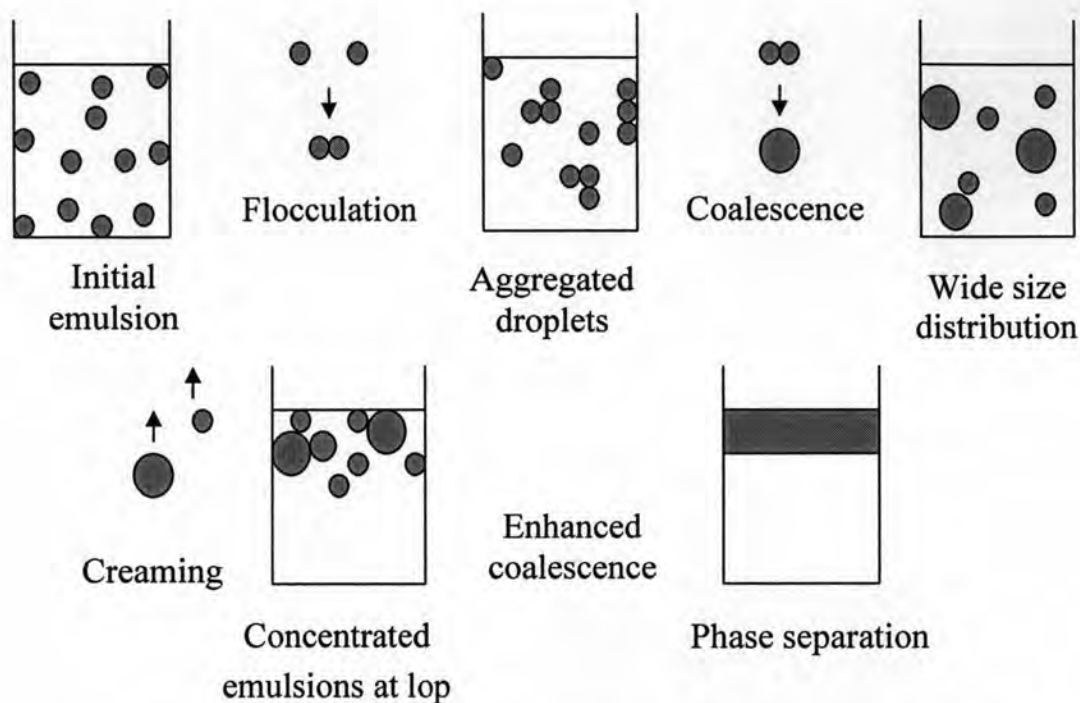


Figure 2.2 The destabilization of an emulsion passes through several stages; flocculation, coalescence and creaming before the final phase separation occur. (Sjoblom, 1996)

In parallel with these phenomena, the droplets rise through the medium (creaming) or sink to the bottom (sedimentation) due to differences in density of the dispersed and continuous phase. This process is enhanced by the fact that larger droplets or aggregates move faster through the medium; in dilute suspensions, the velocity is proportional to the square of the radius. As a consequence, larger droplets pass the smaller ones, causing sedimentation – induced flocculation. The final result is highly concentrated emulsion at the top or bottom of the container and the increased number of droplets per volume increases the flocculation rate in a most decisive manner. The flocculation and coalescence processes lead to larger and larger droplet until finally, a phase separation has occurred.

2.3 Demulsification Methods

In the oil industry, emulsion must be separated almost completely before the oil be transported and processed further. Emulsion separation into oil and water necessarily involves the destabilization of emulsifying films around water droplets. This process is an accomplished by anyone or a combination of the following methods.

- Reducing the flow velocity that allows gravitational separation of oil, water and gas. This is generally accomplished in large volume separators and desalters.
- Adding chemical demulsifiers.
- Increasing the temperature of the emulsion.
- Applying electrical fields that promote coalescence
- Changing the physical characteristics of the emulsion.

Because of the wide variety of oils, brines separation equipment, chemical demulsifiers and product specifications, demulsification methods are very application specific. Furthermore, emulsions and conditions change over time and add to the complexity of the treatment process. The most common methods of emulsion treatment have been the application of heat and appropriate chemical demulsifiers to promote destabilization, followed by a settling time to allow gravitational separation to occur.

