VEGETABLE OIL BASED MICROEMULSION BIOFUELS

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ABSTRACT

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Keywords: Reverse micellar microemulsion/ Palm Oil/ Alcohol exthoxylate surfactants/ Ethanol/ Butanol/ Microemulsion biofuel

The growth of energy demand increases dramatically which has resulted in an increase of exhaust emissions to air quality deterioration. Therefore, there are driving forces in the development of renewable energy production technologies. Vegetable oils based reverse micelle microemulsions have been increased in attention for biofuel production. This work aims to formulate microemulsion biofuel containing palm oil/diesel blend as nonpolar phase, and ethanol/butanol, as a polar phase. The nonionic alcohol ethoxylate surfactant with the different numbers of EO groups, EOn (n=1, 3, 5, and 9) were selected as a stabilizing agent. A pseudo-ternary phase diagram was conducted to determine an isotropic region in the phase behavior of microemulsion systems. The ability of butanol added for reducing the phase separation and amount of surfactant required to form the microemulsified fuels was explored. Together with, the effects of surfactant structures and cosurfactant structures, straight chain (1-octanol) and branch chain alcohol (2-ethyl-1-hexanol) were investigated systematically through their phase behaviors. The fuel properties (i.e., kinematic viscosity, droplet size, density, heating value) were examined and compared with neat biofuels. The results suggest that the percentage of surfactant used to stabilize the microemulsion decreased with increasing butanol fraction in the mixture of butanol/ethanol blend. The microemulsion with branching structure in cosurfactant required more surfactant to formulate the microemulsions. The addition of butanol to palm oil/diesel blended with ethanol affecting fuel properties was noted.

บทคัดย่อ

อุราลักษณ์ เปสน : เชื้อเพลิงชีวภาพที่เตรียมจากน้ำมันพืชด้วยวิธีการไมโครอิมัลชัน (Vegetable Oil Based Microemulsion Biofuels) อ. ที่ปรึกษา : ดร.อัมพิรา เจริญแสง และ ศาตราจารย์ ดร. เดวิด เอ สะบาตินี 90 หน้า

การเติบโตของความต้องการพลังงานเชื้อเพลิงเพิ่มขึ้นอย่างมากซึ่งส่งผลต่อการปล่อยไอเสียที่เพิ่มมากขึ้นโดยจะส่งผลกระทบต่อคุณภาพของอากาศให้แย่ลง ดังนั้นแรงผลักดันในการพัฒนาเทคโนโลยีในการผลิตพลังงานหมุนเวียน ซึ่งน้ำมันพืชที่ผ่านวิธีการไมโครอิมัลชันได้รับความสนใจเพิ่มมากขึ้นในการผลิตเชื้อเพลิงชีวภาพ ในงานวิจัยนี้มีจุดมุ่งหมายเพื่อเตรียมสารเชื้อเพลิงชีวภาพผ่านวิธีการรีเวิร์สไมโครอิมัลชันโดยประกอบไปด้วยน้ำมันพืชปาล์มผสมกับน้ำมันดีเซลเป็นเฟสที่ไม่มีขั้วรวมกับบิวทานอลและเอทานอลเป็นเฟสที่มีขั้วโดยใช้สารลดแรงตึงผิวที่ไม่มีประจุชนิดดีไฮดอลเอทิลีนออกไซด์ที่มีหมู่เอทิลีนออกไซด์ที่แตกต่างกันที่นำมาใช้ ได้แก่ 1 3 5 และ9 ซึ่งใช้เป็นตัวประสานให้สารสองชนิดผสานกัน ซึ่งจะทำการสร้างแผนภาพสามเหลี่ยมเพื่อกำหนดพื้นที่การผสมเข้ากันเป็นเนื้อเดียวของสารน้ำมันเชื้อเพลิงชีวภาพไมโครอิมัลชัน จากนั้นสำรวจผลของการเพิ่มปริมาณของบิวทานอลที่มีผลในการช่วยลดของการแยกของเฟสและปริมาณของสารลดแรงตึงผิวที่นำมาใช้ในการเตรียมสารเชื้อเพลิงชีวภาพไมโครอิมัลชัน ร่วมกับศึกษาผลของโครงสร้างของสารลดแรงตึงผิว และสารลดแรงตึงผิวร่วม ได้แก่ ออคทานอลที่มีโครงสร้างเป็นโซ่ตรง และ 2-เอทิล-1-เฮกซานอล ที่มีโครงสร้างเป็นโซ่กิ่งผ่านพฤติกรรมของเฟส คุณสมบัติทางเชื้อเพลิง ได้แก่ ความหนืด ขนาดของอนุภาพ ความหนาแน่น ค่าความร้อน และคุณสมบัติต่างๆของเชื้อเพลิงชีวภาพนำมาเปรียบเทียบตามมาตรฐานของไบโอดีเซล จากการทดสอบชี้ให้เห็นว่า เปอร์เซ็นต์ของสารลดแรงตึงผิวที่ใช้ในการรักษาเสถียรภาพของน้ำมันเชื้อเพลิงชีวภาพไมโครอิมัลชันลดลงตามการเพิ่มขึ้นของบิวทานอลในส่วนผสมของบิวทานอล/เอทานอล และพบว่าน้ำมันเชื้อเพลิงชีวภาพไมโครอิมัลชันที่ใช้สารลดแรงตึงผิวร่วมเป็นโซ่กิ่งจะใช้ปริมาณของสารลดแรงตึงผิวในการรักษาเสถียรภาพมากขึ้นในการสร้างไมโครอิมัลชัน ยิ่งไปกว่านั้นพบว่าการเพิ่มปริมาณบิวทานอลในอัตราส่วนผสมระหว่างบิวทานอลกับเอทานอล ยังส่งผลกระทบต่อสมบัติของน้ำมันเชื้อเพลิงอีกด้วย

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CHAPTER I

INTRODUCTION

The demand for fossil fuel has been rapidly increased each year. The concerns about the fuel shortages and emissions generated from the production and utilization are driving forces in the development of renewable fuel production technologies. Vegetable oils are considered as an appropriate source for biofuel production due to their advantage that they are not only produced from a renewable resource, but they also have a lower exhaust gas emission due to the less oxygen atom in their chemical structures. Nevertheless, the limitation of using vegetable oils in diesel engines is their high viscosity which leads to the malfunction of diesel engine operation due to poor atomization and engine deposits. There are thermal and chemical methods to reduce vegetable oil's viscosity such as direct vegetable oil/diesel blending, pyrolysis, transesterification and microemulsion (Atmanli *et al*., 2016). In this study, the vegetable oil-based microemulsions are considered as potential biofuel production technology. Because the environmental benefits of microemulsification over transesterification that are eliminating of the chemical reactions of hazardous substances and wastes from unpurified glycerol and water after washing (Attaphong *et.al*, 2012; Kibbey *et al*., 2014).

A reverse microemulsion biofuel is the use of surfactants as an emulsifying agent to form the thermodynamically stable mixtures of liquid fluids with different polarity. The reverse micelle microemulsion biofuels are classified as Winsor type II microemulsions where the polar phase (i.e., alcohol) is solubilized in a nonpolar phase (i.e., vegetable oils, diesel). Several types of vegetable oil (e.g., palm, canola, jatropha) have been studied for microemulsion biofuel formation. Palm oil has been used as nonpolar phase due to a high potential feedstock for biofuel production in Thailand. Ethyl alcohol or ethanol, acting as a viscosity reducer, has been employed as a polar phase because it can be produced from renewable resources (e.g., sugar cane and corn). The presence of ethanol in the vegetable oils based microemulsion using carboxylate-based extended as a surfactant can be improved the fuel properties for using in diesel engines (Attaphong *et al*., 2012).

The butanol has been used to promote the cetane number in diesel blending instead of ethanol. Also, the presence of butanol blending in diesel has lower corrosion risk, higher calorific value and lower polarity (Qureshi *et al*., 2008; Yilmaz *et al*., 2014). The presence of butanol mixing with ethanol in the canola oil/diesel based microemulsion biofuel can improve their systems in engine operating parameter and decrease oxides of nitrogen, carbon monoxide and hydrocarbon emissions (Yilmaz *et al*.,2014) .

Cosurfactants, an amphiphile hydrotrope adsorbing between the head and tail of the surfactant molecules, help the surfactants facilitate in lower the interfacial tension of the water-oil (i.e., alcohols-vegetable oil), thus enhancing microemulsion biofuel formation. Besides, the compatibility of the chain length of surfactant/cosurfactant plays a vital role during microemulsion formation.

In our previous study, the microemulsion biofuels formed by palm oil/diesel blended with ethanol/butanol using sorbitan monooleate as a surfactant and octanol as a cosurfactant. It was observed that the blending ratio of ethanol/butanol is a significant parameter for optimizing the viscosity and other fuel properties of microemulsion biofuels (Waritta, 2015). Even more, a few numbers of the research study on microemulsion systems using vegetable oils based are available to allow formulation to produce optimal fuel performance on the basis of component properties (Kibbey *et al*., 2014).

Therefore, the purpose of this work is to formulate palm oil/diesel based microemulsion biofuels using nonionic alkyl alcohol ethoxylate surfactants with different numbers of ethylene oxide group (EO). Two cosurfactants, 1-octanol and 2-ethyl-hexanol deviated by their structures were selected as a cosurfactant. Hence, this research focuses on the effect of nonionic surfactants and cosurfactant structures on microemulsion phase behavior. The presence of butanol in the alcohol system as a polar phase was investigated to maintain the amount of surfactant concentration used to form the microemulsion biofuels. Finally, basic fuel properties (kinematic viscosity, density, heat of combustion, cold flow properties, and sulfur content) are evaluated for further utilizing microemulsion biofuels as biofuel applications.

CHAPTER II
LITERATURE REVIEW

2.1 Vegetable Oils

Vegetable oils do not dissolve in water comprising of primarily fatty esters of glycerol so-called triglycerides that form by a combination of three fatty acid molecules with the molecule of glycerol by ester linkages as illustrated in Figure 2.1. (Hanna *et al*., 1994).

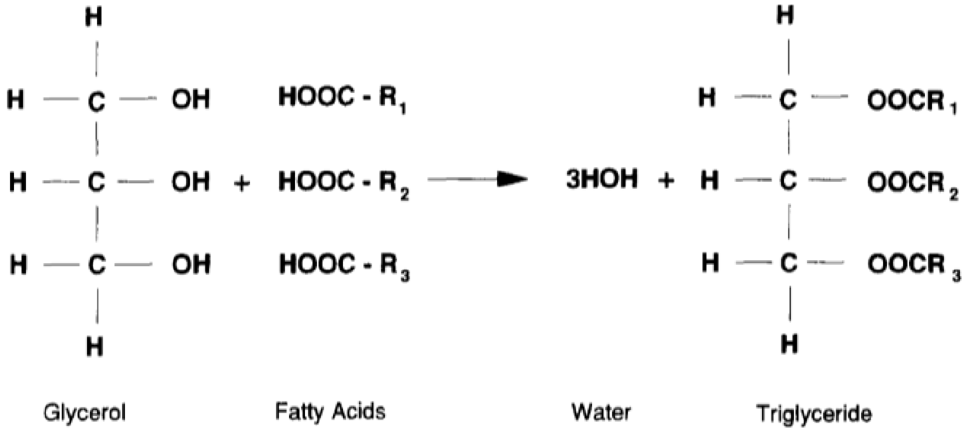


Figure 2.1 Chemical structure of vegetable oil.

The characteristics of fatty acids are varied in relation to the carbon chain length, the amount of unsaturated bonds and presence of other chemical functions. There are two types of fatty acids which are fully saturated with hydrogen bond and no double bonds, and unsaturated with at least one missing hydrogen.

Fully saturated triglycerides are solid at 25±2°C temperature thus they are difficult to use as a fuel, whereas the use of saturated triglycerides leads to excessive carbon deposits in engines (Ali and Hanna, 1994).

The fatty acid compositions found in vegetable oil as shown in Table 2.1 (Ali and Hanna, 1994).

Vegetable oils have several characteristics and properties comparable with those of diesel fuels (Goering *et al.*, 1982). Therefore, several types of vegetable oil (e.g., palm, canola, jatropha) have been selected to utilize as a biofuel depending on their chemical property and production cost. Seddon (1942) indicated that neat vegetable oils could be used directly as fuel in diesel engines under usual operating conditions. Eventhough the neat vegetable oils in diesel engines without modification cause several problems including the poor atomization, injector coking, ring sticking and carbon clogging (National Renewable Energy Laboratory, NREL, 2010; Lin *et al.*, 2013; Yoshimoto *et al.*, 2013).

Table 2.1 The fatty acids compositions found in vegetable oils (Issariyakul and Dalai, 2014)

Common name	Symbol	Formula	Double bond position[a]
Saturated			
Capric	C10:0	$C_{10}H_{20}O_2$	-
Lauric	C12:0	$C_{12}H_{24}O_2$	-
Myristic	C14:0	$C_{14}H_{28}O_2$	-
Palmitic	C16:0	$C_{16}H_{32}O_2$	-
Stearic	C18:0	$C_{18}H_{36}O_2$	-
Archidic	C20:0	$C_{20}H_{40}O_2$	-
Behenic	C22:0	$C_{22}H_{44}O_2$	-
Lignoceric	C24:0	$C_{24}H_{48}O_2$	-
Monounsaturated			
Palmitoleic	C16:1	$C_{16}H_{30}O_2$	9c
Petroselinic	C18:1	$C_{18}H_{34}O_2$	6c
Oleic	C18:1	$C_{18}H_{34}O_2$	9c
Elaidic	C18:1	$C_{18}H_{34}O_2$	9t
Vaccenic	C20:1	$C_{20}H_{38}O_2$	11c
Gadoleic	C20:1	$C_{20}H_{38}O_2$	9c
Gondoic	C20:1	$C_{20}H_{38}O_2$	11c
Erucic	C22:1	$C_{22}H_{42}O_2$	13c
Polyunsaturated			
Linoleic	C18:2	$C_{16}H_{28}O_2$	9c12c
Linolenic-α	C18:3	$C_{18}H_{32}O_2$	9c12c15c
Linolenic-γ	C18:3	$C_{18}H_{30}O_2$	6c9c12c

Common name	Symbol	Formula	Double bond position[a]
Eleostearic	C18:3	$C_{18}H_{30}O_2$	9c11t13t
Calendic	C18:3	$C_{18}H_{30}O_2$	8t10t12c

[a] *c* = *cis* formation; *t* = *trans* formation.

2.1.1 Palm Oil

Palm oil refers to the oil extracted from palm fruit which is spontaneously reddish as it contains high amount of beta-carotene. The palm fruit consists of hard seed, is called Palm kernel, enclosed in a shell which is surrounded by mesocarp as demonstrated in Figure 2.2. The fatty acid compositions of palm oil are shown in Table 2.2. Three main components of fatty acid commonly found in palm oil were palmitic acid (45.6%), oleic acid (38.5%) and linoleic acid (Riba *et al.*, 2012).

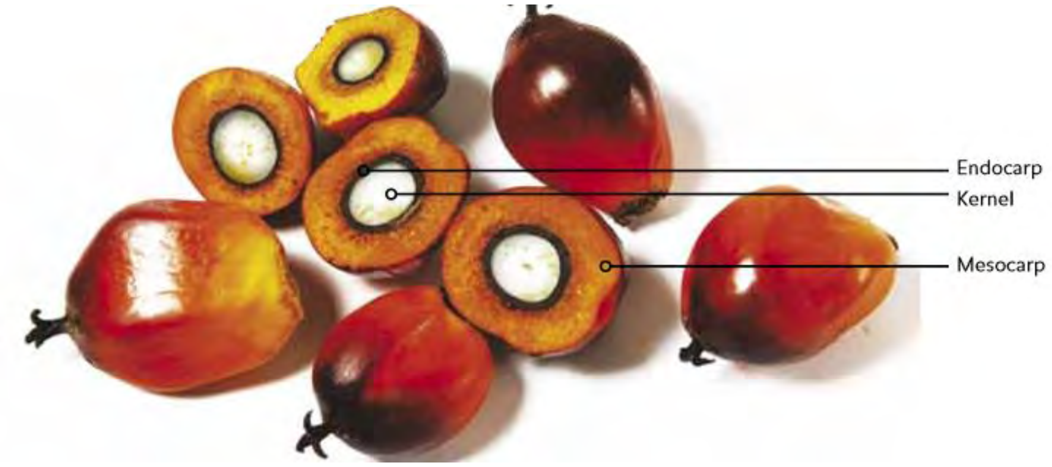


Figure 2.2 Palm fruit.
Source : http://www.simedarby.com/upload/Palm_Oil_Facts_and_Figures.pdf

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 : Esteban *et al*., 2012

Several types of vegetable oil have been utilized as biofuels. Among them, palm oil is a high potential feedstock for biofuel production in Thailand as illustrated in Table 2.3 and Figure 2.4, representing the palm oil production since 1976. It can be seen that the quantity of production of palm oil increased until 2016 (Mukherjee *et al*., 2014).

Table 2.3 Productivity of various vegetable oil sources between 2005 and 2009 in Thailand in unit 1000 Tons

Year	Palm	Coconut	Soybean	Sunflower	Castor
2005	5,003	1,930	226	38	10
2006	6,715	1,815	215	24	10
2007	6,390	1,722	204	23	10
2008	9,265	Nd	187	Nd	0.4
2009	8,313	Nd	190	Nd	Nd

*Nd is data not found

Source: Bureau of Agricultural Economic Research (Sirinee, 2013)

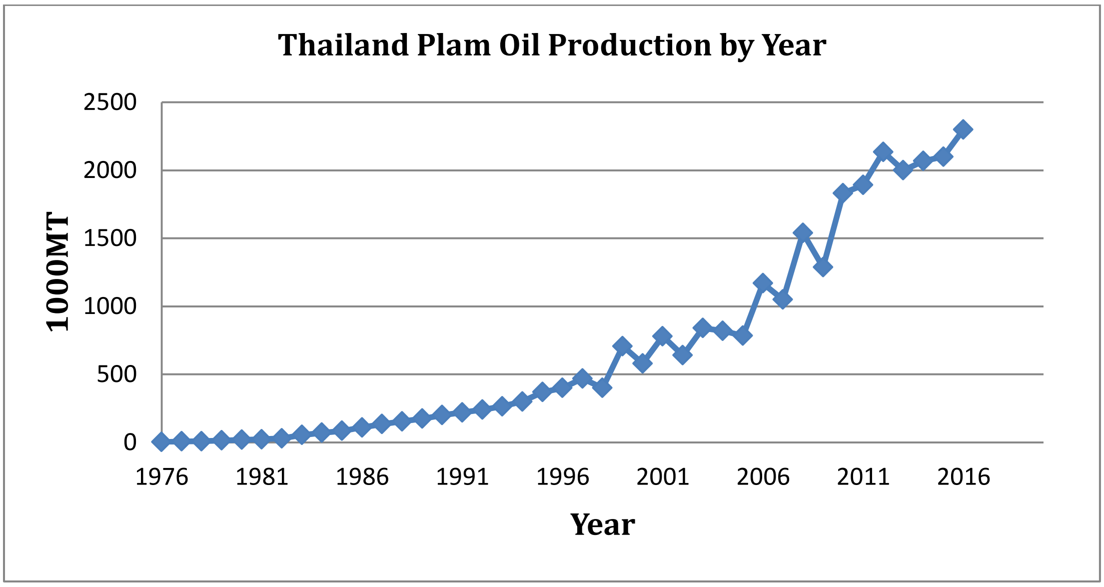


Figure 2.3 Production of palm oil in Thailand (kilotons).

Source:http://www.indexmundi.com/agriculture/?country=th&commodity=palm-oil&graph=production

2.1.1.1 Crude Palm Oil Processing

Crude palm oil (CPO) is derived from the mesocarp part of palm fruit through sterilization, stripping, extraction and purification process as shown in Figure 2.4. The process is following:

- Sterilization : placing sterilize cages in horizontal vessels at steam pressure of 3 kg/cm^2, 143°C and 60 minutes
- Stripping : separation of sterilized fruits from the bunch stalks
- Digestion : reheating the sterilized fruits at 95-100°C and 20 minutes before carrying to oil extraction unit
- Oil extraction : continuous screw pressing to product that mixture of oil 66%, water 24% and non-oily solid 10%
- Purification : dilution with water to facilitate settling and screen to remove fibrous material from that pump oil to settling tank through centrifuge, vacuum dryer into oil storage.

