

CHAPTER IV RESULTS AND DISCUSSION

4.1 Phase Behavior Study

The goal of this study is to determine the effect of surfactant's and cosurfactant's structures on phase behavior of reverse micelle microemulsion fuels. The miscibility and phase behavior of microemulsion biofuels are formulated in Winsor type II microemulsion system using pseudo-ternary phase diagram as shown in Figure 4.1. The upper vertex of the diagram is a surfactant/cosurfactant mixture and the bottom of the triangle represents a vegetable oil/diesel mixture and an ethanol, respectively. The area above the miscibility curve is the composition of a single phase microemulsion. On the other hand, the area below the curve is the composition of a separate phase, which is a Winsor Type II. The phase behavior study of microemulsion fuels was conducted at room temperature ($25\pm 2^\circ\text{C}$).

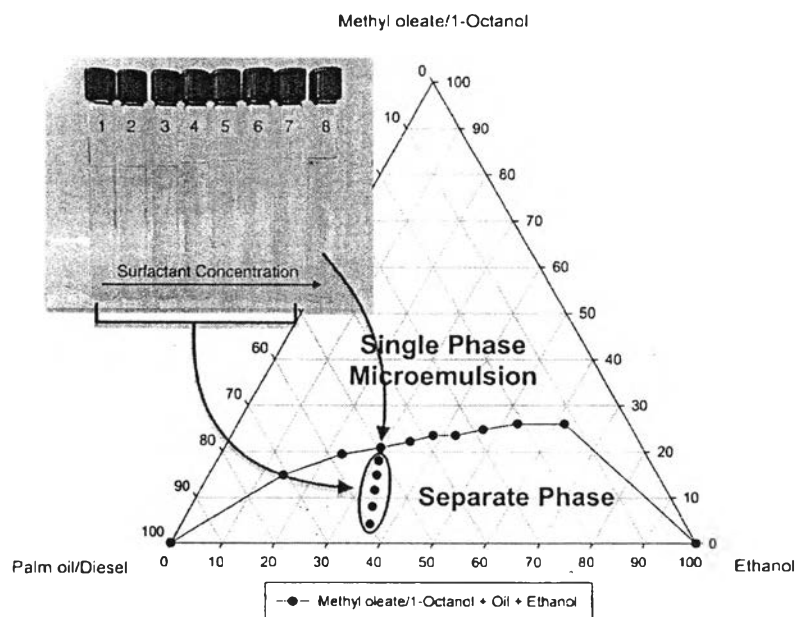


Figure 4.1 The pseudo ternary phase diagram of microemulsion biofuel using methyl oleate/1-octanol as surfactants at 1:8 molar ratio with palm oil/diesel blend at a ratio of 1:1 (v/v).

4.1.1 Effect of Surfactant's Structures

Figure 4.2 and Figure 4.3 present the pseudo ternary phase diagram of microemulsion fuel systems with palm oil/diesel blend at a ratio of 1:1 (v/v) using 1-octanol and 2-ethyl-1-hexanol as a cosurfactant at a molar ratio of 1:8; respectively. The plotted data reveal the miscibility curves of methyl oleate (black circle), Span 80 (white circle) and biodiesel or known as palm oil methyl ester (PME) (black triangle) systems.

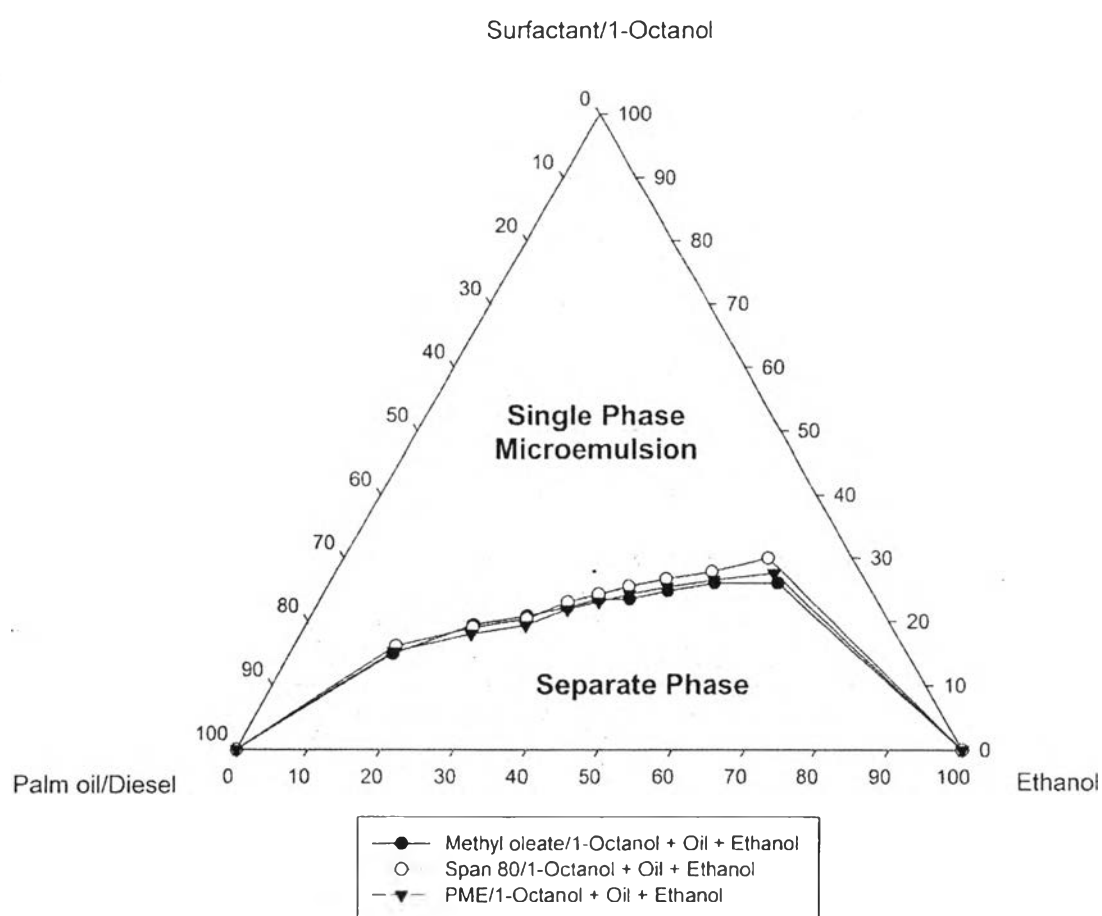


Figure 4.2 Pseudo ternary phase diagram of microemulsion biofuel systems using methyl oleate, Span 80 and PME as a surfactant at surfactant/1-octanol molar ratio of 1:8 with a palm oil/diesel at a ratio of 1:1 (v/v) at room temperature ($25\pm 2^\circ\text{C}$).

Two pseudo ternary phase diagrams in Figure 4.1 and Figure 4.2 indicate that when amount of ethanol in biofuel solutions was increased, surfactant

concentration was more required to formulate a single phase microemulsion biofuel. At very high fraction of ethanol, surfactants which were used to a single phase microemulsion biofuel were decreased and then, no surfactant was required to solubilize at 100% of ethanol. This trend are followed the works of Attaphong *et al.* (2010) and Arpornpong *et al.* (2014).

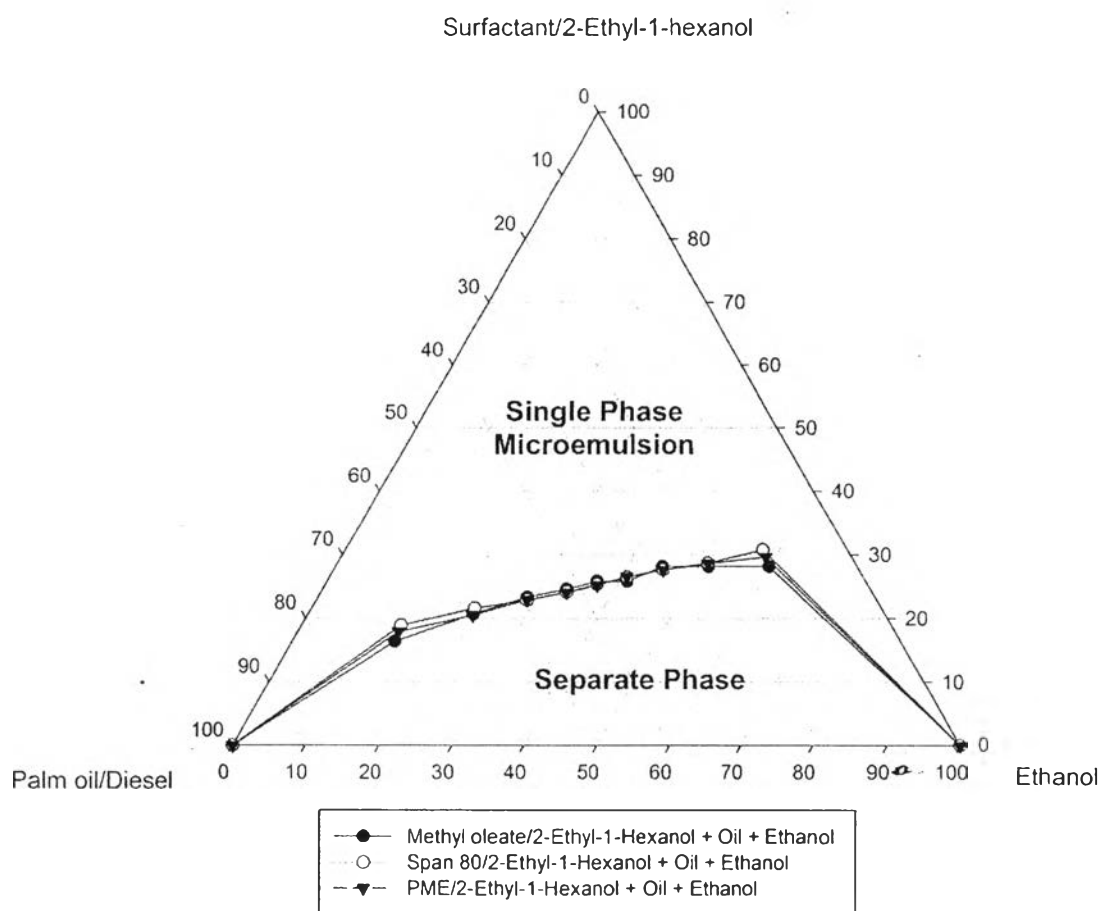


Figure 4.3 Pseudo ternary phase diagram of microemulsion biofuel systems using methyl oleate, Span 80 and PME as a surfactant at surfactant/2-Ethyl-1-hexanol molar ratio of 1:8 with a palm oil/diesel at ratio of 1:1 (v/v) at room temperature ($25\pm 2^\circ\text{C}$).

