

## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Vegetable Oil

Vegetable oil is oils which are extracted from any vegetables or plants such as soy bean, sun flower, coconut, palm, canola and castor. They consist of mono- di- tri- glyceride. Reaction between glycerol and fatty acid(s) produces vegetable oil. Vegetable oil can be oxidized with oxygen in the atmosphere and can be self-polymerized at high temperature. These factors can make an increasing in vegetable oil viscosity.

Recently, using vegetable oil as a fuel can be substituted diesel because vegetable oil has the comparable or similar properties with diesel oil. But the high viscosity of vegetable oil causes diesel engine's problems for example, vegetable oils make incompletely combustion which produced smog inside the diesel engine, reduce diesel engine's life and feed difficultly to combustion chamber (National Renewable Energy Laboratory, NREL, 2010). Table 2.1 shows properties and heating value of each vegetable oil and diesel.

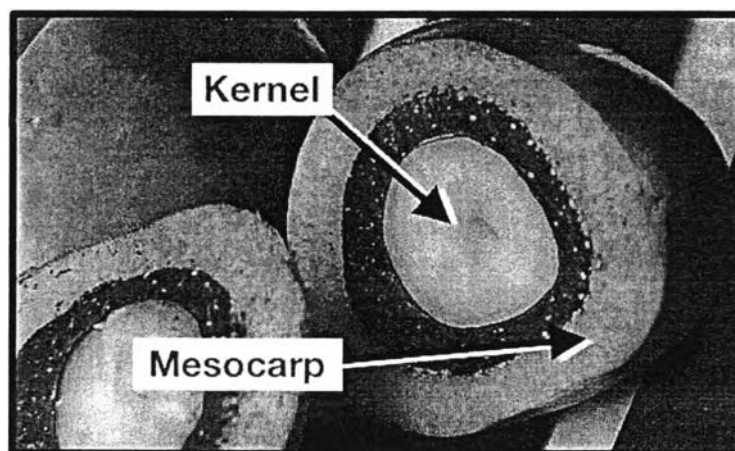
**Table 2.1** Properties and heat of combustion of vegetable oils and diesel

Types of Oil	Density <sup>a</sup> at 40°C (g/ml)	Viscosity <sup>b</sup> at 40°C (cSt)	Heat of combustion <sup>b</sup> (kJ/g)
Diesel	0.8181	2.70	46,800
Rapeseed	0.9027	34.06	40,449
Sunflower	0.9043	33.78	39,800
Soybean	0.9061	31.42	40,000
Palm	0.8996	45.34	39,800

Source : <sup>a</sup>Riba *et al.* (2012), <sup>b</sup>Jenvanitpanjakul *et al.* (2001)

### 2.1.1 Palm Oil

Palm oil is a simply cooking ingredient and used widely in food industries. Oil palm is commercial plants in Malaysia and Thailand originated from South Africa and introduced to East Asia. Palm oil can be extracted from 2 parts; mesocarp and palm kernel which known as palm oil and palm kernel oil, respectively.



**Figure 2.1** Palm fruits (adapted from Liz Lovely, Inc., 2014).

Moreover, palm oil is separated to 2 types (palm olein and palm stearin) by phase separation at ambient temperature (25-30°C). The liquid fraction is called olein and solid or harder fraction of palm oil is called stearin. Palm olein contains high amount of oleic and linoleic acid. On the other hand, the main fatty acid composition in palm stearin is palmitic acid.

Table 2.2 shows fatty acid compositions in palm oil. The major components of fatty acid are palmitic acid (45.6%), oleic acid (38.5%) and others (i.e. linoleic acid, esteric acid) (Riba *et al.*, 2012).

**Table 2.2** Fatty acid composition of palm oil

Fatty acid	Carbon number	Composition (%)
Lauric acid	C12:0	0.1
Mtristic acid	C14:0	0.9
Palmitic acid	C16:0	45.6
Palmitoleic acid	C16:1	0.4
Estearic acid	C18:0	3.8
Oleic acid	C18:1	38.5
Linoleic acid	C18:2	10.5
Linolenic acid	C18:3	0.1

Source : Riba *et al.*, 2012

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

Crude palm oil is extracted from mesocarp and palm kernel of palm fruit, after that the extracted oil is passed thru the process to produce refined bleached deodorized palm oil (RBDPO). This process eliminates free fatty acids, smell, color and clarified impurities from the crude palm oil. The RBDPO has partially solid part as fat. Moreover, RBDPO can be used popularly in fried food industries such as snack, sweetened condensed milk, and production of biodiesel.