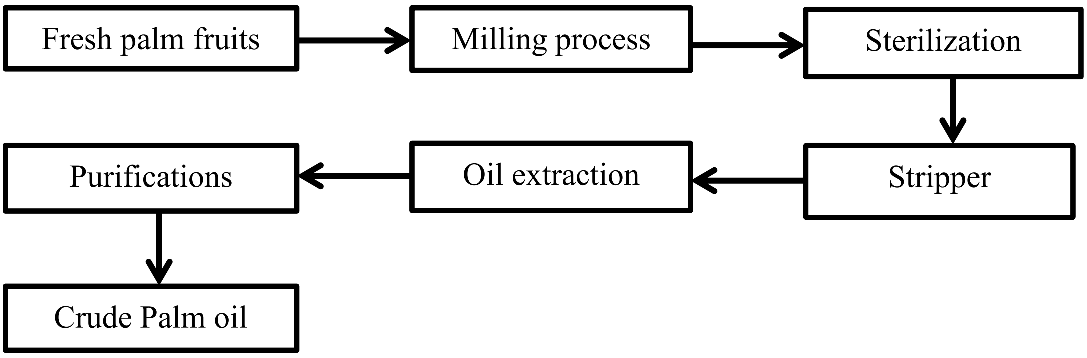


Figure 2.4 Crude palm oil production process (Zin *et al.,*2006).

Higuchi (1983) informed that a crude vegetable oil usually comprises of desirable triglycerides, unspecific substance together with small amount of impurities. These impurities contribute effect to the oil, for example, flavor, color, odor, instability and foaming. Thus, they should be removed by a purification step which is the cause of producing a high quality of refined oil with minimal possible oil loss.

2.1.1.2 Refined Bleached Deodorized Palm Oil (RBDPO) Process

The refined bleached deodorized palm oil is called RBDPO, is produced from a crude palm oil that extracted from mesocarp part of palm fruit as mentioned in 2.1.1.1, then it is passed through the physical refining process comprising pre-treatment and distillation. Pre-treatment processes (degumming and bleaching) use a chemical to react and adsorb the undesirable impurities that can effect to the stability of the final product. Another process, distillation consists of deodorization and deacidification which use a high-temperature heating (240-260°C) under vacuum (2-4 mmHg). During deodorization process, free fatty acids in the form of palm fatty acid distillate are taken away at the top section of deodorizer and the refined bleached deodorized palm oil (RBDPO) is then cooled before filtered and sent to storage tank as shown in Figure 2.5.

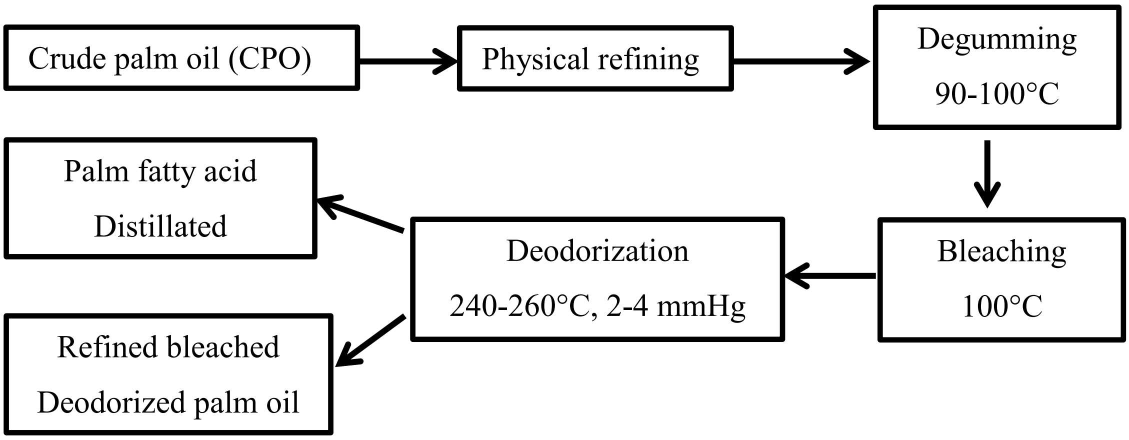


Figure 2.5 Refined bleached deodorized palm oil production.
Source : http://www.slideshare.net/peggydeng/oleochm-phy-refining

Further processes, the fractionation of RBDPO is conducted in order to separate the refined bleached deodorised palm olein (RBD olein) or palm olein as liquid fraction and the refined bleached deodorised palm stearin (RBD stearin) or palm stearin as solid fraction based on the different melting points of each component as illustrated in Figure 2.6 (Hassan *et al*., 2005).

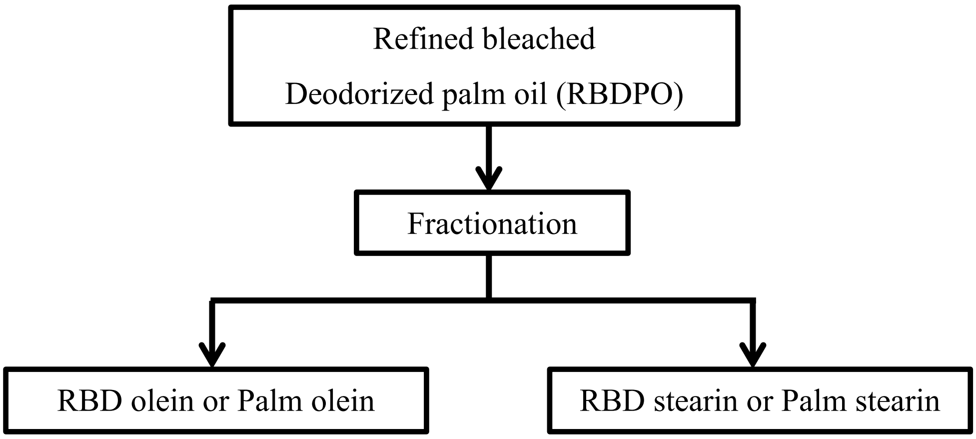


Figure 2.6 Palm olein and palm stearin production.

The RBD olein is used mainly for cooking and frying oils while RBD stearin is used for the production of shortenings and margarine (Salmiah *et al.*, 2000).

The fatty acid compositions of neat RBDPO, palm stearin, palm olein and synthesis RBDPO are shown in Table 2.4. It can be seen that palm olein contains a high amount of oleic and linoleic acids (unsaturated fatty acid) while palm stearin contains mainly palmitic acids (saturated fatty acid). These fatty acids are distributed in the various glyceride molecules as shown in Table 2.5.

However, the containing of high polyunsaturated of palm olein as for use in fuel that causes an indirect diesel engine problem including poor atomization, injector coking and carbon clogging.

Table 2.4 Fatty acid compositions of the neat RBDPO, palm stearin, palm olein and synthetic RBDPO

Fatty acid	**Carbon number**	**Fatty acid composition (%)**			
		Neat RBDPO[a]	**Palm stearin**[a]	**Palm olein**[a]	**Synthetic RBDPO (Palm stearin/ Palm olein ratio**[b]**)**
					30/70
Saturated					
Myristic acid	C14:0	1 - 1.5	1 – 2	1 - 1.5	1.10 - 1.30
Palmitic acid	C16:0	42 – 47	47 – 74	38 - 42	44.90 - 48.90
Stearic acid	C18:0	4 – 5	4 – 6	4 - 5	4.60 - 5.00
Total		47 - 53.5	52 – 82	43-48.5	50.60 - 55.20
Unsaturated					
Oleic acid	C18:1	37 – 41	16 – 37	40 - 44	36.40 - 40.10
Linoleic acid	C18:2	9 – 11	3 – 10	10 - 13	8.40 - 9.40
Total		46 – 52	19 – 47	50 - 57	44.80 - 49.50

[a]The data obtained from Abdul *et al.*, 2013, [b]The data obtained from Soares *et al.*, 2009

Table 2.5 Glyceride compositions of the neat RBDPO, palm stearin, and palm olein

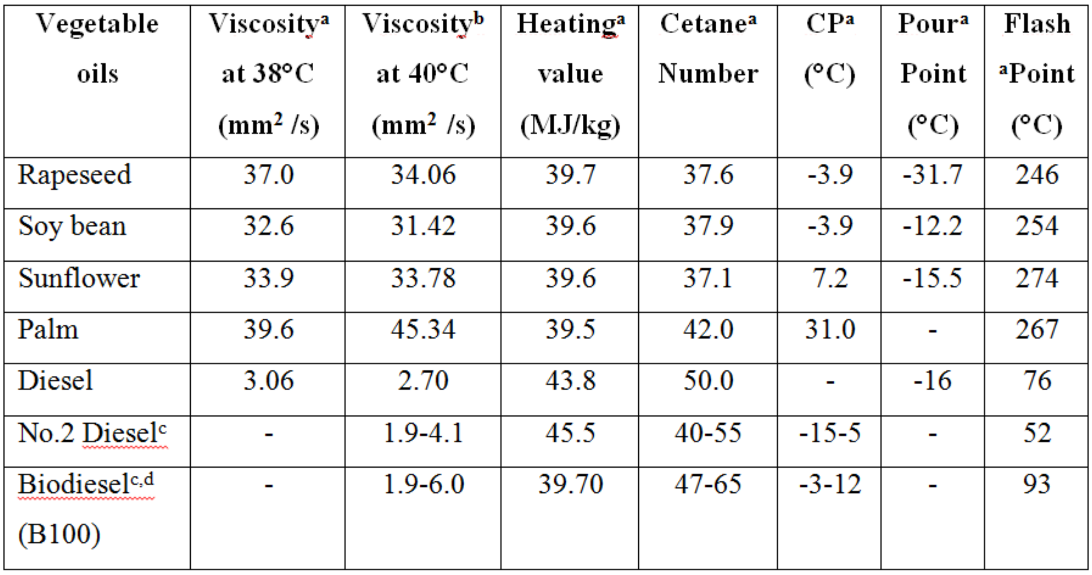
Fatty acid	Glyceride composition (%)		
	Neat RBDPO	**Palm stearin**	**Palm olein**
Diglyceride			
Total	5.20	5.15	5.55
Triglyceride			
Triunsaturated	4.98	3.95	5.27
Monosaturated	35.18	16.40	38.81
Disaturated	45.95	36.61	47.56
Trisaturated	8.69	35.20	2.81
Total	94.80	94.85	94.45

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

2.2 Technology for Reducing Vegetable Oil's Viscosity

Vegetable oils are considered for utilizing as a biofuel because their physical and chemical characteristics are comparable to the fuel properties of No.2 diesel as illustrated in Table 2.6. Although vegetable oils consist of harmless substances leading to lower toxic emissions after combustion, they have improper fuel properties such as high viscosity, cloud point resulting in cold weather limitation (Ali *et al*., 1994; Chang *et al*., 1996), low volatilities and high polyunsaturated compounds. These can cause durability problems of diesel engines including coking of injector nozzles, sticking of piston rings, and lubricating oil contamination (Nitchawan *et al*., 2014, Mofijur *et al*., 2016). Therefore, the viscosity of vegetable needs to be improved before directly utilized as a fuel in unmodified engines. Four technologies have been investigated to reduce vegetable oil's viscosity, are direct blending (Do *et al*., 2011), pyrolysis (Do *et al*., 2011; Stumborg *et al*., 1996), transesterification (Galan *et al*., 2009; Pagliaro *et al*., 2007; Mofifur *et al*., 2016) and vegetable oil -based microemulsification.

Table 2.6 Chemical and physical properties of vegetable oils and diesel



Vegetable oils	Viscosity[a] at 38°C (mm^2/s)	Viscosity[b] at 40°C (mm^2/s)	Heating[a] value (MJ/kg)	Cetane[a] Number	CP[a] (°C)	Pour[a] Point (°C)	Flash [a]Point (°C)
Rapeseed	37.0	34.06	39.7	37.6	-3.9	-31.7	246
Soy bean	32.6	31.42	39.6	37.9	-3.9	-12.2	254
Sunflower	33.9	33.78	39.6	37.1	7.2	-15.5	274
Palm	39.6	45.34	39.5	42.0	31.0	-	267
Diesel	3.06	2.70	43.8	50.0	-	-16	76
No.2 Diesel[c]	-	1.9-4.1	45.5	40-55	-15-5	-	52
Biodiesel[c,d] (B100)	-	1.9-6.0	39.70	47-65	-3-12	-	93

[a]The data obtained from Murugesan *et al.*, 2009, [b]The data obtained from Riba *et al.*, 2012 ,[c]The data obtained from U.S. Department of Energy, Biodiesel Handling and Use Guidelines (2nd Edition, March 2006) and [d]The data obtained from Raman *et al.*, 2009

2.2.1 Transesterification

Transesterification process is the commonly used method to reduce vegetable oil's viscosity, and the derived vegetable oil is well-known as biodiesel production. The transesterification between fat or oil and excess alcohol is the reversible reaction in the presence of the catalyst. The transesterification reaction can be considered by three forward and reversible equations as the following:

$$\text{Triglyceride} + \text{ROH} \longleftrightarrow \text{Diglycerides} + \text{RCOOR}_1 \tag{1}$$

$$\text{Diglyceride} + \text{ROH} \longleftrightarrow \text{Monoglycerides} + \text{RCOOR}_2 \tag{2}$$

$$\text{Monoglyceride} + \text{ROH} \longleftrightarrow \text{Glycerol} + \text{RCOOR}_3 \tag{3}$$

Fatty acid methyl ester (FAME) or biodiesel is the primary product and crude glycerol as a by-product. An improper management of glycerol can lead to adverse environmental problems due to waste disposal (Galan *et al.*, 2009; Pagliaro *et al.*, 2007; Mofifur *et al.*, 2016). Even more, the utilization of glycerol, resulting in an increase in overall energy consumption and environmental emissions.

2.2.2 Direct Vegetable Oil/Diesel Blends

Vegetable oils can blend directly with diesel fuels to use as a biofuel that is the simple way to reduce viscosity. However, the drawback of this technique is that the mixed liquid fuel that leads to the durability problem of diesel engines such as coking of injector nozzles, sticking of piston rings, and lubricating oil contamination (Do *et al.*, 2011). The ratio of vegetable oil and diesel blended at 50% by volume results in the higher viscosity than the diesel no.2 around 18 times (Ma and Hanna, 1991).

2.2.3 Pyrolysis

Pyrolysis is a thermochemical treatment which refers to decompose reaction of larger to smaller molecules by thermal in the vacuum system (Sťávová *et al.*, 2012). Pyrolysis of vegetable oils represents an alternative method of producing renewable liquid products for use in fuel applications. The advantage of pyrolysis possesses over transesterification is that the final product can be altered dependent on reaction conditions thus the process able to adjust the products towards certain applications by tuning various process parameters, including lower processing costs, compatibility with infrastructure, and feedstock flexibility (Stumborg *et al.*, 1996).

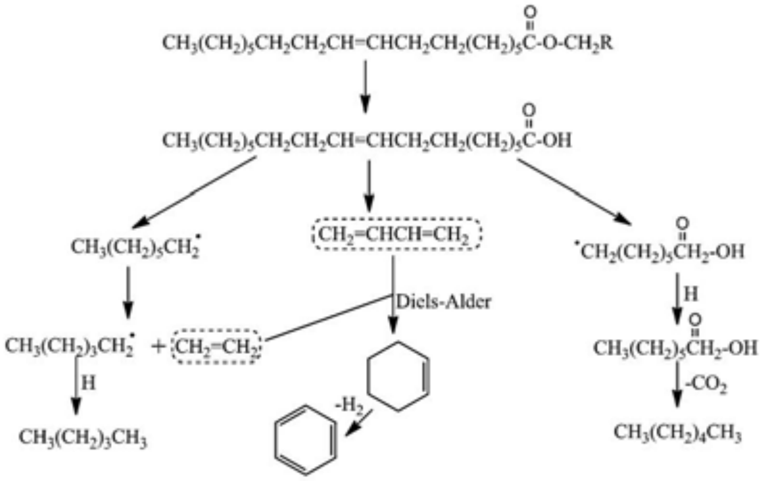


Figure 2.7 Pyrolysis of vegetable oil (Catal. Sci. Technol., 2013).

The composition of pyrolysis oil is hydrocarbon components consisting of alkane, alkene, aromatic and carboxylic acid as illustrated in Figure 2.7. Complex reactions of pyrolysis process frequently lead to several by-products through several reactions which are difficult to control the quality of the fuel and low purity (Do *et al*., 2011).

2.2.4 Microemulsification

Microemulsions are a transparent thermodynamically stable liquid mixture that can be formed by mixing of hydrophilic, hydrophobic, surfactant and co-surfactant together (Rosen, 1989; Wanxu *et al.*, 2015). Moreover, the formation of microemulsion depends on compositions and environmental conditions. Phase study extremely helps to explain different phases that exist in the region depending upon the composition ratios. Construction of phase diagram enables determination of aqueous dilutability and range of compositions that form a monophasic region as shown in Figure 2.8. Microemulsions can exist in four Winsor-Type microemulsion phases as demonstrated in Figure 2.9. Normal micelles are Winsor Type I (oil-in-water or O/W) microemulsions in equilibrium with an excess oil phase, while reverse micelles are Winsor Type II (water-in-oil or W/O) microemulsions in equilibrium with an excess water phase. Winsor type III microemulsions contain with three phases comprising excess oil and water phases in equilibrium with middle phase containing oil, water, and surfactant (Bourrel *et al*., 1988).

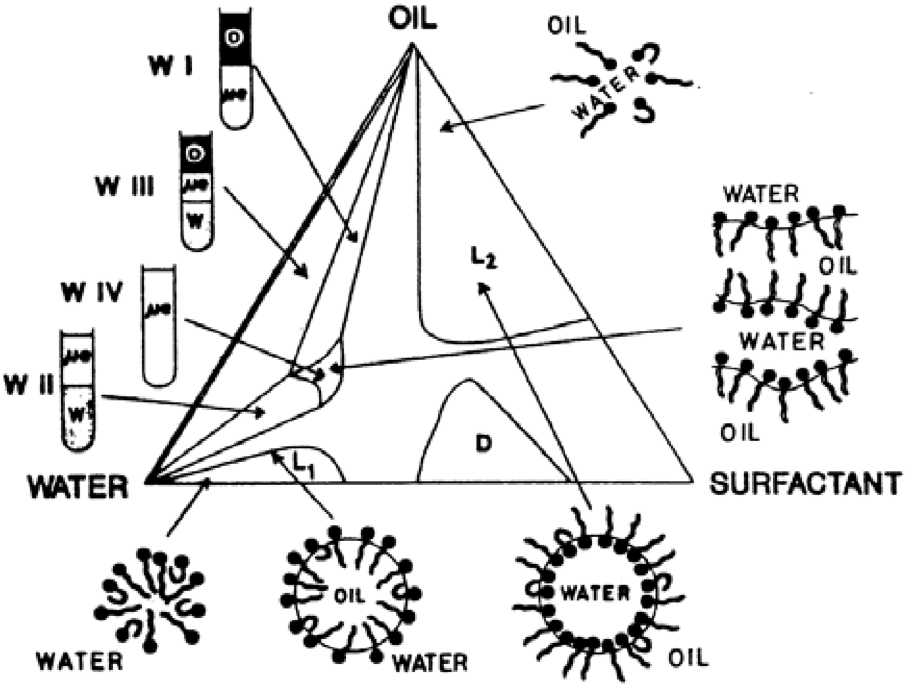


Figure 2.8 A hypothetical ternary phase diagram representing the three components in the system (Bancroft, 1913; Paul and Moulik, 2000).

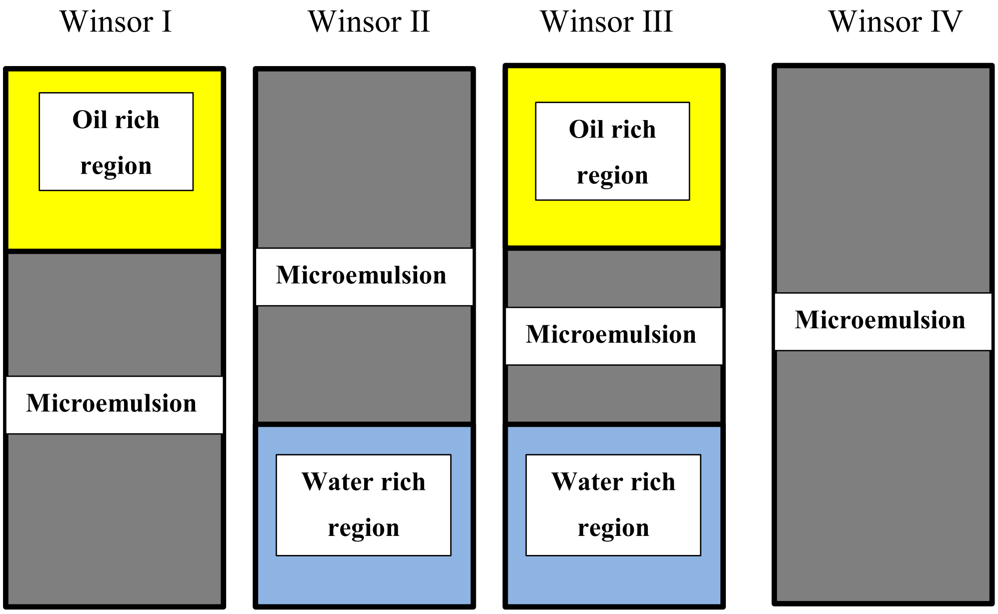


Figure 2.9 Winsor type of phase equilibrium (Mehta *et al.*, 2011).

