

## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Vegetable Oils

The dwindling of petroleum energy sources and their inherent environmental anxiety have caused to the pursuance of renewable biofuels. Vegetable oils, as a result is an alternative fuel source to solve the limitation of fossil fuels. Seddon (1942) demonstrated many types of vegetable oils could be directly used in diesel engine under normal operating conditions. Vegetable oils are pleasing for use as a biofuel because of their several characteristics, but in overall they are renewable and non-toxic natures. While the combustion process, vegetable oils emit less greenhouse gases and other harmful emissions than those of fossil fuels (Dunn *et al.*, 2000; Mondal *et al.*, 2008). However, triglycerides, which are the primary components, are the cause of having high viscosity in vegetable oil. Unfortunately, the use of vegetable oil in diesel engine has some limitations, including poor volatility and higher viscosity than those of diesel, which could lead to a poor atomization, carbon deposits or clogging of fuel lines (Rakopoulos *et al.*, 2006; Lin *et al.*, 2013; Yoshimoto *et al.*, 2013).

##### 2.1.1 Palm Oil

Several types of vegetable oil have been utilized as biofuels, palm oil is high potential feed stock among others. Rupilius and coworker (2007) showed palm oil has the lowest cost for biodiesel production and needs far less agricultural land for production compared with soya bean, rapeseed, sun-flower seed and coconut (Table 2.1). The production and export trends from year 2008 to 2012 of palm oil in Thailand are shown in Table 2.2. The volume of production and exports increased in every year at high rate of production (Mukherjee and Sovacool, 2014). This can be implied that palm oil is an appropriate vegetable oil for utilizing biofuel production in Thailand.

**Table 2.1** Productivity of different plants

<b>Oil</b>	<b>Productivity (MT/Ha/year)*</b>
Palm/palm kernel	4.4
Coconut	2
Rapeseed	1.2
Sunflower	0.7
Soya	0.4

\*Metric ton/Hectare/year

(Rupilius and Ahmad, 2007)

**Table 2.2** Palm oil production and exports of Thailand (kilotons)

	<b>2008/09</b>	<b>2009/10</b>	<b>2010/11</b>	<b>2011/12</b>	<b>2012/13</b>
Production	1,540	1,345	1,288	1,546	1,700
Exports	114	130	382	500	520

(Mukherjee and Sovacool, 2014)

### 2.1.2 Refined Bleached Deodorized Palm Oil (RBDPO)

Palm oil products are made using milling and refining process, the oil is filtered and bleached to remove impurities. Finally, physical refining removes smell and color of oil to produce refined bleached deodorized palm oil (RBDPO). Because of the lower price of RBDPO than that of purified palm olein as shown in Table 2.3. RBDPO is selected to formulate as alternative vegetable oil for microemulsion biofuels in this study.

**Table 2.3** Cost with different types of oil

Raw Materials	Raw Material Price (USD/kg)	Selling Price (USD/kg)
Refined Bleached Deodorized Palm Oil (RBDPO)	146.91	0.96
Palrn. olein	148.87	0.97

(Meilita *et al.*, 2015)

## 2.2 Technologies of Reducing Vegetable Oil's Viscosity

Vegetable oils can be used as alternative diesel fuel because of their physical properties, especially high energy content (about 90 % of diesel) (Schwab *et al.*, 1987). Chemical and physical properties of vegetable oils are showed in Table 2.4. The overall kinematic viscosity of vegetable oils is approximately 10 times more than that of petroleum diesel fuel (Murugesan *et al.*, 2009). Due to the fact that high viscosity of vegetable oils leads to poor atomization of the fuel, engine durability problems such as coking of injector nozzles and sticking of piston rings, and incomplete combustion (Schwab *et al.*, 1987; Ma and Hanna, 1999; Murugesan *et al.*, 2009). Thus, reducing vegetable oil's viscosity is very important for biofuel production technology.