For the effects of surfactant's structure on the phase behavior, a minimum amount of surfactants required to solubilize all components and form a single phase microemulsion were not different significantly. The reason for this

could be due to the fact that the hydrophilic-lipophilic balance (HLB) value of these surfactants is almost similar. The HLB value of methyl oleate, Span 80 and biodiesel (PME) are 4.0, 4.3 and 4.2, respectively. Therefore, the polarity of surfactants interacted similarly to the oil and ethanol phase in microemulsion systems. This result is accordance with the work from Balcan *et al.* (2014).

4.1.2 Effects of Cosurfactant's Structures

Figures 4.4 to 4.6 show the effect of cosurfactant's structures on the phase behaviors of methyl oleate, Span 80 and PME systems, respectively. These fuel systems consist of palm oil/diesel blend at a ratio of 1:1 (v/v) with ethanol and surfactant/cosurfactant at a molar ratio of 1:8 at room temperature. 1-Octanol and 2-ethyl-1-hexanol were used as a cosurfactant for the comparison in this work. For 1-octanol, it is a medium chain alcohol (or alkanol) with linear structure but the structure of 2-ethyl-1hexanol is a branching isomer of octanol.

When the amount of ethanol increases to 30 vol.% of methyl oleate's system, the difference of surfactant concentration between using 1-octanol and 2-ethyl-1-hexanol as a cosurfactant was about 1-2 vol.%. At higher fraction of ethanol, the amount of surfactant used to stabilize all components to become a single phase microemulsion biofuel was slightly increased to 2-3 vol.%.

For the pseudo ternary phase diagram as shown in Figures 4.4 to 4.6, it was found that 2-ethyl-1hexanol's system more slightly required about 1-4% of surfactant than that of 1-octanol system at lower ethanol fraction. These results can be explained that the difference of cosurfactant structures was not affected to surfactant concentration to formulate single phase microemulsion biofuels, since branching structure of cosurfactant has less influence on the phase behavior of microemulsion biofuel than the number of carbon chain length of cosurfactant. This result is in agreement with the studies of Attaphong *et al.* (2010) and Arpornpong *et al.* (2014).

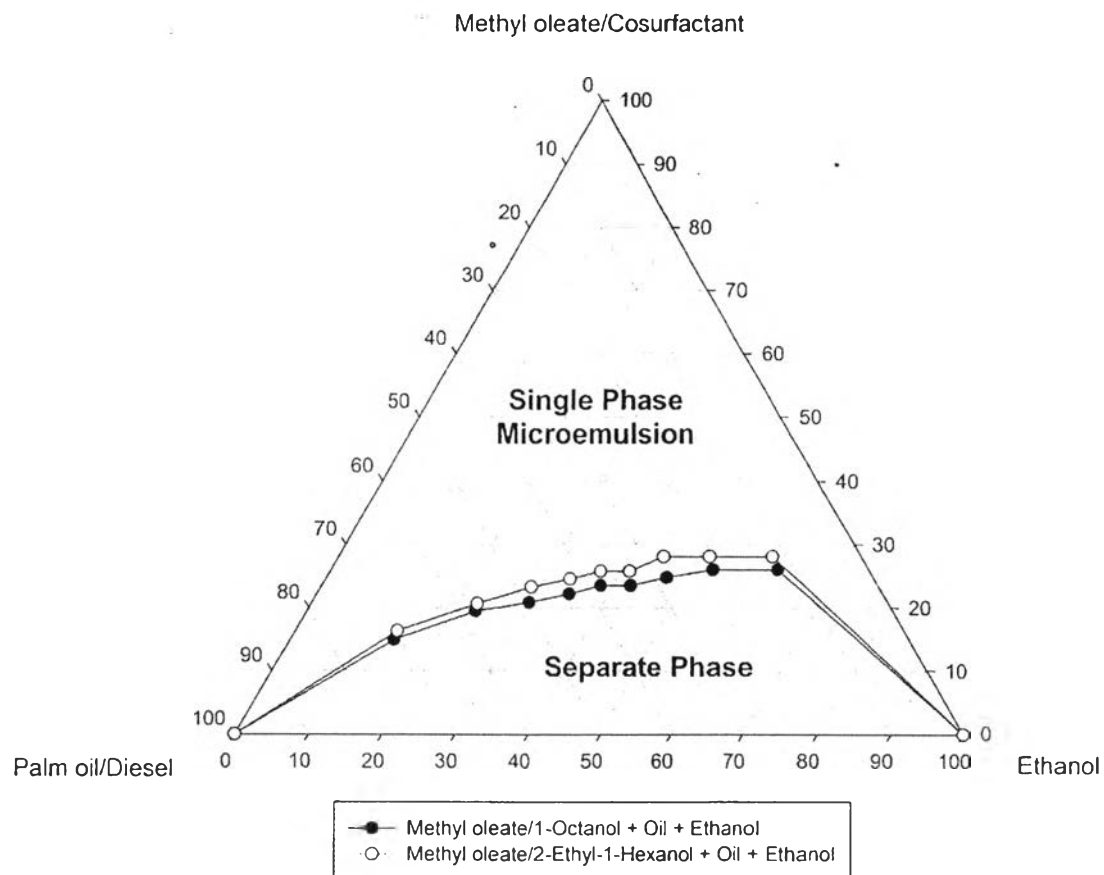


Figure 4.4 Pseudo ternary phase diagram of methyl oleate/1-octanol and methyl oleate/2-ethyl-1-hexanol at surfactant/cosurfactant molar ratio of 1:8 with a palm oil/diesel at ratio of 1:1 (v/v) at room temperature ($25 \pm 2^\circ\text{C}$).

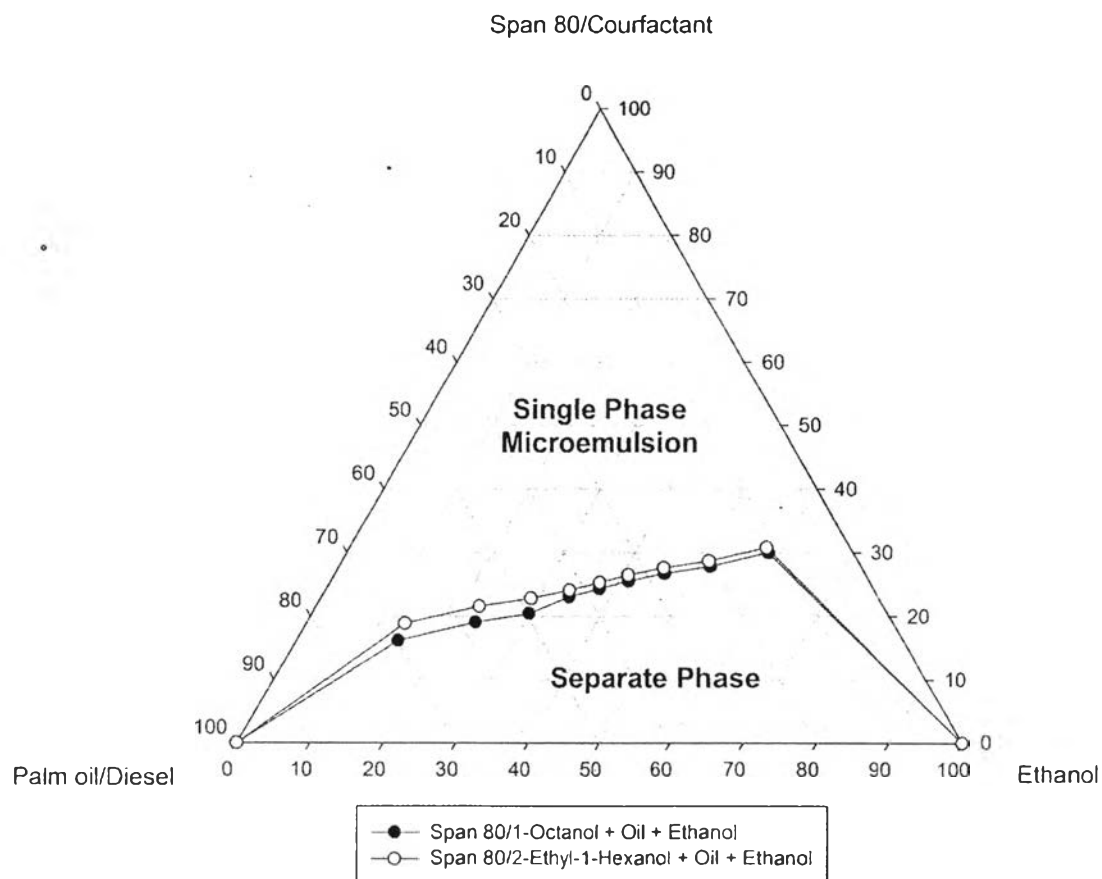


Figure 4.5 Ternary phase diagram of Span 80/1-octanol and Span 80/2-ethyl-1-hexanol at surfactant/cosurfactant molar ratio of 1:8 with palm oil/diesel at ratio of 1:1 (v/v) at room temperature ($25 \pm 2^\circ\text{C}$).