## 2.2 Diesel

Diesel is a hydrocarbon liquid mixture which is commonly used in diesel engine and industry. Its boiling point is about 150-380°C. Therefore, ignition of diesel fuel takes place because inlet air mixture is compressed without spark, after, diesel fuel is injected into the cylinder and it is combusted immediately. (Majewski and Jääskeläinen, 2013)

## 2.2.1 Types of Diesel

### 2.2.1.1 *Automotive Diesel Oil*

Automotive diesel so called high speed diesel (HSD) or solar oil, is typically used for diesel engine has speed more than 1,000 rpm such as vehicles trucks, tractor and fishing boat.

### 2.2.1.2 *Industrial Diesel Oil*

This oil is used for diesel engine which has moderate speed engine (500-1.000 rpm) and it is so called low speed diesel (LSD). LSD engines do not require high cetane number and volatilization rate of fuel in the engine may be lower than that of HSD engine.

## 2.2.2 Standard Diesel Fuels

Diesel fuels can be classified by conventional distillation operation. Diesel fuels are known as No. 1, No. 2 and No. 4 diesel fuel. The difference between No. 1, No. 2 and No. 4 diesel fuel is distillation temperature of diesel fuels and their applications.

### 2.2.2.1 *No. 1 Diesel Fuels*

No. 1 diesel fuel is light product from distillation operation and its distillation temperature is about 290°C. It consists of hydrocarbons which carbon numbers in the range of C<sub>9</sub>-C<sub>16</sub>. The specific standard of No. 1 diesel fuels defined in ASTM D 975. It is used in high speed diesel engines.

### 2.2.2.2 *No. 2 Diesel Fuels*

No. 2 diesel fuel is middle distillate product and has distillation temperature about 340°C. The specific standard of No. 2 diesel fuels defined in ASTM D 975 as the same No. 1 diesel fuels. Carbon chain length of No. 2 diesel fuels is longer than carbon chain length of No. 1 diesel fuels. It is used in high speed diesel engines.

### 2.2.2.3 *No.4 Diesel Fuels*

No. 4 diesel fuel is heavy distillate product and is used in low- and medium-speed diesel engines and industries. The standard of No. 4 diesel fuels defined in ASTM D 396. Carbon chain length of No. 4 diesel fuels is longer than carbon chain length of No. 1 and No. 2 diesel fuels.

## 2.3 Biofuel

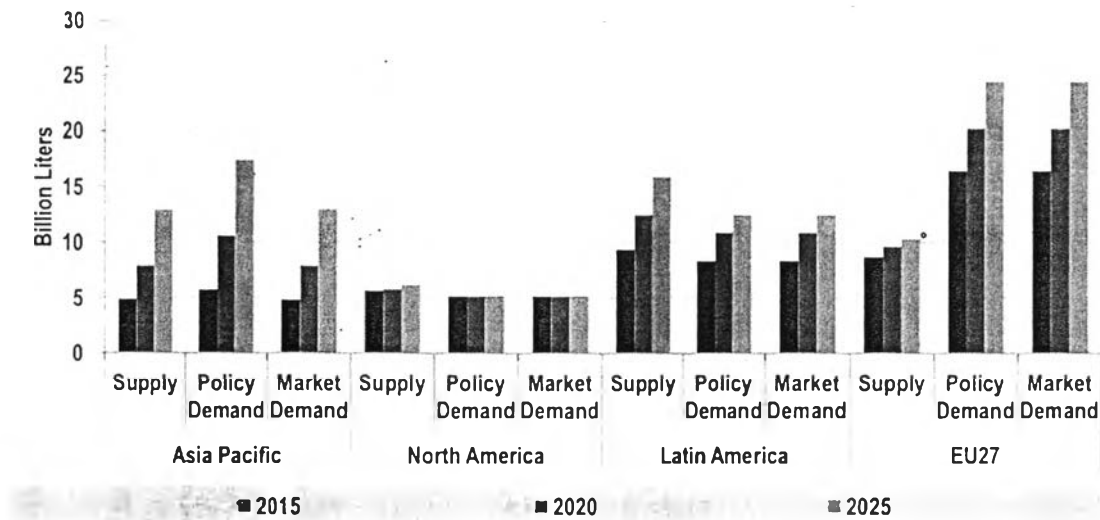
Biodiesel (methyl esters) is derived from vegetable oils or animal fats which can be used as an alternative fuel in diesel engines. In 2008, Mondal and co-workers used vegetable oil and animal fat directly for substitution of diesel fuel. To date, several engine manufacturers have launched full warranty engines with vegetable oil as fuel. The produced process of vegetable oils is extraction from any plants under pressure to squeeze the oil out, but the extraction cannot be used to extract all vegetable oils from the fruits or seeds of plants.