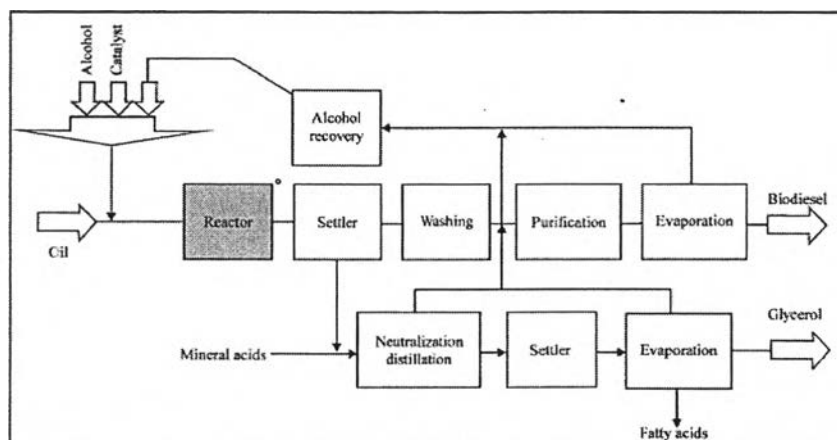
**Table 2.4** Chemical and physical properties of vegetable oils

Vegetable Oils	Kinematic Viscosity at 38 °C (mm <sup>2</sup> /s)	Cetane Number	Heating Value (MJ/kg)	Cloud Point (°C)	Pour Point (°C)	Flash Point (°C)
Corn	34.9	37.6	39.5	-1.1	-40.0	277
Cottonseed	33.5	41.8	39.5	1.7	-15.0	234
Peanut	39.6	41.8	39.8	12.8	-6.7	271
Rapeseed	37.0	37.6	39.7	-3.9	-31.7	246
Soy bean	32.6	37.9	39.6	-3.9	-12.2	254
Sunflower	33.9	37.1	39.6	7.2	-15.5	274
Palm	39.6	42.0	39.5	31.0	-	267
Diesel	3.06	50.0	43.8	-	-16	76

(Murugesan *et al.*, 2009; Singh and Singh, 2010)

Four technologies have been assessed to decrease the high viscosity of vegetable oils in order to conquer diesel engine problems; dilution with less viscous liquid fuels (vegetable oil/diesel blends), pyrolysis (thermal cracking), vegetable oil transesterification to fatty alkyl esters or biodiesel (alcoholysis with short chain alcohols) and vegetable oil-based microemulsification.

Transesterification to produce biodiesel is the most common method to decrease the viscosity of vegetable oils. Because biofuel obtained from transesterification process has fuel properties comparable to those of No.2 diesel (e.g., kinematic viscosity, specific gravity, cetane number and gross heat of combustion) (Attaphong *et al.*, 2012). However, biodiesel also has many undesirable properties including cold weather limitations due to relatively higher cloud point and pour point, and increasing nitrogen oxides (NO<sub>x</sub>) in the exhaust emissions which needs further improvement (Ali *et al.*, 1994; Chang *et al.*, 1996). Moreover, transesterification reaction produces glycerol as a co-product (see Figure 2.1) which requires additional process, and thus increasing in overall environmental emissions (Galan *et al.*, 2009; Pagliaro *et al.*, 2007).



