

# CHAPTER II

# **BACKGROUND AND LITERATURE REVIEWS**

# 2.1 Vegetable oil

Vegetable oil is the fat or oil extracted from plant sources such as peanuts, soybean, sunflower seeds, safflower, palm oil, castor beans, rapeseed etc. Most of vegetable oils are used for several applications such as culinary uses, industries uses, medical uses and fuel. Normally, vegetable oils are obtained from beans or seed by extraction process which can be solvent extraction or mechanical extraction or pressing.

In general the major composition of vegetable oil is triglyceride compound connecting a variety of fatty acids. According to the United States Department of Agriculture (USDA) reported the total world consumption of major vegetable oils in 2000 was as shown in table 2.1;

Table 2.1 World consumption of vegetable oil

Oil source	World consumption (megatonnes)		
Soybeans	26.0		
Palm	23.3		
Rape seed	13.1		
Sunflower seed	8.6		
Peanut	4.2		
Cottonseed	3.6		
Palm Kernel	2.7		
Olive	2.5		

Source: http://en.wikipedia.org/wiki/USDA

In Thailand vegetable oils are used for variety purpose. Normally, the major economic vegetable oils in Thailand are soybean oil, palm oil including palm kernel oil, peanut oil, coconut oil, sesame oil and castor oil. (Janvanishpunjakul, 2007) For soybean oil has the consumption demand about 295137 tons in 2003 (Office of agricultural economics, 2004) and tend to increase demand up to now because this oil consider as the

healthily and versatility vegetable oil for consumption. However, the production capacity of soybean oil in Thailand tends to decrease and higher demand for import from other countries. In case of palm oil, the consumption demand is about 3512000 tons (Office of agricultural economics, 2004) in Thailand which higher than soybean oil and tend to increase the production capacity in Thailand for many applications such as biodiesel.

# 2.1.1 Soybean Oil

Soybeans are native to South East Asia, 45 percent of the world's soybean area, and 55 percent of production, is in the United States. The U.S. produced 75 million metric tons of soybeans in 2000, of which was more than one-third was exported. Other leading producers are Brazil, Argentina, China, and India.

Soybeans are an important global crop, with political ramifications. It is grown for its oil and protein. The bulk of the crop is solvent extracted for vegetable oil and the defatted soy meal is used for animal feed. A very small proportion of the crop is consumed directly for food by humans. Soybean products, however, appear in a large variety of processed foods.

# Chemical composition

The oil and protein content together can account proximately 60% of dry soybeans by weight consisting of 40% protein and 20% oil. The remainder consists of 35% carbohydrate and about 5% ash. Soybean cultivars comprise 7.3% seed coat or hull, 90.3% cotyledons and 2.4% hypocotyl axis or germ. (Perkin, 1995)

To produce soybean oil, the soybeans are cracked, adjusted for moisture content, rolled into flakes and solvent-extracted with commercial hexane. The oil is then refined, blended for different applications, and sometimes hydrogenated. Soybean oils, both liquid and partially hydrogenated, are end up as vegetable oil in a wide variety of processed foods. The remaining soybean husks are used mainly as animal feed.

The major unsaturated fatty acids in soybean oil triglycerides are linolenic acid (C18:3); linoleic acid, C-18:2; and oleic acid (C-18:1) as shown in Table 2.2.

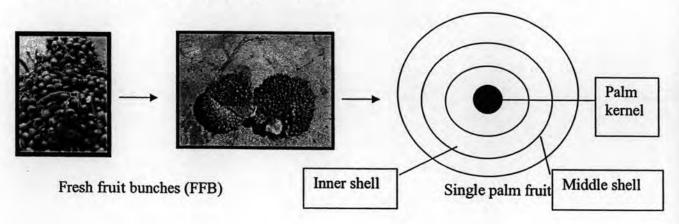
Table 2.2 Composition of fatty acid in soybean oil, palm oil and palm kernel oil

		Composition (%)		
Fatty acid	Туре	Soybean oil*1	Palm oil*2	Palm kernel oil*2
Caprylic C8:0	Saturated		-	3.3
Capric C10:0	Saturated	-	-	3.4
Lauric C12:0	Saturated		0.2	48.4
Myristic C14:0	Saturated	•	1.1	16.2
Palmitic C16:0	Saturated	10.7	44.3	8.4
Stearic C18:0	Saturated	3.4	4.6	2.5
Oleic C18:1	Unsaturated	21.3	39.2	15.3
Linoleic C18:2	Unsaturated	56.4	10.5	2.4
Linolenic C18:3	Unsaturated	8.2	-	