A number of oils have been used in biofuel production. Although diesel engines have been invented, in part, with vegetable oil in mind, diesel fuel is almost exclusively petroleum-based. Rising fossil oil prices have made biodiesel more attractive. Vegetable oils have been evaluated for utilizing as a biofuel based on their emissions and cost of production. Many researchers have developed and improved diesel formula by blending vegetable oils for green fuel. For example, Pryor and co-worker (1982) studied the use of soybean oil fuel in a small diesel engine. A longer term evaluation of the engine when using pure crude soybean oil was prematurely terminated, but power output and thermal efficiency were decreased.

Due to the high viscosity, the use of vegetable oils in diesel engines can cause engine durability problems. Balat *et al.* (2008) investigated potential solutions for solving the problem of vegetable oil viscosity.

### 2.3.1 Demand & Supply of Biodiesel

Figure 2.2 shows global demand and supply of biodiesel will be increased by 70% by 2020 and nearly about by 2025. Therefore, increasing demand and supply of biodiesel are force to develop renewable biofuel in the future.



**Figure 2.2** Demand and supply of biodiesel in the future (Hart Energy's Global Biofuels Center, 2012).

## 2.4 Methods for Vegetable Oil Viscosity Reduction

### 2.4.1 Vegetable Oil/Diesel Blends

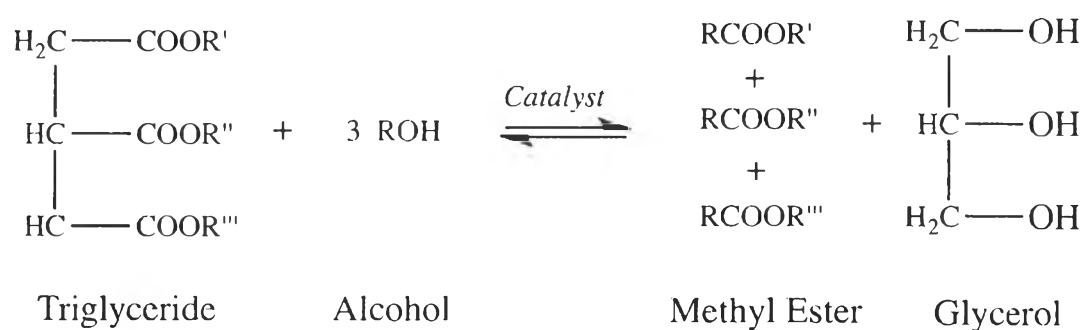
Vegetable oils can be used directly as diesel or combination with diesel for utilizing in engines. However, the use of vegetable oil or partial substituted can cause engine's problem due to the high viscosity. (Do *et al.*, 2011).

### 2.4.2 Pyrolysis

Pyrolysis is dissociated reaction of large molecules to smaller molecules by heating in the vacuum system. When temperature of system increases, triglycerides are converted to many hydrocarbon components such as alkane, alkene, alkyne, aromatic and carboxylic acid compounds. Amount of sulfur, water and precipitate as by-products from pyrolysis reaction is low acceptably, but not ash and carbon residues not because the pour point of oils is unacceptable. Furthermore, pyrolysis reaction consumes high oxygen and operates at high temperature, so the cost of operation is increased.

### 2.4.3 Transesterification

Transesterification or alcoholysis is a common method for reducing viscosity of vegetable oils. Vegetable oil or animal fat (triglyceride) and alcohol react with catalyst to produce ester compounds and glycerol; Figure 2.3 shows transesterification reaction between triglyceride and alcohol.



**Figure 2.3** Transesterification reaction between triglyceride and alcohol.

### 2.4.4 Microemulsion

There are many methods to reduce vegetable oil viscosity; a microemulsion is one of the promising methods. Microemulsion is a system of water and oil mixture which is a single optically isotropic and thermodynamically stable liquid solution (Danielson and Lindman, 1981). Sometimes, microemulsions can be considered as small scale of emulsions, i.e., droplet type dispersions with an average of microemulsion droplet size ranging in 5–50 nm. Formation of microemulsion depends on type and structure of surfactant. If surfactant is used as ionic surfactant and contains a single hydrocarbon chain (e.g., sodium dodecylsulphate, SDS), microemulsion can be formulated to single phase without cosurfactant, but surfactant which is used as double hydrocarbon chain of ionic surfactants or some non-ionic surfactants is not necessary to use cosurfactant for formulating microemulsion (Komesvarakul *et al.*, 2006).