Microemulsion formation can be determined by the hydrophilicity - lipophilicity balance (HLB) which is an empirical expression for the relationship of the hydrophilic and hydrophobic group of the surfactants in the emulsion system as shown in Figure 2.10. It has been demonstrated that a bicontinuous structure corresponds to a zero curvature, (HLB ≈ 10). For HLB <10, water is dispersed in oil (W/O type microemulsion), while the oil is dispersed in the aqueous phase for HLB>10 (O/W type microemulsion).

Many advantages of microemulsion technique compared with the other process are a simple process, no wastewater, no by-product, burning more completely, less carbon monoxide emission, less nitrogen oxide emission, less particulate matters through their exhaust gas quality. Even more, the microemulsion fuels are acceptable kinematic viscosity in the range of 4-6 cSt at 40 °C. The range of microemulsion droplet size of microemulsion biofuels is about 2-200 nm (Arpornpong *et al.*, 2014).

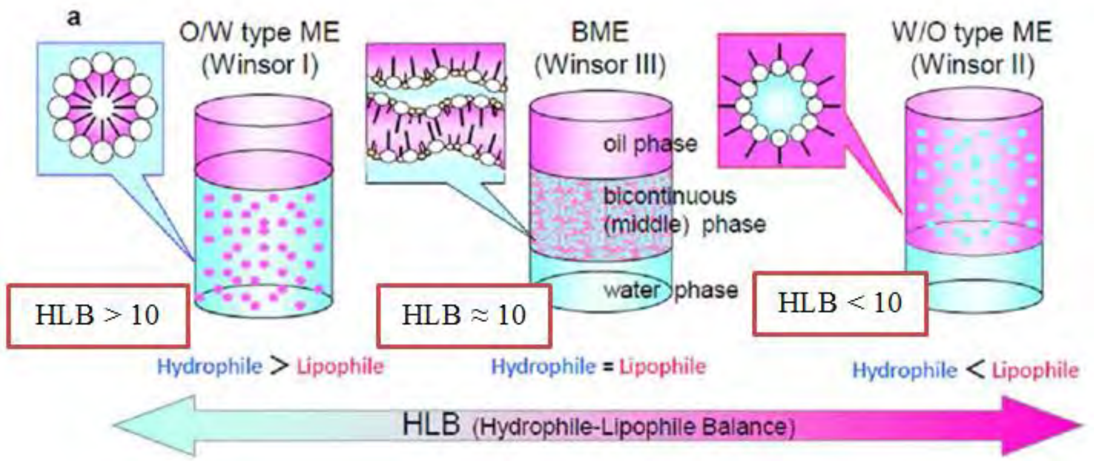


Figure 2.10 Schematic representation and corresponding photographs of a series of microemulsion controlled by HLB.

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

2.3 Alcohol Blended

The utilization of alcohols in diesel fuels can significantly reduce exhaust emissions (CO and NO_x) and particulate matter emissions for vehicles (Chotwichien *et al*., 2009). Alcohols can be produced from common crops such as sugar cane and corn. However, NOx emissions increased linearly with their content of alcohol used involving pentanol and long chain, particularly at the high load condition. The longer chain fatty alcohols (e.g., hexanol, octanol, and dodecanol) are commonly used as cosurfactant for stabilization lower alcohol/diesel blends and diesel-oil microemulsion (Rajesh *et al*., 2016).

Ethanol as a renewable energy source is produced from a variety of biomass sources by the fermentation process. Nevertheless, there are many drawbacks in using ethanol in diesel engine such as lower cetane number, flash point and dynamic viscosity than diesel fuel (Xing-cai *et al*., 2004). Whereas, a diesel engine prefers high cetane number fuels which make it easily auto-ignition and gives a short ignite delay. Therefore, butanol has been promoted instead due to its higher cetane number, higher heating value, and less hydrophilicity when compares with methanol and ethanol. (Lin *et al*., 2013; Yoshimoto *et al*., 2013).

Chotwichien and coworkers (2009) investigated on the utilization of three types biodiesel as an additive in diesohol preparation such as biodiesel-methyl, ethyl and butyl ester. They prepared through transesterification process with a conventional based catalyst. They found that the use of butanol in diesohol can improve the fuel stability at low temperature.

Biswajit and coworkers (2016) investigated the effect of cosurfactant types in the microemulsions containing the mixture of diesel and kerosene as an oil phase with using Tween-80 surfactant, and water or bine as the polar phase by comparison between branching of cosurfactant (iso-butanol) and n-butanol. The finding of the work indicated that a fuel compatibility of the microemulsions comprising branched chain was better than that of the straight chain, thus resulting in the changing in phase behavior, cloud point, conductivity and fuel related characteristics of microemulsion systems.

2.4 Surfactants and Cosurfactants

2.4.1 Surfactants

Surfactants are an amphiphile molecule consisting of hydrophilic part or surfactant's head (soluble in water) and hydrophobic part or surfactant's tail (soluble in lipids or oils). One narrowly studied method for accommodation vegetable oils to fuel applications is the surfactant used to create the thermodynamically stable mixtures of different fluids as vegetable oils/diesel blends (Kibbey *et al.*, 2014).

Surfactants are classified into four types based on the nature of their head group as shown in Figure 2.11.

1) Anionic Surfactants

The surface active portion of the molecule carries a negative charge, for instance, alkylbenzene sulfonates (detegents), soaps (fatty acid), lauryl sulfate (foaming aging), lignosulfonates (dispersants) etc.

2) Cationic Surfactants

The surface active portion of the molecule carries a positive charge, for example, salt of long chain amine and quaternary ammonium chloride. These surfactants are more expensive than conventional anionic surfactants due to the use of high-pressure hydrogenation reaction.

3) Zwitterionic or Amphoteric Surfactants

A single surfactant molecule exhibits both positive and negative charges in the surface active portion, for intsances, sulfobetaine, amino acid and phospholipids.

4) Nonionic Surfactants

The surface active portion bears no apparent ionic charge, for example, monoglyceride of long chain fatty acid, polyoxyethylenated alkylphenol and polyoxyethylenated alcohol.

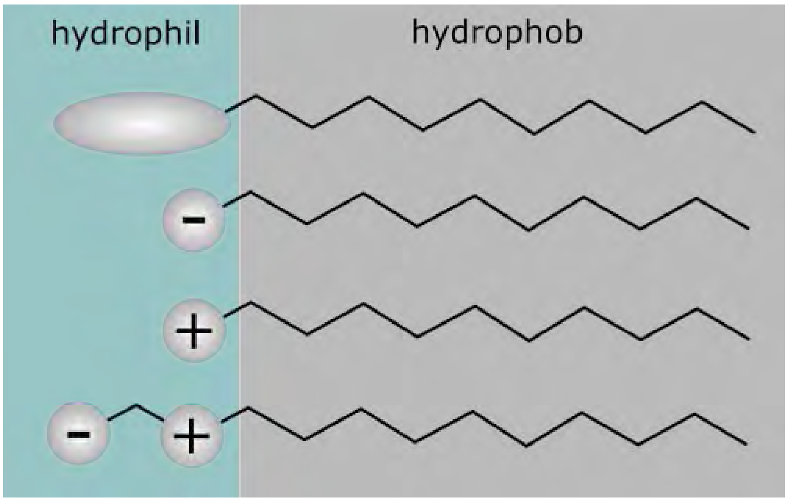


Figure 2.11 Schematic illustration of the various types of surfactants
Source: http://www.wikiwand.com/en/Surfactant.

Arpornpong and coworkers (2014) found that the nonionic surfactants were an appropriate surfactant to formulate a single phase reverse microemulsions of palm oil/diesel blends to stabilize ethanol in the oil phase. The nonionic surfactants have many advantages comparable with other surfactants such as undesirable salt, more oil soluble, no SO_x and NO_x. Thus, a nonionic surfactant is selected to form microemulsion biofuels in this study.

2.4.1.1 Alcohol Ethoxylate Surfactant

Alcohol ethoxylate (AE) is classified as a nonionic surfactant that can be produced by synthetic or natural fatty alcohols. Synthetic alcohols used for ethoxylation are available from the oligomerization of ethylene with Ziegler catalysts.

Natural fatty alcohol surfactants are produced by reduction of fatty acids. Both synthetic and natural alcohol ethoxylates are used as a nonionic surfactant in many industries. AEs with carbon unit range between C8 to C18 are most commonly used in household detergent products. Furthermore, the alcohol ethoxylate surfactants commonly contain ethylene oxide group from 3 to 12 units (EOn) in the molecule as illustrated in Figure 2.12.

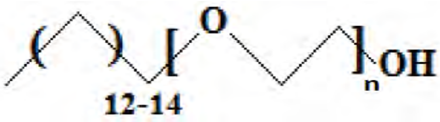


Figure 2.12 Structure of alcohol ethoxylate surfactant.

Many researchers have studied the effects of surfactant and cosurfactant structures on microemulsion biofuel formation. Arpornpong and coworkers (2014) used stearyl alcohol (saturated), oleyl alcohol (unsaturated), methyl oleate (unsaturated fatty acid ester) and Brij-010 (ethylene oxide groups) as a surfactant to stabilize palm oil/diesel blended and ethanol in order to formulate microemulsion biofuels. They found that the methyl oleate unsaturated surfactant can greatly reduce the bulk viscosity and produce the uniform size of microemulsion droplets while using the least amount of surfactant in the system.

Several researchers have investigated the effect of surfactant types to form microemulsion biofuels. Balcan and coworkers (2014) studied phase behavior, interfacial tension and solubilization in microemulsion systems containing diesel and colza oil. They used tetraethylene glycol dodecyl ether (Brij 30) as a nonionic surfactant, sodium bis-(2-ethylhexyl) (AOT) as an anionic surfactant and i-butanol as a cosurfactant. The results showed that the single phase area of Brij 30 is smaller than AOT but larger for anionic-nonionic mixture. The presence of NaCl in the aqueous solution caused a reduction in the microemulsion area. Therefore, the microemulsion area on the pseudo-ternary phase diagram decreases with the hydrophobicity of surfactant and in the presence of electrolyte but increases in mixture system.

Attaphong and coworkers (2013) studied the effects of surfactant and temperature on phase behaviors of vegetable oil-based microemulsion fuels using three types of nonionic surfactant and anionic carboxylate-based extended surfactants with 2-ethyl-1-hexanol. The results showed that salt-free microemulsion fuels could be formulated using single and mixed surfactants with cosurfactants even at low temperature. Among all surfactants used, oleyl alcohol (nonionic surfactant) had the maximum solubilization capacity because the system with oleyl alcohol required the least surfactant concentration to formulate a single phase microemulsion biofuel.

However, the linear alcohol ethoxylate surfactant (L16-1) in the single and mixed systems can be used to form microemulsion fuels, which provided the comparable result to those of the system with oleyl alcohol as a surfactant. Both the increasing of alkyl groups and decreasing of EO groups led to hydrophobicity of surfactants increase. As the result, the polar phase significantly dissolves in the oil phase.

Anantarakitti and coworkers (2014) studied the effects of nonionic surfactant and cosurfactant structures on their fuel properties of microemulsion-based biofuel from palm oil. They varied the number of ethylene oxide groups, EOn (n =1, 5 and 9) in nonionic alcohol ethoxylate surfactants. The results showed that the kinematic viscosity and the microemulsion droplet sized depending on structures of both surfactant and cosurfactant, nonpolar phase, and polar phase. The significant difference in the kinematic viscosity for the microemulsion fuel systems with branch chain alcohol was more remarkable than using straight chain alcohol as a cosurfactant.

Pengpreecha and coworkers (2014) studied the effects of using cosurfactant to formulate microemulsion fuels from vegetable oils (palm oil, used palm oil, soybean oil) blend with diesel or biodiesel on phase behaviors. The phase behaviors of the system, which contained different types of vegetable oil, were not significantly affected by the fatty acid composition of vegetable oils. The results indicated that the vegetable oils blended with biodiesel required a lower surfactant concentration to formulate single phase microemulsion. The microemulsion fuels containing octanol exhibited the separate phase was significantly lower than those of systems with ethylene glycol butyl ether.

Bora and coworker (2015) studied the effect of nonionic surfactants such as FAME (fatty ester), OA (long chain alcohol) and EGBE (alkyl ether and anti-freezing agent) on structure, dynamics and other fuel characteristics of microemulsion based hybrid biofuels (MHBF) from *Thevetia peruviana* seed oil (TPO). The result showed that the structural and dynamic behavior of MHBF system were developed using nonionic surfactants. The physical stability was increased in both FAME and OA as surfactants by modifying the structure and dynamics of the simple crude TPO based system. The effect of EGBE was opposed to the role played by FAME and OA. Nevertheless, the anti-freezing agent EGBE contributed significantly in improving the cold flow properties of MHBFs.

Wang and coworker (2015) studied the formation and characterization of fully dilutable microemulsion with fatty acid methyl esters (FAME) as the oil phase mixture with alkyl polyglycerol (APG) and alkylpolyethoxy carboxylates (AEC) as the surfactant, and alkanol as a cosurfactant. The result showed that a full water dilutable microemulsions with 3:1 by weight of APG/AEC as the surfactant, 2:1 by weight of 1- butanol/1-propanol as the cosurfactant and methyl laurate as the oil phase was optimized from pseudo-ternary phase diagrams. It was found that FAMEs could replace toxic and volatile organic solvents as the oil phase. The DLS results showed that the primary destabilization mechanism for these dilute microemulsion was Ostwald ripening at the beginning of the dilute process. The diluted microemulsions exhibited the excellent wetting and spreading properties on hydrophobic surfaces.

2.4.2 Cosurfactant

Cosurfactant, such as a long-chain alcohol, is added into the process to enhance the effectiveness of a surfactant, further reducing the surface tension of liquid. Typically, cosurfactant is used to increase the oil-solubilizing capacity in microemulsion surfactant systems (Schlumberger Company, 2015).

Several researchers have investigated the effect of cosurfactants on microemulsion biofuel formation. Anantarakitti and coworkers (2014) studied the effect of cosurfactants structures which are straight chain (1-octanol) and branch chain alcohols (2-ethyl-1-haxanol) in vegetable oil/diesel blends to form reverse micelle microemulsion fuel formation. The result showed that the solubility of ethanol in the palm oil/diesel blends was improved by increasing the hydrophobicity of the surfactant/cosurfactant. They found that the kinematic viscosity of the microemulsion fuel system with branch chain alcohol was less than the system with straight chain alcohol as a cosurfactant. Furthermore, the droplet size of microemulsion fuel systems using 2ethyl-1-hexanol was larger than the system with 1-octanol as cosurfactant.

Acharya and coworkers (2016) studied the effect of branching of cosurfactant which is iso-butanol to compare with n-butanol in the microemulsion properties that included the mixtures of diesel and kerosene at difference proportion, non-ionic Tween-80 surfactant, and water as the aqueous phase. They found that the use of branched alkyl chains as a cosurfactant led to the formation of more disordered microemulsion due to weaker intermolecular cohesive forces and their shorter sufficient alkyl chain length and steric hindrance which cause to efficient molecular packing (Rodrigue *et al*. 2006; Knothe 2005).

2.5 Pseudo-ternary Phase Diagram

The phase diagram in triangle vertices is used to determine the miscibility of the microemulsion mixture. Of which, the pseudo-ternary phase diagram of the microemulsion biofuel system consists of five components i.e., vegetable oil/diesel, ethanol, surfactant, and cosurfactant. The surfactant/cosurfactant at fixed molar ratio is represented by the upper vertex, while vegetable oil/diesel blended (non-polar phase) and ethanol (polar phase) are shown at the left side and right side, respectively.

Bora and coworker (2016) studied the phase diagram of microemulsion as illustrated in Figure 2.13. It can be seen that the upper of vertices is GMO/butan-2-ol mixture, while the bottom of vertices represents P-TPO (oil phase) and ethanol (polar phase) at the left side and right side, respectively. The separate and single phases are represented in shading and without shading portion, respectively, while between the portion that is called miscibility curve.

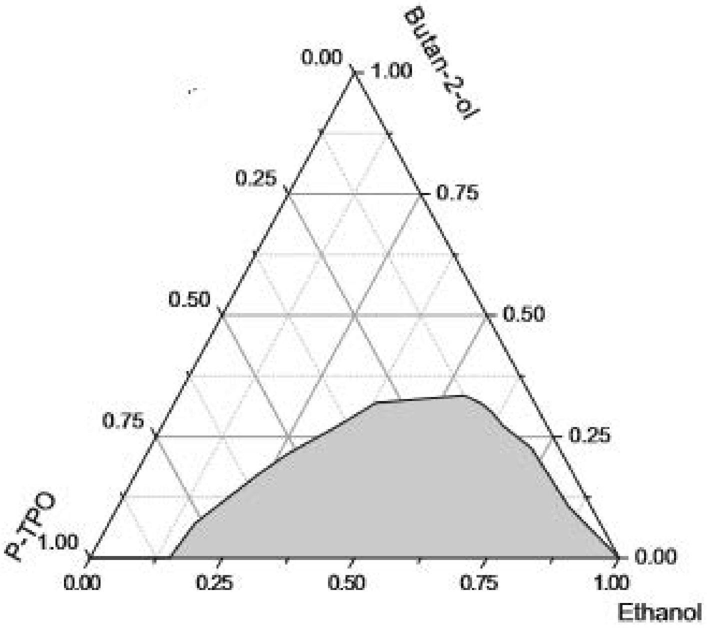


Figure 2.13 Pseudo-ternary phase diagram of oil/ethanol/surfactant (Bora *et al.*, 2016).

2.6 Diesel Fuel

Diesel consists of hydrocarbons liquid mixture and generally used as a fuel in vehicle and industry.

2.6.1 Types of Diesel Oil

The types of diesel oil are classified into 3 types such as automotive and industrail diesel oil which are described below:

2.6.1.1 Automotive Diesel Oil

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

2.6.1.2 Industrial Diesel Oil

Industrial diesel oil so-called low-speed diesel (LSD) is used for a diesel engine which has moderate speed engine approximate 500-1,000 rpm.

LSD engines do not require high cetane number and volatilization rate of fuel in the engine may be lower than that of HSD engine.

2.6.2 Standard Diesel Fuels

Diesel fuels can be classified by conventional distillation operation which is distillation temperature of diesel fuels and their applications.

2.6.2.1 No. 1 Diesel Fuels

No. 1 diesel fuel is a light product from distillation operation, and its distillation temperature is about 290ºC. It consists of hydrocarbons which carbon numbers in the range of C_9-C_{16}. The specific standard of No. 1 diesel fuels is defined in ASTM D 975. It is used in high rpm engines requiring frequent changes in load and speed.

2.6.2.2 No. 2 Diesel Fuels

No. 2 diesel fuel is middle distillate product and has distillation temperature about 340ºC. The specific standard of No. 2 diesel fuels is defined in ASTM D 975 as the same as No. 1 diesel fuels. Carbon chain length of No. 2 diesel fuel is longer than the carbon chain length of No. 1 diesel fuels. It is more widely used in truck fleets because of its greater heat value per gallon, particularly in warm to moderate climates.

2.6.2.3 No.4 Diesel Fuels

No. 4 diesel fuel is heavy distillate product and is used in small and medium-speed diesel engines. The standard of No. 4 diesel fuels is defined in ASTM D 396. Carbon chain length of No. 4 diesel fuels is longer than the carbon chain length of No. 1 and No. 2 diesel fuels. It is used in stationary constant-speed engines or marine transport applications.

2.7 Biodiesel

Biodiesel is known as methyl esters derived from renewable sources such as vegetable oils, animal fats or other types of biomass and can be used as an alternative fuel in diesel engines. Biodiesel is non-explosive, biodegradable, non-flammable as well as non-toxic properties. As a result, biodiesel is being used in developing countries (Mofifur *et al*., 2016). Many researchers have developed and improved diesel formula by blending vegetable oils for producing green fuel. For example, Nguyen and coworker (2010) demonstrated the feasibility of production fuel via vegetable oil extraction using diesel-based reverse micellar microemulsion as an extraction solvent. The results showed that diesel based reverse micellar extract oil from peanut which has more effectively than only both diesel and hexane under the same condition. The extracted peanut oil/diesel blend has viscosity, cloud point and pour point that meet requirements for biodiesel fuel.