Sources \*1 Gunstone, 2002 and \*2 Ang et al., 1999

#### 2.1.2 Palm Oil

The oil palm is a tropical palm tree. There are two species of oil palm, the better known one is the one originating from Guinea, Africa and its name is *Elaeis guineensis* Jacq. The fruit is reddish about the size of a large plum and grows in large bunches. A bunch of fruits can weigh between 10 to 40 kilograms each. Each fruit contains a single seed (the palm kernel) surrounded by a soft oily pulp. Oil is extracted from both the pulp of the fruit. The extracted palm oil from the pulp is edible oil while the oil extracted from kernel seeds are mainly used for soap manufacture.



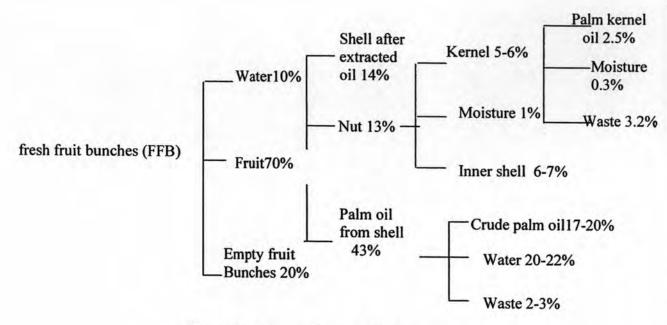


Figure 2.1 Composition of palm oil Source: Prengampei, 2005

# Chemical composition

Both palm and palm kernel oil contain high saturated fatty acids. The oil palm is given its name according to the 16 carbon saturated fatty acid palmitic acid found in palm oil; monosaturated oleic acid is also a constituent of palm oil while palm kernel oil contains mainly 12 carbon saturated fatty acid or lauric acid. Palm oil is the largest natural source of tocotrienol, part of the vitamin E family. Palm oil is one of the few vegetable oils relatively high in saturated fats, though it is not as high as found in palm kernel oil. The application of palm and palm kernel oil are different because the different chemical composition. The proximate concentration of fatty acids in palm oil and palm kernel oil is also shown in Table 2.2.

Compared the two oils in this study; soybean and palm kernel, the majority of fatty acid in soybean oil are most unsaturated fatty acid while the ones in palm kernel oil are saturated fatty acid.

# 2.1.3. Vegetable oil extraction process

Basically, three are three methods for vegetable oil extraction; traditional method, mechanical and solvent extraction, with hexane is the most common solvent for solvent extraction. Solvent extraction is a conventional method for extraction of oil from seed due to its high efficiency. However, solvent extraction is not suitable method for small scale extraction plant because of high capital and operation cost, the risk of fires and solvent explosion in case of poor safety and the complexity of process. Consequently, solvent extraction by using hexane are commonly found only in the large vegetable oil industry which are the major producer of cooking oil in the market is.

# 2.1.3.1 Soybean oil Extraction Process

Soybean oil extraction process consists of this following step;

#### - Pre-Treatment

Soybeans are carefully cleaned and dried before and then are passed into the pretreatment process consists of four operation: cracking, dehulling or hull removal, conditioning and flaking.

Soybeans are fed into cracking rolls to crack the beans for facilitating separation the hulls from bean, followed by separation of the hulls with the use of shaker screens and aspiration in order to separate the lighter hulls from the heavier beans and kernels, with the use of fan aspiration and screens to strain for heavy objects and also using the magnets to separate any metals.

After that the cracked beans and residual bean chips are conveyed to the conditioning area, where make them pliable and keep them hydrated by application of indirect steam to adjust the moisture content and temperature. The cracked beans are exposed to temperatures to approximately 74 - 79 °C for 30 - 60 minutes (Erickson et al., 1980) prior to using smooth-surface rollers to flatten into large flakes of uniform thickness which vary in thickness from approximately 0.25 to 0.51 millimeter (Allen et al., 1982). The purpose of the conditioning is the heat denaturation to prevent soybean chips being broken into smaller particles and subsequent coagulation of proteins present in addition to the coalescence of oil droplets and reduction in the affinity of oil for the solid materials, making it easier to extract (Allen et al., 1982). Lastly, Flaking is the process which allows

the soybean oil cells to expose and the oil to be easily extracted. The schematic diagram for soybean oil extraction is shown in Figure 2.2.