## 2.5 Surfactant

Surfactant, known as detergent, is a surface active agent. When added to a liquid (i.e. water), it reduces an interfacial tension between two miscible phases, thereby increasing its spreading and wetting properties. Thus, it has been used in microemulsion formation of vegetable oil/diesel/ethanol systems. The molecule of surfactants has partly hydrophilic part (surfactant's head) and hydrophobic part (surfactant's tail). Surfactant's head will be located to dissolve the water phase. Similarly, surfactant's tail will be located to dissolve the oil or lipid phase. The surfactants will aggregate to droplets of water and those of oil, or lipid, to act as an emulsifier.

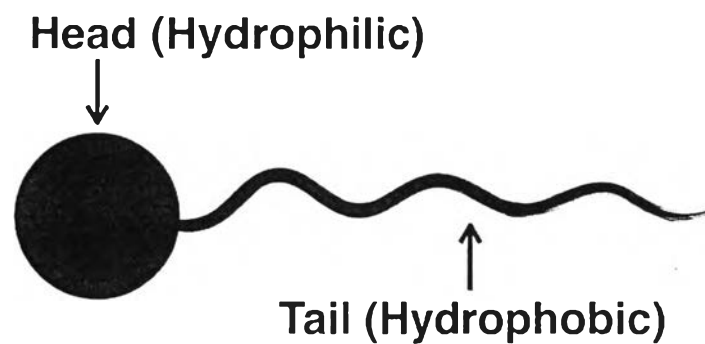


Figure 2.4 Surfactant's structure.

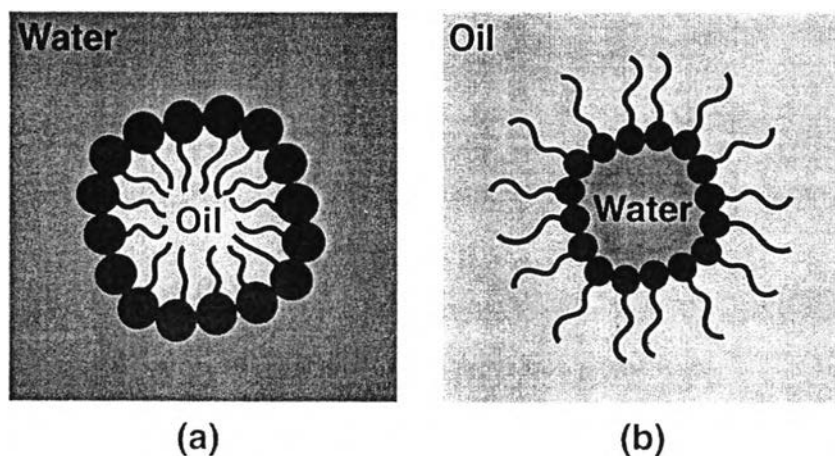
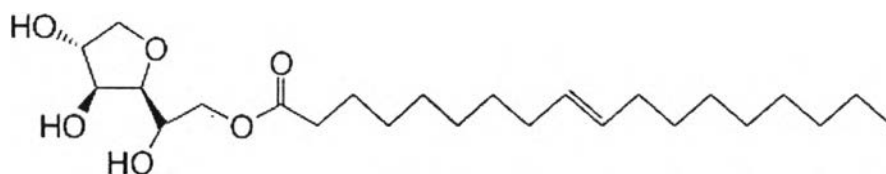


Figure 2.5 (a) normal micelle and (b) reverse micelle.



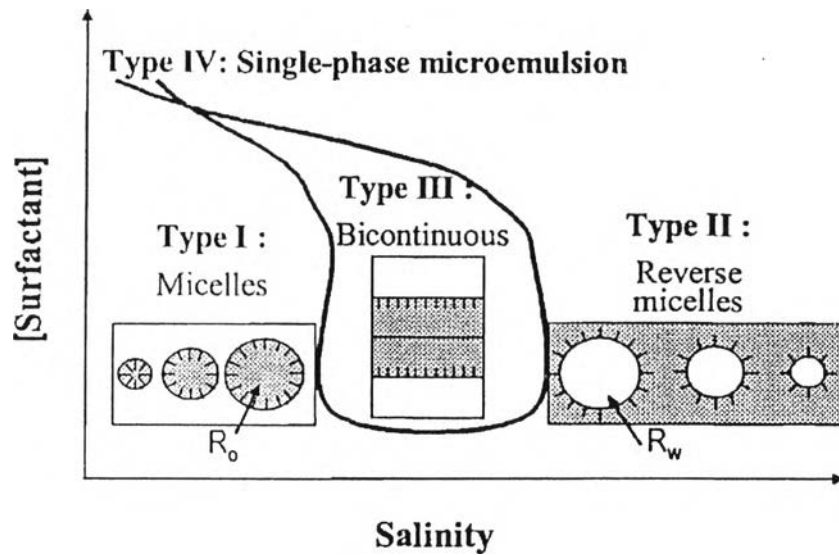
Recently, many researchers have studied the effects of surfactant and cosurfactant structure to formulate microemulsion of vegetable oil and diesel with ethanol on phase behavior. For example, Sabatini and coworkers (2013) used nonionic surfactants compared with anionic carboxylated-based extended surfactants and sugar-based surfactants (e.g. sorbitan monooleate, Span 80) with canola oil/diesel and ethanol to formulate microemulsion biofuel in their study.