2.8 Fuel Properties

2.8.1 Kinematic Viscosity

One of the importance parameters to determine the quality of fuel is kinematic viscosity because it affects to the fuel drop size, the jet penetration, quality of atomization, spray characteristic and the combustion quality (Mofifur *et al*., 2016). The viscosity of palm oil at 40 ºC is 45.34 mm^2/s (Esteban *et al.,* 2012) while the viscosity of diesel at 40 ºC is 2.70 mm^2/s (Martinez, 2015). Kinematic viscosity is a measure of the resistive flow of a fluid under the influence of gravity. The high viscosity of vegetable oils leads to poor fuel atomization during the injection process including ring sticking (Attaphong *et al.,* 2012). On the other hand, the viscosity is very low then it will not provide enough lubrication which leads to increase wear and leakage.

2.8.2 Droplet size

The droplet diameter and droplet size distribution of the reverse micelle microemulsion droplets can be measured by dynamic light scattering (DLS). Arpornpong and coworkers (2014) and Anantarakitti and coworkers (2014) investigated the droplet size distributions to observe the correlation with the kinematic viscosity of microemulsion-based biofuel systems. The ranges of the mean droplet size of reverse micelle microemulsions are 2-200 nm (Rosen, 2004).

2.8.3 Cloud Point

Cloud point is the temperature at the fuel which is initially to form crystals and 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 necessary to use for several applications because using fuels at low temperature may be formed crystals which can clog fuel filter and supply lines. The cloud point of vegetable oil/diesel blend is higher than diesel fuel (Ali and Haan, 1994).

2.8.4 Gross Heat of Combustion

Heating values or gross heating values is the energy released as heat when a compound undergoes complete combustion with oxygen under standard conditions. Typically, evaluating the fuel consumption in a diesel engine can be measured by a heat of combustion. Arpornpong and coworkers (2014) showed that heating value of the microemulsion-based biofuels (38.6–39.5 MJ/kg) had slightly lower than the heating value of regular diesel fuel (45.1 MJ/kg). Do and coworkers (2011) indicated the area of the gas phase combustion in the fuels with higher degrees of oxidation because of the presence of oxygen in the fuel.

CHAPTER III

EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Equipment

- Canon Fenske type Viscometer
- Circulating temperature bath (MGW LAUDIA, model S - 1)
- DLS (Goniometer CGS-II)
- Glass vials 15 ml
- Syringe
- Pipette and Auto-Pipette
- vacuum filter kit
- Fourier transform infrared spectroscopy (FTIR)
- Vortex
- Hot plate with stirrer
- Density meter
- Sulphur analyser

3.1.2 Materials

3.1.2.1 Surfactants

Nonionic surfactants used in this research were alcohol ethoxylate surfactants containing C12-14 carbon atoms with different numbers of ethylene oxide groups, EOn (n =1, 3, 5 and 9). The linear alkyl alcohol ethoxylate surfactants with 99% purity were obtained from Thai Ethoxylate Company, Ltd. (Bangkok, Thailand). The structures and properties of surfactants used are shown in Figure 3.1 and Table 3.1, respectively.

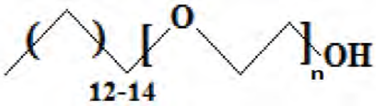


Figure 3.1 Structure of alcohol ethoxylate series contain C12-14 carbon atoms.

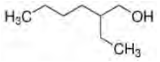
3.1.2.2 Cosurfactants

The cosurfactants used in this study were 1-Octanol (99% purity) and 2-ethyl-1-hexanol (≥99.6% purity) and purchased from Acros Organic. They can work well together with a nonionic surfactant for improving the formation of single phase microemulsion (Pengpreecha *et al.*, 2014; Anantarakitti *et al.*, 2014). The structures and properties of cosurfactants used are shown in Figure 3.2 and Table 3.1, respectively.

1-Octanol 2-ethyl-1-hexanol

Figure 3.2 Structure of cosurfactants.

Table 3.1 Properties of the surfactants and the cosurfactant

Materials	Chemical structure	Symbol	M.W.[a] (g/mol)	Density[a] (g/mL)	HLB[b]
Surfactants					
$C_{12,14}H_{25,29}$–(EO)$_1$–OH		EO1	244	0.837	3.60
$C_{12,14}H_{25,29}$–(EO)$_3$–OH		EO3	332	0.890	7.95
$C_{12,14}H_{25,29}$–(EO)$_5$–OH		EO5	420	0.924	10.48
$C_{12,14}H_{25,29}$–(EO)$_9$–OH		EO9	569.31	0.966	12.97
Cosurfactant					
1-Octanol		Oct	130.23	0.825	-
2-ethyl-1-hexanol		2-ethyl	130.2	0.833	-

Source : [a] Insom, 2016, [b] The data from calculation as shown in appendix G

3.1.2.3 Polar Phase or Alcohol Phase

Absolute ethanol and butanol, with 99% purity from Merck Company (Thailand), were selected for use as a viscosity reducer in the microemulsion system.

3.1.2.4 Non-polar Phase or Oil Phase

In this study, a food-grade pure palm oil (Morakot Industries Public Company, Thailand) was purchased from a local market (Bangkok, Thailand). The diesel fuel (The Shell Company Ltd., Thailand) was purchased from a local gas station (Bangkok, Thailand).

3.2 Experimental Methods

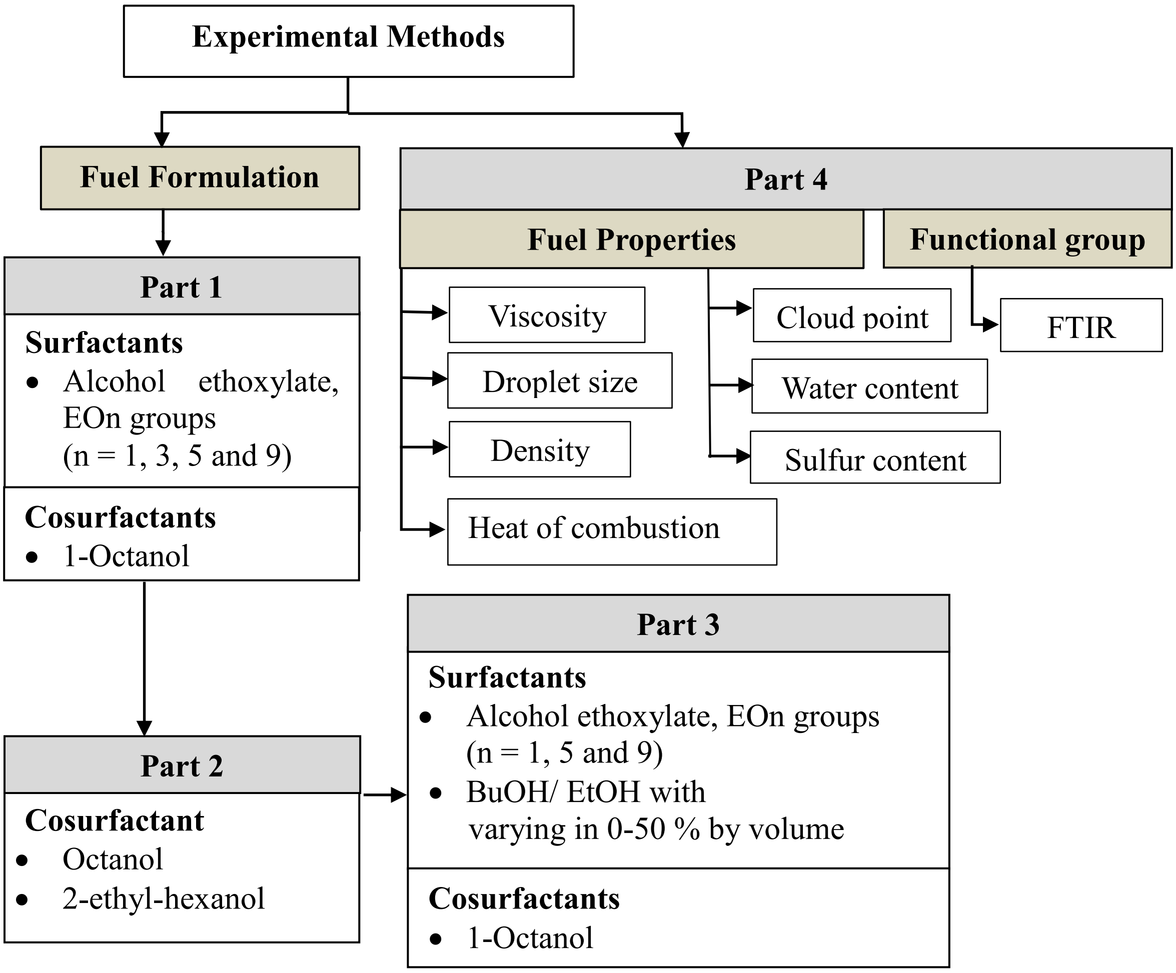


Figure 3.3 Experimental methods flow diagram of this study.

3.2.1 Microemulsion Preparation

1) The microemulsion biofuels were prepared in a 15 mL glass vial by palm oil/diesel mixture at ratio 1:1 by volume and surfactant/cosurfactant (S/C) at the molar ratio of 1:8, and the amount of ethanol added to each vial were varied. The sample was gently mixed by hand-shaken and then placed at room temperature (25 ± 2ºC) to observe the phase separation. The microemulsion phase behavior of each sample was observed for 30 days to ensure its stability.

2) The microemulsion fuels were prepared at fixed 20% by volume of alcohol as a polar phase, in which the amount of butanol in butanol/ethanol mixture were varied from 10:90, 20:80, 30:70, 40:60 and 50:50. The prepared alcohol solution at different fraction was added to the surfactant/cosurfactant mixture (1:8 by molar ratio), and palm oil/diesel blend (1:1 by volume ratio) to study the effect of alcohol blending in the microemulsion fuel formation.

3.2.2 Pseudo-ternary Phase Diagram

The isotropic region is determined by a pseudo ternary diagram, which is constructed through the stepwise addition of ethanol to concentrated stock solutions of oil, surfactant, and cosurfactant in different volume ratios (Bora *et al.*, 2016). The upper vertex of the diagram represents the surfactant/cosurfactant (S/C) mixture (A) at a constant ratio, while the two vertices at the bottom are vegetable oil/diesel blend (B) and ethanol (C) at the left side and right side, respectively. Each point in the diagram is calculated relation with three components of A, B, C in volume percentage as follows:

$$x\%A + y\%B + z\%C = 100\% \text{ total components}$$

The miscibility curves are plotted between separate phase and single phase areas as shown in shading and without shading areas, respectively.

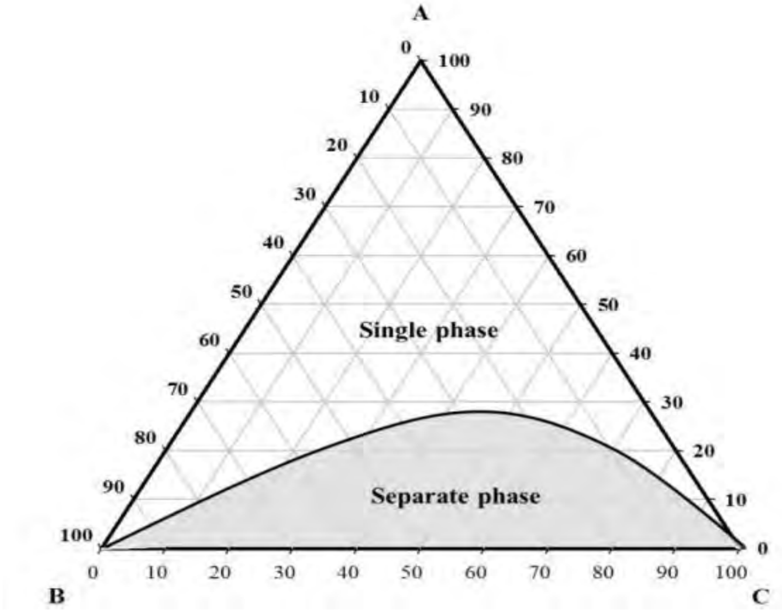


Figure 3.4 Pseudo-ternary phase diagram.

3.2.3 Functional group Analyzer

3.2.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

The infrared spectroscopic analysis of microemulsion biofuels systems was carried out using the Nicolet iS5 FT-IR Spectrometer. Each sample was scanned for 16 times. For any oil, it was scanned at least two separate spectra. The functional group and chemical transformation during the process of microemulsion biofuels systems were characterized to confirm the non-involvement of chemical reactions by Fourier transform infrared spectroscopy (FTIR).

3.2.4 Fuel Properties of Microemulsion Biofuels

3.2.4.1 Kinematic Viscosity

The kinematic viscosity of the microemulsion biofuels was measured by Cannon-Fenske Routine viscometer according to ASTM D 445. The flow rates, described in cSt/sec unit, were calculated by counting time at 25ºC, 40ºC and 60ºC. Finally, the kinematic viscosity can be calculated by Equation (3.1) as follows:

$$\mu = Kt \tag{3.1}$$

Where μ is the kinematic viscosity (cSt)

K is viscosity constant

t is the time of sample flow in the viscometer

Table 3.2 Viscosity constant varying in temperature

Temperature(°C)	Viscosity constant (cSt)
25	0.01549
40	0.01547
60	0.01545

3.2.4.2 Droplet Size Measurement

The size distribution of the microemulsion droplets was investigated by dynamic light scattering (DLS). The measurement was performed by Nano Zeta Sizer (Malvern) in the range 1-10^4 nm at 25ºC, a scattering angle of 173º and light source was a He-Ne laser using 4MW at wavelength 633 nm.

3.2.4.3 Density

The density of the sample was measured at 20°C by density meter (DMA 4500 M).

Figure 3.5 DMA 4500 M density meter.

3.2.4.4 Cloud Point

The cloud point was determined following ASTM D 2500 by cooling bath. The test fuel was visually observed for turbidity as the temperature was decreased every 1°C.

3.2.4.5 Gross Heat of Combustion

Gross heat of combustion was measured by oxygen bomb calorimeter (Ac-500) according to ASTM D 240. The fuel was placed in a crucible inside calorimeter to test the heating value and to collect carbon residuals. The heat of combustion is calculated by the measured temperature increase of the water bath surrounding the bomb.

3.2.4.6 Water Content Measurement

The water content in the microemulsion fuel samples was analyzed by coulometer 831 KF including titration cell and generator electrode with the diagram for water content determination down to trace levels. The results were obtained using Karl Fischer standards of varying concentration.

Figure 3.6 Water content measurement by Coulometer 831 KF.

3.2.4.7 Sulfur Content Measurement

The sulfur content in the microemulsion fuel samples was analyzed by sulfur analysis method complying with ASTM D2622, D7039 and ISO 20884 methods (Sindie ® 2622 benchtop analyzer).

Figure 3.7 Sulfur analyzer.

CHAPTER IV
RESULTS AND DISCUSSION

The microemulsion biofuels of palm oil/diesel blend using renewable-based nonionic alcohol ethoxylate surfactants were formulated. The influence of ethylene oxide group (EOn) in the nonionic surfactants on the reverse micellar microemulsion phase behavior was investigated. The effect of cosurfactant structures such as straight and branch chain structure on the surfactant required to achieve a single phase microemulsion system also examined. Butanol, an alcohol that can be derived from bio-based feedstocks, was introduced into the alcohol phase to enhance the solubilization ethanol and palm oil/diesel blend. The minimum of surfactant concentration required to form the single phase was conducted to evaluate the effect of butanol/ethanol blending ratios. The explanation of the solubilization mechanism of alcohol in the oil phase of the reverse micellar system was discussed. Finally, the improvement in fuel performances such as kinematic viscosity, density, the heat of combustion as well as some cold flow properties through the incorporation of nonionic surfactant and alcohols were measured and compared with the No.2 diesel fuel.

4.1 Phase behavior Study

The pseudo-ternary phase diagram is typically used to represent the phase behavior of a microemulsion biofuel divided into three vertices. The five components in the microemulsion biofuel are located as a pseudo phase in the diagram according to their polarity. The top vertex of the diagram represents the constant ratio of surfactant/cosurfactant at 1:8 by molar, while the palm oil/diesel blend as an oil phase and ethanol as a polar phase represent on the left and right sides at the bottom of the triangle, respectively. Also, the miscibility curve which plots between single and separate phases indicates the lowest composition for each component to form a single phase microemulsion as illustrated in Figure 4.1.

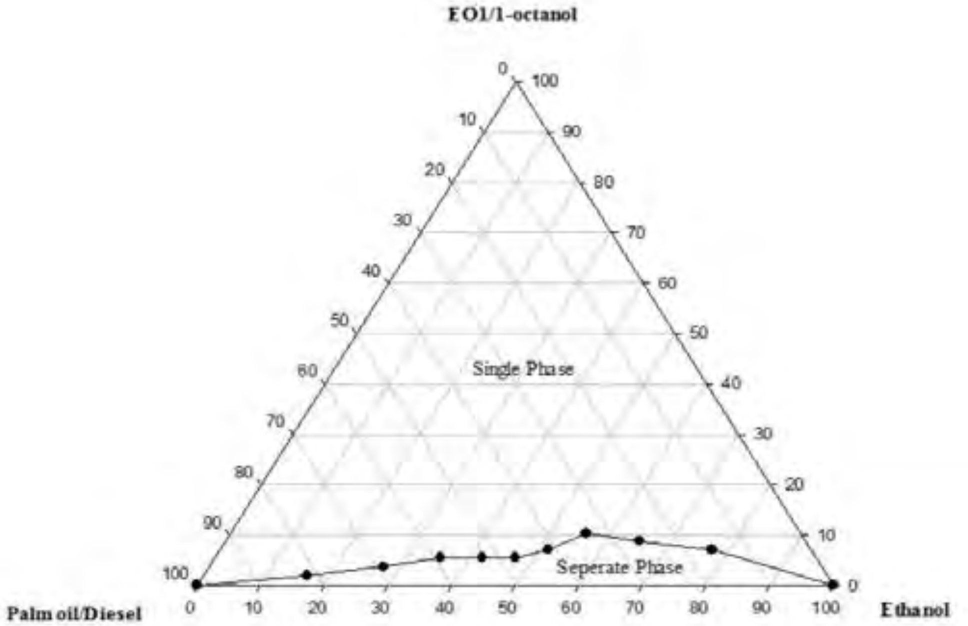


Figure 4.1 Pseudo-ternary phase diagram of microemulsion biofuel systems using EO1 as a surfactant and 1-octanol as a cosurfactant at molar ratio of 1:8 (S/C) in palm oil/diesel blend ratio at 1:1 by volume, at room temperature (25 ± 2ºC).

4.1.1 Comparison of the System with Different Structures of Surfactant

The microemulsion biofuels were formulated by the palm oil/diesel blend (1:1 v/v) with ethanol using by using nonionic alcohol ethoxylate surfactants containing various numbers of EOn group (n = 1, 3, 5 and 9) as a stabilizing agent. Noted that, the hydrophilic-lipophilic balance (HLB) value is an important parameter to select an appropriate surfactant for formulating w/o microemulsions (Balcan *et al.,* 2014). The HLB values of nonionic surfactant used in this study are reported by the manufacturer as shown in Table 3.1., the HLB value of EO1, EO3, EO5 and EO9 are 3.6, 7.95, 10.48 and 13.4, respectively. It can be seen that the HLB value increase with the increasing the number of EO group in the surfactant molecules.

Figure 4.2 illustrates the pseudo ternary phase diagram of microemulsion biofuels consisting of the palm oil/diesel blend as an oil phase, ethanol as a polar phase, and different nonionic surfactants (EO=1, 3, 5 and 9) mixed with 1-octanol at a fixed molar ratio of 1:8 as a surfactant system. The area above miscibility curve represents the single phase microemulsion and the area below the curve is the phase separation. The minimum surfactant required and other components to formulate the biofuels were obtained from the area just above the miscibility curve. For all surfactant systems, it can be observed that more surfactant concentration required to stabilize the microemulsion fuels when percentages of ethanol are up to 50% (v/v). At above 50% of ethanol content, less surfactant concentration was required to solubilize all liquid fuel components .These results are consistent with Pengpreecha et al. (2014) and Arpornpong et al. (2014).

Turning to investigate of the effect of surfactant structure on the microemulsified fuel phase behavior as shown in Figure 4.2, the result was found that the single phase area decreased with increasing the number of EO groups in the surfactant. For w/o, the number of EO groups increasing leads to an increase in the hydrophilicity of the fuel system which results in the higher surfactant concentration used to be able to dissolve into the hydrophobic oil phase. According to the HLB values, at 20% of ethanol, the lowest required surfactant was obtained for EO1 which have the lowest HLB.

As the HLB of surfactant increased due to increasing the number of ethylene oxide group from EO1 to EO9, the higher amount of required surfactant were achieved to stabilize the microemulsified fuels.