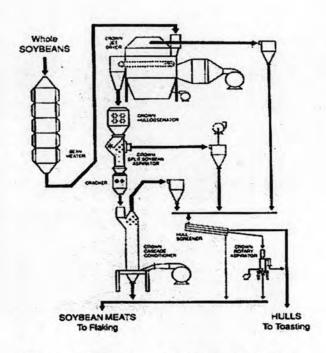


Figure 2.2. Process of soybean oil extraction Source: Carlson and Scott, 1991

# Extraction of soybean oil

Firstly, Oil is washed from soybean flaked with hexane solvent in a countercurrent extractor. Soybean flakes are conveyed into the extractor, where they are washed counter currently with various hexane/oil mixtures and finally, with pure hexane. The initial oil content of the soybeans is approximately 18 to 20 percent by weight. After extraction, the defatted flakes contain approximately 0.5 to 2.0 percent oil by weight. And then the oil/hexane mixture is removed from the extractor separately from the defatted flakes. The mixture is first pumped through heaters, then through film evaporators under vacuum and, finally, through a stripping column to remove the hexane. The hexane/water vapor mixture is removed from each oil desolventizing unit and condensed in a "separation" tank to separate the solvent; hexane from the water. Once separated from the water, the hexane is reused in the extraction process. The desolventized oil, called "crude" soybean oil, is stored in tanks for further processing or load out.

# Purification of soybean oil

The further processing for crude soybean oil is purified of soybean oil because the crude soybean oil contains many oil-insoluble and oil-soluble impurities that must be removed. Oil-insoluble material may be removed through filtration; however, the soluble materials must be removed by implementing several different techniques depending on the application of soybean oil such as degumming and lecithin recovery, alkali refining, bleaching, hydrogenation, deodorization, winterization, dewaxing

#### 2.1.3.2 Palm kernel oil extraction

Palm kernel oil extraction process consists of this following step;

#### Kernel Separation

This process consists of bunch reception and quality check of bunch before bring these materials into extraction unit. The field factors that affect the composition and final quality of palm oil are genetic, age of the tree, agronomic, environmental, harvesting technique, handling and transport. After checking the specification of palm fruit, threshing is the later process for removal of fruit from the bunches following by Sterilization of bunches or cooking means the use of high-temperature wet-heat treatment of loose fruit. Cooking normally uses hot water; sterilization uses pressurized steam. The cooking action serves several purposes. Heat treatment destroys oil-splitting enzymes and arrests hydrolysis and auto-oxidation and also helps to solidify proteins in which the oilbearing cells are microscopically dispersed. The protein solidification (coagulation) allows the oil-bearing cells to come together and flow more easily on application of pressure. After fruit cooking weakens the pulp structure, softening it and making it easier to detach the fibrous material and its contents during the digestion process. The high heat is enough to partially disrupt the oil-containing cells in the mesocarp and permits oil to be released more readily after that the fruit will pass in to digestion in order to release the palm oil in the fruit through the rupture or breaking down of the oil-bearing cells. After that palm oil was extracted from shell by mechanical process, the residual parts consists of a mixture of fiber and palm nuts or kernel. Kernel recovery process in the large-scale plant follow this step; the nuts contained in the press cake are separated from the fiber in a depericarper are then dried and cracked in centrifugal crackers to release the kernels. The kernels are normally separated from the shells using a combination of winnowing and hydrocyclones. The kernels are then dried in silos to a moisture content of about 7 percent before stroage for further use.

# Kernel pre-treatment

Proper kernel pre-treatment is necessary to efficiently extract the oil from the kernels. The feed kernels must first be cleaned of foreign materials in order to prevent the contamination of products. Magnetic separators commonly are installed to remove metal debris, while vibrating screens are used to sieve sand, stones or other undesirable materials. A swinging hammer grinder, breaker rolls or a combination of both then breaks the kernels into small fragments. This process increases the surface area of the kernels, thus facilitating flaking. The kernel fragments subsequently are subjected to flaking in a roller mill. A large roller mill can consist of up to five rollers mounted vertically above one another, each revolving at 200-300 rpm. The thickness of kernel cakes is progressively reduced as it travels from the top roller to the bottom. This progressive rolling initiates rupturing of cell walls. The flakes that leave the bottom nip are from 0.25 to 0.4 mm thick.

The kernel flakes are then conveyed to a stack cooker for steam conditioning, the purpose of which is to:

- Adjust the moisture content of the meal to an optimum level
- Rupture cell walls (initiated by rolling)
- Reduce viscosity of oil
- Coagulate the protein in the meal to facilitate separation of the oil from protein materials.