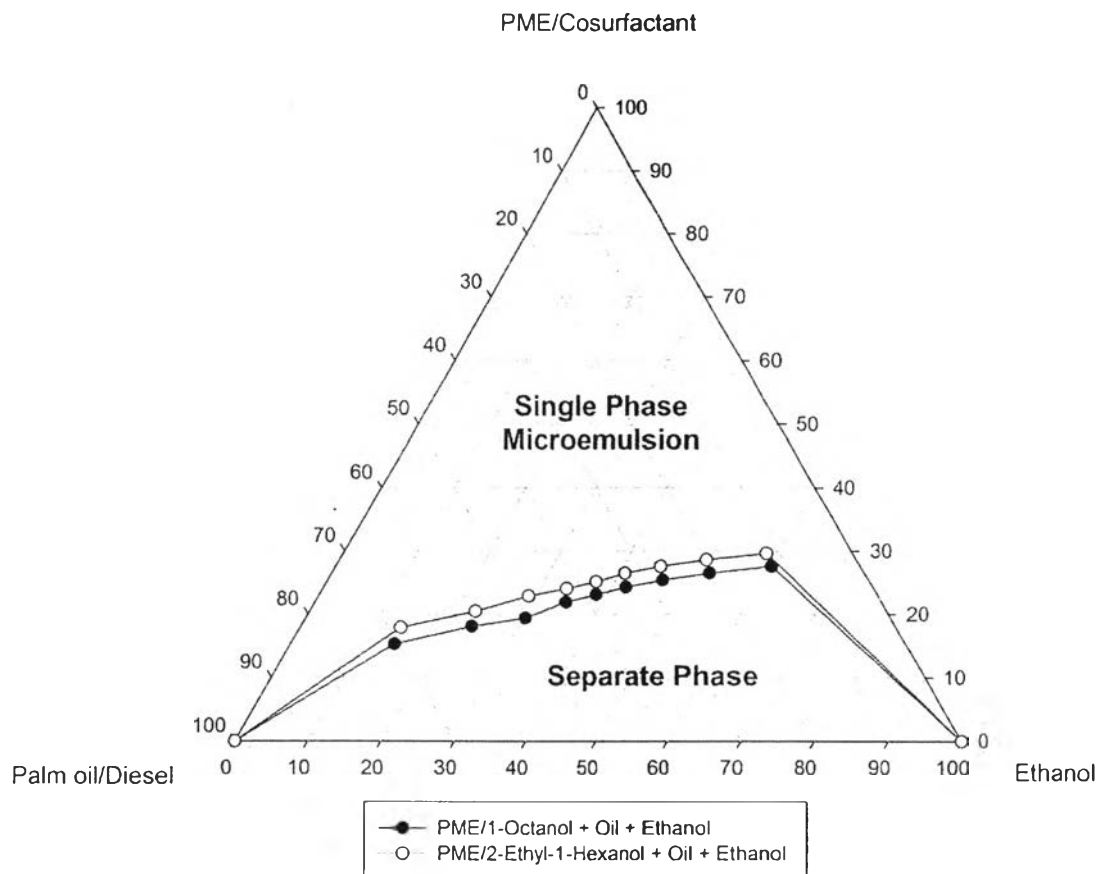


Figure 4.6 Ternary phase diagram of PME/1-octanol and PME/2-ethyl-1-hexanol at surfactant/cosurfactant molar ratio of 1:8 with a palm oil/diesel at ratio of 1:1 (v/v) at room temperature ($25 \pm 2^\circ\text{C}$).

4.2 Effect of Types of Palm Oil

For this study, two types of palm oil used were food-grade commercial palm oil and refined bleached deodorized palm oil (RBDPO). This study aimed to compare the effects of surfactant's and cosurfactant's structures and the amount of surfactant consumed to form microemulsion biofuels with different types of vegetable oil. Each palm oil was combined with diesel at a ratio of 1:1 (v/v) and ethanol of 20 vol.% and then added surfactant and cosurfactant mixture at a molar ratio of 1:8 to form microemulsion biofuels.

4.2.1 Amount of Surfactant Required to Formulate Single Phase Microemulsion Study

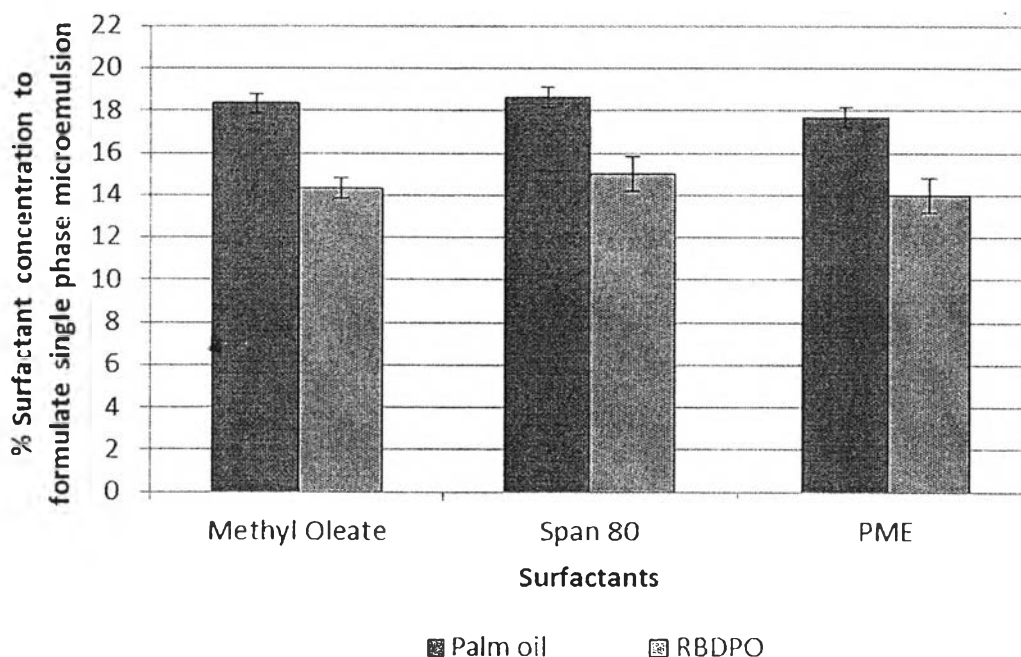


Figure 4.7 Minimum total surfactant concentration (%) to formulate single phase microemulsion versus types of surfactant and 1-octanol as a cosurfactant at a molar ratio of 1:8 compared with a palm oil/diesel and RBDPO/diesel blends at a ratio of 1:1 (v/v) with 20 vol.% of ethanol at room temperature ($25\pm 2^\circ\text{C}$).

The effect of palm oil type, palm oil-olein (PO-olein) and palm oil – RBDPO, on minimum surfactant concentration required to formulate single phase microemulsion shown in Figure 4.7 and Figure 4.8 respectively. In comparison with same type of the surfactant, the RBDPO's systems used surfactant concentration slightly less than those of palm oil's system by 2 to 5 %. This could be the fact that RBDPO is a mixture of palm olein (65%) and palm stearin (35%) (Nusantoro, 2007) and/or perhaps the fatty acids in RBDPO can facilitate the surfactant to form a single phase microemulsion. Most types of fatty acid in palm oil are oleic acid (C18:1). For RBDPO, palmitic acid (C16:0) is the major fatty acid composition followed Table 4.1.

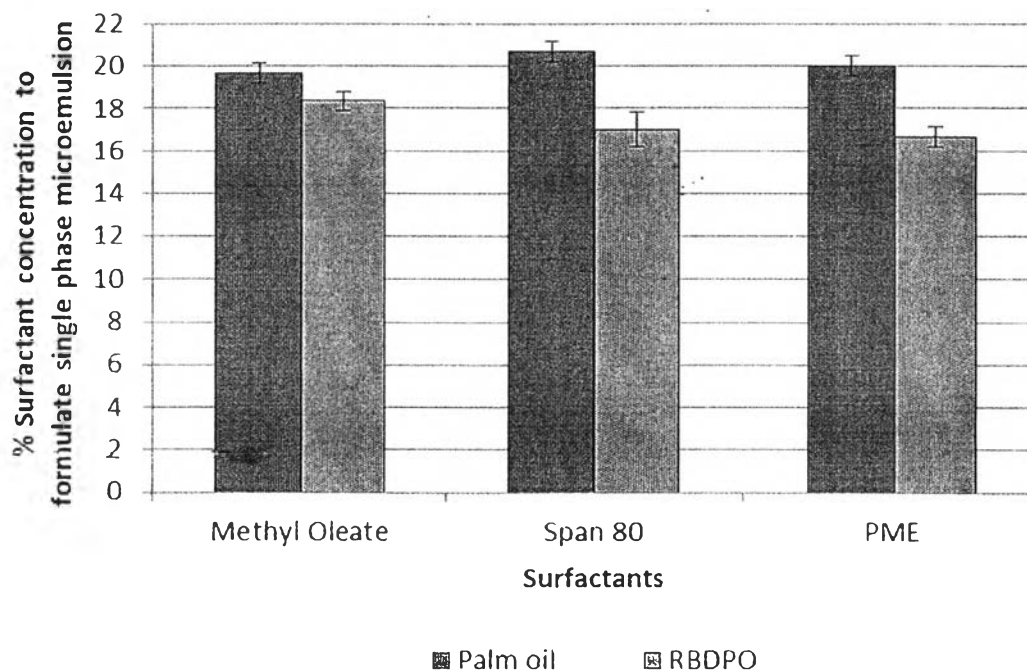


Figure 4.8 Minimum total surfactant concentration (%) to formulate single phase microemulsion versus types of surfactant and 2-ethyl-1-hexanol as a cosurfactant at a molar ratio of 1:8 compared with a palm oil/diesel and RBDPO/diesel blends at a ratio of 1:1 (v/v) with 20 vol.% of ethanol at room temperature ($25 \pm 2^\circ\text{C}$).