2.3.1 Chemical

An emulsion will often break if the emulsifying agent is chemically altered. Emulsions stabilized with alkali – metal soaps are broken on adding acid or metal ions. Emulsions stabilized with anionic agents can be broken by adding a cationic detergent. A more subtle chemical effect is to alter the HLB (Hydrophile – Lipophile Balance) number. This procedure depends on the two solutes being able to comicellize, which allows them to blend so intimately that the mixture behaves as a unit of intermediate HLB. Thus an O/W emulsion stabilize with an agent of high HLB may be vulnerable to the addition of an agent of low HLB. Bolster and Little (1980) studied chemical demulsification of seawater in residual oil emulsions. Oil slick emulsions were modeled using residual type oils such as Navy Special Fuel Oil and No.6 Fuel Oil. Chemical demulsification of these emulsions was demonstrated

using Aerosol GPG (practical grade of Aerosol OT) and a combined two part demulsifier composed of Aerosol OT and polyethylene oxide. The time required to break the emulsions was a function of oil type, water content, temperatures and demulsifier concentration. Aerosol GPG shows promise as a chemical demulsifier of collected oil slick emulsions provided ambient temperatures are not severe. The two part demulsifier seems capable of high speed demulsification of seawater – in – oil emulsions especially when used close to optimum concentration and temperature conditions. Because of the sensitivity of the two part demulsifier to small excesses in polyethylene oxide content this demulsifier system seems more suited to the oily waste treatment plant where greater control and technical assistance are available.

2.3.2 Mechanical

Mechanical obstacles to the flow that increase the collision frequency are by far the most developed and most diverse enhancement technique in the oil industry many different geometric configurations are available on the market;

- Grids
- Baffles
- Parallel plate interceptors/coalescers and tilted plate interceptors
- Corrugated plate interceptors/coalescers, the most famous process in this category being the Performax matrix plate coalescer
- Fixed fibrous beds (glass fibers, polymer fibers, metal wires)
- Packed coalescers or loose media filters (walnut shells, gravel, sand, “coalescer balls”)
- Membrane Processes

These obstacles present occasions for the droplets to encounter each other and coalesce. The presence of the inclined plates within a separator vessel, for example, shortens the time necessary for a droplet to encounter an interface. The coalesced droplets form a liquid film on the inclined plates, and films flow out much easier than isolated droplets. The principle of fiber beds is the same as for grids: the presence of physical obstacles heightens the possibility of droplet collision and thus the coalescence probability. Single droplets adhere to the fibers and become bigger by capturing other droplets or by coalescing with other droplets immobilized on the fiber. Once a critical volume is reached, these large drops detach from the fiber, reenter the

bulk flow, but this time, due to their higher volume, sediment easily. Such separator packing present the process compared to conventional separators without consuming a lot of energy. During the design phase though, some precautions have to be taken in order not to raise turbulence in the flow unnecessarily (which increases droplets breakup) or not to raise the pressure drop (unnecessary energy costs). The upstream flow also has to be virtually free of sand and other solid matter in order not to clog up fiber beds or corrugated plate equipment in particular. Sun et al. (1998) studied demulsification of water – in – oil emulsion by using porous glass membrane. The hydrophilic porous glass membranes were used to demulsify water – in – oil emulsion and demulsification efficiency can reach more than 96.2%. Effects of pore size of the membrane, transmembrane pressure and volumetric ratio of oil phase to internal aqueous phase in the emulsion on demulsification were investigated. It was found that pore size of membrane and transmembrane pressure can significantly affect demulsification efficiency. The smaller the pore sized of the membrane, the better the demulsification efficiency. However, smaller pore size of the membrane has to be exerted a greater transmembrane pressure in order to make internal aqueous phase enter the membrane pore. In addition, recover – oil phase by the demulsification were reused five times to extract cadmium from simulated aqueous waste. The results indicated that the extracting efficiency could arrive at 96.5%.