The meal flows from the top compartment down to the fifth compartment in series. At each stage a mechanical stirrer agitates the meal. Steam trays heat the cookers, and live steam may be injected into each compartment when necessary. In the palm kernel, the meals are normally cooked to a moisture content of 3 percent at 104-110°C.

# - Palm Kernel oil extraction

Kernels flakes which pass the pre-treatment process are conveyed into the screw-pressing unit or solvent extraction unit. Hexane is normally the solvent for extraction. In this case, Solvent extraction process for palm kernel oil will be mentioned only. Solvent extraction is diffusion process achieved by immersing kernel in solvent or by percolating solvent though a bed of kernels. Palm kernel seed normally contain oil about 48-50% by weight (Gustone, 2002). The extraction process is similar to soybean oil. Palm kernel flakes are conveyed into extractor, where they are washed with pure hexane. After palm kernels are extracted. Separation of oil and solvent is accomplished by conventional distillation methods or desolventizers. The solvent from the desolventizer is condensed, so that the heat of condensation can be applied to the distilling of the solvent from the miscella by using a series of stills, striping columns, and associated condensers. The hexane-free oil is cooled and filtered before storage or further treatment. Most of the solvent is recovered for repeated use.

# Purification of palm kernel oil

The extracted palm kernel oil generally required purification steps. There are water degumming before refining by water treatment following by centrifugation to remove the phosphatides as hydrated gums, acid degummed and treated with soda in order to saponifity impurities.

The air and vapors from the solvent condensors and other parts of the extraction plant must be essentially solvent free before being discharge to the atmosphere because solvent extraction in vegetable oil extraction production has been recognized by the United State Environmental Protection Agency (USEPA) as a major source for hazardous air pollutant. Normally, most of the vegetable oil extraction plants use scrubbing system. All of the recovered solvent is separated from water in a gravity separation tank and reused in the solvent extraction operation. However, there are still founded that hexane loss 1 gallon per ton of seed to the atmosphere (Gustone, 2002). Consequently, the USEPA set the new National Emission standards for Hazardous Air Pollutant (NESHAP) for vegetable oil extraction plant is 0.2 gallon per ton of seed. This standard aims to

protect the environment and human from hazardous substance because hexane is potential toxic chemical and risk to human health. Hence, the new technology which can reduce hexane emission by using cleaner process should be introduced.

#### 2.2 n-Hexane

n-Hexane is a chemical made from crude oil. Pure n-hexane is a colorless liquid with a slightly disagreeable odor. Normally, pure n-hexane is used in laboratories. Most of the n-hexane used in industry is mixed with similar chemicals called solvents. Common names for these solvents are commercial hexane, mixed hexanes, petroleum ether, and petroleum naphtha. The major use for solvents containing n-hexane is to extract vegetable oils from crops such as soybeans, flax, peanut, palm kernel, corn and sunflower seed. These solvents are also used as cleaning agents in the printing, textile, furniture, and shoemaking industries. Figure 2.3.shows the structure hexane.

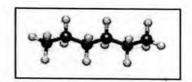


Figure 2.3 Structure of hexane

# Chemical properties

The molecular formula for hexane is C<sub>6</sub>H<sub>14</sub>. Synonyms for n-hexane are hexane and hexyl hydride. N-hexane is a colorless liquid with a slightly disagreeable odor. It evaporates very easily into the air and dissolves only slightly in water. It is highly flammable, and its vapors can be explosive. It may be ignited by heat, sparks, and flames. Flammable vapor may spread away from a spill. N-hexane can react vigorously with oxidizing materials such as liquid chlorine, concentrated oxygen, and sodium hypochlorite. It will attack some forms of plastics, rubber, and coatings. It is insoluble in water and miscible with alcohol, chloroform, and ether. It is incompatible with strong oxidizers.

Table 2.3 Physical properties of hexane

Molecular weight (g/mol)	86.13		
Melting point	-95 <sup>0</sup> C		
Boiling point	68.74 <sup>0</sup> C		
Flash point	-21.7ºC		
Auto ignition temperature	225° C		
Reflextive index	1.342		
Vapour density	3 (air = 1)		
Vapour pressure	132 mm Hg at 20 <sup>0</sup> C		
Specific gravity	0.659		
Explosive limit in air(%v/v)	1.1-7.5		

Source: McParland, 2002

# Health effects

Exposure to n-hexane may lead to human health risk since hexane can cause toxicity in peripheral nerves, muscle wasting, and atrophy. It can cause numbness to the feet and hands and muscle weakness in the feet and lower legs, which can lead to paralysis of the arms and legs. It can also cause dermatitis, nausea, confusion, jaundice, and coma. Thus, a main group of people who have potential to be affected to this potential health risk is a worker who works in the environmental where hexane can leak such as vegetable oil extraction plant.