For the effect of surfactant types with similar system of palm oil, the result demonstrated that the structure of surfactant did not affect to surfactant concentration required to formulate a single phase microemulsion. The reason of this result is because of the HLB value of surfactant as presented in 4.1.1 section.

Table 4.1 Fatty acid compositions of palm oil and RBDPO

Materials	Fatty acid composition (%)	
	Palm oil	RBDPO
Saturated		
Myristic acid (C14:0)	0.89	0.92
Palmitic acid (C16:0)	41.54	46.30
Stearic acid (C18:0)	3.51	3.52
Total	45.94	50.74
Unsaturated		
Oleic acid (C18:1)	43.63	39.58
Linoleic acid (C18:2)	10.43	9.68
Total	54.06	49.26

The data from Che Man *et al.*, 1999

4.2.2 Amount of Surfactant with the Different Types of Cosurfactant Required to Formulate Single Phase Microemulsion Study

The results in Figures 4.9 to 4.11 show the effect of cosurfactant's structures in various surfactant systems; methyl oleate, Span 80 and PME, the surfactant concentration with 1-octanol systems as a cosurfactant required to produce to a single phase microemulsion was less than those of 2-ethyl-1-hexanol system for both palm oil olein and RBDPO systems. Furthermore, the RBDPO systems needed lower surfactant concentration than those of palm oil olein systems (16% for 2-ethyl-1-hexanol system and 15% for 1-octanol system).

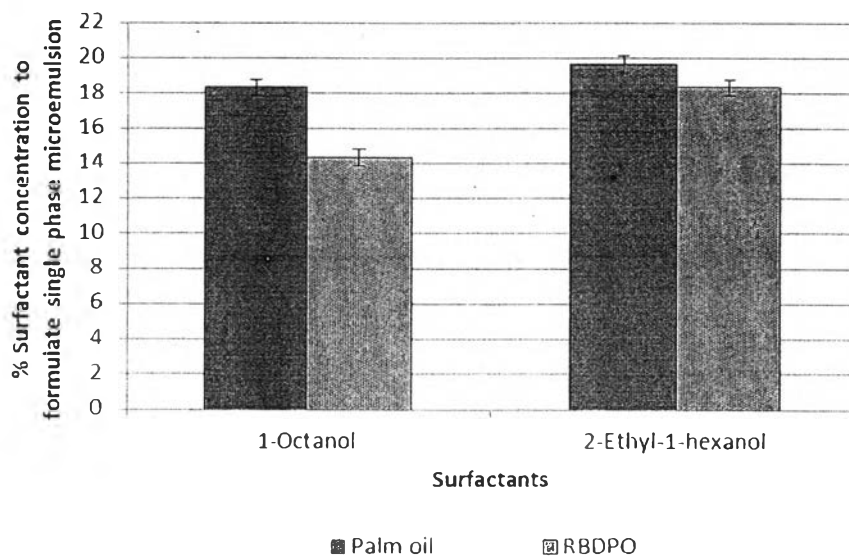


Figure 4.9 Minimum total surfactant concentration (%) to formulate single phase microemulsion of methyl oleate systems versus types of cosurfactant at a molar ratio of 1:8 with a palm oil/diesel blends at a ratio of 1:1 (v/v) and 20 vol.% of ethanol at room temperature ($25\pm 2^\circ\text{C}$).

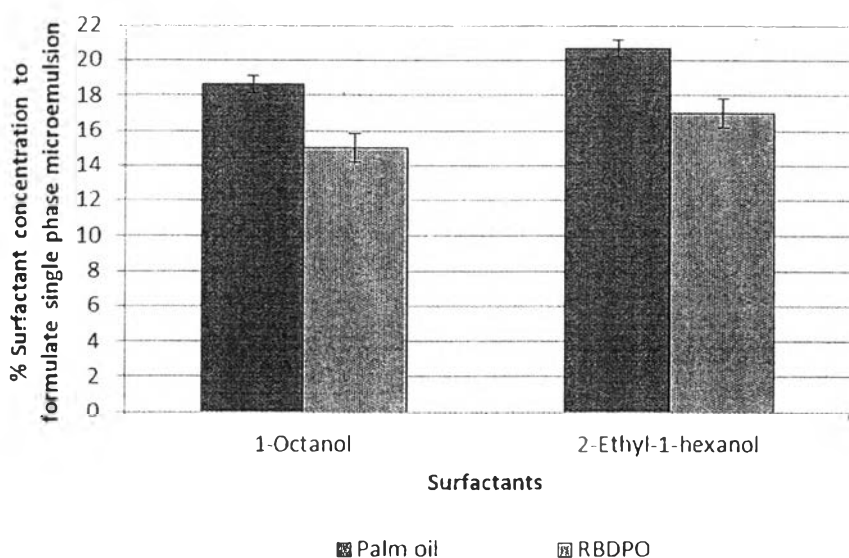


Figure 4.10 Minimum total surfactant concentration (%) to formulate single phase microemulsion of Span 80 systems versus types of cosurfactant at a molar ratio of 1:8 with a palm oil/diesel blends at a ratio of 1:1 (v/v) and 20 vol.% of ethanol at room temperature ($25\pm 2^\circ\text{C}$).

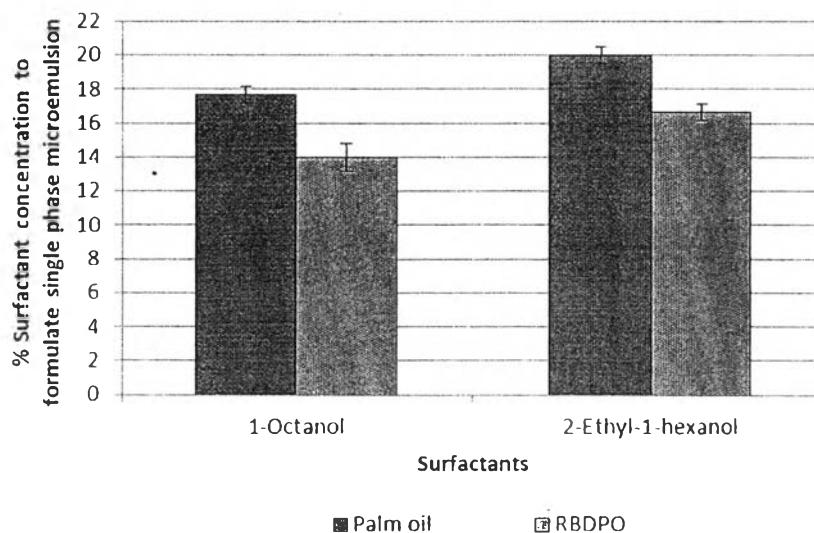


Figure 4.11 Minimum total surfactant concentration (%) to formulate single phase microemulsion of Span 80 systems versus types of cosurfactant at a molar ratio of 1:8 with a palm oil/diesel blends at a ratio of 1:1 (v/v) and 20 vol.% of ethanol at room temperature ($25\pm 2^\circ\text{C}$).

Even though, there are evidences that palm oil - RBDPO has a remarkable benefit in terms of surfactant loading, it can be a potential option to replaced palm oil olein. However, the limitation of RBDPO is the phase separation due to wax or solid fat formation at its below melting point. The RBDPO generally contains palm stearin fraction (35%) (Nusantoro, 2007) which could form a crystalline semi-solid fat at low temperature.

4.3 Fuel Properties Determination

Property of biofuels is an important factor to utilize for many applications such as vehicles and industries. In this section, the effect of surfactant's and cosurfactant's structures and types of palm oil on their fuel properties including kinematic viscosity, droplet size, turbidity, cloud point, density and heat of combustion were evaluated. The microemulsion biofuel systems were palm oil/diesel and RBDPO/diesel blends with 20 vol.% of ethanol. In addition, the appropriate

surfactant concentration of each system to formulate all microemulsion biofuels was selected at 5% (v/v) of upper miscibility curve.

Table 4.2 and Table 4.3 show the composition of microemulsion biofuels of palm oil's and RBDPO's system with 20 vol.% of ethanol, respectively. Surfactant and cosurfactant of a molar ratio of 1:8 was prepared and blended with oil phase, a ratio of palm oil/diesel and RBDPO/diesel blends 1:1 (v/v).

Table 4.2 Composition of microemulsion biofuels in palm oil - olein system with 20 vol.% of ethanol used for fuel property determination

Sample	Composition (vol. %)		
	Surfactant/ cosurfactant	Palm oil/ diesel	Ethanol
Methyl oleate/1-octanol	23.3	56.7	20.0
Methyl oleate/2-ethyl-1-hexanol	24.7	55.3	20.0
Span 80/1-octanol	23.7	56.3	20.0
Span 80/2-ethyl-1-hexanol	25.7	54.3	20.0
PME/1-octanol	22.7	57.3	20.0
PME/2-ethyl-1-hexanol	25.0	55.0	20.0

Table 4.3 Composition of microemulsion biofuels in RBDPO's system with 20 vol.% of ethanol used for studied fuel properties determination

Sample	Composition (vol. %)		
	Surfactant/ cosurfactant	RBDPO/ diesel	Ethanol
Methyl oleate/1-octanol	19.3	60.7	20.0
Methyl oleate/2-ethyl-1-hexanol	23.3	56.7	20.0
Span 80/1-octanol	20.0	60.0	20.0
Span 80/2-ethyl-1-hexanol	22.0	58.0	20.0
PME/1-octanol	19.0	61.0	20.0
PME/2-ethyl-1-hexanol	21.7	58.3	20.0

4.3.1 Kinematic Viscosity Measurement

Kinematic viscosity of microemulsion biofuels can be measured by Cannon-Fenske Routine viscometer followed the ASTM D 445. In this study, the kinematic viscosity of the microemulsion fuels are compared with neat diesel fuel followed the ASTM No.2 diesel fuel at 40°C. The kinematic viscosity of No.2 diesel standard is about 4.1 cSt (Nakkash N.B. and Al-Karkhi S.R., 2012). By analyzing the kinematic viscosity, the various effects including surfactant's and cosurfactant's structures and types of palm oil were investigated.