2.3.3 Thermal

Heating the emulsion enhances its breaking or separation. It reduces the viscosity of the oil and increases the water – settling rates. Increased temperatures also result in the destabilization of the rigid films caused by reduced interfacial viscosity. Furthermore, the coalescence frequency between water droplets is increased because of the higher thermal energy of the droplets. In other words, heat accelerates the emulsion – breaking process. Partal et al. (1997) studied the influence that concentration and temperature exert on the viscous behavior of emulsions stabilized by a sucrose ester (SE) of high hydrophilic – lipophilic balance (HLB), flow curves and droplet size distributions were determined. Flow curves of presheared emulsions always exhibited behavior at intermediate shear rates, a tendency to a limiting viscosity at high shear rates, and a meta-stable region at low rates. This behavior can be fitted to a Carreau model. Both SE and oil concentration were increase emulsion viscosity as a result of a more structured system with a lower

droplet size and polydispersity. An increase in temperature usually leads to decrease in emulsion viscosity. However, at high oil concentration, coalescence and phase separation take place at low temperature. On the other hand, at high temperature, droplet, bursting due to shear forces, leading to an increase in viscosity, may result. Despite the strong structural breakdown caused by steady shear, master flow may be obtained by using superposition methods.

2.3.4 Acoustic

Ultrasound is most often used to characterize dispersions or emulsions, namely to measure droplet size distributions distribution and follow their evolution over time, but the technology has recently also been used to aid the separation of emulsions. Acoustic spectroscopy deals with measuring the attenuation of ultrasound within a certain frequency range, while electroacoustic spectroscopy superimposes an electrical field. The former is used mostly to measure droplet size distribution and the latter seems to be more promising for the measurement of the ζ -potential. The acoustic spectrometer generates sound pulse that after passing through a sample are measured by a receiver. The passage through the sample system causes the sound energy to change in intensity and phase. The acoustic instrument measures the sound energy losses (attenuation) and the sound speed. The sound attenuates due to the interaction with the particles and liquid in the sample system. Rajakovic and Skala (2006) studied separation of water – in – oil emulsions by freeze/thaw method and microwave radiation. The demulsification has been achieved with the use of freeze/thaw (F/T) method and microwave radiation (MWR). The object of investigation was emulsion samples prepared by mixing the metal – working – oil, FESOL 09, produced by FAM, Krusevac, Serbia, and deionized water. F/T method has been successfully applied for the removal of oil from emulsions in our previous work. In this work, MWR has been additionally used for separation and enhanced heating of emulsion samples. The efficiency of oil removal has been improved with the assistance of MWR, up to 90%.

2.3.5 Electromagnetic

Two very different microwave treatments have to be distinguished: thermal and non – thermal microwave treatment. Separation based on thermal microwave treatment (TMT) derived basically from the same principles as conventional heating:

a reduction of viscosity, which eases the sedimentation and coalescence of droplets. The main advantage of TMT compared to conventional heating is the relative rapidity of temperature increase by increasing molecular movement instead of convection and conduction for conventional heating and the relative environment a friendliness compare gas or oil combustion. Non – thermal microwave treatment (NTMT), on the other hand, is a much more innovative technology.

2.3.6 Electrical

Electricity (electric grids) is often an effective means of breaking emulsions. It is generally theorized that water droplets have an associated charge and, when an electric field is applied, the droplets move about rapidly, collide with each other, and coalesce. The electric field also disturbs the rigid interfacial film by rearranging the polar molecules, there by weakening the tight film and enhancing coalescence. The electrical system consists of a transformer and electrodes that provide high voltage alternating current. The electrodes are placed in such a way as to provide an electric field that is perpendicular to the direction of flow. The distance between the electrodes (in some designs) is adjustable so that the voltage can be varied to meet the requirement of the emulsion being treated.

Electrostatic dehydration is rarely used alone a method of breaking emulsions. It is generally used in conjunction with chemical and heat requirements. Invariably, the use of electrostatic dehydration will result in a reduction of heat addition. Lower temperatures result in fuel economy, reduced light – end loss.