# Exposure Values

IDLH: 1100 ppm (NIOSH, 1997)

TLV TWA: 50 ppm for n-hexane (@ACGIH)

NIOSH REL: TWA 50 ppm (180 mg/cm<sup>3</sup>)

OSHA PEL: TWA 500 ppm (1800 mg/cm<sup>3</sup>)

#### 2.3 Surfactants

Surfactant is the term derived from Surface Active Agent. Because of its properties when present at low concentration in the system, it can adsorb on the surface or interface and change the free energy of the system. Surfactants tend to adsorb at interfaces and self-assemble results in unique physical properties and behavior. The structure of surfactant molecule contains of two parts. The first part is called hydrophilic part (waterloving) or lyophobic (oil-hating) which is a polar or ionic head and can be charge or uncharged group and another part is called hydrophobic part (water-hating) or lyophilic (oil-loving) which is hydrocarbon chain. Due to two dissimilar parts in one molecule of surfactant, it is called an amphiphalic structure as show in figure 2.4



Figure 2.4 Molecule of surfactant

A single molecule of surfactant is called a monomer and at sufficiently concentration in solution, surfactant monomer will aggregate to form micelles. The micelle formation is a phenomenon at sufficiently high concentration in solution. The concentration at which this occurs is called critical micelle concentration (CMC), depended on the characteristic of each surfactant. This process is known as "micellization". There are two types of micelles; normal and reverse micelle. For aqueous solution, normal micelles are formed with the hydrophobic tail part in the interior and the hydrophilic head group toward aqueous phase. In contrast, reverse micelles are formed in non-polar solvent or in oil with the hydrophilic head group interior and the hydrophobic tail group toward to non-aqueous phase. Figure 2.5 shows the formation of micelle.

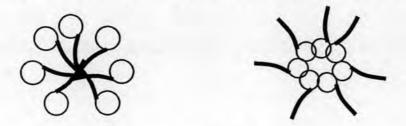


Figure 2.5 Normal micelle and Reverse micelle

Because of the unique characteristic of surfactant such as formation of micelles, surface tension reduction and improving wettability of aqueous solutions, several phenomena of surfactants become interested as a unique branch of physical chemistry as well as leading to many practical applications of chemical industry such as pharmaceutical, paints, cosmetic and detergent (Scamehorn, Sabatini, and Harwell, 2004).

# 2.3.1 Type of surfactants

Surfactants are divided into four types which depending on the nature of the hydrophilic head group.

- Anionic surfactant The surfactants that surface active portion bear a negative charge
  and tend to adsorb onto positively hydrophilic surface. This surfactant type is the
  largest surfactant class for so many applications.
- Cationic surfactant The surfactants that surface active portion bear a positive charge
  and tend to adsorb onto negatively hydrophilic surface. This surfactant type is used
  for subsurface remediation because of their strongly absorb onto most surfaces.
- Zwitterionic surfactant The surfactants that surface active portion bear both positive
  and negative charge without changing the charge of surface significantly. This
  surfactant type is compatible with all other classes of surfactants.
- 4. Non-ionic surfactant The surfactants that surface active portion bear no apparent charge and tend to adsorb onto surface with either hydrophilic and hydrophobic group and oriented toward the surface depending on the nature of surface. The ethylene oxide is usually the polar group of non-ionic surfactants.

#### 2.4 Microemulsions

Microemulsion is one of phenomena occurred in a system consisting of oil, water and surfactant at suitable composition. Microemulsions are a transparent dispersion with particle size less than 100 nm. They are thermodynamically stable, isotropic dispersion of otherwise immiscible oil and water stabilized by surfactant. This type of emulsions are

widely studied due to their unique property in side of providing ultralow interfacial tension which results in the solubilization of the otherwise immiscible component.