**Figure 2.1** Transesterification of biodiesel. (Y.K. Ho *et al.*, 2009)

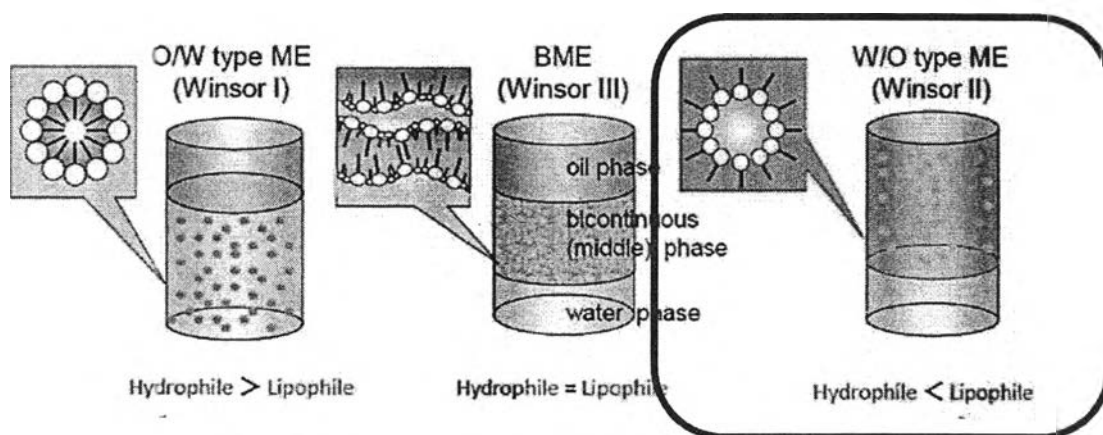
In addition, the blend of ethanol and diesel, so called “diesohol”, is being investigated in public transport vehicles. Because diesohol can be made from very ordinary crops such as sugar cane and corn. However, ethanol-diesel blends are limited by the fact that they are immiscible over a wide range of temperatures (Fernando *et al.*, 2005).

Microemulsification of vegetable oils overwhelm the transesterification process in terms of environmental benefits by avoiding the production of water waste stream and unpurified glycerol or co-product of transesterification. Moreover, the microemulsification approach assists to conquer the immiscibility of ethanol and diesel blend

### 2.2.1 Vegetable Oil based Microemulsification

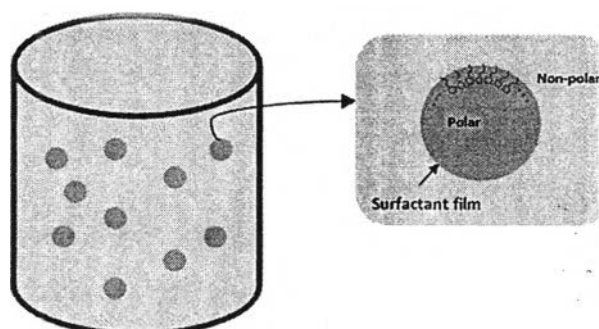
Microemulsions are thermodynamically stable emulsions that include water and oil domains separated by surfactant film (Rosen, 1989). Microemulsions can exist in four Winsor Type microemulsion phases (Figure 2.2). Winsor Type I (oil-in-water or O/W) microemulsions are normal micelles in equilibrium with an excess oil phase, while Winsor Type II (water-in-oil or W/O) microemulsions are reverse micelles (Figure 2.3) in equilibrium with an excess water. Winsor Type III microemulsions exhibit three phases, excess oil and water phases in equilibrium with

a middle phase containing oil, water, and surfactant. In a middle phase microemulsion, increasing surfactant concentration causes the amount of the middle phase to increase until all of the oil and water coexists in a Winsor Type IV single phase microemulsion (Rosen, 1989). Microemulsion-based biofuels, or hybrid fuels, are transparent and thermodynamically stable of Winsor Type II microemulsion which the polar phase is solubilized in reverse micelles occurring in the non-polar phase (vegetable oil/diesel blended). Alcohol is used in place of water as the polar phase which disperses in the vegetable oil/diesel blend.



**Figure 2.2** Winsor-type microemulsion phases.

<http://chem.chem.kumamoto-u.ac.jp/~polymers/eng/research/bme.html>



**Figure 2.3** Reverse micelle structure.

### 2.3 Alcohol Blended

The utilization of ethanol in diesel fuel can yield a significant reduction of exhaust emissions in terms of CO and NO<sub>x</sub> (Ajav *et al.*, 1999) and particulate matter (PM) emissions for motor vehicle. However, there are many hindrances in using ethanol in diesel engine (Xing-cai *et al.*, 2004);