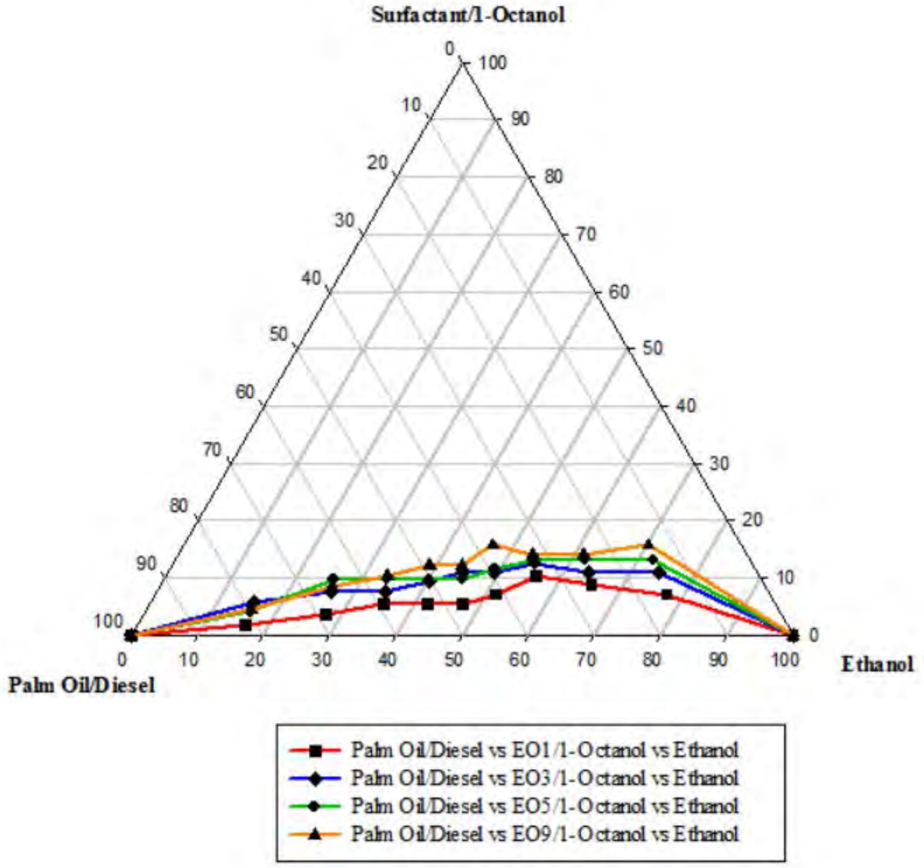


Figure 4.2 Pesudo-ternary phase diagram of the microemulsion biofuel systems using different alkyl alcohol ethoxylate, EOn groups (n = 1, 3, 5 and 9) as a surfactant and 1-octanol as a cosurfactant at surfactant/1-octanol ratio of 1:8 by molar in palm oil/diesel blended ratio at 1:1 by volume, and controlled at room temperature (25 ± 2°C).

4.2 The effect of Cosurfactant Structures Study

The addition of cosurfactant in the surfactant system resulted in the solubility enhancement of ethanol. In this study, the straight (1-octanol) and branch chain (2-ethyl-hexanol) structure of alcohol were investigated as a cosurfactant mixed with the nonionic surfactant with different numbers of EO group.

The microemulsified fuels comprised of palm oil/diesel blended as an oil phase at 50:50 by volume and ethanol as a polar phase at 20% by volume. The surfactant systems were prepared by alcohol ethoxylate surfactants deviated by the numbers of EO group and mixed with 1-octanol or 2-ethyl-hexanol as a cosurfactant at a molar ratio of 1:8 (S/C). Figure 4.3 shows the amount of surfactant used to formulate the single phase microemulsion biofuels in different cosurfactants. It can be seen that the surfactant required increased with the numbers of EO group for both cosurfactant systems, 1-octanol and 2-ethyl-1-hexanol. However, the results of the microemulsion biofuel systems with 2-ethyl-1-hexanol needed more percentage of surfactant by +0.5% for all surfactant with different EO group. The reason could be due to the steric effect of its branching structure affecting the orientation of the cosurfactant in reverse micelle surfactant aggregates. Therefore, the structure of the cosurfactant has an influence on the formation of the microemulsified fuels of the palm oil/diesel and ethanol systems.

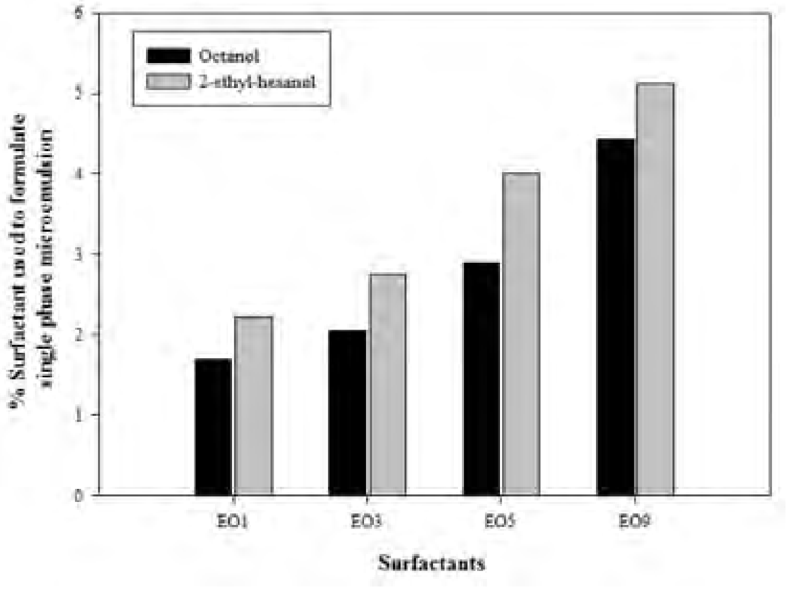


Figure 4.3 The amount of surfactant used to formulate the palm oil/diesel microemulsion biofuels with different cosurfactant structures mixed with alkyl alcohol ethoxylate surfactant with varying numbers of EO group (EO = 1, 3, 5 and 9), at room temperature (25 ± 2ºC).

4.3 The Effect of BuOH/EtOH Study

4.3.1 Comparisons the Effect of BuOH/EtOH Ratios on the Minimum Surfactant Concentration Required to Form the Microemulsion Fuels with Different Surfactant

In our previous work, the addition of a mixture of two alcohols, butanol and ethanol blends (BuOH/EtOH) as an alcohol phase in the microemulsion biofuels showed a significant reduction of surfactant required to formulate the biofuels. Notwithstanding, the more percentages of butanol used, the higher viscosity of the microemulsified fuels was obtained. Thus, this study the amounts of butanol in the BuOH/EtOH blend are varied within 50% by volume to maintain the property of the microemulsion biofuel.

Figure 4.4 illustrates the minimum surfactant required to formulate the microemulsion biofuel systems using the nonionic surfactants with different EO groups (n = 1, 3 and 5) as a surfactant and with varying the percentages of butanol in the alcohol phase. The results show that the surfactant concentration required to form the single phase decreased with the fraction of butanol increased for in all surfactant systems. It is apparent that the presence of butanol at 10% by volume of the alcohol resulted in a significant reduction of surfactant used comparing with the microemulsion systems contained ethanol alone as alcohol phase. In the presence of butanol, the microemulsion system with EO1 required lower surfactant concentration to form the single phase than the EO5 system and the EO9 system, respectively. It alternatively calculated in gram of surfactant used as shown Appendix H. As the numbers of EO group in the surfactant molecule increase, the more polar phase (i.e., alcohol) solubilized in the core of reverse micelle thus resulting in an increase the hydrophilicity of the microemulsion system. However, the microemulsion systems that composes of butanol in the BuOH/EtOH blend has less percentage of surfactant used to solubilize the microemulsified fuels than that of the system with ethanol alone. For the addition of butanol in the alcohol phase at 50:50 by volume, the surfactant concentrations required were about 5% for the EO1, EO5 and EO9 systems.

Therefore, the addition of short chain alcohol – butanol as in this case, can facilitate the usability of surfactant to form a single phase microemulsion due to increasing the hydrophobicity in the polar phase.

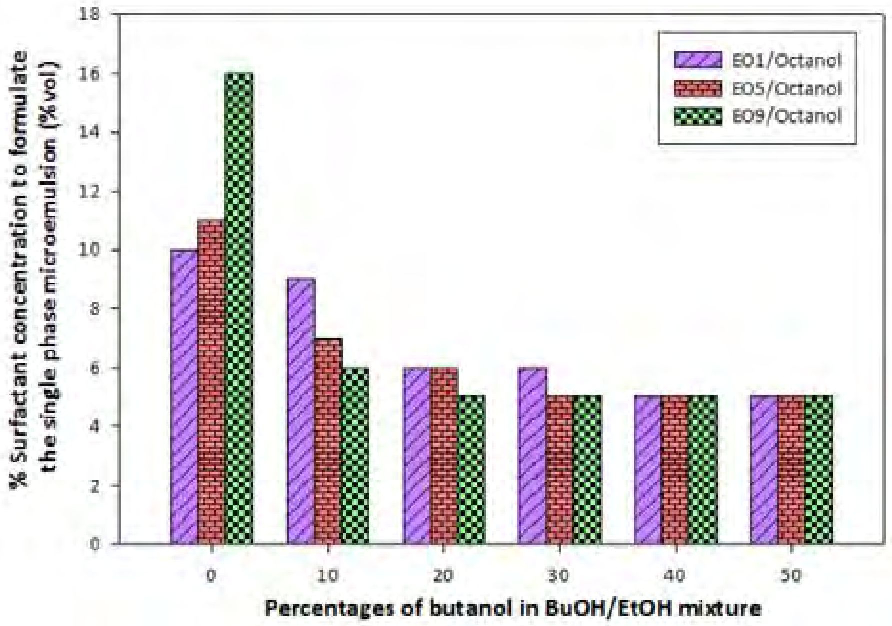


Figure 4.4 The amount of surfactant concentration required to formulate microemulsion biofuel systems in various BuOH/EtOH blending ratios using the nonionic surfactant with different EO groups (n = 1, 5 and 9) as a surfactant at room temperature (25 ± 2ºC).

4.4 Fuel Properties Determination

4.4.1 Kinematic Viscosity Determination

For this study, the kinematic viscosity of the palm oil/diesel based microemulsion biofuels was measured by Cannon-Fenske Routine viscometer following ASTM D 445 at 25 °C, 40 °C and 60 °C. The kinematic viscosity is determined to evaluate their compatibility with that of the regular diesel fuel (4.0 cst) and neat biodiesel (B100) (6.0 cSt) (Jan *et al.*, 2010) at 40 °C.

4.4.1.1 Effect of Surfactant and Cosurfactant Structures

Figure 4.5 illustrates the kinematic viscosity of the microemulsion biofuels which composes of the palm oil/diesel blend and 20% volume of ethanol, using nonionic surfactants with different EOn groups (n = 1, 3, 5 and 9) as a surfactants, and mixed with 1-octanol and 2- ethyl-hexanol as a cosurfactant at molar ratio of 1:8 (surfactant/cosurfactant). It can be seen that the viscosity of the microemulsion fuels containing octanol was slightly higher than that of 2-ethyl-hexanol as a cosurfactant for all surfactant system.

In addition, the numbers EO group in the surfactants increased with slightly increasing the viscosity of the microemulsion fuels. For the effect of cosurfactants structures, the microemulsion fuels formulated by the straight chain octanol had higher viscosity than that of the branch chain, 2-ethyl-hexanol system.

This result is in line with the study of Anantarakitti (2014) that the arrangement of hydrophobic parts of surfactants and cosurfactants structure impacted the interfacial region between oil phase and ethanol phase.

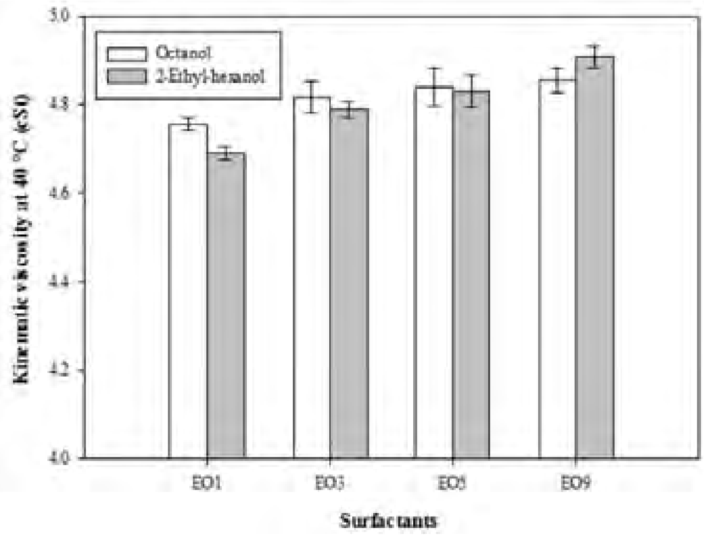


Figure 4.5 Kinematic viscosity of the microemulsion systems prepared by nonionic surfactant with different EO groups (n = 1, 3, 5 and 9) as a surfactant, and compared with the microemulsion systems prepared by different cosurfactants, 1-octanol and 2-ethyl-hexanol.

4.4.1.2 *Effect of BuOH/EtOH Ratio*

The kinematic viscosity of microemulsion biofuels comprising of palm oil/diesel blend as an oil phase and 20% of BuOH/EtOH blends as an alcohol phase, using alcohol ethoxylate surfactants, EOn (n= 1,5 and 9) and 1-octanol as cosurfactant was investigated as shown in Figure 4.6. It can be observed that the kinematic viscosity of the microemulsion biofuel systems increased with increasing of butanol fraction in the polar phase.

According to the Figure 4.6 representing the effect of EO groups in the alcohol ethoxylate surfactants, it is interesting to note that the influence of butanol on viscosity of the microemulsions was clearly observed when butanol fraction in the BuOH/EtOH blends were more than 30%, especially for the system with higher number of EO group.

Therefore, the addition of butanol affects the overall kinematic viscosity of the microemulsion systems. Even though, the presence of butanol in the alcohol phase can significantly reduce the amount of surfactant usage to formulate the single phase microemulsion.

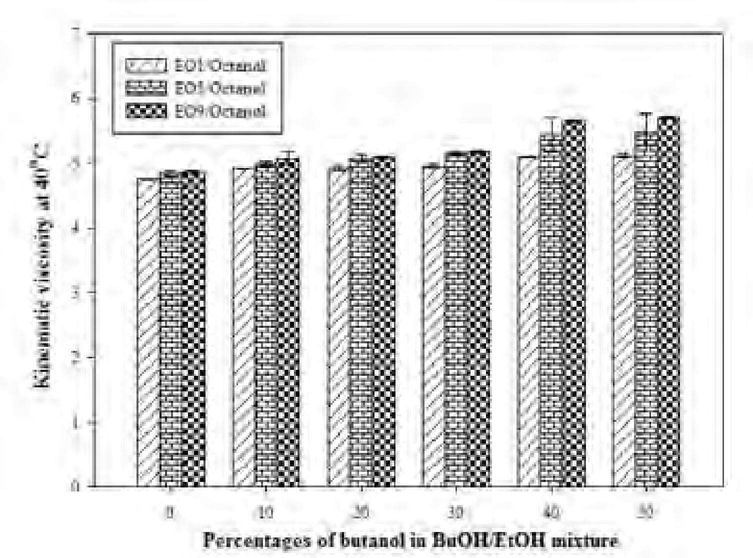


Figure 4.6 Kinematic viscosity (at 40°C) versus the microemulsion biofuels prepared by alcohol ethoxylate with different EO groups, EOn (n = 1, 5 and 9) as a surfactant with 1-octanol as a cosurfactant with varying butanol fraction in 20% of the alcohol phase by volume.

4.4.1.3 Effect of Temperature

Table 4.1 shows the kinematic viscosity of microemulsion biofuels containing alcohol ethoxylate surfactants, EOn groups (n = 1, 5 and 9) at different temperature 25°C, 40°C and 60°C. The results correspond to the fact that the viscosity decreased with increasing temperatures of the microemulsion fuels, which is similar to the effect of temperature on viscosity of microemulsion with the presence of butanol in alcohol phase.

Therefore, the temperature has a significant impact on the viscosity of microemulsion biofuels (Kibbey *et al.*, 2014).

Table 4.1 The effect of temperature on the kinematic viscosity of the microemulsion biofuels prepared by alcohol ethoxylate surfactants with different EO groups and ethanol alone as an alcohol phase.

Temperature (°C)	**Kinematic viscosity (cSt)**		
	EO1	**EO5**	**EO9**
25	6.89±0.0300	7.00±0.0058	7.00±0.0115
40	4.76±0.0153	4.84±0.0416	4.85±0.0265
60	2.97±0.0115	2.96±0.0058	3.01±0.0100

4.4.2 Droplet Size Measurement

The droplet size distribution of the microemulsion biofuels was carried out using dynamic light scattering (Zetasizer, model ZEN 3600, Malvern instrument) to determine the dilution stability of the dilute solution of the microemulsion fuels (Wang *et al.*, 2015).

For this study, the effect of surfactant structure of microemulsion biofuels systems containing alcohol ethoxylate surfactant with different EO group (EO3 and EO5) and octanol as a cosurfactant at ethanol 20% by volume were investigated. Noted that the droplet size was measured the droplet size after placing the emulsion for 1 month.

Table 4.2 illustrates the droplet size distribution of the microemulsion biofuel systems. It can be seen that the numbers of EO group in the nonionic surfactant increases while the size of microemulsion droplets dramatically increases as expected in the schematic diagram of reverse micellar aggregate formation of the microemulsion biofuel systems as illustrated in Figure 4.7. When fact that the EO groups in nonionic surfactant increase which result in the more of the hydrophilic property leading to an increasing the diameter size of reverse micellar aggregate (Anantarakitti *et al*., 2014).

This could be concluded that the droplet size of the microemulsion fuels depending on the structure of surfactant which causes from the arrangement of hydrophilic and hydrophobic parts of surfactants impacted the interfacial region between oil phase and ethanol phase (Anantarakitti *et al*., 2014).

Table 4.2 The droplet size and distribution of the microemulsion biofuels prepared by alcohol ethoxylate surfactant with different EO group

Sample	**Size Distribution (nm)**	
	$D_{1\ mean}$ (%intensity)	**$D_{2\ mean}$ (%intensity)**
EO3/Octanol	493 (100%)	- (0%)
EO5/Octanol	4415 (100%)	- (0%)

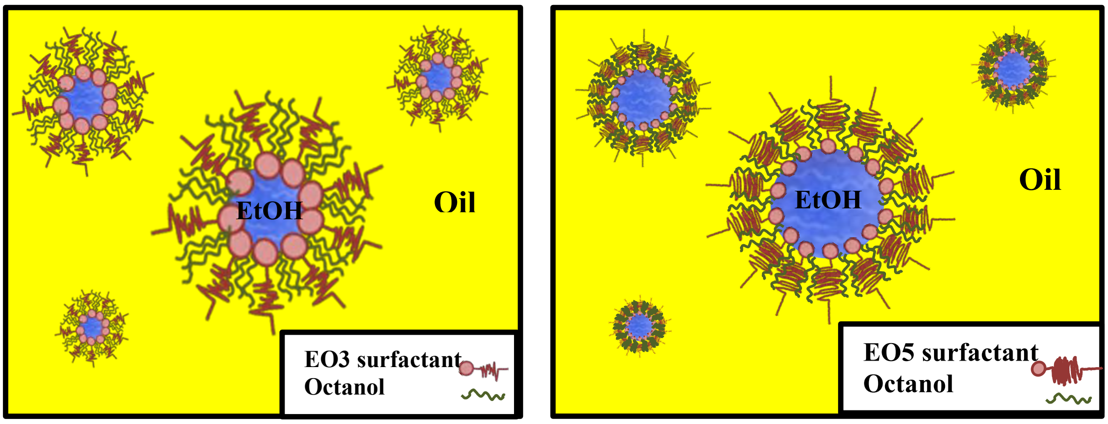


Figure 4.7 Schematic reverse micellar aggregate formation of the microemulsion biofuels systems.

4.4.3 Density

The density of microemulsion biofuels containing different component was evaluated in the range of diesel and biodiesel 0.876 g/mL (Bernat *et al*., 2012).

4.4.3.1 Effect of Surfactant and Cosurfactant Structures

Table 4.3 illustrates the density (at 20°C) of the formulated microemulsion biofuels containing alcohol ethoxylate with different EO groups, EOn (n=1, 3, 5 and 9) as a surfactant and different cosurfactant structures, which are 1-octanol and 2-ethyl-hexanol as cosurfactants. It can be seen that the density depends on the density of the composition of component (surfactant, oil, alcohol) in the microemulsion system with 1-octanol and 2-ethanol as a cosurfactant.