2.4 Electrical Demulsification Methods

Electrical cannot completely replace tried and true emulsion resolution methods such as time, temperature and chemical. However, when a properly applied, electrical methods may reduce the reliance on them. A variety of electrostatic treatment techniques available to the designer and operator include AC, DC, AC/DC, modulated and pulsed fields. Whichever electrostatic method is selected, an understanding of the water droplet behavior within a voltage field will aid the designer to optimize the treatment rate, chemical dosage and applied voltage.

2.4.1 Water Dipole

In an AC type electrostatic field, the driving force for droplet coalescence is based on the dipole to the water molecule. Applying voltage to an AC – electrode aligns the water molecule creating a chain of water droplets with positive and negative poles. Droplets that are close together will migrate towards each other and coalesce.

However, a 60 Hz AC field alters polarity up to 120 times per second and the droplet interface is not charged. Nor will the AC field promote film rupture that exposes a clean water surface to adjacent droplets.

2.4.2 Charging

In a DC electrostatic field a sustained movement of electrons charges the water droplet interface. The ability to charge the droplet interface is primarily dependent on the voltage magnitude and the oil conductivity. Studies have shown that higher DC voltage levels are capable of delivering a significant charge to even the smallest water droplets and thereby promoting coalescence.

Furthermore, the DC field promotes droplet stretching that ruptures the outer film and enhances the droplet coalescence rate.

2.4.3 Conductivity

In general, for electrostatic treatment processes, crude oil is considered a non-conductive continuous phase. Pure organic components may be treated by electrostatically, however the low conductivity generally reduces the droplet charge and hinders droplet movement, coalescence and separation. In highly refined oils where the conductivity is extremely low, AC and DC electrostatic fields rely on the dipole of the dispersed water to promote droplet coalescence. However, in DC treatment processes, the oil conductivity is essential in delivering a charge to the dispersed water droplets. The DC field transfers a charge to dispersed water droplet proportional to the voltage gradient and the oil conductivity. Small – scale lab studies have shown that a limited increase in the oil conductivity can improve water droplet coalescence by a significant amount in some crude oils. Unfortunately, high oil conductivity requires an increase in the connected power supply and limits the voltage gradient developed between electrodes.

2.4.4 Coalescence/Separation

As water droplet progresses through the electrostatic field and coalescence and separation occur, the characteristics of the dispersed phase changes, there were changes tend to slow the coalescence and separation rate leaving a small percentage of untreated water. The following changes occur to the dispersed phase.

Coalescence of the dispersed phase will

- Increase the droplet diameters.
- Increase the droplet spacing.
- Reduce the droplet population.
- Increase the attractive forces between droplets.
- Reduce the total interfacial area.
- Reduce droplet mobility.

Separation of the dispersed phase will

- Reduce the droplet volume percentage.
- Reduce the interfacial surface area.
- Increase the droplet spacing.
- Decrease the attractive force between droplets.
- Reduce droplet mobility.

Separation without coalescence accumulates an unresolved emulsion at the vessel interface between the oil and water phases. This accumulation of emulsion forms a hindered settling zone that, if unresolved, will “short” the electrical field, limit the voltage gradient and slow further droplet coalescence.

2.4.5 Mobility

For vertical flow, oil dehydrators, the water droplet mobility must be controlled in both the horizontal and vertical directions. Insufficient horizontal movement (velocity) fails to promote coalescence of the dispersed water droplets.

Since AC fields rely solely on the water dipole to promote coalescence, droplet mobility is limited. However, once a net droplet charge is acquired in DC field droplet mobility is increased significantly. Higher electrostatic voltages improve the horizontal droplet mobility. However, if higher voltages lower the interfacial tension, the result can be a dispersion of the water droplets rather than coalescence.

2.4.6 Dispersion

Increasing the droplet dispersion improves the contact efficiency between the produced, brine water and the injected, dilution water. Techniques used to achieve high levels of dispersion are pressure drop across static mixers or valves and high voltage gradients. Either dispersion technique produces smaller, finely dispersed water droplets. These smaller droplets increase the interfacial surface area for better contact efficiency.

2.5 Batch and continuous process

There are three major classification of processes:

Batch process

In a batch process, material is placed in the vessel at the start and (only) removed at the end --no material is exchanged with the surroundings during the process.