- Ethanol has limited solubility in diesel fuel
- Ethanol fuel has a substantially low cetane number, whereas diesel engines prefer high cetane number fuels, which makes auto-ignition easy and gives a short ignition delay.
- The dynamic viscosity of ethanol is much lower than that of diesel fuel, so that the lubricity, as a result is a potential concern of ethanol-diesel blend fuel.
- Ethanol has low flash point

To stretch the utilization of diesel/biodiesel blends in diesel engine, the addition of alcohols, mainly ethanol, to the blends has been considered (Altun *et al.*, 2011; Lujaji *et al.*, 2011; Lin *et al.*, 2013; Sukjit *et al.*, 2013; Yoshimoto *et al.*, 2013). The lower viscosity and higher volatility of alcohols recompense for these opposite properties in biodiesel (Lin *et al.*, 2013; Yoshimoto *et al.*, 2013).

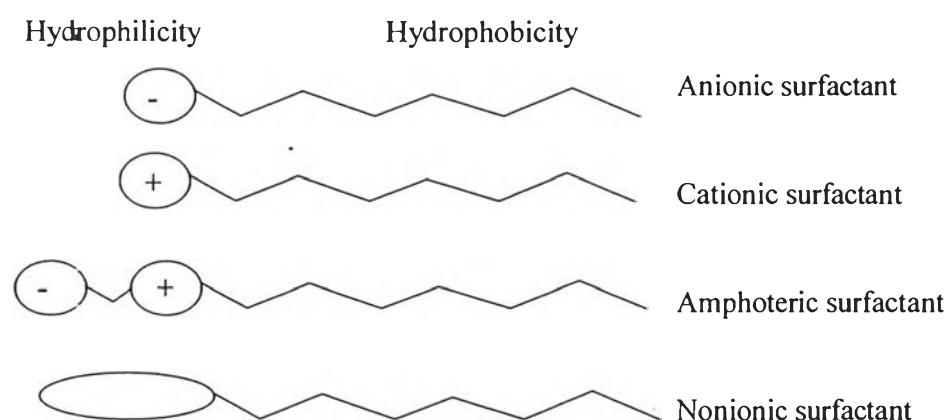
Among alcohols, butanol has recently drawn particular attention as a renewable biofuel for diesel engines due to its higher heating value and cetane number and less hydrophilicity compare to diesel, and more miscibility compared to methanol and ethanol (Altun *et al.*, 2011; Sukjit *et al.*, 2013; Yoshimoto *et al.*, 2013). Recent studies recommended that butanol can be a better alternative biofuel than ethanol for using in diesel engine (Sukjit *et al.*, 2012). However, there is a lack of detailed examinations on the effects of butanol addition to diesel blends on engine performance and particulate emissions.

Although ethanol is generally used for blending in diesohol, butanol is an alcohol which has higher solubility in diesel than ethanol. Areerat and coworkers (2009)

investigated on the utilization of biodiesel as an additive in diesohol preparation, three types of biodiesel-methyl, ethyl, and butyl esters-were prepared from palm oil through transesterification using a conventional based catalyst. They found that the use of butanol in diesohol could solve the problem of fuel instability at low temperatures because of its higher solubility in diesel fuel. The fuel property study showed that the blends containing butanol have better properties than those of the blends containing ethanol (properties closer to diesel).

## 2.4 Surfactants and Cosurfactants

To overcome the immiscibility of alcohol and diesel, surface active agents or surfactants can be used as emulsifiers to stabilize the miscibility phases of alcohol and diesel through microemulsification process. Surfactants are typically divided into four types as shown in Figure 2.4;



**Figure 2.4** Types of surfactants. (Rosen, 1989)

### 1) Anionic Surfactant

Anionic surfactants contain anionic functional groups at their head (has a negative charge on their hydrophilic end). It is normally in the sulfonate or sulfate



group of chemicals such as sodium laureth sulfate, that acts as an active surface agent to lower the surface tension of liquids.