For the effect of cosurfactants, the result was found that microemulsion biofuels with straight chain (1-octanol) had less density than the branch chain (2-ethyl-hexanol) system. This could be because the octanol system requires less surfactant concentration than that of the 2-ethyl-hexanol system to form the single phase microemulsion.

Therefore, the density of microemulsion biofuel depending on the fraction of each component which is affected by the arrangement of hydrophobic parts of surfactants and cosurfactants structure impacted the interfacial region between oil phase and ethanol phase as well as the kinematic viscosity as expected in Figure 4.8.

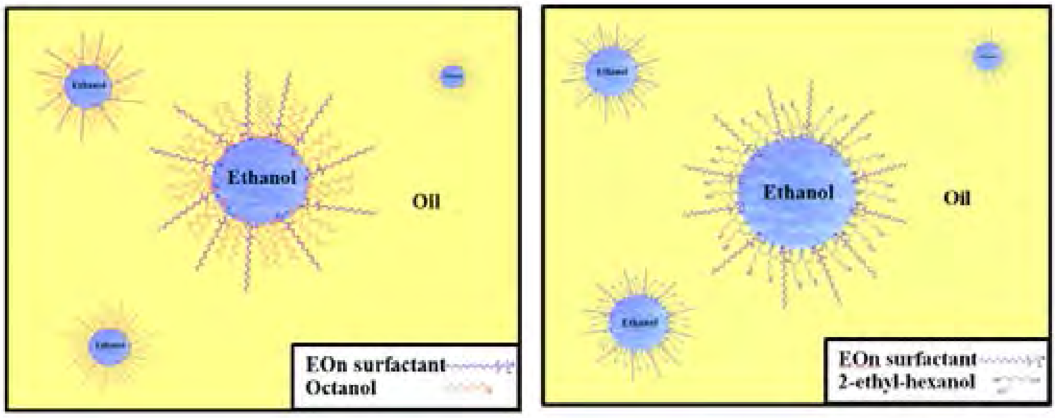


Figure 4.8 Schematic reverse micellar aggregate formation of the microemulsion biofuels systems with different of cosurfactant structure

Table 4.3 Density of microemulsion biofuels at 20°C

Sample	Palm oil/Diesel at 1:1 by volume	EtOH	Surfactant	Co surfactant	Density (g/ml) at 20°C
1-octanol					
EO1/Oct	72	20	1.69	8.31	0.8496±0.0001
EO3/Oct	71	20	2.04	6.96	0.8504±0.0001
EO5/Oct	69	20	2.90	8.10	0.8506±0.0001
EO9/Oct	66	20	4.43	9.57	0.8521±0.0001
2-ethyl-hexanol					
EO1/2-ethyl	67	20	2.23	10.77	0.8487±0.0006
EO3/2-ethyl	68	20	2.75	9.25	0.8513±0.0003
EO5/2-ethyl	65	20	4.00	11.00	0.8533±0.0009
EO9/2-ethyl	64	20	5.12	10.88	0.8554±0.0010

4.4.3.2 Effect of BuOH/EtOH Ratio

Figure 4.9 shows the density of microemulsion biofuels system containing alcohol ethoxylate surfactants with different EO groups, EOn (n = 1, 5 and 9) as a surfactant in various BuOH/EtOH blends. It can be observed that the density of microemulsion biofuels system increases with the increasing butanol in the alcohol phase. Moreover, Figure 4.10 shows the correlation between density and kinematic viscosity of the microemulsion biofuels containing EO1 as a surfactant and 1-octanol as a cosurfactant at varying BuOH/EtOH blending ratio as an alcohol phase. It can be observed that the increment of viscosity was in agreement with that of the density of the microemulsion with an increasing the presence of butanol in alcohol phase.

Hence, the density of microemulsion biofuels was affected by the presence of butanol in the alcohol phase.

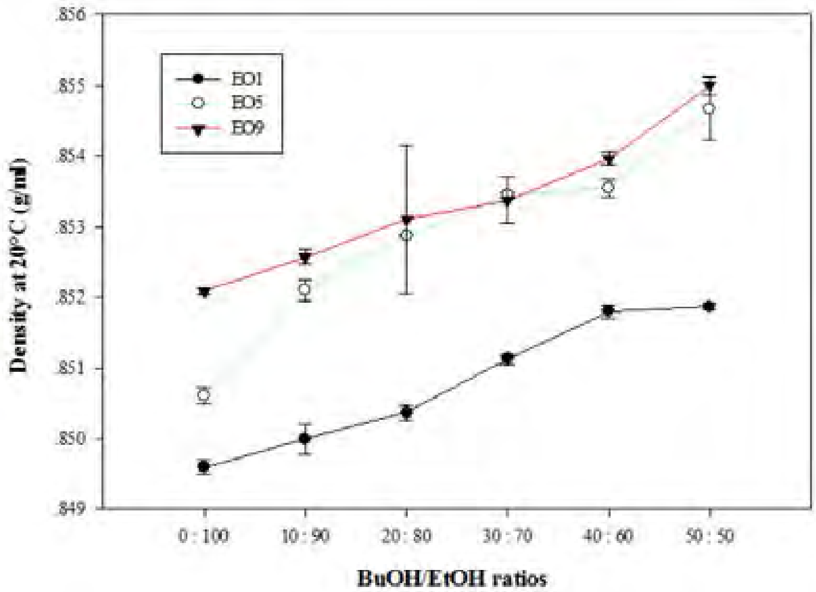


Figure 4.9 The density of the microemulsion fuels using alcohol ethoxylate surfactants with different EOn groups (n =1, 5 and 9) in varying BuOH/EtOH blending ratio as an alcohol phase.

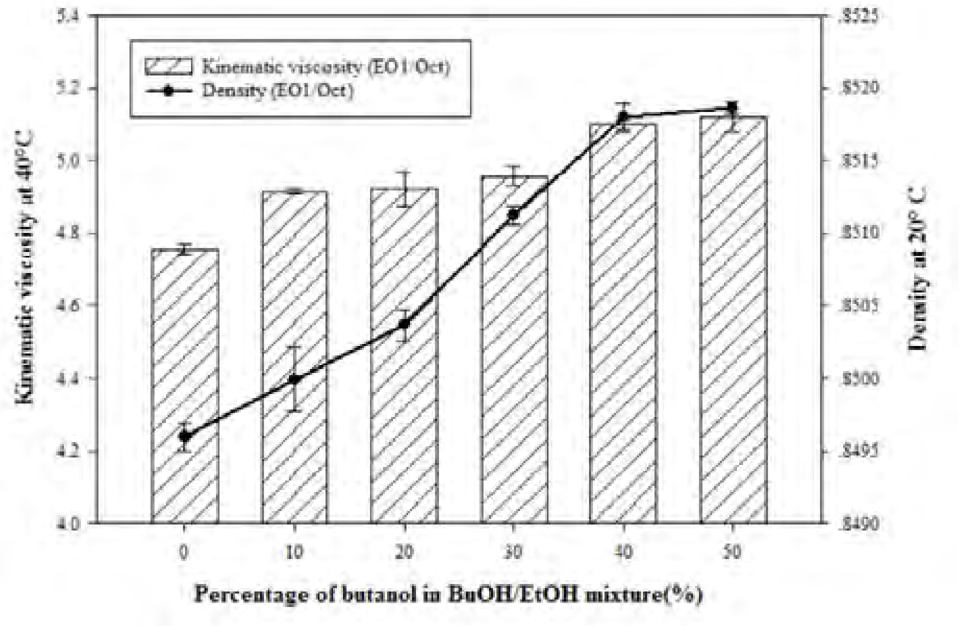


Figure 4.10 The density and kinematic viscosity of the microemulsion fuels using EO1 as a surfactant in varying BuOH/EtOH blending ratio as an alcohol phase.

4.4.4 Cloud Point

The cloud point of microemulsion biofuels is the temperature at which fuel becomes a turbid solution that lead to plug in the engine (Mofijur *et al.*, 2016). The experimental measurement was conducted using temperature controlled water bath following ASTM D2500. These were observed by temperature decreasing by 1°C intervals. The surfactant structure and amount of butanol added in the microemulsion system did not affect the turbidity formation (10°C±0.1°C) significantly as demonstrated in Table 4.5 and Table 4.6. In the observation, the cloud points of microemulsion biofuels (10±0.1°C) are more than a regular diesel and diesel no.2 but less than biodiesel as shown in Table 4.4. In addition, the turbid point defined as the temperature of concentrated alcohol ethoxylate surfactant becomes a turbid solution at controlled cooling temperature was considered as illustrated in Table 4.4. It can be seen that the numbers of alcohol ethoxylate group, EOn (n = 1, 3, 5 and 9) increased leading to increasing in the turbid point. This could be implied that the turbid point depends on the structure of the surfactant while the number of EO groups was not affected to the cloud point of microemulsion biofuels.

Table 4.4 turbid point of surfactant used

Sample	**Turbid point (°C)**
Alcohol ethoxylate surfactant with EO1	10 ± 0.1
Alcohol ethoxylate surfactant with EO3	12 ± 0.1
Alcohol ethoxylate surfactant with EO5	14 ± 0.1
Alcohol ethoxylate surfactant with EO9	19 ± 0.1
Palm oil	12 ± 0.1
Diesel (regular)	7 ± 0.1
Palm oil/diesel (1:1 by volume)	7 ± 0.1
Diesel No.2[a]	-15-5
Biodiesel[a]	-3-12

[a] the data obtained from Raman *et al.,* 2009

Table 4.5 Cloud point of microemulsion biofuels for difference of surfactant structures

✓ means microemulsion biofuel from cloudy

✗ means microemulsion biofuel do not form cloudy

Sample	**Temperature (°C)**									
	12	11	10	9	8	7	6	5	4	3
EO1/Octanol	✗	✗	✓	✓	✓	✓	✓	✓	✓	✓
EO3/Octanol	✗	✗	✓	✓	✓	✓	✓	✓	✓	✓
EO5/Octanol	✗	✗	✓	✓	✓	✓	✓	✓	✓	✓
EO9/Octanol	✗	✗	✓	✓	✓	✓	✓	✓	✓	✓

Table 4.6 Cloud point of microemulsion biofuels for difference of butanol in BuOH/EtOH mixture by using EO1 as a surfactant

Sample (BuOH:EtOH)	**Temperature (°C)**									
	12	11	10	9	8	7	6	5	4	3
0:100	×	×	✓	✓	✓	✓	✓	✓	✓	✓
10:90	×	×	✓	✓	✓	✓	✓	✓	✓	✓
20:80	×	×	✓	✓	✓	✓	✓	✓	✓	✓
30:70	×	×	✓	✓	✓	✓	✓	✓	✓	✓
40:60	×	×	✓	✓	✓	✓	✓	✓	✓	✓
50:50	×	×	✓	✓	✓	✓	✓	✓	✓	✓

4.4.5 Heat of Combustion

The heat of combustion or calorific value of fuels is an important property to define its suitability of alternative fuels. The calorific value of microemulsion biofuels was investigated following ASTM D 240. Figure 4.11 exhibits the calorific values of palm oil/diesel blend at 1:1(v/v) with alcohol ethoxylate group, EOn (n=1, 3, 5 and 9) as a surfactant and 1-octanol as a cosurfactant at fixed molar ratio 1:8 at 20% ethanol as an alcohol phase by volume. It can be seen that the calorific value of the microemulsion from range 38.58-39.23 MJ/kg did not depend on the number of EO group. The obtained calorific value and biodiesel (39.70 MJ/Kg) (Raman *et al.*,2009) are approximately the same. When compared to diesel no.2, the result shows that the calorific values of microemulsion biofuels had still lower than that of diesel no.2 (45.3 MJ/kg) (Goering *et al.,*1982) around 4%. These results are in the similar range with the study of Arpornpong *et al.* (2014). In this context, the surfactant structure does not effect to the calorific value of microemulsion biofuels.

Turning to the investigation of butanol/ethanol blending ratio in the microemulsion biofuel with EO1 were conducted as demonstrated in Figure 4.12. The results indicated that the calorific value slightly increased with the amount of butanol in the BuOH/EtOH mixture increased compared with the microemulsion with ethanol alone. Because the heating value of butanol (33 MJ/Kg) is higher than that of ethanol (26.8 MJ/Kg, Evangelos *et al.*, 2013). However, the calorific values of microemulsion biofuels with the presence of butanol slightly increased with butanol added increased to 40% by volume of the alcohol phase and then slightly dropped. This could be concluded that the use of butanol in the microemulsion biofuels can improve the calorific values than that of the system with ethanol alone.

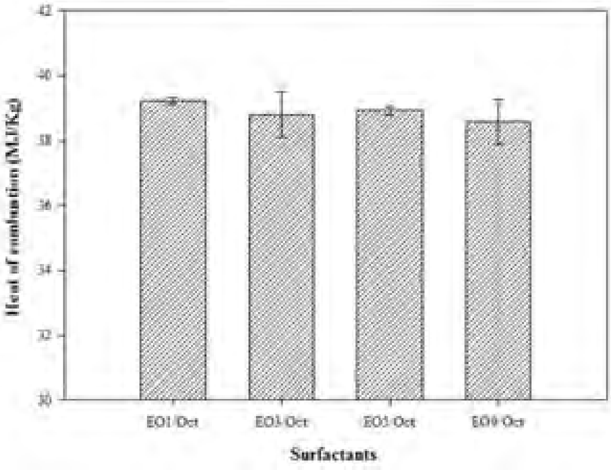


Figure 4.11 Comparison of calorific value of the microemulsion biofuels using alkyl alcohol ethoxylate with different EO groups, EOn (n = 1, 5 and 9) as a surfactant with 1-octanol as a cosurfactant at molar ratio of 1:8 (surfactant/cosurfactant) in palm oil/diesel blend ratio at 1:1 by volume.

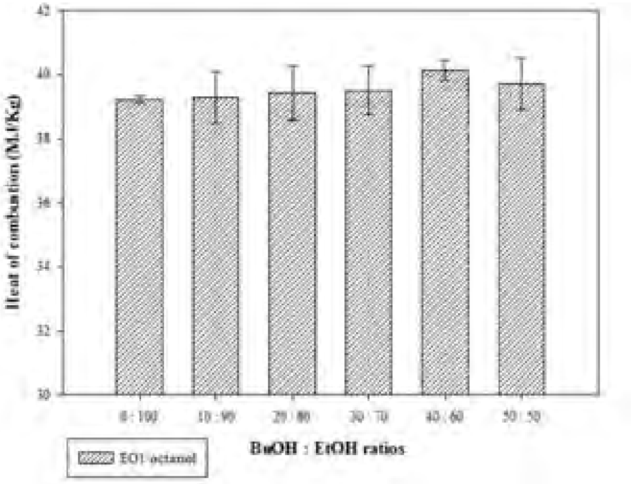


Figure 4.12 Comparison of calorific value of the microemulsion biofuels using EO1 as surfactants with 1-octanol as cosurfactants at various BuOH/EtOH blending ratios as an alcohol phase.

4.4.6 Water Content of Microemulsion Biofuels

Figure 4.13 illustrates the water content of microemulsion biofuels system containing alcohol ethoxylate surfactants with different EO groups, EOn (n=1, 3, 5 and 9) as a surfactant. It can be indicated that the water content increased with increasing number of EO groups in the surfactant as tabulated in Table 4.7.

Table 4.7 Water content of all chemical used

Sample	Water content (% volume)
Diesel (regular)	0.01 ± 0.0004
Palm oil	0.09 ± 0.0028
Butanol	0.23 ± 0.0011
Ethanol	0.55 ± 0.0033
Octanol	0.1[a]

[a] the reported by the manufacturer

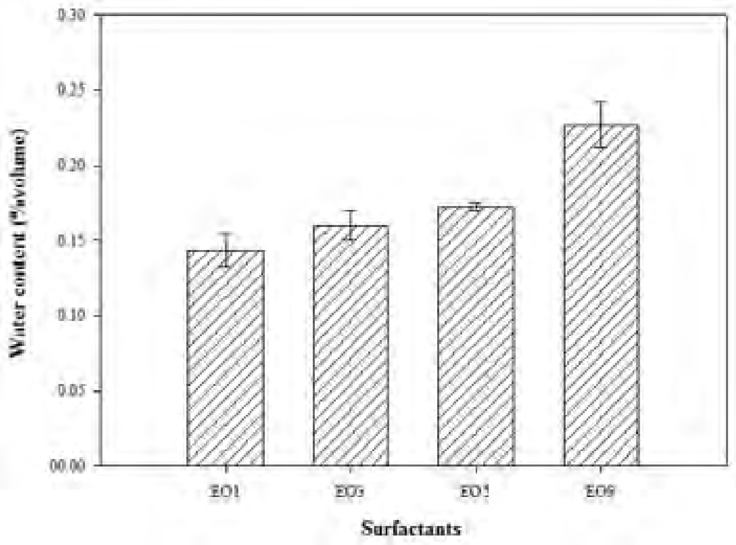


Figure 4.13 Water content of the microemulsion biofuels using alkyl alcohol ethoxylate with different EOn groups (n =1, 5 and 9) as a surfactant with 1-octanol as a cosurfactant at the molar ratio of 1:8 (surfactant/cosurfactant) in palm oil/diesel blend ratio at 1:1 by volume.

Figure 4.14 demonstrates that water content of microemulsion biofuels system containing EO1 as a surfactant with octanol as a cosurfactant in varying butanol in BuOH/EtOH mixture at 20 % by volume of an alcohol phase. It can be seen that the water content of microemulsion biofuel was not significantly different when the percentage of butanol increased.

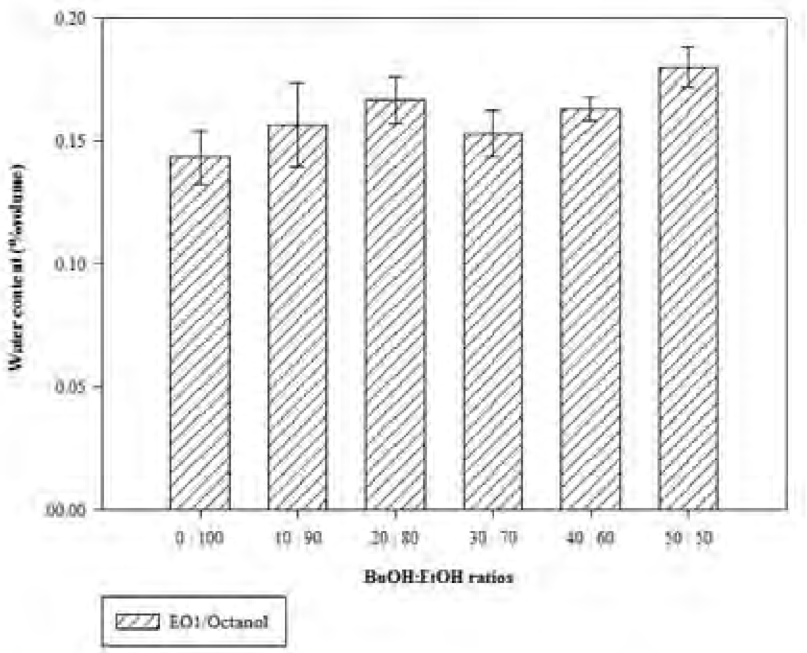


Figure 4.14 The water content of the microemulsion biofuels containing alcohol ethoxylate surfactant with EO1 as a surfactant with 1-octanol as a cosurfactant at the molar ratio of 1:8 (surfactant/cosurfactant) at varying BuOH/EtOH blending ratios.

4.4.7 Sulphur Content of Microemulsion Biofuels

The microemulsion biofuel, comprising alcohol ethoxylate group, EOn (n=1, 3, 5 and 9) as a surfactant and 1-octanol as a cosurfactant in palm oil/diesel blend and 20% ethanol by volume, was observed. For determination of sulfur content, it can be seen that the sulfur content in microemulsion biofuels was less ranging from 9.35-9.83 ppm that of diesel (29.25 ppm). Because the sulfur content of the vegetable oil based microemulsion biofuels depends on the fraction of diesel, which is the main source of sulfur in the fuel see Table 4.8. Therefore, the microemulsion biofuels have less sulfur, leading to lower greenhouse gas emissions after combustion.