Semi – batch process

A semi – batch process is one that does not neatly fit into either of the other categories (i.e., it is a catch – all classification).

Continuous process

In a continuous process, material flows into and out of the process during the entire duration.

The advantages and disadvantages for batch and continuous processes.

1. Size
 - Smaller throughput favors batch processes.
 - Large throughput favors continuous processes.
2. Product quality
 - Batch operations are preferred, when the product quality of each batch of material must be verified and certified.
 - Continuous of product quality is carried out, but some potentially large quantities of off – specification product can be produced.
3. Feedstock Availability
 - Batch operations are favored when feedstock availability is limited.
4. Product demand

- Seasonal demand for products favors batch processes. Because batch plants are flexible, other products can be made during off – season.
5. Rate of reaction to produce products
- Processes that involve very slow reactions and, hence, require very long reactor residence times are favored by batch operation

2.6 Study of Electric fields

2.6.1. Batch system

Goyer et al. (1960) studied effects of electric fields on water droplet coalescence. Growth of incipient precipitation particles by collision and coalescence with cloud droplets is one of the primary mechanisms of natural rain. Comparison of previous research shows wide divergence between various theoretical and laboratory values of collision efficiency and coalescence efficiency. In an effort to obtain additional laboratory measurements of droplets coalescence, high – speed photographs were taken of colliding droplets at the breakup point in a Rayleigh jet. It appears that the observed coalescence – electric fields relationship might result from either of two factors: (a) the effect of droplet polarization in the electric fields, with the result that approaching droplets present surface of opposite charge, or (b) an effect of droplet charge, operating independently of the electric fields. With 700 – micron diameter droplets, less than 30% of the result in coalescence under no field condition. At fields of about 40 per cm, the coalescence was about 100 percent under all conditions of field.

Hano et al. (1988) studied the demulsification kinetics of W/O emulsion in a high AC electric field was investigated by using a batch cylindrical demulsifier in which a glass – sealed electrode was placed above a grounded copper disk electrode. The effect of emulsion preparation conditions (oil – phase viscosity, water drop size, water – phase holdup and surfactant concentration) and demulsifying conditions (agitation speed and temperature) on the demulsification rates were examined experimentally while keeping the applied voltage constant. Used 1.5 kV of 60 Hz was applied between the two electrodes in all experiments. Demulsification behavior was affected by both emulsifying and demulsifying conditions. The demulsification rate increased considerably with increasing water – drop size and with decreasing oil phase viscosity, water phase holdup and surfactant concentration. Stirring of the

emulsion during the operation was found to promote demulsification. The temperature dependence of thermal demulsification was close to that of electrostatic demulsification. Therefore, the acceleration by temperature rise under an electric field was thought to be caused by a decrease of emulsion stability and oil – phase viscosity.

Wang et al. (1994) studied the demulsification of water – in – oil emulsions by use of a high voltage ac field. The demulsification kinetics of water – in – oil (W/O) emulsions in a electric field was investigated by using a batch cylindrical demulsifier. The oil phase was liquid paraffin containing 1 – 10 wt% SPAN80 or ECA4360 as surfactant. The aqueous phase was deionized water containing 0 – 40 wt% H₂SO₄ solution. The rate of demulsification was increased with applied electric field strength. When a higher electrolyte concentration in the aqueous phase enhances the electric shielding effect and results in reducing the electrostatic force. From experimental, they proposed of application and easy demulsification, the surfactant concentration in the oil phase should be formulated at approximately 5%.

Ichikawa et al. (2004) studies rapid demulsification of dense oil – in – water (O/W) emulsions has been found to be induced by applying a low electric field of the order of 1 – 10 V/cm. The apparatus was composed of a rectangular glass vessel in which two rectangular stainless steel plates were fixed as electrodes. The intensity of an internal electric field in the emulsion layer was measured with a voltmeter. The demulsification simultaneously takes place over the entire space between two electrodes with two shielded copper electrodes that were inserted in the emulsion layer. Dilute O/W emulsions are demulsified only near an electrode after being condensed by electrophoresis of the droplets, which indicates that the mutual contact of oil droplets through thin water layers is necessary for the rapid demulsification. Increase of the concentration of electrolyte accelerates the demulsification, whereas increase of the concentration of an ionic surfactant retards the demulsification. O/W emulsions stabilized with a nonionic polymer surfactant are not demulsified. Water – in – oil (W/O) emulsions are not demulsified even the chemical components are the same as those of the O/W emulsion. Application of an alternating electric field with the frequency higher than 10 kHz does not cause the demulsification.