# Characteristic of Microemulsions

Microemulsions are transparent dispersions containing two immiscible liquids with particles of 10-100 nm diameter that are generally obtained upon mixing gently the oil and water in the present of surfactant solution in the system. Normally, microemulsions are consisting of at least 3 components, water oil and surfactant which may be one type or more than one or mixture of surfactant in some system. Generally, a second surfactant, called cosurfactant, is added into the microemulsions system. The role of cosurfactant is to prevent formation of rigid structures such as gel, liquid crystal, precipitated etc. A cosurfactant can make the system lower viscosity, reduce the interfacial tension, increase the fluidity of the interface and thereby increasing the entropy of the system, increase the mobility of the hydrocarbon tail and allow greater penetration of the oil and influence the solubility properties of the aqueous and oleic phase due to its partition between the phases. Moreover, other components such as additive, cosolvent, and electrolyte may be added into some system. As a consequence of many potential advantage of microemulsion for example their clarity, high stability and interfacial area and ease of preparation interest has rapidly grown in the use of microemulsions in so many application such as oil recovery (Bidyut and Satya, 2001)

# 2.4.1 Types of microemulsions

Most studies of phase equilibrium of microemulsions are related to Winsor Type microemulsions (Winsor, 1954) which consist of four types of microemulsions known as Winsor Type I, II, III and IV

- Winsor Type I: With two phases, the lower, oil in water (o/w) microemulsions phase
  is in equilibrium with the upper excess oil phase (i.e. in a case of oil is lighter than
  water). Oil droplet disperses in water phase. Oil is solubilized in aqueous micelles
  which surfactant aggregates hydrophobic interior and hydrophilic exterior.
- Winsor Type II: With two phases, the upper microemulsions phase, water in oil (w/o) is in equilibrium with an excess water phase. Water droplet disperses in oil phase.
   This type corresponds to water solubilized in reverse micelle present in oil phase.

- 3. Winsor Type III: The three-phase system consists of non-droplet type microemulsions or middle microemulsions phase (o/w plus w/o) which is called bicontinuous, in equilibrium with upper excess oil and lower excess water phase. This type corresponds to an oil and water bicontinuous phase that is stabilized by a surfactant membrane. The IFT between the middle phase and oil equals to the IFT between the middle phase and water.
- Winsor Type IV: Single phase with oil water and surfactant homogenously mix.
   The Winsor phase diagram is illustrated in Figure 2.6

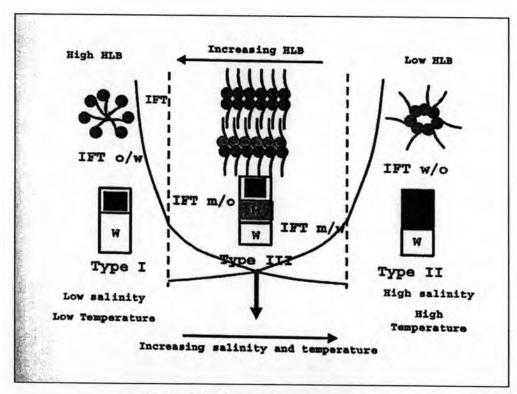


Figure 2.6 Winsor phase diagram

The transformation of microemulsion phase from Winsor Type I to Type III and Type II is related to its hydrophile-lipophile balance (HLB). This parameter shows the partition of surfactant between oil phase and water phase relative to surfactant hydrophobicity. The transition of microemulsion for ionic surfactant is induced by increasing salinity which results to decreasing of HLB. The concentration of salt that

produce minimum IFT and balanced hydrophilic and lipophilic properties is called the optimum salinity. While the phase transition for non-ionic surfactant is occurred by increasing temperature of the system. The temperature at the microemulsion inversion is known as the phase inversion temperature or PIT (Rosen, 2004).

# 2.4.2 Microemulsion properties

Microemulsions have their special properties such as thermodynamically stable, isotropic dispersions of otherwise immisicible oil and water solubilized by surfactant (Bidyut and Santya, 2001) that results in pysico-chemical properties for instance extremely low interfacial tension and high solubilization.

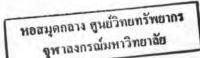
#### Solubilization

Solubilization is the one of the most important properties of microemulsion system. This property directly related to micelle formation of surfactant. It may be defined as the spontaneous dissolving of the substance by the reversible interaction with the micelles of surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material (Rosen, 2004). Micelle forming of a surfactant can enhance the solubility of highly hydrophobic compounds at the micellar core while moderately, soluble polar and ionic compounds can also be solubilized into outer palisade layer of micelle, which consists of the polar moiety of amphipathic surfactant molecule.

#### Interfacial tension

Microemulsions have their unique properties, namely, ultralow interfacial tension, large interfacial area, thermodynamic stability and the ability to solubilize otherwise immiscible liquid. The numerous of microemulsions application require low interfacial tension between oil phase and water phase hence the interfacial tension is one of the most commonly measured properties of microemulsions. The interfacial tension is defined as surface free energy per unit area that is the minimum work requires to bring sufficient molecules from the interior to the surface in order to expand the surface by unit area.