Table 4.8 Sulphur content in microemulsion biofuels, diesel and palm oil

Sample	**Sulphur content (ppm)**	**Palm oil(%volume)**	**Diesel (%volume)**
EO1/Octanol	9.75 ± 0.63	35.0	35.0
EO3/Octanol	9.52 ± 0.48	35.5	35.5
EO5/Octanol	9.83 ± 0.99	34.5	34.5
EO9/Octanol	9.35 ± 1.19	33.0	33.0
Diesel (regular)	29.25	-	100
Palm oil	0.4	100	-

4.4.8 Functional Group Analysis

The functional group analysis was conducted to ensure the presence of surfactant molecule in the homogeneous solution of the microemulsion biofuels through the FTIR spectroscopy. The microemulsion biofuels prepared by mixing palm oil/diesel blend at 1:1 by volume and using different alcohol ethoxylate group, EOn (1, 3, 5 and 9) as surfactants with 1-octanol as a cosurfactant at fixed mole ratio 1:8 at 20% of ethanol. The results of FTIR spectra as illustrated in Figure 4.15, it indicated that the peak of each formulated microemulsion biofuel with different Eo groups in the alcohol ethoxylate as a surfactant was not significantly different. The palm oil, be confirmed in each microemulsion biofuels, were observed at 2,921 and 2,852 cm^{-1} assign to C-H asymmetrical and symmetrical stretching vibration of the saturated carbon-carbon bond and the carbonyl group of triglycerides (C=O) were observed at 1,746 cm^{-1},which result from stretching vibration. The bending of CH_2 and CH_3 appear at 1,459 and 1,377 cm^{-1}, respectively. From Figure 4.15, it can be observed that the peaks appear at 1,161, 1,093 and 1,050 cm^{-1} assign to the C-O stretching of the functional group of alcohol ethoxylate, EOn (1, 3, 5 and 9), which can be investigated at peak in range 1,200-1,000 cm^{-1}. The peak at 3,382 cm^{-1} complied with hydrogen-boned O-H stretching as a very board and intense peak in the range 3,400 to 3,300 cm^{-1}.

The FTIR spectra of diesel, palm oil, EO1 and the microemulsion system with EO1 as a surfactant were compared as shown in Figure 4.16. It can be observed that the peak approximately 1,740 cm^{-1} appeared on the spectra of the palm oil, the microemulsion with EO1 system and diesel but this peak disappears on the spectra of EO1 as a surfactant. Moreover, the significant peaks approximately 3,400 1,100 and 720 cm^{-1} appeared on the spectra of EO1 (Ngee *et al*., 2008). In Figure 4.16, the spectra of the functional group of the EO1/octanol microemulsion were observed clearly in spectra of all the microemulsion comprising of surfactant.

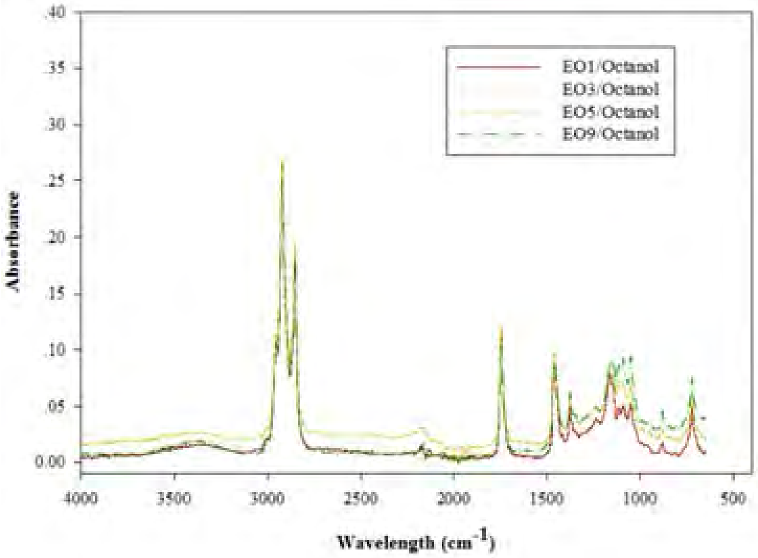


Figure 4.15 FTIR spectrum of microemulsion biofuels systems which comprising of linear alkyl alcohol ethoxylate surfactants with different EO groups (n =1, 3, 5 and 9) as a surfactant with 1-octanol as a cosurfactant by surfactant/1-octanol at molar ratio of 1:8 in palm oil/diesel blend at 1:1 by volume ratio and 20% volume of ethanol.

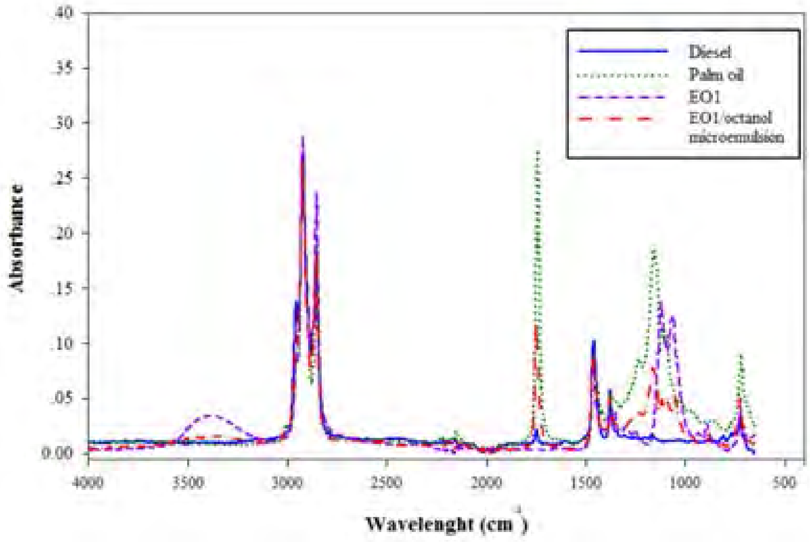


Figure 4.16 FTIR spectrum of diesel, palm oil, EO1 and EO1/octanol microemulsion system.

4.4.9 Emulsion Stability

The formation of microemulsion biofuels samples was left for 6 months at ambient temperature and then observed the phase separation and phase behavior after every 2 weeks. It can be seen that the phase behaviour of microemulsion biofuels with alcohol ethoxylate surfactant with the different of EO group and the increasing butanol in the alcohol phase were still single phase until 6 months as shown in Figure 4.17 and Figure 4.18, respectively.

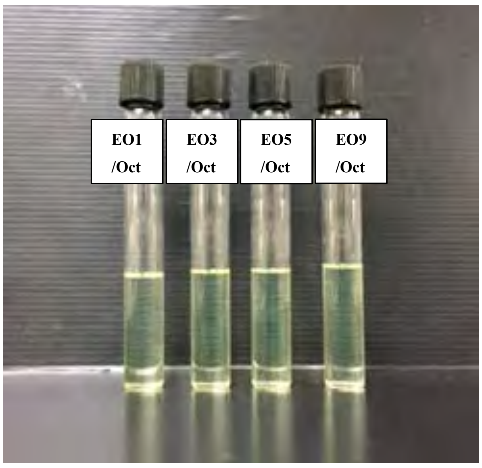


Figure 4.17 The microemulsion biofuels systems containing the palm oil/diesel microemulsion biofuels with octanol as a cosurfactant mixed in alkyl alcohol ethoxylate surfactant at molar ratio 1:8 (surfactant/cosurfactant) with varying number of EO group (EO = 1, 3, 5 and 9), at room temperature (25 ± 2ºC) for 6 months.

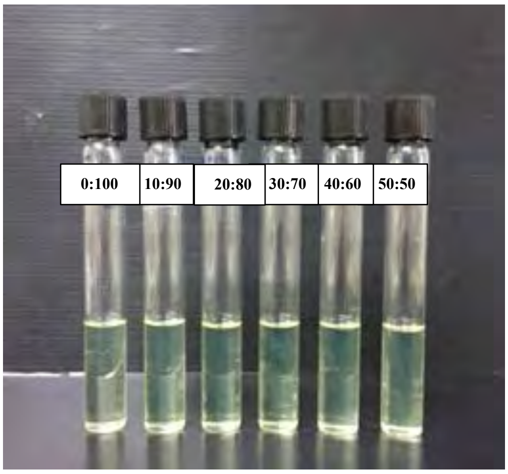


Figure 4.18 The microemulsion biofuels systems containing the palm oil/diesel microemulsion biofuels with EO1 as a surfactant and octanol as a cosurfactant at molar ratio 1:8 (surfactant/cosurfactant) at varying BuOH/EtOH blending ratio alcohol, at room temperature (25 ± 2ºC) for 6 months.

4.5 Summarized Results

This palm oil/diesel based microemulsion biofuels were formulated with the aim to enhance the microemulsion stability with minimum surfactant used and also maintain their fuel properties. The microemulsion fuels used prepared by the palm oil/diesel blend as a nonpolar phase, butanol/ethanol blends as a polar or alcohol phase. The nonionic alcohol ethoxylate surfactants (C12-EOn-OH) having different number of polyethylene oxide group, EOn (n= 1, 3, 5 and 9) were selected as a stabilizing agent for the selection of the surfactant and alcohols, this study investigated the effects of surfactant and cosurfactant structures and ratios of blending butanol/ethanol on a single phase microemulsion formation.

In microemulsion phase behavior, the pseudo-ternary phase diagram was employed to investigate the amount of each component (surfactant, oils, alcohols) in the minimum requirement that can form a single phase microemulsion where represented in the area above miscibility curve. The effect of surfactant structures deviated by the number of EO groups (n=1, 3, 5 and 9) in the alcohol ethoxylate surfactants was observed for microemulsion biofuels formulation. It was found that the surfactant concentration used to formulate a single phase increased with an increase in a number of EO groups due to an increase in the hydrophilicity of the microemulsion systems lead to higher surfactant used to dissolve the hydrophobic oil phase.

The effect of cosurfactant structure, straight chain (1-octanol) and branch chain (2-ethyl-hexanol) in the microemulsion formation were investigated. The microemulsion systems were prepared by branch chain as a cosurfactant required more the surfactant concentration to form a single phase. This can be summarized that the steric effect of cosurfactant structure influences the formation reverse micelle surfactant aggregates.

The addition of butanol in ethanol as an alcohol phase has a significant impact on the amount of surfactant required to form a single phase. The use of butanol in the alcohol blends as a polar phase provides the benefit in case of minimizing the surfactant used. The interesting result was noted the amount of surfactant added are less influent when the microemulsion system contained butanol fraction more than 30% by volume of the alcohol mixture.

Fuel properties of microemulsion biofuels were investigated and compared with No.2 diesel including kinematic viscosity, droplet size, density, heat of combustion, cloud point, sulfur content and water content. For kinematic viscosity study, the kinematic viscosity of microemulsion biofuels systems compared to No.2 diesel and neat biodiesel (B100). The viscosity of microemulsion systems gradually increased with the number of EO group increasing as surfactants. The kinematic viscosities of microemulsion systems increased with increasing of butanol fraction in the alcohol phase due to butanol having a higher viscosity than the ethanol. The viscosities of formulated microemulsion biofuels in the presence of butanol were in the range of the biodiesel but did not approach to the viscosity of the diesel.

For the effect of surfactant structure on droplet size of the microemulsion biofuels, the droplet size dramatically increased with increasing of the number of EO group. The density of the microemulsions increased with the number of EO group in the alcohol surfactants. Moreover, the microemulsion systems with butanol had the higher density than those of ethanol alone systems. Noted the kinematic viscosity and density of microemulsion biofuels are affected by the arrangement of hydrophobic parts of surfactants and cosurfactants structures as a result of the impact on the interfacial region between oil phase and polar phase.

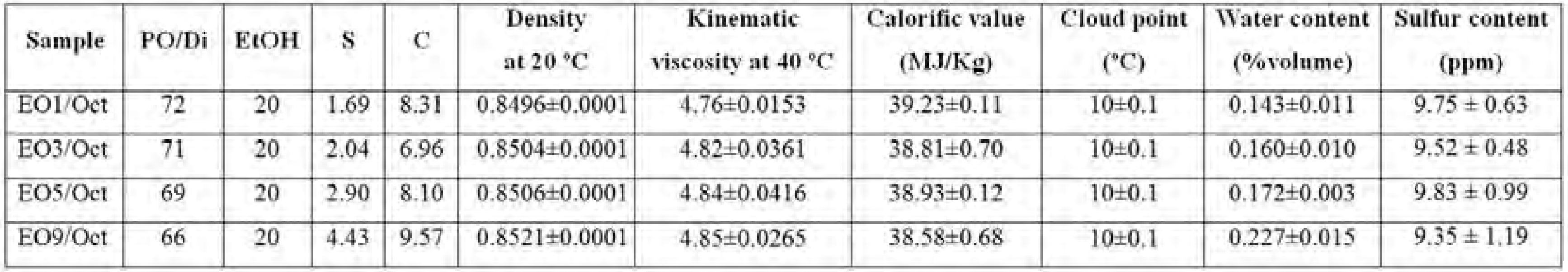
For cloud point, the structure of surfactants and amount of butanol added did not affect the temperature of turbidity formation (10°C±0.1°C) of the microemulsion biofuels. In comparison, the cloud point of microemulsion has still higher than regular diesel (7°C±0.1°C). The calorific value of microemulsion biofuels was less than that of diesel. When varying BuOH/EtOH ratios, the calorific value slightly increased with increasing the amount of butanol in the BuOH/EtOH mixture compared with only the use of ethanol alone as a polar phase. This could be concluded that the presence of butanol in the microemulsion biofuels could improve the calorific values than that of ethanol alone.

For water and sulfur contents of microemulsion biofuels, they depend on the fraction in each component in the microemulsion biofuels system. In addition, the water contents of microemulsion biofuels were higher than diesel due to increasing the fraction of the amount of surfactant, palm oil, and alcohol. It is interesting to note that the sulfur contents of all microemulsion biofuels were less than diesel in range 9.35-9.83 ppm.

For the characterization study, the functional groups of surfactants determined by the FTIR. The resulted of the microemulsion biofuels indicated that the microemulsion biofuels contained the surfactant represented by the peak of the surfactant appearing on the spectra of the microemulsion systems.

Based on this finding, the structure of surfactant and cosurfactant are the factors influencing to the arrangement of reverse micellar aggregates and also attributed to the fuel properties including kinematic viscosity and droplet size. In addition, the presence of butanol in the microemulsion biofuels benefits in term of surfactant used and calorific value. Notwithstanding, the amount butanol added reflects the viscosity properties. The fuel properties of the microemulsion can be adjusted by appropriate formulation of surfactant, alcohol and oils phase.

Table 4.9 The microemulsion biofuel systems using alcohol ethoxylate nonionic surfactant and 1-octanol as a cosurfactants at a molar ratio of 1:8 (S/C), in palm oil/diesel blended ratio at 1:1 by volume at room temperature (25 ± 2ºC).



Sample	PO/Di	EtOH	S	C	Density at 20 °C	Kinematic viscosity at 40 °C	Calorific value (MJ/Kg)	Cloud point (°C)	Water content (%volume)	Sulfur content (ppm)
EO1/Oct	72	20	1.69	8.31	0.8496±0.0001	4.76±0.0153	39.23±0.11	10±0.1	0.143±0.011	9.75 ± 0.63
EO3/Oct	71	20	2.04	6.96	0.8504±0.0001	4.82±0.0361	38.81±0.70	10±0.1	0.160±0.010	9.52 ± 0.48
EO5/Oct	69	20	2.90	8.10	0.8506±0.0001	4.84±0.0416	38.93±0.12	10±0.1	0.172±0.003	9.83 ± 0.99
EO9/Oct	66	20	4.43	9.57	0.8521±0.0001	4.85±0.0265	38.58±0.68	10±0.1	0.227±0.015	9.35 ± 1.19

CHAPTER V
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This work aims to formulate microemulsion biofuels containing palm oil/diesel blend as a nonpolar phase, and ethanol/butanol, as a polar alcohol phase. The nonionic alcohol ethoxylate surfactants containing polyethylene oxide group, EOn (n=1, 3, 5, and 9) were selected as a stabilizing agent with two cosurfactants which are 1-octanol and 2-ethyl-hexanol.

From the research results, the conclusions are made as follow:

The pseudo-ternary phase diagram of the microemulsion biofuels systems was conducted to determine an isotropic region or a single phase in the phase behavior of microemulsion systems. The single phase of the microemulsion biofuels systems was obtained at the minimum surfactant concentration increased with an increase the percentage of ethanol until approximately 55% by volume, and then, less surfactant was required to solubilize all liquid fuel components.

For the effect of surfactant and cosurfactant structures, the structure of surfactant and cosurfactant had an influence on the formation of reverse micellar surfactant aggregates of the system. Together with, the surfactant and cosurfactant structures also affect to fuel properties, for example, kinematic viscosity, droplet size, and cloud point.

For the effect of butanol added, the ability of butanol can reduce the phase separation and amount of surfactant required to from the microemulsified fuels. Although the presence of butanol in the alcohol phase can reduce the amount of surfactant usage to form the stable microemulsion fuels, the addition of butanol in the BuOH/EtOH also affects the overall viscosity of the microemulsion systems at which to the inappropriate zone above the diesel no.2 standard.

However, the fuel properties, kinematic viscosity, density, heating value, and cloud point of the palm oil/diesel based microemulsion biofuels are inappropriate levels for regular diesel but can be comparable with the diesel no.2 standard and neat biodiesel (B100). The palm oil/diesel blend with the alcohol ethoxylate surfactant exhibits a low sulfur content according to a fraction of vegetable oil, which results in less toxic emission after combustion.

5.2 Recommendations

The surfactant selection has an influence on the formulation of microemulsion biofuels and fuel properties including the viscosity and cloud point. Therefore, there is a limitation for utilizing of microemulsion biofuels in diesel engines. The palm oil based microemulsion biofuels can be applied for a single-cylinder diesel engine which typically used in truck fleets and agricultural application.

REFERENCES

Abdul Hadi, N. (2013) Physico-chemical Properties of Palm Stearin, Soybean Oil and Their Binary Blends. Universiti Teknologi MARA.

Ajav, E.A., Singh, B., and Bhattacharya, T.K. (1999) Experimental study of some performance parameters of a constant speed stationary diesel engine using ethanol-diesel blends as fuel. Biomass and Bioenergy, 17, 357-365.

Altin, R., Cetinkaya, S., Yucesu, H.S., (2001) The potential of using vegetable oil fuels as fuel for diesel engines. Energy Conversion and Management, 42, 529-538.

Anantarakitti, N, Arpornpong, N., Khaodhiar, S. and Charoensaeng, A. (2014) Effect of nonionic surfactant structure on fuel properties of microemulsion-based biofuel from palm oil. Paper presented at International Conference On Advances In Civil, Structural, Environmental And BioTechnology - CSEB 2014, Kuala Lumpur, Malaysia.

Arpornpong, N., Attaphong, C., Charoensaeng, A., Sabatini, D.A. and Khaodhiar, S. (2014) Ethanol-in-palm oil/diesel microemulsion-based biofuel: Phase behavior, viscosity, and droplet size. Fuel, 132, 101-106.

Attaphong, C., Do, L. and Sabatini, D.A. (2012) Vegetable oil-based microemulsions using carboxylate-based extended surfactants and their potential as an alternative renewable biofuel. Fuel, 94, 606-613.

Attaphong, C. and Sabatini, D.A. (2013) Phase behaviors of vegetable oil-based micro-emulsion fuels: the effects of temperatures, surfactants, oils, and water in ethanol. Energy & Fuels, 27(11), 6773-6780.

A. W. Schwab, M. 0. Bagby and B. Freedman (1987) Preparation and properties of diesel fuels from vegetable oils. Fuel, 1987, 66, October, 1372-1377.

Bora, P., Konwar, L.J., Phukan, M.M., Deka, D., Konwar, B.K., (2015) Microemulsion based hybrid biofuels from Thevetia peruviana seed oil: , -Structure and dynamic investigations. Fuel, 208-218.

Dantas Neto, A. A. 1; a Fernandes, M. R.; a Barros Neto, E. L.; a Castro Dantas, T. N.; a Moura, M. C. P. A. (2013) Effect of biodiesel/diesel-based microemulsions on the exhaust emissions of a diesel engine. Brazilian Journal of Petroleum and Gas, 7(4), 141-153.

Esteban, B., Riba, J.R., Baquero, G., Rius, A., and Puig, R. (2012) Temperature dependence of density and viscosity of vegetable oils. Biomass and Bioenergy, 42, 164-171.

Forson, F.K., Oduro, E.K., Hammond-Donkoh, E. (2004) Performance of jatropha oil blends in a diesel engine. Renewable Energy, 29, 1135-1145.

Ito, T., Sakurai, Y., Kakuta, Y., Sugano, M., and Hirano, K., (2012) Biodiesel production from waste animal fats using pyrolysis method. Fuel Processing Technology, 94, 47-52.

Inoue, T., Ohmura, H., and Murata, D., (2003) Cloud point temperature of polyoxyethylene-type nonionic surfactants and their mixture. Journal of Colloid and Interface Science, 258, 374–382

Issariyakul, T., Dalai, A.K., (2014) Biodiesel from vegetable oils. Renewable and Sustainable Energy Reviews, 31, 446-471.

Jing-Liang, L., Dong-Shun, B., Bing-Hung, C. (2009) Effect of additives on the cloud points of selected nonionic linear ethoxylated alcohol surfactants. Colloids and Surfaces A : Physicochemical and Engineering Aspects, 346, 237-243.