**Figure 2.6** Structure of Span 80.

## 2.6 Fish Diagram

Fish diagram shows phase behavior with surfactant concentration and formulation hydrophobicity by salinity. Fish diagram is typically separated into four areas including Winsor Type I, II, III and IV. Winsor Type I microemulsion with excess water phase, surfactant's head will be located outside the micelle. Winsor Type II microemulsion with excess oil phase, surfactants can be formulated to reverse micelles and surfactant's head will be located inside the droplet. The next, Winsor Type III microemulsion consists of oil, water, and bicontinuous phase of microemulsion coexisting in three phase equilibrium. Winsor Type IV microemulsion is defined as completely solubilized between water and oil to single phase microemulsion at high concentration of surfactant.

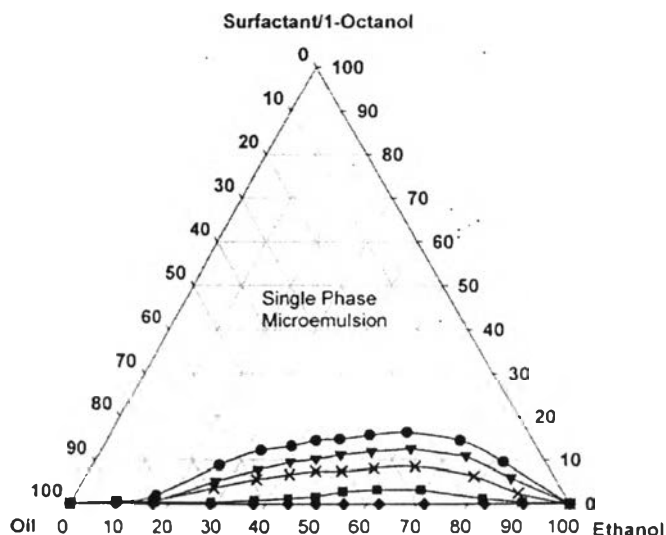


**Figure 2.7** Fish diagram shows phase behavior with surfactant concentration and formulation hydrophobicity by salinity (Komesvarakul *et al.*, 2006).

### 2.7 Pseudo-ternary Phase Diagram

Pseudo-ternary phase diagram is a triangle diagram consists of at least three components in the system uses for phase behavior study of microemulsion. The upper vertex represents the surfactant and cosurfactant mixture at a constant ratio. The vertex at the bottom in the left hand side represents vegetable oil and diesel blend at a constant ratio, and the right hand side represents a polar phase i.e. water and ethanol. This is system a given temperature.

From Figure 2.8 shows a sample of pseudo-ternary phase diagram of diesel/vegetable oil and ethanol blend with surfactant and cosurfactant from Sabatini and coworkers (2012). In Figure 2.8, the upper of the diagram is surfactant/1-octanol mixture and the bottom of the triangle represents oil mixture (vegetable oil and diesel) and ethanol. The area above the miscibility curve is composition of single phase microemulsion. On the other hand, the area below the curve is composition of separate phase.



**Figure 2.8** A sample of pseudo-ternary phase diagram (Sabatini *et al.*, 2012).

## 2.8 Fuel Properties

### 2.8.1 Kinematic Viscosity

Kinematic viscosity of the microemulsion fuel can be measured using a Canon-Fenske type viscometer No. 100 (ASTM D 445). Kinematic viscosity can be calculated using Equation 2.1, which is provided by the manufacturer of the viscometer:

$$\mu = Kt \quad (2.1)$$

where  $\mu$  Kinematic viscosity (cSt)  
 K Viscosity constant ( $K=0.01606$  cSt/s)  
 t Time of sample flow in vescometer

In this study, the kinematic viscosity of the microemulsuion fuels are compared with neat diesel fuel followed ASTM No.2 diesel fuel at 40 °C and the standard kinematic viscosity value is 4 cSt. In addition, kinematic viscosity of biofuels depends on unsaturated structure, branching, double bond position, carbon chain length and temperature (Knothe *et al.*, 2005).