Microemulsions are utilized in a variety of chemical and industrial processes such as pharmaceuticals, fuels, cosmetics, detergency, biotechnology, coating and textile



finishing. Microemulsion formation often requires additive beyond the surfactant alone since synergism of a surfactant and additive or co-surfactant tent to promote their formation. Additives for enhancing microemulsion formation can be co-surfactants, cosolvent, electrolyte, hydrotropes and linkers (Tongcumpou et al., 2003). The behavior of mixed surfactant shows a result of increasing electrostatic interaction between mixed micelle due to the incorporation of charged surfactant (Holland and Rubingh, 1992). In addition, the relative hydrophile-lipophile balance (HLB) of the mixed surfactant system is optimum in the midst the three phase region when the microemulsion exist with excess water and oil phases, the solubilization capacity reaches its maximum and ultralow interfacial tensions are attainted due to critical solution phenomena of microemulsion (Kunieda et al.,1998). There are many researches focus on the mixed surfactant system for example; Aramaki, Ozawa, and Kunieda (1997) studied the effect of temperature on the phase behavior of ionic and nonionic microemulsion while using brine/ sodium dodecyl sulfate(SDS) /polyoxyethylene dodeccyl ether (C12EO2 or C12EO3)/ decane system. The experiment was carried out by forming the microemulsion system over a wide range of temperature. The results show temperature insensitive microemulsion is formed in the SDS-C<sub>12</sub>EO<sub>3</sub> system. Raney (1991) studied optimization of nonionic and anionic surfactant blends for enhanced oily soil removal from polyester cotton and fabric in order to find the high effectiveness formation of nonionic and anionic mixture that temperature insensitive.

Moreover, there are many publications used microemulsions for environmental applications in field of extraction contaminant such as Dierkes et al. (1998) studied low-temperature microemulsions for the in situ extraction of hydrophobic contaminants from soil such as toluene and polychlorinated biphenyls using rape oil and use anionic and nonionic surfactant system at temperature10 °C. This work reveals that microemulsion system seems to be an excellent media for in-situ remediation of hydrophobic contaminant in soil. Dantas et al. (2003) investigated the heavy metal extraction by microemulsion, using regional vegetable oils as surfactants. This work showed the great efficiency of the microemulsion, indicating that it is possible to extract selectively the heavy metals from the aqueous phase. Neto, Dantas, and Moura (2004) studied chromium removal from tannery effluent by microemulsion in the Morris extractor using surfactant

derived from a vegetable oil (coconut oil). This work shows the promising technique for chromium removal by microemulsion system.

Furthermore than that mentioned earlier, microemulsions application have been introducing in the area environmental aspect on vegetable oil extraction in order to replace conventional organic solvent. This is because it provides ultra low interfacial tension that expects to be a major key for extracting oil from their seeds. Recently, there is growing of the interest in replacing solvent extraction by surfactant aqueous base extraction in microemulsion system. Guar et al. (2006) studied the method of using enzyme assisted three phase partitioning (EATPP) in order to replace hexane in conventional extraction process. However their work was found to release t-butanol and ammonium sulphate from the system which is considered not preferable to the environment. Surfactant aqueous-based for vegetable oil extraction is thus considered as a promising alternative approach. In addition, some literatures have shown possibilities to from microemulsion with vegetable oil.

Dantas, Sliva and, Neto (2001) studied the new microemulsions systems containing diesel and various types of vegetable oils (soybean, palm and ricin) that can be used as alternative fuels in order to serve for emission controlling. The main parameters that influence the microemulsion system have been studied in this work such as nature of surfactant (T), cosurfactant (C), C/T ratio and composition of the oil phase. The surfactants that selected for this work were Texapan HBN (Sodium laurylsulfate) and Comperlan SCD (coconut fatty acids diethanolamide). Ethyl, propyl and isoamyl alcohols were used as cosurfactant. The results showed that it was possible to obtain the new microemulsion systems with different oil phase composition (mixtures of diesel and vegetable oils) though a simple methodology and, seemingly, of low cost.

Hsu and Naca (2003) studied the behavior of soybean oil in water emulsion stabilized by nonionic surfactant; Tween series surfactants including Tween 20, Tween 60, Tween 80 and Tween 85. The effect of temperature, hydrophile-liprophilic balance (HLB) value of surfactant and surfactant to oil ratio on the size of emulsion drop were investigated with an acoustic electroacoustic devices. The electrokinetic properties of soybean oil in water emulsions solubilized with surfactants were examined. Moreover, the effect of electrolyte and pH on the potential of vegetable oil stabilized by a non-ionic

surfactant were studied, the results showed that the stability of the emulsions strongly dependent on pH. In addition, it was found that high concentrations of Na<sup>+</sup> and K<sup>+</sup> are capable for separating the oil phase from the emulsion.

