CHAPTER II
BACKGROUND AND LITERATURE SURVEY

The API separator sludge consists of a mixture of oil, water and solid. To study the light components recovery from the sludge, it is assumed that the mechanism of light components recovery consists of 3 steps. First, the oil is detached from the surface of solid particle. Second, detached and free oil will disperse in the solution in the form of emulsion. Finally, destabilization of oil droplets is used to separate the emulsion droplets from the aqueous solution.

2.1 Detachment of Oil from the Solid Surface

The oil, which attaches to the solid surface, is not soluble in water and cannot be removed by using pure water. As a consequence, there is an interfacial tension between the oil and water. This tension corresponds to the energy needed to bring the oil in contact with the solid surface. It arises because the cohesive energy of the oil is not the same as that of the solid surface. Water is not able to wet the surface of the oil.

Surfactants need to be added into the water to reduce the interfacial tension, allowing water to wet the solid surface, which actually means the displacement of air by the aqueous medium. This step is important because it must be completed before any detachment can occur. Depending on the nature of the oil, the surfactant used, the temperature, and the mechanical work, different mechanisms can happen (Lange,1994).

2.1.1 Roll-up

Removal of oil by aqueous solution is mainly achieved via roll up mechanism in which the contact angle between the oil and solid surface is increased by adsorption of surfactant from the aqueous solution. An interfacial tension γ_{OS}, at the oil-solid interface occur when the oil (O) is on the solid surface (S.) (Figure 2.1).

The oil droplet forms an angle θ with the solid surface resulting from the balance between the surface forces. The surface tension γ_{SG} between the solid and

the gas phase tends to spread the oil on the surface to reduce the area of contact. The interfacial tension γ_{OS} between the oil and solid tends to reduce the oil-solid contact and re-form the drop. The surface tension γ_{OG} between the oil and the gas phase is not in the plane of the solid. However, its projection on the plane must be considered to balance the force.
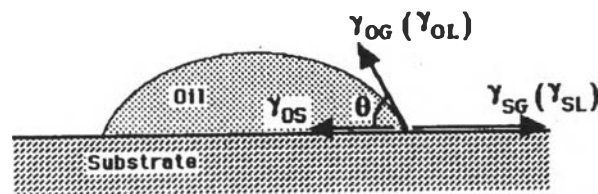

Figure 2.1 Drop of oil on a solid substrate.

The interfacial tension between the solid and gas phase is usually higher than the surface tension between the oil and solid. The result is that the contact angle is usually small, which is synonymous with good wetting, and sometimes zero, which is synonymous with perfect wetting. When the solid and the oil are submerged, the surface tension between the solid and the gas phase is replaced by the interfacial tension γ_{SL} between the solid and water. The surface tension between oil and gas is replaced by the interfacial tension γ_{OL} between the oil and water.

If an appropriate surfactant is dissolved in water, the effect is a strong reduction of the solid-water and oil-water interfacial tensions, due to the adsorption of surfactant molecule at the water-oil and water-solid interface. Of course, the oil-solid interfacial tension is not affected, since the water does not diffuse to that interface. The system evolves toward a new equilibrium state, characterized by a higher contact angle. It is evident that the higher the contact angle, the more easily the oil is removed. If the reduction of interfacial tension is so strong that the sum of the oil-water and solid-water interfacial tensions reaches the oil-solid interfacial tension, the contact angle is 180° ($\cos \theta = 1$). This means there is no oil left on the solid surface as seen from Figure 2.2 (Lange, 1994).
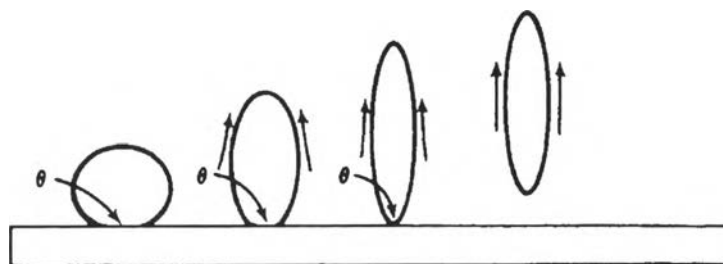
Figure 2.2 Complete removal of oil droplets from the solid surface when θ remains constant at > 90°.