**Figure 2.9** Cannon-Fenske routine viscometer ([http://www.cannoninstrument.com/P10-0103%20CFO%20\(reverse%20flow\)%20instructions.pdf](http://www.cannoninstrument.com/P10-0103%20CFO%20(reverse%20flow)%20instructions.pdf)).

### 2.8.2 Droplet Size

Droplet size of the microemulsion fuels can be measured by dynamic light scattering (DLS) for determining diameter of the microemulsion droplets and their size distribution. The principle of DLS is done using photon from LASER through the sample and the angle from the light scattering will be detected by detector. Measurement is a time correlation function of the scattered intensity. And then, the mean of “lag time” is a decreased correlation function with displacement time and it can be used to diffusion coefficient of a particle or droplet for solution. The diffusion coefficient can be calculated by a hydrodynamic radius ( $R_h$ ) of the droplet using the Stokes–Einstein’s equation:

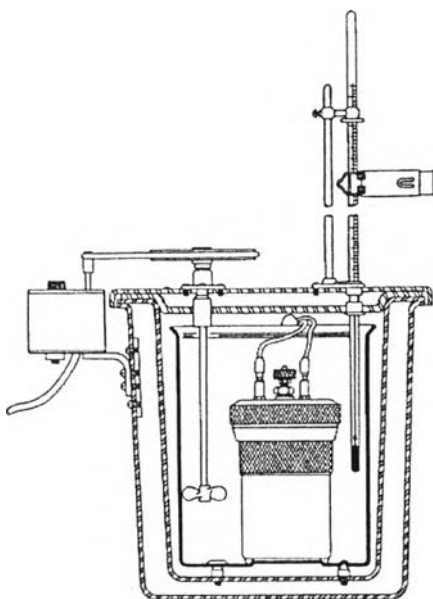
$$R_h = \frac{kT}{6\pi\eta D} \quad (2.2)$$

where,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature,  $\eta$  is the viscosity of the continuous phase and  $D$  is the diffusion coefficient.

### 2.8.3 Cloud Point

Cloud point is the temperature at the fuel which is initial to form crystals and the fuel appears to the cloudiness. The cloud point of petroleum products and biodiesel fuels can be measured by following to ASTM D 2500. This property of fuels is important to use for several applications because using fuels at low temperature may be affected to separated phase of fuels and make engine's problem. Thus, we could concern about this property of fuels.

### 2.8.4 Gross Heat of Combustion



**Figure 2.10** Schematic diagram of bomb calorimeter (<http://www.scimed.co.uk/wpcontent/uploads/2013/03/Introduction-to-bomb-calorimetry.pdf>).

Normally, gross heating values can be measured using many methods. One of the methods is using an oxygen bomb calorimeter followed ASTM D 240 for heating value of liquid hydrocarbon fuel. The heating value can be measured by temperature's increase of the water bath surrounding the bomb of calorimeter. Moreover, the heat released by the combustion in calorimeter of all hydrogen and carbon with oxygen to convert to carbon dioxide ( $\text{CO}_2$ ) and water ( $\text{H}_2\text{O}$ ).

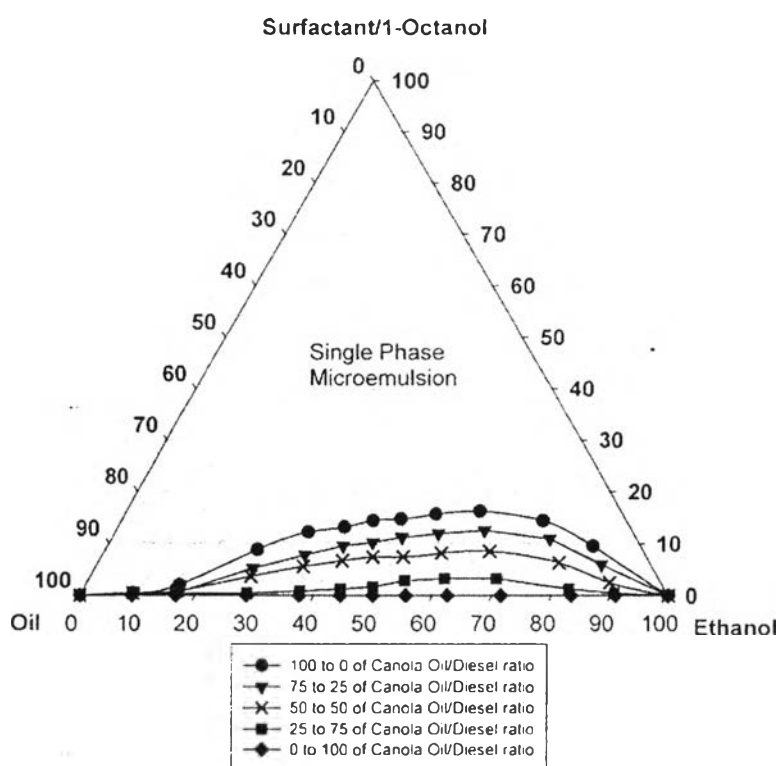
**Table 2.3** The standard properties of No.2 diesel and biodiesel fuel