#### 2) Cationic Surfactants

They have positively charged end, which makes them ideal in antistatic formulas like fabric softeners and automobile. The cationic structure consists of, e.g., bromide or chloride group such as alkylbenzene ammonium chloride.

#### 3) Amphoteric Surfactants

These unique molecules consist of both a positive and a negative charge on their hydrophilic end, giving them a net charge of zero. This means that they can act as two state; anionic surfactant in an alkalic solution or as cationic surfactant in an acidic solution. The examples of amphoterics are betaines and amine oxides.

#### 4) Nonionic Surfactants

Nonionics have no charge on their hydrophilic end, which helps make them superior oily soil emulsifiers. They have a wide application within cleaning detergents and include groups like fatty alcohol polyglycosides, alcohol ethoxylates and etc.

Nonionic surfactants have been found to be an appropriate surfactant for microemulsion formation of vegetable oil/diesel and ethanol blends from many reasons (Arpornpong *et al.* 2014) including; it has low HLB or it can work well with oil systems. For phase transition, nonionic surfactants can work without salt and they are no SO<sub>x</sub> and NO<sub>x</sub> emissions. Some special types of nonionic surfactant are biodegradable because it can derived from renewable feedstocks.

##### 2.4.1 Alcohol Ethoxylates Surfactant

Alcohol ethoxylates are nonionic surfactants that can be derived from bio-based product as shown in equation 2.1. In industrial ethoxylation, an alcohol is treated with ethylene oxide and potassium hydroxide (KOH), which serves as a catalyst. The reactor is pressurised with nitrogen and heated to about 150 °C. Typically, 5 to 10 units of ethylene oxide (EO) are added to each surfactant molecule.



The amount of ethylene oxide group and the reaction time determine the degree of ethoxylation (the value of  $n$  in the equation above), which in turn determines the surfactant properties of the ethoxylated product. The hydrophilicity of the surfactant increases with the value of ethylene oxide group.

Many researchers have been investigated on various types of surfactant for microemulsion biofuels; Attaphong and coworkers (2012) used the extended-surfactants, which have the intermediate polar groups enclosed between the head and the tail of the surfactant molecule, for forming microemulsions. The extended-surfactants have ethylene oxide (EO) or propylene oxide (PO) groups enclosed between the hydrophilic head and hydrophobic tail to improve polar phase and non-polar phase interaction, respectively. They determined the phase behaviors of carboxylated-based extended surfactant on reverse micelle microemulsion formation with ethanol and canola oil/diesel blends. 1-octanol and 2-ethyl-1-hexanol were used as cosurfactant. 2-ethyl-1-hexanol is an isomer of octanol with a branched eight-carbon alcohol. Mixtures of surfactant and cosurfactant at fixed molar ratios (1-8, 1-16, and 1-32) were investigated. Different amounts of ethanol (0.5, 1, 2, 3, 4 and 5 mL) with 5 mL of canola oil/diesel blend were added into surfactant/cosurfactant mixture to formulate reverse micelle microemulsions. The results showed that the linear extended surfactants required less amount of surfactant than branched extended surfactants to solubilize all components and produce a single phase microemulsion. When the number of EO groups decreased from 5 to 3 in the extended surfactants led to 3 % to 4 % reduction of the amount of surfactant used. So, the linear surfactant which has the least number of EO groups was identified as the preferred surfactant due to the fact that it needed the least amount of surfactant to achieve the single phase microemulsion. Moreover, they studied the effect of surfactant to cosurfactant ratio, the resulted showed that the phase behavior of microemulsion is not significantly affected by adjusting the ratio of surfactant to cosurfactant.