4.3.1.1 Effect of Types of Palm Oil

Comparing with types of palm oil from Figure 4.12 and Figure 4.13, the palm oil olein/diesel and RBDPO/diesel blends with the same type of surfactants/cosurfactants system had no difference in kinematic viscosity at 40°C. The kinematic viscosity of neat palm oil and RBDPO are 40.88 (Anantarakitti *et al.*, 2014) and 38.9 cSt (Sukirno *et al.*, 2010), respectively.

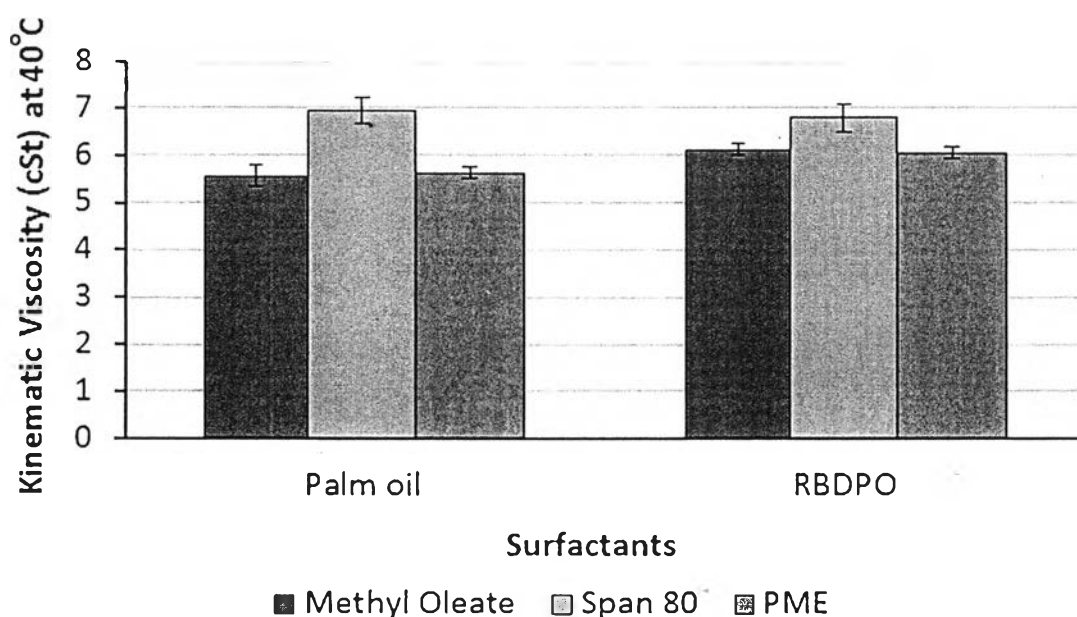


Figure 4.12 Kinematic viscosity (cSt) at 40°C versus types of surfactant and 1-octanol as a cosurfactant at a molar ratio of 1:8 compared with a palm oil/diesel and RBDPO/diesel blends at a ratio of 1:1 (v/v) with 20 vol.% of ethanol.

4.3.1.2 Effect of Surfactant's Structures

To study the effect of surfactant's structures on kinematic viscosity at 40°C, the various surfactants including methyl oleate, Span 80 and biodiesel (PME) were selected as a surfactant which was mixed with 1-octanol and 2-ethyl-1-hexanol at a ratio of 1:8 as shown in Figure 4.12 and Figure 4.13; respectively. It was found that, the kinematic viscosity of each of microemulsion biofuel was ranging from 5.0-7.0 cSt and the viscosity of Span 80 systems was higher than those of methyl oleate and PME systems, respectively. This is due to the fact that the larger head (hydrophilic part) of Span 80 surfactant and more hydrogen bond between the molecules than methyl oleate and PME, resulting in the Span 80 has higher viscosity than those of the other surfactants, therefore, the kinematic viscosity of Span 80's system was higher than that of both methyl oleate and PME systems. Because of the similar structures between methyl oleate and PME, their kinematic viscosities were not significantly different in figure.

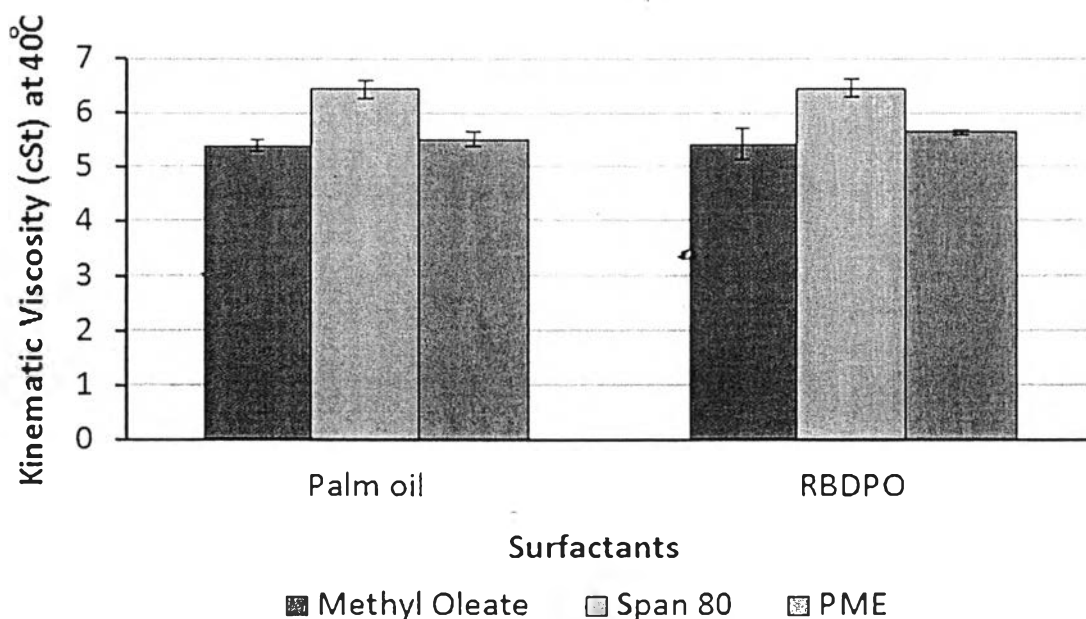


Figure 4.13 Kinematic viscosity (cSt) at 40°C versus types of surfactant and 2-ethyl-1-hexanol as a cosurfactant at a molar ratio of 1:8 compared with a palm oil/diesel and RBDPO/diesel blends at a ratio of 1:1 (v/v) with 20 vol.% of ethanol.

4.3.1.3 Effect of Cosurfactant's Structures

The results from Figure 4.14 and Figure 4.15 display the kinematic viscosities of palm oil/diesel and RBDPO/diesel blended with 20 vol.% of ethanol. In comparison between types of surfactant and cosurfactant, the kinematic viscosity of 2-ethyl-1-hexanol's systems was less than those of 1-octanol's systems. It can be in line with previous study (Anantarakitti *et al.*, 2014) that the different structures of straight chain (1-octanol) and branching chain alcohol (2-ethyl-1-hexanol) were not affected to kinematic viscosity of microemulsion biofuels.

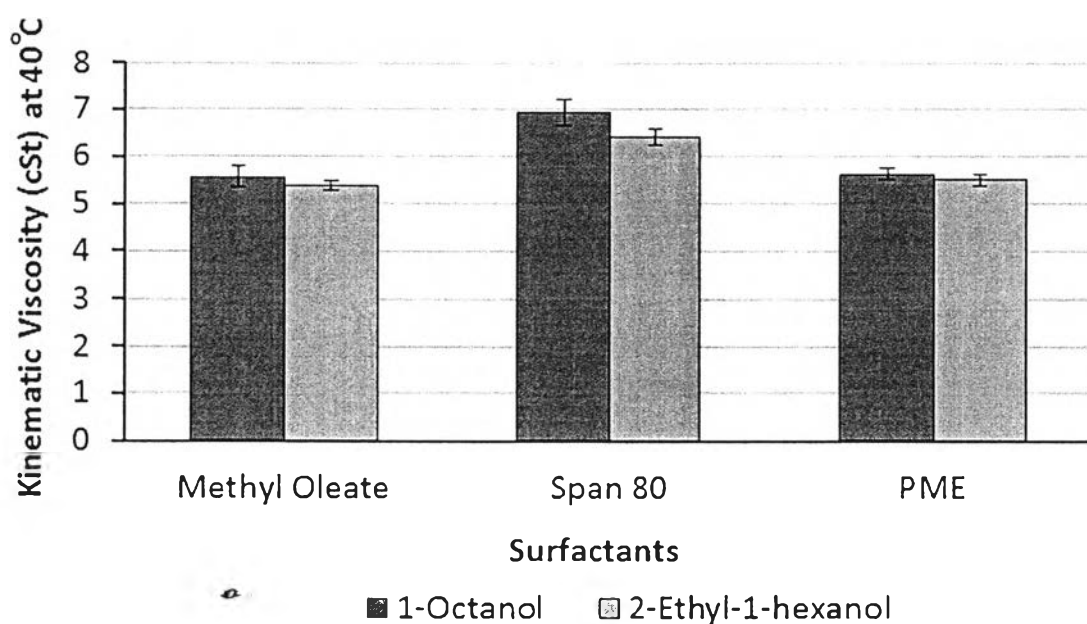


Figure 4.14 Kinematic viscosity (cSt) at 40°C versus types of surfactant and cosurfactant at a molar ratio of 1:8 with a palm oil/diesel blends at a ratio of 1:1 (v/v) and 20 vol.% of ethanol.