<b>Properties of fuel</b>	<b>No.2 Diesel</b>	<b>Biodiesel</b>
Standard No.	ASTM D 975	ASTM D 6751
Kinematic Viscosity at 40°C (cSt)	1.9-4.1	1.9-6.0
Lower Heating Value (Btu/gal)	~129,050	~118,170
Specific Gravity at 60°C (g/mL)	0.85	0.88
Boiling Point (°C)	180 to 340	315 to 350
Cloud Point (°C)	-15 to 5	-3 to 12
Pour Point (°C)	-35 to -15	-15 to -10
Flash Point (°C)	52	93
Cetane Number	40 to 55	47 to 65
Water Content (%Vol)	0.05 max	0.05 max
Ash Content (%mass)	0.01	0.02
Carbon Residue (%mass)	0.35	0.05
Acid Number (mg KOH/g)	-	0.5

Source : U.S. Department of Energy, Biodiesel Handling and Use Guidelines (2nd Edition, March 2006)

## 2.9 Literature Review

Many researchers studied the effects of surfactant types for forming microemulsion. Sabatini and co-worker (2012) studied phase behavior using carboxylate-based extended surfactants with canola oil and diesel blend with ethanol. They found that no salt was needed to formulate the microemulsion fuel by their surfactant system. Their results also showed that the branching of surfactant and the number of EO groups of this extended surfactants affect the amount of the surfactant required to form single phase microemulsion because the branching in surfactant molecule increases the performance of oil solubility. However, the increasing of EO group in extended surfactant made poorly oil soluble.



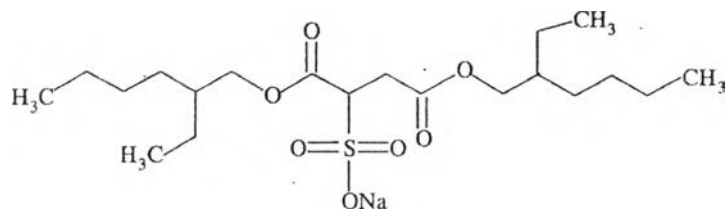
**Figure 2.11** Comparison of the systems of C16-18 4PO-2EO-carboxylate at surfactant/1-Octanol ratio of 1-16 at 25 °C where the oil is canola oil/diesel ratio at 0-100, 25-75, 50-50, 75-25, and 100-0 (Sabatini *et al.*, 2012).

Furthermore, they found that the surfactant/cosurfactant ratio that was not significantly affected the microemulsion fuel formation. They selected the ratio of surfactant/cosurfactant based on the cost-effective and limitation of surfactant preparation.

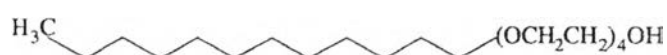
Figure 2.10 shows the effect of canola oil and diesel blend ratios, they found that microemulsion system without canola oil (or 0 to 100 of canola oil/diesel ratio) did not require surfactant to solubilize ethanol in pure diesel because ethanol can be completely miscible in diesel at 25°C. Therefore, increasing canola oil's fraction in the canola oil/diesel mixture. The system required more amount of surfactant to formulate a single phase microemulsion. The kinematic viscosity study indicated that the viscosity of diesel fraction over 50% by vol. of the oil phase close to the standard viscosity of the ASTM No. 2 diesel fuel.

Dan-Florin *et al.* (2014) used Brij 30 and AOT as surfactants to form microemulsion fuels. Brij 30 (tetraethylene glycol dodecyl ether) can be grouped as a sugar based surfactant. AOT (sodium bis-(2-ethylhexyl) sulphosuccinate) is a nonionic surfactant. The cosurfactant used was i-butanol. Their study presents phase behavior, interfacial tension and solubilization of biofuel microemulsions of colza oil and diesel blend with water. It can be seen that the single phase of region in pseudo-ternary phase diagram of AOT with i-butanol was smaller than Brij 30 with i-butanol but larger than AOT and Brij 30 mixture with i-butanol. The single phase area of microemulsion decreased when NaCl was added in the solution. When they considered in the Winsor Type III systems, the interfacial tension values of o/w are the lowest, the solubilization between oil and water was the greatest and the dispersed particles of microemulsion droplet have the largest size. The highest water and oil solubilization parameters can be obtained with the anionic–nonionic surfactant blend and the colza oil and diesel mixture. Thus, they concluded that diesel and colza oil/diesel blend can be mixed with water to formulate single phase microemulsion for developing biofuel formulation.