This mechanism was investigated by Thompson (1994). He concluded that a detergency maximum attributable to the roll-up mechanism occurred when the surfactant system was of higher effective HLB (as it was for nonionic surfactant at temperature below the PIT). The failure of this mechanism of the operation under the low interfacial tension conditions of the phase inversion region was because of a sudden drop in contact angle, which has been attributed to the formation and deposition of the middle oil/water/surfactant phase (Thompson, 1994).

2.1.2 Necking or Snap-off

When the contact angle is less than 90° at least part of oil will remain attached to the solid surface (Figure 2.3). This mechanism is called necking or snap-off. In this case, mechanical work required to remove the residual oil from the solid (Lange, 1994). Kolev and coworker studied the consecutive photos of an oil drop on the surface. Initially it had an approximately spherical shape. With elapsed time the contact line shrinks, the oil-solid contact area decreased, and the drop became slightly elongated under the action of buoyancy. At the final stage a neck was formed. Next, the drop detached very fast (Kolev *et al.*, 2003).
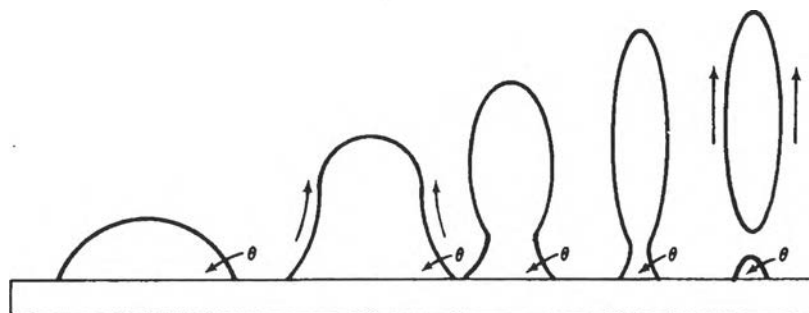
Figure 2.3 Rupture and incomplete removal of large oil droplets when θ remains constant at < 90°. A small droplet remains attached to the substrate.

There are many researchers studying the detachment of the oil from the solid surface. Carroll (1996) concluded that the detachment of high molecular weight alkane squalane from polyester plate seems to be only partial, a residual droplet remaining attached to the plate. Starkweather and coworkers observed the detachment of hydrocarbon from metal surface. Their results indicated that the increase in the surfactant concentration and pH of the solution enhanced the displacement of oil from metal surface. In addition, the volume of the detached oil droplet increased with increasing both the surfactant concentration and pH of the solution (Starkweather *et al.*, 1999).

2.2 Emulsification and Emulsion Stability

Most of oil droplets detached from the solid surface will disperse in the solution in the form of emulsion. As a consequence of the small droplet size and the presence of an interfacial film on the oil droplet in emulsion, which is quite stable, dispersions of these species can be made. That is, the suspended droplets do not settle out or float rapidly, and the droplets do not coalesce quickly.

Emulsion droplets are stabilized by electrostatic force or charged interfaces. Most substances acquire a surface electric charge when they are brought into contact with a polar medium such as water. For emulsions, the origin of the charge can be ionization, as when the surface acid functionalities ionize when the oil droplets are dispersed into the aqueous solution, or the origin can be adsorption, as when

surfactant ions or charged particles adsorb onto an oil droplet surface. Ions of opposite charge are attracted to the surface, but those of like charge are repelled. An electrical double layer, which diffuses because of mixing caused by thermal motion, is thus formed. A term often associated with the electrical double layer, and one that is misused, is zeta potential (ζ) or electrokinetic potential (Shramm, 1992).