Table 4.4 Comparison of the droplet size and distribution of microemulsion biofuels with palm oil/diesel blend (1:1 v/v) at room temperature ($25\pm 2^\circ\text{C}$)

Sample	Size distribution (nm)	
	Average $D_{1\text{ mean}}$ (% intensity)	Average $D_{2\text{ mean}}$ (% intensity)
Methyl oleate/1-octanol	5,342 100%	- 0%
Methyl oleate/2-ethyl-1-hexanol	5,467 100%	- 0%
Span 80/1-octanol	20.31 97%	4,985 3%
Span 80/2-ethyl-1-hexanol	16.16 91%	5,207 9%
PME/1-octanol	5,495 100%	- 0%
PME/2-ethyl-1-hexanol	5,228 100%	- 0%
Palm oil/diesel blend	4.32 100%	- 0%

4.3.2.1 Effect of surfactant's structures

From Table 4.4, the microemulsion biofuel systems were prepared at $25\pm 2^\circ\text{C}$, with surfactant/cosurfactant molar ratio of 1:8. Surfactant and cosurfactant were added in palm oil/diesel blend at a ratio of 1:1 (v/v) with 20 vol.% ethanol. For the effect of surfactant's structure on droplet size, the results displayed that methyl oleate's and PME's systems had microemulsion droplet size ranging from 5,228-5,495 nm with 100% intensity, the proximity of droplet size and distribution of those affected from the similarity of methyl ester group in the head group (hydrophilic group) of both surfactants. Most droplet size of Span 80's systems ranging from 16.16-20.31 nm at 91-97% and another size ranging from 4,925-5,207 nm had about 3-9% which was much smaller than methyl ester surfactants. It could be due to the fact that head group of Span 80 comprising of hydroxyl groups that has more hydrogen bond than the other surfactant systems.

Therefore, Span 80 can stabilize ethanol in oil phase less than methyl oleate and PME, the microemulsion droplet size of Span 80's system was smaller than other systems.

Note that palm oil/diesel blend without surfactant system, the droplet size of palm oil /diesel blend was about 4.32 with 100% intensity which was lower than those of all microemulsion fuel performed in this study.

4.3.2.2 Effect of Cosurfactant's Structures

The effect of cosurfactant's structure on microemulsion droplet size can be explained by Table 4.4 that the droplet size of 1-octanol's systems were in proportion to 2-ethyl-1-hexanol's system. Therefore, it can be concluded that cosurfactant's structures in terms of branch and linear structure did not affect to the size of reverse micelle microemulsion.

Table 4.5 Comparison the time that the sample of Span 80's systems with palm oil/diesel blend (1:1 v/v) and 20 vol.% ethanol was placed before measured droplet size and distribution at 25±2°C

Sample	Condition	Size distribution (nm)	
		Average $D_{1, \text{mean}}$ (% intensity)	Average $D_{2, \text{mean}}$ (% intensity)
Span 80/1-octanol	freshly prepared	3,287 64%	22.39 36%
Span 80/1-octanol	Placed for 7 days before measured	20.31 97%	4,985 3%
Span 80/2-ethyl-1-hexanol	freshly prepared	2,656 79%	18.77 21%
Span 80/2-ethyl-1-hexanol	Placed for 7 days before measured	16.16 91%	5,207 9%

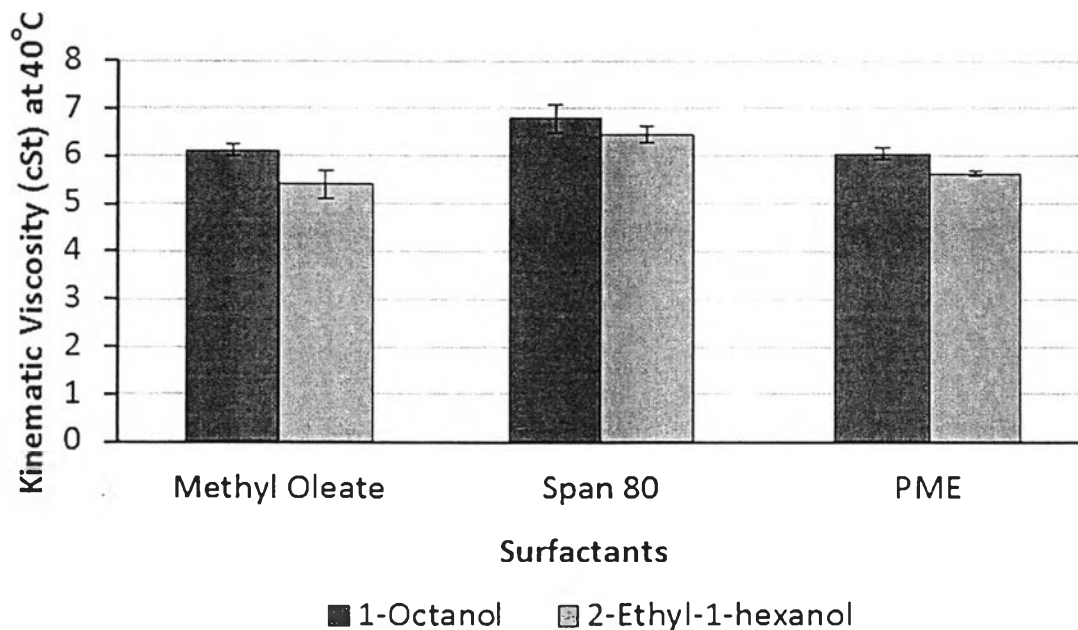


Figure 4.15 Kinematic viscosity (cSt) at 40°C versus types of surfactant and cosurfactant at a molar ratio of 1:8 with a RBDPO/diesel blends at a ratio of 1:1 (v/v) and 20 vol.% of ethanol.

4.3.2 Droplet Size and Size Distribution

Microemulsion droplet size and size distribution of biofuels was analyzed by monomodal or multimodal between intensity versus diameter of droplet from dynamic light scattering (DLS), Nano Zetasizer 3600 (Malvern). The scattering intensity from measuring by DLS can be used to define the amount of microemulsion droplets (percentage) of each mean droplet size. Microemulsion droplet size was studied to determine the correlation of kinematic viscosity of biofuels with other biofuel's properties. This section, the effects of surfactant's and cosurfactant's structures on droplet size in palm oil/diesel blend with ethanol were study.

It is interesting to note that the microemulsion aggregate size has changed with time. Based on experimental setup, the microemulsion biofuels of palm oil/diesel blend with ethanol using Span 80 as a surfactant mixed with different cosurfactants were conducted to observe the droplet size with a certain period of time. According to the droplet sizes in Table 4.5, the freshly prepared samples appeared with droplet sizes and droplet size distribution of 3,287 nm (64% intensity) and 2,656 nm (79% intensity) for Span 80/1-octanol and Span 80/2-ethyl-1-hexanol, respectively.

Considering the samples which have placed at room temperature of $25\pm 2^\circ\text{C}$ for 7 days before measured, the droplet size distribution of 1-octanol's and 2-ethyl-1-hexanol's system ranging from 2,500-5,500 nm had decreased to 3-9 % intensity. On the other hand, the droplet size of both systems ranging from 15-25 nm had increased after holding the sample for 7 days. This fact, indicates a time evolution in microemulsion stability of microemulsion droplet and size distribution. We concluded that much smaller size of microemulsion droplet affected to their stability due to very large entropy of dispersion (Akhtar ,1996).

4.3.2.3 Relation of Droplet Size Distribution with Kinematic Viscosity

Stokes–Einstein's equation (2.2) can be used to explain the correlation between droplet size and kinematic viscosity of microemulsion biofuels. Hydrodynamic radius (R_h) or referred as microemulsion droplet size is inversely proportional to viscosity of biofuels.

The results from Table 4.6 show that the droplet size of Span 80's systems were smaller than those of methyl oleate's and PME's systems. Span 80's systems had higher viscosity than those of the other fuel systems. This results are followed the Stokes–Einstein's equation and in accordance with Arpompong *et al.* (2014). In comparison with droplet size distribution and kinematic viscosity, there was no significant trend observed between two microemulsion biofuels with different types of cosurfactant.

Table 4.6 Comparing relation of droplet size with kinematic viscosity of palm oil/diesel blend (1:1 v/v) and 20 vol.% ethanol with surfactant/cosurfactant at molar ratio of 1:8 at 25±2°C

Sample	Size Distribution D _{1 mean} (nm)	Kinematic viscosity (cSt)
Methyl oleate/1-octanol	5,342 100%	5.57
Methyl oleate/2-ethyl-1-hexanol	5,467 100%	5.39
Span 80/1-octanol	20.31 97%	6.96
Span 80/2-ethyl-1-hexanol	16.16 91%	6.43
PME/1-octanol	5,495 100%	5.64
PME/2-ethyl-1-hexanol	5,228 100%	5.51

4.3.3 Turbidity

For turbidity of microemulsion biofuels, the measurement was carried out using by UV spectroscopy. Due to the limit of detection, however, the absorbance of microemulsion biofuels could not be observed in which the appeared noise peaks ranging in 200-500 nm were overlapped with interesting peak. The turbid solution was then observed by visual observation.

Figure 4.16 shows the phase behavior of palm oil/diesel blend with ethanol with methyl oleate/1-octanol as surfactants. It can be noted that the vial No. 1 to No. 7 depicted a separate phase. When added more surfactants, the mixture of liquid fuels can form a single phase microemulsion as illustrated in vial No. 8.