Sanfeid et al. (2005) studied the energy barrier in dense W/O emulsions. A study has been made of the interactions between non – deformed charged spherical droplets in concentrate emulsions. Based on Albers – Overbeek model, which was restricted to electrostatic effect, we calculate the repulsive interaction energy by taking also into account a quantity β that depends on the distance between the surfaces of the droplets and their sizes. Its meaning lies in the fact that, when particles come into each other's field, the fields lose their spherical symmetry. We show that in concentrate emulsions, the high volume fraction is responsible for a decrease of the energy barrier. When reaching a maximum packing, the energy barrier equals zero. However, for medium dense emulsions our calculations show that the electrical repulsion increases with the volume fraction. In all cases the corrective term β decreases the repulsive energy. A more refined calculation, taking into account the van der Waals attraction leads also to a decrease, although low, of the height of the energy barrier. The analysis of this height shows its strong dependence on the thickness of the double layer and on the volume fraction: the thicker the double layer, the lower the volume fraction that causes the decrease of the height of the barrier.

Ichikawa et al. (2006), studies stability of oil – in – water emulsion with mobile surface charge. Experimental and theoretical studies have been carried out for clarifying the effect of the migration of surface charges on the stability of electrically charged oil – in – water (O/W) emulsion droplets. A rectangular glass vessel of a cross section and a height of 33 mm x 3 mm and 70 mm, respectively, in which two stainless steel parallel electrodes of an area of 32 mm x 50 mm and a separation distance of 30 mm were immersed. One of the electrodes was connected to the ground and the other was connected to a programmable power supply. Application of a 10 kHz +20 V/-20 V square wave to a dense oil – in – water emulsion does not accelerate the demulsification, because the migration of surface charges during a half cycle is compensated during the next half cycle. On the other hand, application of a 20 V/0 V square wave of the same frequency shortens the demulsification time from 1 h to only 1 min, because the migration of the charges during a 20 V half cycle is not completely compensated during the next half cycle. This experimental result confirms that the migration of surface charges induced by the approach of emulsion droplets also plays a crucial role in the coalescence of emulsion droplets under no

external electric field. The effect of the migration of surface charges on the stability of oil – in – water emulsion systems under no external electric field has been theoretically estimated in the framework of the DLVO theory by calculating the height of energy barrier preventing the coalescence of two-charged oil droplets. The energy is expressed by

$$U = \frac{2\varepsilon_1\kappa\zeta^2(z_d^2e^2\eta + \varepsilon_1\kappa kT)e^{-\kappa w}}{z_d^2e^2\eta(1 + e^{-\kappa w}) + \varepsilon_1\kappa kT(1 - e^{-\kappa w})} - \frac{A_H}{12\pi\omega^2}$$

where ε_1 is the dielectric constant of water; κ , the Debye–Hückel reciprocal length; w , the separation distance between two oil surfaces; ζ , the zeta potential; $\pm z_d e$ are electric charges of adsorbed positive and negative ions on the surfaces; kT , the thermal energy; A_H , the Hamaker constant; and η , the total number density of the adsorbed positive and negative ions and is equal to the absolute value of $(\varepsilon_1\kappa/z_d e)\zeta$ if only positive or negative ions are adsorbed. The height of the energy barrier estimated from the above equation is much different from that estimated from a conventional equation that is derived under the assumption that the electrostatic potential between two-charged droplets is given by the superposition of the electrostatic potentials of the isolated droplets.