Zeta potential is the potential of a charged particle as determined from electrokinetic phenomena. It is the potential of the charged surface at the plane of shear between the particle and the surrounding solution as the particle and the solution move with respect to each other (Rosen, 1988). Stachurski and Michalek found that the emulsion droplets of hydrocarbons C_9 to C_{16} revealed a completely different course of changes of the ζ potential due to pH rather than the n-alkanes of the shorter hydrocarbon chains (C_6 to C_8). They revealed a negative value of the ζ potential, lower by almost twice. Unlike the pH of aqueous solution, the ζ potentials of emulsion droplets of the n-alkanes, from n-nonane to n-hexadecane, are not practically influenced by the hydrocarbon chain length. This observation indicated a close correlation between the emulsion droplets of the tested aliphatic hydrocarbon in water and the value changes of the ζ potential (Stachurski and Michalek, 1996). Their results were confirmed by Al-Shamrani and coworkers (2002). They concluded that the oil droplets were negatively charged and the magnitude of zeta potential was sufficiently large to stabilize the oil-water emulsions electrostatically.

Emulsion can clump together in various different ways. In the definition of emulsion stability, it is considered against three different processes: creaming (sedimentation), aggregation and coalescence. Creaming is the opposite process of sedimentation and results from a density difference between the two liquid phases. For aggregation, two or more droplets clump together, touching only at a certain points, and with virtually no change in total surface area. This process is sometimes referred to as flocculation or coagulation. As for the term of coalescence, two or more droplets fuse together to form a single larger unit with a reduced total surface. Aggregation of droplets may lead to coalescence and the formation of larger droplets until the phases become separated (Shramm, 1992).

2.3 Demulsification (Emulsion Breaking)

Demulsification is used to separate the emulsion droplets from the aqueous solution. This process involves two steps. The agglomeration or coagulation of the droplets must take place first. Then, the agglomerated droplets must coalesce. Only after these two steps can complete phase separation occur.

The first step in systematic demulsification is to characterize the emulsion in term of its nature (O/W or W/O), the nature of the two phases and the sensitivity of the emulsifiers. On the basis of such an evaluation, the effect of the emulsifier could be made to neutralize by chemical addition, followed by mechanical methods to complete the phase separation. It directly depends on emulsion stability. If an emulsion is stabilized by electrical repulsive forces, the demulsification could be brought about by overcoming or reducing these forces. Any or all of the following methods of aiding this process may be employed (Shramm, 1992):

1. Providing low-turbulence and low-velocity environments (treating vessel) that allow gravitational separation and removal of oil, water and solids. Gas may also be removed.

2. Increasing the temperature of the emulsion.

3. Applying chemical designed to break emulsion.

4. Applying electrical fields that promote coalescence.

5. Changing the physical characteristics of an emulsion by the addition of diluent water.

2.3.1 Chemical Method

The most common method of demulsification is a combination of heat and application of chemicals to reduce or neutralize the effect of negative zeta potential. Addition of appropriate chemicals which have specific properties will generally provide quick, cost-effective and flexible solution of emulsions. The success of chemical method depends on the following (Shramm, 1992):

1. A sufficient quantity of a suitable chemical must add into the emulsion.

2. Thorough mixing of the chemical in the emulsion must occur.

3. Adequate heat may be required to facilitate an emulsion.

4. Sufficient residence time must exist in treating process to allow the complete phase separation.

2.3.2 Chemicals Used in Demulsification

Numerous chemicals used in demulsification are commercially available. They are used in coagulation and flocculation processes.

2.3.2.1 Coagulants

Commonly used coagulants are based on aluminum such as aluminum sulfate and aluminum polymer or on iron such as ferric chloride and ferric sulfate. When a coagulant is added into water, it ionizes, producing cations some of which neutralize the negative charge on the oil droplets (Drinan, 2001). Al-Shamrani and coworker found that the addition of highly charged cations in the form of aluminium and ferric salts had effectively induced the destabilization of the emulsions, leading to the significant oil separations with the removal efficiency more than 99% (Al-Shamrani et al., 2002). The pH showed a marked effect on aluminum sulfate performance and the time necessary to produce the clarification of the system was shorter for higher coagulant concentration (Pinotti and Zaritzky, 2001).