In addition, it can be explained according Figure 4.16 that when increased the surfactant concentration, the phase behavior of microemulsion biofuels had changed from Winsor Type II to a single phase microemulsion as it can be seen from that the phase behavior and turbidity between RBDPO and palm oil olein systems when using Span 80/1-octanol as a surfactant system. This trend was also

observed in Figure 4.17. However, based on Figure 4.17 and Figure 4.18, it is interesting to note that there was a solid-fat precipitates in RBDPO's system after placed the sample at room temperature ($25\pm 2^{\circ}\text{C}$) for 48 hours. The melting point of RBDPO was reported ranging from $33\text{-}39^{\circ}\text{C}$ (Morad *et al.*, 2006). This precipitate could be a solid fat from crystallization of fatty acids in vegetable oil.

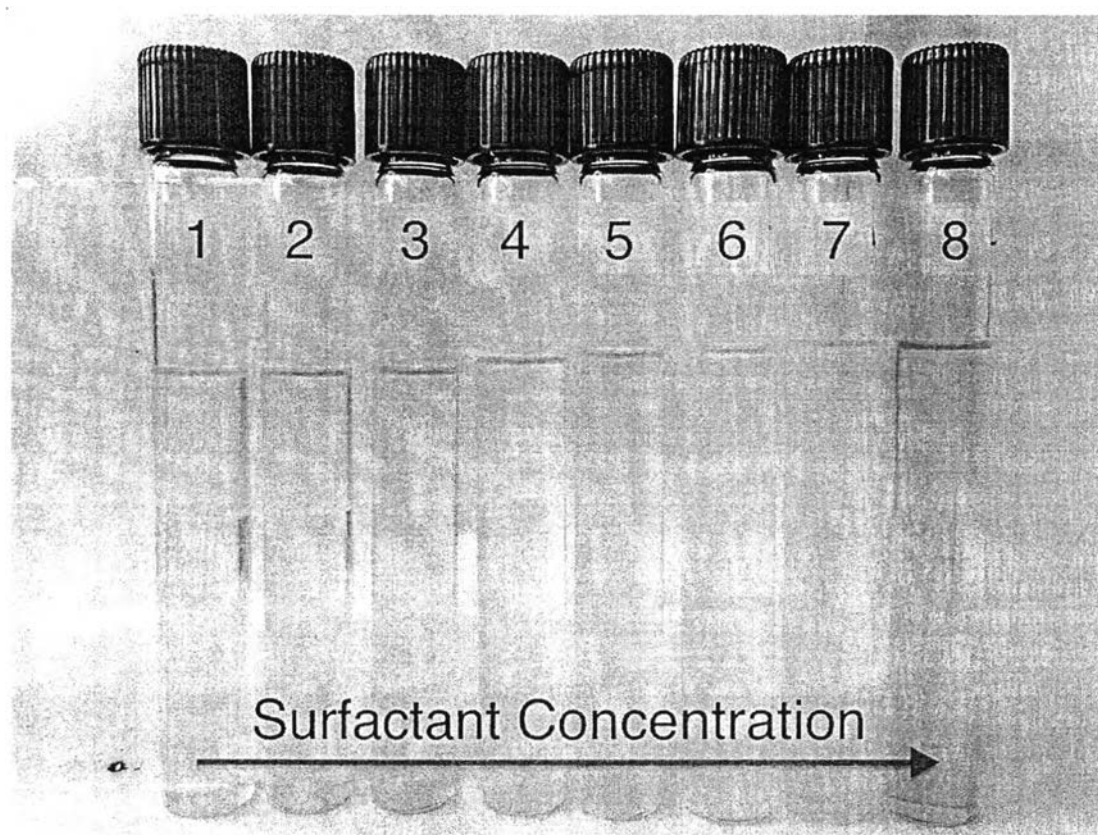


Figure 4.16 Phase behavior and turbidity varying surfactant concentration of methyl oleate/1-octanol with a palm oil/diesel blends at a ratio of 1:1 (v/v) and ethanol.

Miskandar *et al.* (2006) studied crystallization and crystal behavior of palm oil and RBDPO. They found that the crystal memory can be interrupted when held oils at 80°C for 30 min (De Man *et al.*, 1989). The fact that RBDPO used in this study tend to form a solid crystalline phase more than purified palm oil or palm oil olein.

In addition, Normah *et al.* (2012) investigated the effects of time and temperature on crystallization of RBDPO. They found that the crystal precipitates from vegetable oil were slightly larger with increasing in crystallization time and at higher crystallization temperature.

This can be noted that further observation according to microemulsion biofuel derived from crude vegetable oils where the effect of crystallization of RBDPO and palm oil can be minimized throughout the surfactant based formulations.

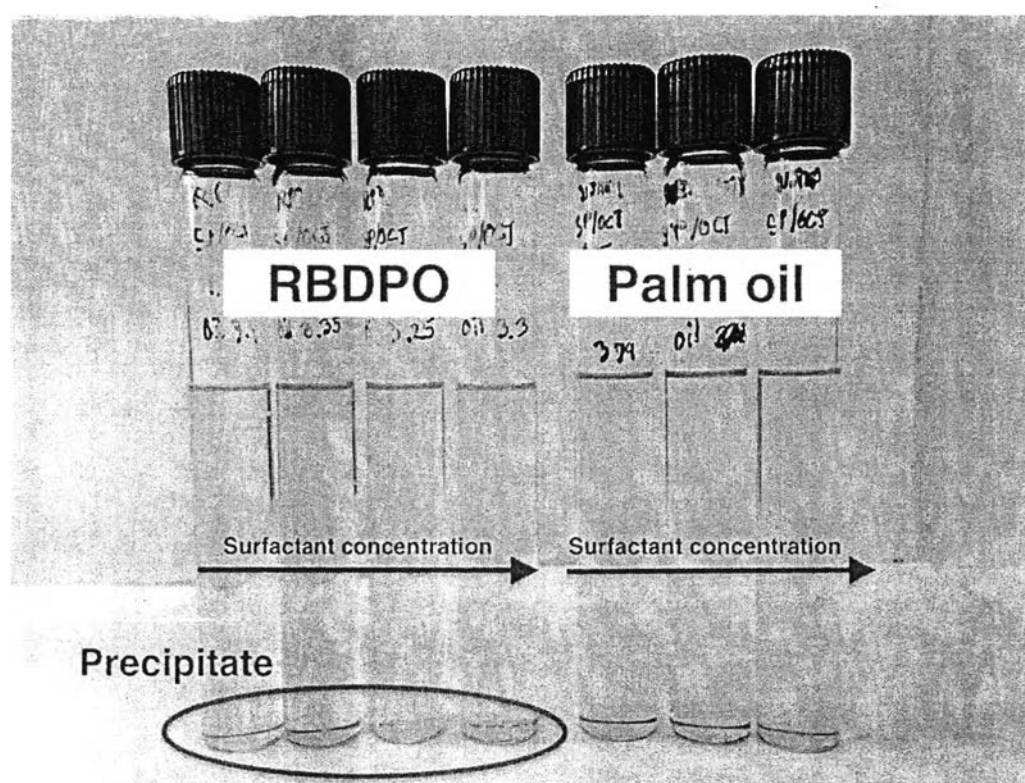


Figure 4.17 Phase behavior and turbidity comparison of Span 80/1-octanol system in RBDPO/diesel blend and palm oil/diesel blend at a ratio of 1:1 (v/v) with ethanol.

The comparison of turbidity for all microemulsion biofuels with regular diesel fuel is shown in Figure 4.19, there is no significant difference through visual observation. The appearance of microemulsion solutions were clear and transparent and their color were naturally yellow. Additionally, the color intensity of

the biofuels depending on fraction of vegetable oil and diesel used for forming microemulsion biofuels and natural color of raw materials.

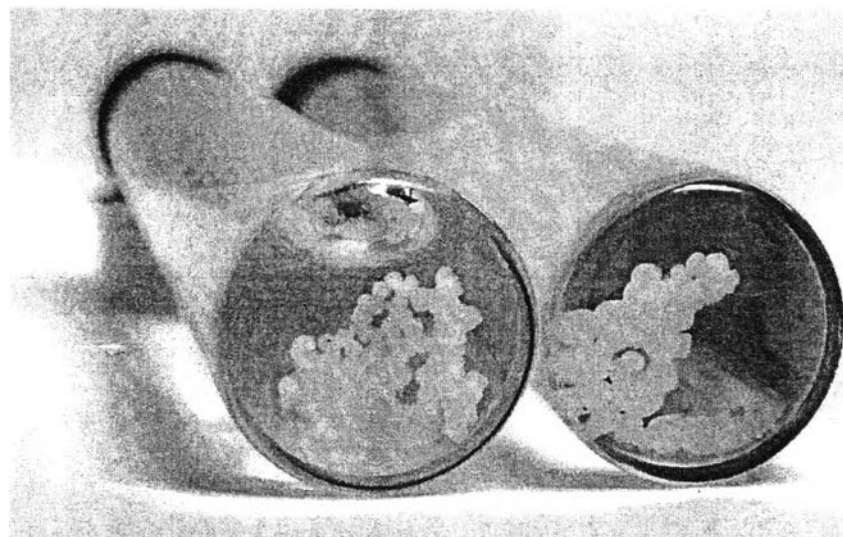


Figure 4.18 Precipitates of microemulsion biofuels within RBDPO's system after held at room temperature ($25\pm 2^\circ\text{C}$) for 48 hours.