Bunyen (2006) studied the demulsification of crude palm oil and palm olein in water emulsions by electric fields in batch system. The vessel was made by glass in size 3.0 cm x 2.5 cm x 7.5 cm. Electric field was generated to stainless steel plate at 2, 4, 6 and 10 V/cm. The emulsions was composed of oil concentration at 2, 5, 10 and 15 %wt and sodiumsulfate concentration 0.3, 0.6, 3.0, 15.0 and 30.0 mmol. The results show that application of low electric fields to palm oil in water emulsion increase demulsification phenomena. Oil droplets in the electric field was moved and collision to form larger droplets. Increasing electric field (V/cm), concentration of oil in emulsion and concentration of electrolyte were increased the rate of demulsification. The rate of demulsification of Crude palm oil from emulsion was less than palm olein.

2.6.2. Continuous system

Drelich et al. (1992) studied the effect of electric of electric field pulsation frequency on breaking water-in-oil emulsions. The electrostatic separation apparatus consisted of a coalescence cell and a high-voltage pulse generator. The polymethylmethacrylate electrostatic coalescence cell (150, 100, 70 mm) contained two electrodes. The cathode (copper plate) was fixed to the bottom of the cell and the anode was installed in the cell cover guides which permitted easy replacement of the anode. The anode was made of copper sheet insulated with an epoxy resin having a dielectric constant of 3.6 to prevent short-circuiting. The effect of the thickness of there was evaluated at both 0.2 mm and 2.0 mm. Separation of a water-in-aromatic solvent emulsion has been studied in a continuous flow electrostatic coalescer. Emulsions containing 0.08 wt% to 0.2 wt% dispersed water with droplet diameters below 20/ μm have been separated with an efficiency exceeding 80% for a 25 s nominal residence time. The process efficiency, ~63%, was observed when the field strength was increased up to 140kV/m, where as an increase in field strength from 140kV/m to 1100 kV/m only resulted in an additional 15% increase in separation efficiency. The DC electric field pulsation frequency exerted no significant influence on the demulsification yield in the range studied (5 Hz to 25 Hz), nevertheless, a maximum in separation efficiency was observed for pulsation frequencies between 8 Hz and 11 Hz.

Harpur et al. (1997) studied the destabilization of water – in – oil emulsions under the influence of an A.C. electric field: experimental of performance. The destabilization of water – in – oil emulsions is an important process and is often the rate determining step in the dewatering and desalting of crude oils. In them studied the influence of a 50 Hz sinusoidal electric field on flowing water – in – oil emulsions is reported. A horizontal rectangular duct was used, with emulsion flowing through at flow rates up to 100 l/min, giving Reynolds numbers (Re) in the range 1,000 to 12,000. Electrocoalescer performance was assessed by measuring water droplet growth, using a specially developed technique with a laser diffraction particle size. 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.

Kim et al. (2001) studied demulsification of water – in – crude oil emulsions by a continuous electrostatic dehydrator. The demulsification rates of water – in – crude oil emulsion in high AC fields were investigated under various conditions by using a model dehydrator. A continuous electrostatic dehydrator was constructed using a glass vessel of 6.5 cm diameter and 10 cm height equipped with a copper electrode and a perforated plate. The separation rate of water from the simulated crude oil increased along with the applied field, frequency, demulsifier concentration, temperature, and contact time. As the applied field increased up to 2.5kV/cm, the separation percentage increased up to 90%, and as the concentration of the demulsifier reached 100 ppm, 80% of the water was separated at 2.5kV/cm. Also it was observed that the separation percentage increased as the temperature, frequency of field, and contact time. It is proposed that the breakup of droplets depends on the interfacial polarization and the proper deformation of water droplets in the field induced by the electrostatic charge.

Inan et al. (2003) studied the removal of chemical oxygen demand (COD), color and suspended solid (SS) from olive oil mill wastewater (OMWW) was experimentally investigated by using electro-coagulation (EC). The size of reactor was 15 cm x 8 cm x 8 cm. Aluminum and iron were used in the reactor simultaneously as materials for electrodes. Distance between anode and cathode was 3 mm. The reactor voltage was 12 V, current density (CD) was changing between 10 and 40 mA cm⁻², pH was taken equal to 4, 6, 7, and 9 units, and duration varied in the limits of 2 – 30 min. Under the 30 min retention time, 52% COD was removed by the aluminum anode and 42% was removed by the iron anode. CD efficiency versus the percent of COD removal was examined at the 10-min retention time for pH 6.2 ± 0.2. It appeared that with the CD increase, the percent of COD removal was increasing as well. The color removal yield was examined as the result of using different retention times, current densities, and iron and aluminum as materials for anodes. CD values in the range of 10 – 40 mA cm⁻² were tested at the 10 min retention time each one; color removal was 90 – 97% by this. In this study the EC process was examined with the aim of determining the highest rate of SS removal from the OMWW as well.