Another research work of Attaphong and coworkers, they studied the phase behaviors of microemulsion fuels using renewable surfactants (alcohol

ethoxylate, and sugar-based surfactants) and compared their results to the surfactant systems used in their previous study (carboxylated-based extended surfactants). They studied three types of nonionic surfactant (linear C<sub>10-12</sub>3EO OH, linear C<sub>12-16</sub>1EO OH and linear C<sub>12-16</sub>3EO OH) and anionic carboxylated-based extended surfactant (linear C<sub>16-18</sub> 4PO 2EO carboxylate surfactant) with 2-Ethyl-1-hexanol as a cosurfactant. The result from their study showed that salt-free single phase microemulsion fuels were formed with all the surfactants used in this research even at low temperatures. Moreover, they demonstrated that all sugar-based surfactants required higher concentrations than carboxylate-based extended, alcohol ethoxylate, and fatty alcohol surfactants to produce a single phase microemulsion. For alcohol ethoxylate surfactants, linear C<sub>12-16</sub>1EO OH (L16-1) required the lowest concentration of surfactant. This is because increasing alkyl groups and decreasing EO groups increase hydrophobicity of surfactants which can facilitate the polar phase to solubilize in the oil phase.

#### 2.4.2 Methyl Oleate with Cosurfactants

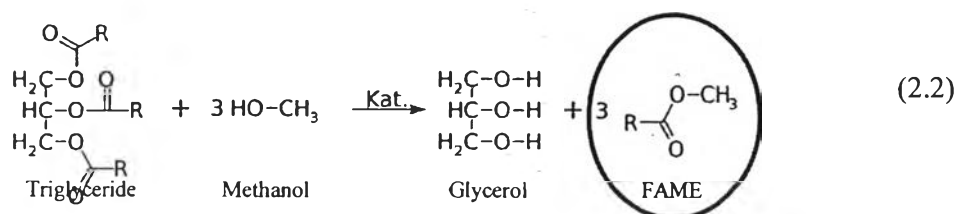
Most of research works on the use of nonionic surfactants in the fuel formulation have been conducted on ethoxylate fatty alcohol. Dunn and Bagby (1994) showed that mixed amphiphile systems composing of a long-chain fatty alcohol and an n-alkanol are effective in solubilizing methanol/ethanol in triglycerides, which has been referred to microemulsification in general. Methyl ester of oleic acid (methyl oleate) and alcohol of oleic acid, gained from natural raw materials, can also use as a nonionic surfactant. Although fatty acid esters in common are not considered as surfactant since they do not form micelles in water phase, they can be considered as surfactants in the oil phase when they have been demonstrated to form reverse micelles in oil phase (Dunn *et al.*, 2000; Do *et al.*, 2011; Attaphong *et al.*, 2012).

Arpornpong and coworkers (2014) studied the effects of surfactant structures including, surfactant saturation, unsaturation, and ethylene oxide groups on phase behavior, kinematic viscosity, and microemulsion-droplet size with the purpose of formulating and optimizing surfactant used in microemulsion biofuel.

They used four types of nonionic surfactants, stearyl alcohol (saturated), oleyl alcohol (unsaturated), methyl oleate (unsaturated with ester groups), and Brij-010 (EO groups). They found that methyl oleate could dramatically reduce the bulk viscosity and produce uniformly size of microemulsion droplets while required the least amount of surfactant to achieve a single phase microemulsion. Its kinematic viscosity at 40 °C of the appropriate fuel condition was 4.0 mm<sup>2</sup>/s, which is nearly compared to that of No.2 diesel (1.9-4.1 mm<sup>2</sup>/s). They concluded that methyl oleate (MO) is the most appropriate surfactant for this system when compared to others. Moreover, the cosurfactant-chain length was varied from n-butanol (C4) to n-decanol (C10). The results showed that increasing the cosurfactant chain length, decreased the amount of surfactant required because the long chain cosurfactant is more suitable for producing stable ethanol-in-oil. For fuel viscosity study, the results showed that increasing the carbon chain length of cosurfactants insignificantly increased the kinematic viscosity (from 4.4 to 4.8 mm<sup>2</sup>/s at 40 °C). Because the van der Waals forces of the hydrocarbon bonds in cosurfactant or alkanol are likely to be a main factor in determining the overall viscosity of palm oil/ethanol-diesel (Dunn *et al.*, 1994).