$CaCl_2$ and $AlCl_3$ were also used as coagulants. The addition of an electrolyte lowered the zeta potential of the oil droplet and destabilization of the emulsions was observed. A cream layer appeared at the top of the container where the coalescence phenomena occurred and resulted in an oil phase separation (Ríos et al., 1998).

2.3.2.2 Coagulant Aids or Flocculants

The addition of some chemicals will enhance coagulation by promoting the growth of large flocs. Their usual dosage is 5 to 10 mg/l. Polyelectrolytes are high molecular weight polymer which contains adsorbable groups and forms bridges between particles or charged flocs. Large flocs are thus created when small dosages of polyelectrolyte are added in the combination with alum or ferric chloride (Eckenfelder, 2000). It has been suggested that the role of the polyelectrolyte in the oil-in-water emulsion treatment was to enhance flotation of oil by increasing floc size. In addition, the increased of charge density of the oil and

polyelectrolyte improved flocculation and flotation performance. However, the increase in polyelectrolyte molecular weight had no effect on flotation performance or optimum polyelectrolyte addition (Gray *et al.*, 1997).

There are several researches involving the performance of polyelectrolytes. Pinotti and Zaritzky found the reversion droplet charge in polyelectrolyte treatment. Moreover, restabilization of the emulsion occurred when an excess of the destabilizer was added (Pinotti and Zaritzky, 2001). The inversion of droplet charge was also observed by Al-Shamrani and coworker. They found the inversion even at very low polyelectrolyte concentration (Al-Shamrani *et al.*, 2002).

2.3.3 Coagulation and Flocculation

Coagulation is a chemical process which provides the sedimentation of the particles more efficient. Flocculation is a physical process which enhances the effectiveness of coagulation's chemical addition. Very small oil droplets have the natural repulsion which is created by the negative zeta potential of the oil droplets. This electrostatic repulsion keeps the oil droplets isolate and suspend in the solution (Drinan, 2001).

The addition of cations depresses the oil droplets charge and the effective distance of the double layer, so reducing the zeta potential. When the coagulant dissolves into the solution, its cations serve to neutralize or reduce the negative charge on the oil droplets. Microflocs then form. These microflocs also serve to neutralize and coat the oil droplets. Then, flocculation will help to agglomerate the microflocs.

Riddick (1964) has concluded a sequence of effective coagulation procedure. If necessary, alkalinity may first be added. Alum or ferric salts are rapidly added next, they coat the oil droplets with Al^{3+} or Fe^{3+} and positively charged microflocs. Coagulant aid or flocculants such as activated silica and polyelectrolyte for floc buildup and zeta potential control are added last (Eckenfelder, 2000).

2.3.4 Flotation

Flotation is a method to separate the oil from an aqueous solution. The small bubbles of air or gas are introduced to the emulsion. They will attach

themselves to the oil droplets and float them to the surface of the solution where they can be coalesced and skimmed. The bubble will also tend to float any solids. This fact must be taken into account in any separation process (Lissant, 1983).

Coagulation and flocculation are very important as a pre-treatment process for flotation. Moreover, these processes are used to improve the flotation efficiency. Zouboulis and coworker (2000) reported that destabilization of oil-in-water emulsion was successfully performed by the application of a combination of coagulation and dissolved air flotation, which showed a synergistic enhancement for the effective separation of emulsified oil (Zouboulis *et al.*, 2000). The flotation process depends strongly on the charge of the oil droplets and bubbles. Therefore, the maximum of flotation can be accomplished when the zeta potential of the oil droplets is zero. The chemicals which are added into the system in pre-treatment process will reduce the repulsive effects of zeta potential to allow the small oil droplets to form large droplets. Under these conditions, dissolved air flotation yielded near complete oil separation even at moderate working pressure and recycle ratio when the oil droplets were destabilized (Al-Shamrani *et al.*, 2002).