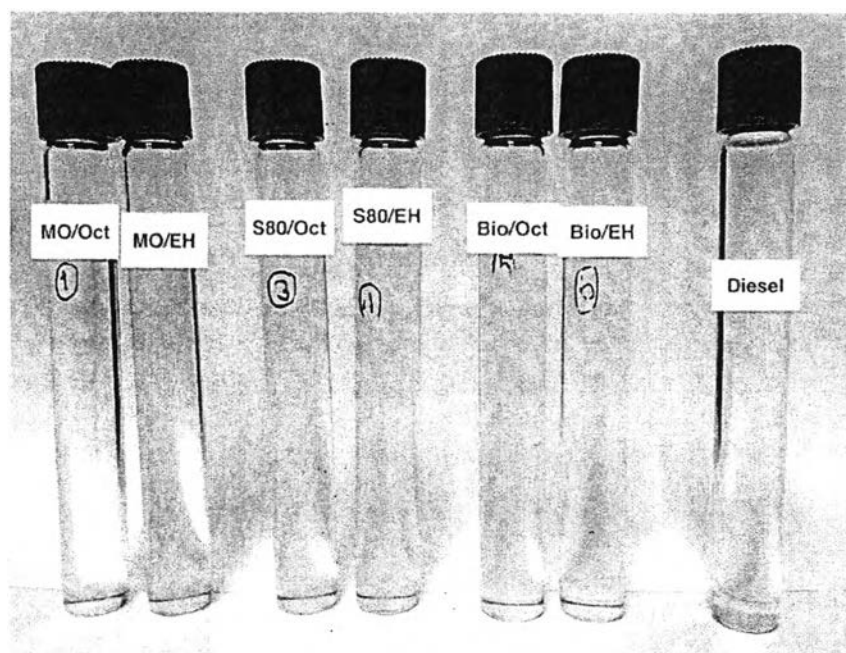


Figure 4.19 Turbidity of all of palm oil/diesel blend with 20 vol.% of ethanol systems after held at room temperature ($25\pm 2^\circ\text{C}$) for 48 hours.

4.3.4 Cloud Point

Cloud point is the temperature of the fuel in which starting to form crystals or cloud solution. In typical, petroleum industries substantially concerned about operating temperature because at temperature lower cloud point, solidified wax from the oil clogs injectors and filters in diesel engines and makes fouling's problem in pipeline and heat exchanger (Mittelbach, 2004). In this study, the cloud point of microemulsion biofuels was measured using cooling bath following to ASTM D 2500. The effects of types of surfactant and cosurfactant on cloud point of palm oil/diesel blend (1:1 v/v) with ethanol 20 vol. % systems were evaluated. The fuel was observed to be the cloudiness when the temperature decreased in every 2°C.

Table 4.7 Cloud point, density and heat of combustion of microemulsion biofuels compared with diesel and palm oil/diesel blend and 20 vol.% of ethanol

Sample	Dynamic viscosity (at 40°C)	Cloud point (°C)	Density (g/mL)	Heat of combustion (MJ/kg)
Methyl oleate/1-octanol	5.57	5	0.874	38.9
Methyl oleate/2-ethyl-1-hexanol	5.39	5	0.841	39.0
Span 80/1-octanol	6.96	3	0.878	38.5
Span 80/2-ethyl-1-hexanol	6.43	3	0.854	38.4
PME/1-octanol	5.43	5	0.855	39.0
PME/2-ethyl-1-hexanol	5.51	5	0.838	38.5
Diesel ^a	4.1	-15	0.847	45.8
Biodiesel (B100) ^a	4.4	5	0.890	41.2
Palm oil/diesel blend ^a	11.7	16	0.879	42.5

^a The data from Arpornpong *et al.*, 2014

The result from Table 4.7 demonstrates the phase change of the microemulsion biofuels with methyl oleate and PME. The cloud points were appeared at both methyl oleate and PME systems at 5°C, but the cloud point of Span 80 systems was 3°C which slightly lower than those of methyl oleate and PME

systems. However, these biofuels' cloud point were similar to cloud point of biodiesel (B100) while these were higher than that of diesel standard (-15°C) while these were close. In comparison with palm oil/diesel blend and regular diesel, it can be seen that the cloud point of the microemulsion fuel was substantially higher than that of regular diesel standard. This could be because the cloud point of vegetable oil/diesel blend depends on the nature of vegetable oils such as cloud point of palm oil (15°C) and rapeseed oil (-4°C) (Balat *et al.*, 2008).

4.3.5 Density

Density is mass per unit volume at a specific temperature. The density of all microemulsion biofuels at $25\pm 2^{\circ}\text{C}$ varied in a range 0.838-0.878 g/mL followed Table 4.7. When we compared density of microemulsion biofuels with density of commercial diesel fuels, it is clear that the density of diesel (0.825-0.845 g/mL at $25\pm 2^{\circ}\text{C}$) (Jin *et al.*, 2011) was slightly lower than those of microemulsion biofuels.

4.3.6 Heat of Combustion

Heat of combustion is an important property of fuels. It can be measured by oxygen bomb calorimeter following in ASTM D 240. The results from Table 4.7 indicate that heat of combustion of all microemulsion biofuels ranging from 38.4-39.0 MJ/kg were not different significantly, but the heat of combustion of these were lower than those of diesel fuel and palm oil/diesel blend which were 45.8 and 42.5 MJ/kg, respectively. The main reason of lower heat of combustion of microemulsion biofuels could be due to ethanol content in fuel's formulation. Even through the use of ethanol in microemulsion biofuel can dramatically reduce the viscosity of the system, ethanol content in the formulation also affects directly to the fuel properties such as heat of combustion and also the method to handling and stage due to the flash point.

4.4 Summarized Results

This work aims to formulate new hybrid microemulsion biofuel from vegetable oil/diesel blend with ethanol using renewable based surfactant system. The nonionic surfactants with linear and branch chain of cosurfactant were used for forming reverse micelle microemulsion. The fuel properties was then evaluated and discussed their fuel's performance and the potential use in appropriate application.

For w/o microemulsion biofuel formulation, palm oil and RBDPO were selected to combine with diesel at 1:1 (v/v) ratio and ethanol was used as the polar phase and viscosity reducer. Surfactant and cosurfactant were as emulsifier to stabilize single phase microemulsion with a fixed surfactant/cosurfactant molar ratio of 1:8. Methyl oleate, Span 80 and biodiesel or known as palm oil methyl ester (PME) were selected as a surfactant. Methyl oleate is methyl ester as the same as PME and Span 80 (sorbitan monooleate) is sugar based-biodegradable surfactant. Then, 1-octanol and 2-ethyl-1-hexanol or branching chain of octanol were used for study the effect of cosurfactant structures. Phase behavior, kinematic viscosity, microemulsion droplet size determination, and fuel property testing were conducted to optimize fomula of microemulsion biofuel.

Pseudo ternary phase diagram was used to observe that phase behavior of each microemulsion fuel formulation, the minimum surfactant concentration to formulate single phase can be observed by the miscibility curve. The results of phase behavior can be summarized that palm oil/diesel blend at low amount of ethanol fraction (below 10 vol. %), the microemulsion system no need surfactant to formulate single phase microemulsion biofuel. Similarly, at high ethanol fraction with low amount of oils, the system did not require amount of surfactant to form a single phase solution. Additionally, the types of surfactant were not significant to phase behavior of microemulsion biofuels because the HLB values of these surfactants are almost similar in figure. In addition, cosurfactant structure was not also affected to phase behavior.

In comparison, the effect of the use of palm oil olein and RBDPO on minimum surfactant concentration to formulate a single phase microemulsion. With the same type of surfactant and cosurfactant, the palm oil system was more required

surfactant concentration than that of RBDPO due to the difference of fatty acid composition in palm oil and RBDPO.

Biofuels for fuel properties determination were fixed amount of ethanol at 20 vol. % and surfactant and cosurfactant mixture was added 5 vol. % of above miscibility curve of each system. The kinematic viscosity of all systems was measured at 40°C and compared with the kinematic viscosity of No.2 diesel. The results show that the kinematic viscosity of the Span 80 systems was higher than methyl oleate and PME systems because Span 80 has formerly higher viscosity than those of the other surfactants. For cosurfactant structures and types of palm oil, there was no effect to their kinematic viscosity.

Size distribution and stability of microemulsion droplets can be analyzed by dynamic light scattering (DLS). Considering the effects of surfactant and cosurfactant structures, most droplet size of Span 80's systems was much smaller than methyl oleate and PME. It could be due to the fact that more polarity (has more hydrogen bond) of head group of Span 80 limits the solubilization of ethanol. However, the types of cosurfactant did not affect to size and distribution significantly. When we observed the effect of emulsion stability with a function of time, the results indicated that, the droplet size and droplet size distribution which can be referred to stability of microemulsion between ethanol and oil phase had increased with the size of droplet was attenuated. However, microemulsion droplet size of biofuels directly affected to their kinematic viscosity. The relation of droplet size with viscosity can be described by Stokes–Einstein's equation; the kinematic viscosity of biofuels was increased with decreasing microemulsion droplet size.

The measurement of turbidity study was observed through visual observation. Increasing of the surfactant concentration, the phase behavior of microemulsion biofuels was changed from Winsor Type II to a single phase microemulsion. When compared turbidity of palm oil and RBDPO, no difference was observed but color intensity of RBDPO's solution was more than that of palm oil's solution. Nevertheless, we found that there are solid fat from crystallization of RBDPO after placed the sample at room temperature ($25\pm 2^\circ\text{C}$) where the melting point of RBDPO reported is ranging from 33-39°C.

As compared cloud point, density and heat of combustion of microemulsion biofuels with the standard of diesel No.2 and palm oil/diesel blend. The results show that the fuel properties of all biofuels as mentioned above were not considerably different. The cloud point of the biofuels was about 3-5°C, which is higher than that of standard diesel No.2 (-15°C), but lower than that of palm oil/diesel blend (16°C) without an emulsifier. Density of commercial diesel, palm oil/diesel blend and all biofuels was ranging from 0.83-0.88 g/mL. Additionally, heat of combustion of diesel fuels was higher than palm oil/diesel blend and microemulsion biofuels, respectively. The main reason of higher heat of combustion could be due to increasing fraction of ethanol in fuel's formulation.