#### 2.4.3 Fatty Acid Methyl Ester (FAME) or Biodiesel

Fatty acid methyl esters (FAME) are a type of fatty acid ester that can be produced by an alkali-catalyzed reaction between fats or fatty acids and methanol known as transesterification product (Equation 2.2). Absolute biodiesel is referred to B100. A biodiesel blend is absolute biodiesel blended with petrodiesel which is defined as BXX (XX indicates the amount of biodiesel in the blend such as a B85 blend is 85 % biodiesel and 15% petrodiesel).



Biodiesel is environmental friendly because of lower hydrocarbon emissions, smoke and lampblack reductions, lower CO emissions, reduction of greenhouse gases. Biodiesel has many advantages as the fact that, it is derived from biodegradable and renewable resources. It helps to lubricate the diesel engine itself reducing diesel engine wear. Biodiesel can be used directly in compression ignition engines with no substantial modifications of the engine (Sarin, 2012).

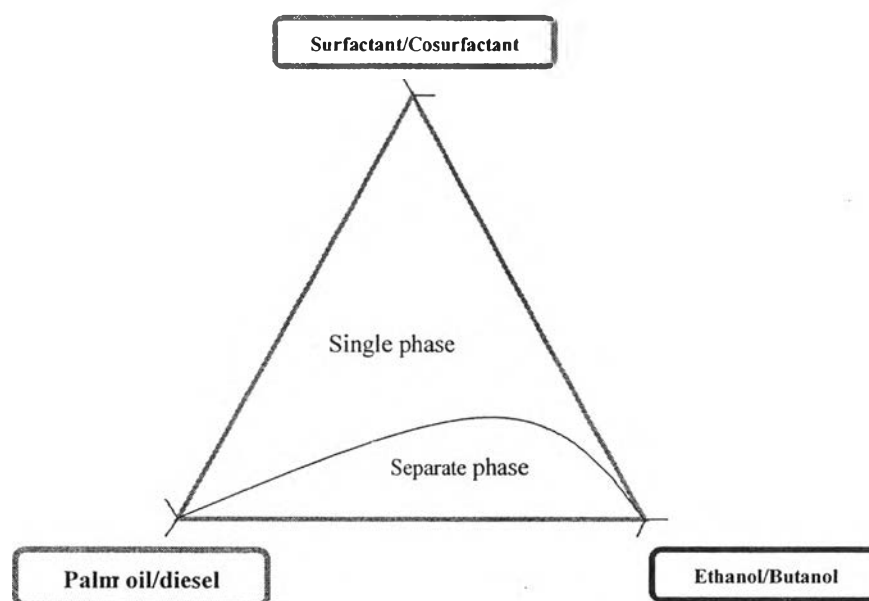
Babadagli and Ozum (2010) studied the use of biodiesels as a surfactant additive for reducing heavy oil/bitumen-water interfacial tension in steam assisted recovery processes. Advantages of using biodiesel as a surfactant additive are that biodiesel is chemically stable under the operating pressure and temperature of the reservoir, it causes no harm on bitumen quality and released water chemistry and its use is economically feasible.

## 2.5 Pseudo-Ternary Phase Diagram

Principle of pseudo-ternary phase diagram representing three-component system is typically used, in order to study phase behavior and miscibility of the microemulsion. It calls pseudo diagram because this systems have more than three component but they have three main material groups (oil phase, alcohol phase, and surfactant phase). A pseudo-ternary phase diagram is an equilateral triangle which consists of three vertices of three main components (Fernando *et al.*, 2005). Two vertices at the bottom of triangle represent palm oil/diesel and alcohol mixtures at the left side and the right side, respectively. While the upper vertex represents the surfactant/cosurfactant mixture at a constant ratio for a given temperature (Figure 2.5) (Neuma *et al.*, 2001; Ploysrimongkol *et al.*, 2009). The composition at each point in the ternary phase diagram demonstrates the volume percent of the three components (A,B,C) as Equation 2.3 (Dorfler *et al.*, 1993):

$$x\%A + y\%B + z\%C = 100\% \quad (2.3)$$

The miscibility curve is plotted as the boundary between separate phase and single phase microemulsions. The regions above the curve are single phase systems where sufficient surfactant has been added to solubilize all of components. Note that; this is a thermodynamically stable and transparent microemulsions. Below the curve, two visibly separate phases occur which in our case is a Winsor Type II (Schwab *et al.*, 1985; Singh *et al.*, 2010).