**Figure 2.12** Structure of Brij 30 (Anghel *et al.*, 2014).



**Figure 2.13** Structure of AOT (Anghel *et al.*, 2014).

Thu *et al.* (2012) studied canola oil, diesel and alcohol formulation. Ethanol and sec-butanol were used as a polarity phase and oleyl amine/1-octanol was used as a surfactant and cosurfactant. In their study, the ethanol and sec-butanol ratios were varied, while other components were fixed at the same concentration.

At ethanol and sec-butanol ratio greater than 1:2, the phase separation of the biofuel occurred at lower than  $-10^{\circ}\text{C}$ . On the other hand, at 30% by volume sec-butanol with no added ethanol, it can be stabilized to single phase microemulsion fuel. However, sec-butanol has a higher viscosity than ethanol, but it has higher heat of combustion than ethanol. When they considered the ethanol and sec-butanol concentration which was varied and fixed the ratio of ethanol to sec-butanol at 1:2, the result indicated that amount of ethanol as viscosity reducer in mixture decreased that affected to overall viscosity of microemulsion fuel and lower cetane number and decreased diesel engine's performance.

Sabatini *et al.* (2013) studied phase behaviors comparing five types of nonionic surfactants with anionic carboxylate-based extended surfactant. Three types of sugar-based surfactants, oleyl alcohol, and 2-ethyl-hexanol was selected as surfactant in this study. It was found that oleyl alcohol required the lowest amount of surfactant to formulate single phase microemulsion. For nonionic surfactants, the number of EO groups decreased as increasing hydrophobicity of the surfactants, the

use of surfactant concentration was lower to form single phase. When temperature decreased, the fuel needed more added surfactants to single phase. Cetane enhancer and antifreezing agent can improve fuel's performance and can help to form microemulsion below 0°C. The systems of oleyl alcohol/2-ethyl-hexanol with canola oil/diesel mixture in ethanol with and without additives can formulate similarly microemulsion below 0°C, and both meet closely kinematic viscosity standard of the No.2 diesel, and had heat of combustion comparably to the No.2 diesel.

Tohren C.G.K. et al. (2014) studied on the prediction of kinematic viscosity of biofuel reverse micelle microemulsion. The aim of their research was exploring of viscosity prediction models. The Chevron's models were used for calculation of viscosity depending on temperature for the fuel components, and used to predict the viscosity of reverse microemulsion fuels. Canola, algae and palm kernel oil as the vegetable oil, mixed with diesel and ethanol were investigated. They concluded that viscosity calculation of microemulsion fuels by the Chevron model can be used for prediction of kinematic viscosity of biofuels from the viscosity of each of the components. This model can calculate viscosity blending index for each components in the mixture. Their study could well predict from consideration of the microemulsion fuels to liquid mixtures. Trends were predicted correctly by viscosity with changing temperature, although the accurate prediction of increasing viscosity can be predicted by increasing surfactant concentration.

## **2.10 Objectives**

The main objective of this study is to formulate hybrid biofuel with palm oil/diesel blend using nonionic surfactant reverse micelle microemulsion; the specific objectives are;

1. To study effect of surfactant and cosurfactant structure on the phase behavior of reverse micelle microemulsion with ethanol and vegetable oil/diesel blend systems.
2. To investigate the effects of the chemical structure of surfactants (with different hydrophilic parts) on their microemulsion formation, kinematic

viscosity, microemulsion droplet size, cloud point and turbidity to enhance ethanol solubilization in reverse micelle microemulsion.

3. To compare some of the basic fuel properties, microemulsion based biofuels neat diesel fuel and other biofuel systems.

### **2.11 Scope of Research**

The scope of this research covers the following:

1. Nonionic surfactants which are used in this study are methyl oleate, biodiesel (palm oil methyl ester), and Span 80.
2. 1-octanol and 2-ethyl-1-hexanol are used as a cosurfactant.
3. Pseudo-ternary phase diagram is used to conduct the phase behaviors of the microemulsion biofuel.
4. Kinematic viscosity, pour point, droplet size and turbidity properties of biofuels are measured in this study.
5. In the kinematic viscosity study, temperature is controlled at 40°C but other studies are investigated at room temperature ( $25 \pm 2^\circ\text{C}$ ).
6. This research, the samples are prepared in batch experiment.