Raman, Suhaimi, and Bidyut (2003) studied phase behavior and microemulsions formed by mixture of non-ionic surfactant with palm olein (PO) and its derivatives oils (Palm oil methyl esters and medium chain triglycerides) with Imbentin coco 6.9 EO, an ethoxylate C<sub>12-14</sub> alcohol in order to identify the composition where microemulsion occur by using the optical microscope phase penetration scan and small angle X-ray diffraction (SAXS). Mix surfactant and oil were prepared at weight ratios of 0.1:1, 0.25:1, 0.5:1 and 1:1 for the phase penetration scan. For SAXS analysis, the initial concentration of surfactant in water (W) was fixed at 38% w/w, which forms a hexagonal mesophase (H<sub>1</sub>). Palm oil methyl esters (POME) and medium chain triglycerides (MCT) were added to this at 0.04:1(or 0.05:1 for MCT), 0.1:1, 0.2:1 (or 0.25:1 for MCT), 0.5:1 and 1:1 ratios of oil to surfactant. The extent of microemulsions formation decreases in the sequence POME> MCT>PO and increases substantially with temperature, particularly for POME and MCT.

Rajib and Bidyut (2005) studied physicochemical of microemulsification of eucalyptus oil and water using single and mixing surfactants (AOT+Brij-35), cosurfactant of different lipohilicity (isomers of butanol) and water at different surfactant and cosurfactant mixing ratios. The microemulsion zone was found to be dependent upon mixing ratios of surfactant and cosurfactant; the largest microemulsion zone was formed with 1:1 w/w S:CS. The effects of temperature and additives (NaCl, urea, glucose and bile salts at different concentrations) were examined in phase behavior part. The mixed microemulsion system showed temperature insensitivity behavior, whereas the system of only Brij-35 exhibited a smaller microemulsion zone at elevated temperature. It was also reported that NaCl and glucose increased the microemulsion zone up to a certain concentration and the additives decreased the microemulsion zone as the temperature was increased.

Klongklaew et al. (2005) studied hexane replacement for soybean extraction process using surfactant based aqueous system. The objective of this study was to investigate the appropriate microemulsion system for soybean oil extraction in order to

maximize soybean oil mobilization while minimize soybean oil solubilization. From this study, the result shows that the system of mixed surfactant 3% Comperlan KD and 0.1% Alfoterra145-5PO with soybean oil was able to form microemulsion. By using this system the maximum soybean oil extraction yield 86% from soybean seeds at the condition of 0.212-0.425 mm size of 1 g ground soybean seeds with 10 ml of the surfactant solution in 30 min contact time.

Engelskirchen, et al (2006) studied the stability of a microemulsion system of triacylglycerol and alkyl ethoxylate surfactants. Thier study focused on the phase behavior, interfacial tension microstructure of H<sub>2</sub>O/ NaCl/ Triacylglycerols-allkylpoly glycoether. Triacylglycerols are the main components of natural fat and oils including all vegetable oils, such as palm oil, sunflower oil. The interfacial tension between water and oil was found to be high in microemulsion system containing triolein and need high surfactant mass fraction to formulate a single phase microemulsion. This is true not only for triolein but also for saturated long chain triglycerols.

Consequently, for this work in order to obtain low interfacial tension which will be the key factor to detach oil from seed meal, extended surfactants are selected for microemulsion formation. This is because extended surfactants have found to provide microemulsion with the vegetable oil and provide very low interfacial tension (Witthayapanyanon et al., 2006).

From literature reviews, this research conducted by selecting the mixture between nonionic surfactant and anionic surfactant because of the occurrence of microemulsion formation with long chain fatty acid or triacylglycerol which are the major component of vegetable oils and considered that difficult to form microemulsion. The vegetable oils which selected for this study were palm kernel oil and soybean oil because the literature reviews showed the possibilities to form microemulsion. The selected nonionic surfactant was Comperlan KD while the selected anionic extended surfactants were Alfoterra145-5PO and Alfoterra5-8PO due to extended surfactant can achieve ultra low interfacial tension from previous study. The mixture of 3% Comperlan KD and 0.1% Alfoterra145-5PO showed the highest extraction efficiency for soybean oil hence in this study used this condition for palm kernel oil. In addition, the optimum condition for soybean oil extraction from previous study was used for oil quality study.