**Figure 2.5** Pseudo ternary phase diagram.

## 2.6 Fuel Properties

The fuel properties of biofuels containing alcohol in their composition are determined to explore its short-term and the long-term effects on the diesel engine. Since addition of alcohols (ethanol and butanol) affects physic-chemical properties of the diesel fuel; decreasing of cetane number, heat content, kinematic viscosity, flash point, and cloud point.

Chotwichien and coworkers (2009) studied the usability of biodiesel as an additive in diesohol preparation. Because they used butanol instead of ethanol for

improving the fuel properties including; kinematic viscosity (at 40 °C), flash point, pour point, heat of combustion and cetane index. The results showed that the blends containing butanol had properties closer to diesel than those of the blends containing ethanol.

In 2012, Nguyen and coworkers formulated microemulsion fuels consisting of diesel fuel and canola oil as the oil phase with ethanol and sec-butanol as viscosity reducers. Moreover, they used oleyl amine and 1-octanol as surfactant/cosurfactant. They confirmed the results by comparing the fuel properties of formulated microemulsion fuels to No.2 diesel fuel. Kinematic viscosity, cloud point, and pour point was investigated in this work.

#### 2.6.1 Kinematic Viscosity

Kinematic viscosity is one of the important parameters in the usability of vegetable oils as fuel. Palm oil has viscosity of 45.34 mm<sup>2</sup>/s (40 °C) while diesel oil's viscosity is 2.70 mm<sup>2</sup>/s (40 °C) (Esteban *et al.*, 2012). The viscosity of a fluid is a measure of its resistance to gradual deformation by shear stress or tensile stress. Vegetable oils have high viscosity, which leads to poor fuel atomization during the injection process. Furthermore, the operation of diesel engine with a viscous fuel results in deposit formation, ring sticking, and fuel dilution from excessive lubricant oils (Attaphong *et al.*, 2012). With appropriate conversion processing, the kinematic viscosity of vegetable oils can be decreased to a level close to diesel fuel.

#### 2.6.2 Cloud Point

The cloud point of a fluid is referred to the temperature at which dissolved solids are no longer completely soluble, precipitating as a second phase giving the fluid a cloudy appearance. This term is essential to several applications with different consequences. For fuel, cloud point referred to the temperature below which wax in diesel or biowax in biodiesel formed a cloudy appearance because of the formation of crystals, which can clog fuel filters and supply lines. Cloud point of diesel oil is lower than that of vegetable oil (Ali and Hanna, 1994).

### 2.6.3 Gross Heat of Combustion or Heating Value

The heat of combustion is the energy released as heat when a compound undergoes complete combustion with oxygen under standard conditions. It is measured in units of energy per unit of the substance, usually mass, such as: MJ/kg, kJ/mol, kcal/kg, Btu/lb. Heating value is generally determined by a bomb calorimeter followed by ASTM D240. Heat of combustion is frequently used for evaluating the fuel consumption in diesel engine.

The mean droplet size (droplet diameters) of reverse micelle microemulsions are in the range of 2 to 200 nm (Rosen, 2004). Arpornpong and coworker (2014) investigated the droplet size distributions of microemulsion-based biofuel to observe the correlation with kinematic viscosity.

### 2.6.4 Droplet Sizes

Microemulsion droplet sizes depends on preparation method and composition in microemulsion-based biofuel system. Dynamic light scattering (DLS) measurements were performed to determine the droplet diameter and droplet size distribution of the reverse micelle microemulsion droplets.