Elektorowicz et al. (2005) studied the effect of electrical potential on the electro-demulsification of oily sludge. They use the six rectangular polyethylene cells and stainless steel material was used to build flat anodes and cathode in them experiment. The sludge was used in them experiment was taken from the bottom of a crude oil storage tank. The behavior of sludge mixture and additive (amphoteric surfactant C_{12}/C_{14} alkyldimethylbetain) was both under the influence of DC fields. They are applied electric field 0.5 and 1.5 V/cm between electrodes. They found, colloidal particles of oily sludge and the separated solid phase moved toward the anode area as a result of electrophoresis, while the separated liquid phase, which consisted of water and hydrocarbon, flowed toward the cathode area as a result of electro-osmosis. When lower the applied electrical potential is, the higher the demulsification rate. The best demulsification result was obtained for the cell with lower electrical potential and without surfactant; it was almost 16% higher than in the cell with the same electrical potential and with surfactant. Resistance changes in each cell during the experiment are well related to the dynamics of the process. By drawing comparisons between cells, it was found that the cells that contained sludge and surfactant showed high resistance. At higher pH values, solid particles become more hydrophilic so that they are desorbed from the oil – water interface. Consequently, demulsification can be performed in higher pH environment.

Yang (2007) studied electrochemical coagulation for oily water demulsification. He used the motor oil and industrial surfactants were used to prepare synthetic oily water. When stabilized with surfactant, the turbidity shows a positive correlation with the oil content in the emulsion with a correlation coefficient of 1.78 FAU (mg/l). The oil – water emulsion was tested with gravity separation, centrifugation, flotation, and electrochemical coagulation for the effectiveness of each process on demulsification. Electrochemical coagulation was them selected of further study. A DC voltage was applied to the electrodes, dissolving ferrous ions (Fe (II)) at the anode and forming hydrogen (H_2O) gas and hydroxyl (OH^-) ions at the surface of the cathode. A few 100 mg/l of sodium chloride (NaCl) were assed to the solution to provide ionic conductivity and to prevent passivation of the or on electrode. The ferrous ions were oxidized into ferric ions (Fe (III)), destabilizing the emulsion. The coalesced oil droplets were adsorbed into the highly dispersed and reactive ferric hydroxide (Fe (OH)₃) coagulant. The oil – rich sludge that was completed in 4 min.

When the reactor was operated for this amount of time, a measure of 165.8 mg/l of ferric ions was generated. The treatment reduced the turbidity of the emulsion from 1800 to 60 FAU. Beyond the 4 min treatment period, the addition of more iron to the system resulted in turbidity change at a much slower rate. When the operated occurred continuously with a current of 2 A. and a throughput of 320 ml/min, the turbidity of the electrically treated effluent was less than 14 FAU.

Hu et al. (2007) studied a continuous electrocoagulation – flotation (ECF) system was employed to treat synthetic high fluoride-content wastewater following calcium precipitation. The electrolysis cell comprised nine aluminium electrodes in size 100 mm x 40 mm. The distance between each electrodes was 10 mm. The volume of the reactor is 320 ml. The dose of sodium dodecyl sulfate (SDS) in a continuous ECF system was higher than that in the batch system indicating the SDS acted not only as frother, but also as collector in the continuous system. The removal of suspended solids (SS) in the continuous system was less than that in the batch system because the scum was disturbed by the flow of wastewater in the flotation tank. It decreased with the increase in flow rate when the flow rate reaches higher than 800 ml/min, yet it increased with the increase in flow rate when the flow rate falls under 200 ml/min.