Kalam, M.A., Masjuki, H.H., (2002) Biodiesel from palm oil - an analysis of its properties and potential. Biomass and Bioenergy, 23, 471-479.

Knothe, G., Matheaus, A.C., Ryan, T.W. (2003) Cetane numbers of branched and straight-chain fatty esters determined in an ignition quality tester, Fuel, 82, 971–975.

Knothe, G. (2005) Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. Fuel processing Technology, 86, 1059-1070.

Knothe, G., Steidley, K.R., (2005) Kinematic viscosity of biodiesel fuel components and related compounds. Influence of compound structure and comparison to petrodiesel fuel components. Fuel, 84, 1059-1065.

Mofijur, M., Rasul, M.G., Hyde, A., Azad, A.K., Mamat, R., Bhuiya, M.M.K., (2016) Role of biofuel and their binary(diesel-biodiesel) and ternary(ethanol-biodiesel-diesel) blends on internal combustion engines emission reduction. Renewable and Sustainable Energy Reviews, 53, 265-278.

Mukherjee, I., Savacool, B.K. (2014) Palm oil-based and sustainability in southeast Asia: A review of Indonesia, Malaysia, and Thailand. Renewable and Sustainable Energy Reviews, 37, 1-12.

Murugesan, A., Umarani, C., Subramanian, R., Nedunchezhian, N., (2009) Bio-diesel as an alternative fuel for diesel engines-A review. Renewable and Sustainable Energy Reviews, 13, 653–662

Nwafor, O.M.I., (2004) Emission characteristics of diesel engine running on gvegetable oil with elevated fuel inlet temperature. Biomass and Bioenergy, 27, 507-511.

Pengpreecha, S., (2013) The effect of vegetable oil properties of the biofuel, prepared by microemulsion base using nonionic surfactants. Thesis, Faculty of engineering Chulalongkorn University, Bangkok, Thailand.

Ramos, M.J., Fernandez, C.M., Casas, A., Rodriguez, L. and Perez, A. (2008) Influence of fatty acid composition of raw materials on biodiesel properties. Bioresource Technology, 100, 261-268.

Rattanarat, P., (2007) Optimal feed rate for biosurfactant production from crude palm oil by Pseudomonas sp.A41 in fed batch fermentation. Thesis, Faculty of engineering Chulalongkorn University, Bangkok, Thailand.

Rosen, M.J. (2004) Surfactants and Interfacial Phenomena. Hoboken, NJ.: Wiley-Interscience.

Sadaghinia, A.S., and Khan, A., (1990) Clouding of a nonionic surfactant: the effect of added surfactants on the cloud point. Journal of Colloid and Interface Science, 144(1), 191-200.

Sembiring, M.T., Sukardi, Suryani, A., Romli, M., (2015) Biodiesel production cost assessment from different palm oil raw material as feedstock. Industrial Engineering Letter, 5(2), 13-19.

Sharma, K.S., Patil, S.R., Rakshit, A.K., (2003) Study of the cloud point of C12EOn nonionic surfactants: effect of additives. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 219, 67-74.

Shay, E.G. (1992) Diesel fuel from vegetable oils: status and opportunities. Biomass and Bioenergy, 4(4), 227-242.

Sorate, K.A., Bhale, P.V., (2015) Biodiesel properties and automotive system compatibility issues. Renewable and Sustainable Energy Reviews, 41, 777-798.

Srivastava, A., Prasad, R., (2000) Triglycerides-based diesel fuels. Renewable and Sustainable Energy Reviews, 4, 111–133.

Thiago de, O., Macedo, Roberto, G., Pereira, Juan, M., Pardal, Alexandre, S., Soares, and Valdir de J. Lameira, (2013) Viscosity of vegetable oils and biodiesel and energy generation. International Scholarly and Scientific Research & Innovation, 7(5), 251-256.

Wen-Huei Lim (2000) Isotropic region of alpha-sulfonated methyl esters derived from palm strearin in mixed surfactants solution. Malaysian Journal of Analytical Sciences, 7(1), 169-171.

Yoshimoto, Y., Kinoshita, E., Shanbu, L., and Ohmura, T. (2013) Influence of 1-butanol addition on diesel combustion with palm oil methyl ester/gas oil blends. Energy, 61, 44-51.

Yusuf Ali & M. A. Hanna (1994) Alternative diesel fuels from vegetable oils. Bioresource Technology, 50, 153-163.

Zarate-Munoz, S., Troncoso, A.B., and Acosta, E., (2015) The cloud point of alkyl ethoxylates and its prediction with the hydrophilic-lipophilic difference (HLD) framework. Langmuir, 31, 12000-12008.

APPENDICES

Appendix A Supplemental Materials for Phase Diagram

Table A1 Composition of EO1/1-octanol at the molar ratio of 1:8, the palm oil/diesel blend at the ratio of 1:1 (v/v)

EtOH/Oil	Concentration (M)		Fraction for Phase Diagram (%)			
	EO1	Oct	EtOH	EO1/Oct	Oil	Total
0/5	-	-	0	0	100	100
1/5	0.0125	0.1	16.3527	1.8836	81.7637	100
2/5	0.0250	0.2	27.5150	3.6976	68.7875	100
3/5	0.0375	0.3	35.4579	5.4457	59.0965	100
4/5	0.0375	0.3	42.0242	5.4457	52.5302	100
5/5	0.0375	0.3	47.2772	5.4457	47.2772	100
5/4	0.0500	0.4	51.5936	7.1314	41.2749	100
5/3	0.0750	0.6	56.0445	10.3288	33.6267	100
5/2	0.0625	0.5	65.1728	8.7581	26.0691	100
5/1	0.0500	0.4	77.3905	7.1314	15.4781	100
5/0	-	-	100	0	0	100

Table A2 Composition of EO3/1-octanol at the molar ratio of 1:8, the palm oil/diesel blend at the ratio of 1:1 (v/v)

EtOH/Oil	Concentration (M)		Fraction for Phase Diagram (%)			
	EO3	Oct	EtOH	EO3/Oct	Oil	Total
0/5	-	-	0	0	100	100
1/5	0.0375	0.3	15.6956	5.8261	78.4782	100
2/5	0.0500	0.4	26.3942	7.6202	65.9856	100
3/5	0.0500	0.4	34.6424	7.6202	57.7374	100
4/5	0.0625	0.5	40.2902	9.3471	50.3627	100
5/5	0.0750	0.6	44.4946	11.0107	44.4946	100
5/4	0.0750	0.6	49.4385	11.0107	39.5508	100
5/3	0.0875	0.7	54.6160	12.6144	32.7696	100
5/2	0.0750	0.6	63.5638	11.0107	25.4255	100
5/1	0.0750	0.6	74.1577	11.0107	14.8315	100
5/0	-	-	100	0	0	100

Table A3 Composition of EO5/1-octanol at the molar ratio of 1:8, the palm oil/diesel blend at the ratio of 1:1 (v/v)

EtOH/Oil	Concentration (M)		Fraction for Phase Diagram (%)			
	EO5	Oct	EtOH	EO5/Oct	Oil	Total
0/5	-	-	0	0	100	100
1/5	0.0250	0.2	15.9751	4.1492	79.8757	100
2/5	0.0625	0.5	25.7814	9.7651	64.4535	100
3/5	0.0625	0.5	33.8381	9.7651	56.3968	100
4/5	0.0625	0.5	40.1044	9.7651	50.1305	100
5/5	0.0625	0.5	45.1174	9.7651	45.1174	100
5/4	0.0750	0.6	49.1702	11.4937	39.3361	100
5/3	0.0875	0.7	54.2767	13.1573	32.5660	100
5/2	0.0875	0.7	62.0305	13.1573	24.8122	100
5/1	0.0875	0.7	72.3690	13.1573	14.4738	100
5/0	-	-	100	0	0	100

Table A4 Composition of EO9/1-octanol at the molar ratio of 1:8, the palm oil/diesel blend at the ratio of 1:1 (v/v)

EtOH/Oil	Concentration (M)		Fraction for Phase Diagram (%)			
	EO9	Oct	EtOH	EO9/Oct	Oil	Total
0/5	-	-	0	0	100	100
1/5	0.0250	0.2	15.9235	4.4587	79.6177	100
2/5	0.0500	0.4	26.1323	8.5368	65.3309	100
3/5	0.0625	0.5	33.5820	10.4480	55.9700	100
4/5	0.0750	0.6	38.9862	12.2810	48.7328	100
5/5	0.0750	0.6	43.8595	12.2810	43.8595	100
5/4	0.1000	0.8	46.8163	15.7307	37.4530	100
5/3	0.0875	0.7	53.7247	14.0404	32.2348	100
5/2	0.0875	0.7	61.3997	14.0404	24.5599	100
5/1	0.1000	0.8	70.2244	15.7307	14.0449	100
5/0	-	-	100	0	0	100

Appendix B Supplemental Materials for Effect of Surfactant and Cosurfactant Types on Amount of Surfactant to Formulate Single Phase Microemulsion Study

Table B1 Surfactant/1-octanol at mole ratio of 1:8, palm oil/diesel 1:1 (v/v) with 20 vol.% of ethanol

Sample	Fraction of microemulsion biofuels (%)				
	Surfactant Phase		Oil Phase		Alcohol Phase
	Surfactant	cosurfactant	Palm Oil	Diesel	EtOH
EO1/Octanol	1.69	8.31	35	35	20.0
EO3/Octanol	2.04	6.96	35.5	35.5	20.0
EO5/Octanol	2.90	8.10	34.5	34.5	20.0
EO9/Octanol	4.43	9.57	33	33	20.0

Table B2 Surfactant/2-ethyl-hexanol at mole ratio of 1:8, palm oil/diesel 1:1 (v/v) with 20 vol.% of ethanol

Sample	Fraction of microemulsion biofuels (%)				
	Surfactant Phase		Oil Phase		Alcohol Phase
	Surfactant	cosurfactant	Palm Oil	Diesel	EtOH
EO1/2-ethyl-hexanol	2.23	10.77	33.5	33.5	20.0
EO3/2-ethyl-hexanol	2.75	9.25	34	34	20.0
EO5/2-ethyl-hexanol	4.00	11.00	32.5	32.5	20.0
EO9/2-ethyl-hexanol	5.12	10.88	32	32	20.0

Appendix C Supplemental Materials for Effect of BuOH/EtOH Ratios on Amount of Surfactant to Formulate Single Phase Microemulsion Study

Table C1 Composition of microemulsion biofuels with Surfactant/1-octanol at mole ratio of 1:8, palm oil/diesel 1:1 (v/v) with 20 vol.% of alcohol as polar phase

Sample	Fraction of microemulsion biofuels (%)					
	Surfactant Phase		Oil Phase		Alcohol Phase	
	Surfactant	cosurfactant	Palm Oil	Diesel	BuOH	EtOH
EO1/Octanol	1.69	8.31	35	35	0	20
	1.52	7.48	35.5	35.5	2	18
	1.02	4.98	37	37	4	16
	1.02	4.98	37	37	6	14
	0.85	4.15	37.5	37.5	8	12
	0.85	4.15	37.5	37.5	10	10
EO5/Octanol	2.9	8.1	34.5	34.5	0	20
	1.84	5.16	36.5	36.5	2	18
	1.58	4.42	37	37	4	16
	1.32	3.68	37.5	37.5	6	14
	1.32	3.68	37.5	37.5	8	12
	1.32	3.68	37.5	37.5	10	10
EO9/Octanol	5.07	10.93	32	32	0	20
	1.90	4.10	37	37	2	18
	1.58	3.42	37.5	37.5	4	16
	1.58	3.42	37.5	37.5	6	14
	1.58	3.42	37.5	37.5	8	12
	1.58	3.42	37.5	37.5	10	10

Appendix D Supplemental Materials for Viscosity Study

1. Kinematic viscosity calculation

The kinematic viscosity of the microemulsion fuel can be measured using a Canon-Fenske type viscometer (ASTM D 445). Kinematic viscosity can be calculated using Equation D.1, which is provided by the manufacturer of the viscometer:

$$\mu = Kt \tag{D.1}$$

where μ Kinematic viscosity (cSt)

K Viscosity constant

t Time of sample flow in vescometer (second)

Table D.1 Viscosity constant varying in temperature

Temperature(°C)	Viscosity constant (cSt)
25	0.01549
40	0.01547
60	0.01545

Example : The sample kinematic viscosity calculation of EO1/Octanol in palm oil/diesel blend with ethanol at 40°C can be shown as follows;

t = 307.40 sec (average time)

K = 0.01547 cSt/s

Therefore;

μ = (0.01547 cSt/s)(307.40 sec)

= 4.76 cSt

2. Raw data for effect of surfactant and cosurfactant types on kinematic viscosity at 40°C

Table D2 Time for measured kinematic viscosity of microemulsion biofuels, using octanol as a cosurfactant which surfactant/cosurfactant 1:8 mole ratio, palm oil/diesel 1:1 (v/v) with 20 vol.% of ethanol

Sample	Time				
	#1(min)	#2(min)	#3(min)	Average(min)	Average(sec)
EO1/Octanol	5.11	5.14	5.12	5.12	307.40
EO3/Octanol	5.22	5.15	5.20	5.19	311.40
EO5/Octanol	5.26	5.18	5.20	5.21	312.80
EO9/Octanol	5.24	5.25	5.20	5.23	313.80

Table D3 Kinematic viscosity of microemulsion biofuels, using octanol as a cosurfactant which surfactant/cosurfactant 1:8 mole ratio, palm oil/diesel 1:1 (v/v) with 20 vol.% of ethanol

Sample	Kinematic viscosity at 40°C (cSt)				
	#1	#2	#3	Average	SD
EO1/Octanol	4.74	4.77	4.75	4.76	0.0153
EO3/Octanol	4.85	4.78	4.83	4.82	0.0361
EO5/Octanol	4.88	4.81	4.83	4.84	0.0416
EO9/Octanol	4.86	4.87	4.83	4.85	0.0265

Table D4 Time for measured kinematic viscosity of microemulsion biofuels, using 2-ethyl-hexanol as a cosurfactant which surfactant/cosurfactant 1:8 mole ratio, palm oil/diesel 1:1 (v/v) with 20 vol.% of ethanol

Sample	**Time**				
	#1(min)	**#2(min)**	**#3(min)**	**Average(min)**	**Average(sec)**
EO1/2-ethyl-hexanol	5.05	5.07	5.04	5.05	303.20
EO3/2-ethyl-hexanol	5.15	5.15	5.18	5.16	309.60
EO5/2-ethyl-hexanol	5.20	5.17	5.24	5.20	312.20
EO9/2-ethyl-hexanol	5.29	5.26	5.31	5.29	317.20

Table D5 Kinematic viscosity of microemulsion biofuels, using 2-ethyl-hexanol as a cosurfactant which surfactant/cosurfactant 1:8 mole ratio, palm oil/diesel 1:1 (v/v) with 20 vol.% of ethanol

Sample	**Kinematic viscosity at 40ºC (cSt)**				
	#1	**#2**	**#3**	**Average**	**SD**
EO1/2-ethyl-hexanol	4.69	4.71	4.68	4.69	0.0153
EO3/2-ethyl-hexanol	4.78	4.78	4.81	4.79	0.0173
EO5/2-ethyl-hexanol	4.83	4.80	4.86	4.83	0.0351
EO9/2-ethyl-hexanol	4.91	4.88	4.93	4.91	0.0252

3. Raw data for effect of BuOH/EtOH ratios on kinematic viscosity at 25°C, 40°C and 60°C

Table D6 Time for measured kinematic viscosity of microemulsion biofuels at 25°C, using octanol as cosurfactant which surfactant/cosurfactant 1:8 mole ratio, palm oil/diesel 1:1 (v/v) with varying butanol contained in butanol and ethanol blends at 20% volume of alcohol.

Sample	**BuOH:EtOH**	**Time (sec)**			
		#1	**#2**	**#3**	**Average**
EO1/Octanol	10:90	446.40	444.60	448.20	446.40
	20:80	487.80	489.60	492.00	489.80
	30:70	491.40	492.00	493.20	492.20
	40:60	512.40	511.20	540.00	521.20
	50:50	511.80	514.20	513.60	513.20
EO5/Octanol	10:90	489.00	482.40	486.60	486.00
	20:80	495.00	501.00	493.80	496.60
	30:70	502.80	504.60	502.20	503.20
	40:60	514.80	511.80	513.60	513.40
	50:50	541.20	514.80	514.80	523.60
EO9/Octanol	10:90	507.60	505.80	505.20	506.20
	20:80	515.40	514.80	515.40	515.20
	30:70	547.20	545.40	545.40	546.00
	40:60	554.40	548.40	547.80	550.20
	50:50	551.40	546.00	543.00	546.80

Table D7 Kinematic viscosity of microemulsion biofuels at 25°C, using octanol as cosurfactant which surfactant/cosurfactant 1:8 mole ratio, palm oil/diesel 1:1 (v/v) with varying butanol contained in butanol and ethanol blends at 20% volume of alcohol.

Sample	**BuOH:EtOH**	**Kinematic viscosity at 25°C (cSt)**				
		#1	**#2**	**#3**	**Average**	**SD**
EO1/Octanol	10:90	6.91	6.89	6.94	6.91	0.03
	20:80	7.55	7.58	7.62	7.59	0.04
	30:70	7.61	7.62	7.64	7.62	0.02
	40:60	7.94	7.92	8.36	8.07	0.27
	50:50	7.93	7.96	7.95	7.95	0.02
EO5/Octanol	10:90	7.57	7.47	7.54	7.53	0.06
	20:80	7.67	7.76	7.65	7.69	0.06
	30:70	7.79	7.81	7.78	7.79	0.02
	40:60	7.97	7.93	7.95	7.95	0.03
	50:50	8.38	7.97	7.97	8.11	0.25
EO9/Octanol	10:90	7.86	7.83	7.82	7.84	0.02
	20:80	7.98	7.97	7.98	7.98	0.01
	30:70	8.47	8.45	8.45	8.46	0.02
	40:60	8.59	8.49	8.48	8.52	0.06
	50:50	8.54	8.46	8.41	8.47	0.07

Table D8 Time for measured kinematic viscosity of microemulsion biofuels at 40°C, using octanol as cosurfactant which surfactant/cosurfactant 1:8 mole ratio, palm oil/diesel 1:1 (v/v) with varying butanol contained in butanol and ethanol blends at 20% volume of alcohol.

Sample	**BuOH:EtOH**	**Time (sec)**			
		#1	**#2**	**#3**	**Average**
EO1/Octanol	10:90	318.00	318.00	317.40	317.80
	20:80	315.00	320.40	319.20	318.20
	30:70	319.80	319.20	322.20	320.40
	40:60	330.00	328.80	330.00	329.60
	50:50	328.80	330.60	333.60	331.00
EO5/Octanol	10:90	324.60	321.60	321.60	322.60
	20:80	323.40	329.40	330.60	327.80
	30:70	333.60	331.80	333.60	333.00
	40:60	361.80	360.00	333.00	351.60
	50:50	334.80	366.00	362.40	354.40
EO9/Octanol	10:90	333.60	327.60	322.80	328.00
	20:80	327.60	330.00	328.80	328.80
	30:70	334.20	335.40	333.60	334.40
	40:60	363.60	364.80	366.60	365.00
	50:50	367.80	368.40	370.20	368.80

Table D9 Kinematic viscosity of microemulsion biofuels at 40°C, using octanol as cosurfactant which surfactant/cosurfactant 1:8 mole ratio, palm oil/diesel 1:1 (v/v) with varying butanol contained in butanol and ethanol blends at 20% volume of alcohol.

Sample	BuOH:EtOH	Kinematic viscosity at 40ºC (cSt)				
		#1	#2	#3	Average	SD
EO1/Octanol	10:90	4.92	4.92	4.91	4.92	0.01
	20:80	4.87	4.96	4.94	4.92	0.05
	30:70	4.95	4.94	4.98	4.96	0.03
	40:60	5.11	5.09	5.11	5.10	0.01
	50:50	5.09	5.11	5.16	5.12	0.04
EO5/Octanol	10:90	5.02	4.98	4.98	4.99	0.03
	20:80	5.00	5.10	5.11	5.07	0.06
	30:70	5.16	5.13	5.16	5.15	0.02
	40:60	5.60	5.57	5.15	5.44	0.27
	50:50	5.18	5.66	5.61	5.48	0.28
EO9/Octanol	10:90	5.16	5.07	4.99	5.07	0.09
	20:80	5.07	5.11	5.09	5.09	0.02
	30:70	5.17	5.19	5.16	5.17	0.02
	40:60	5.62	5.64	5.67	5.65	0.03
	50:50	5.69	5.70	5.73	5.71	0.02

Table D10 Time for measured kinematic viscosity of microemulsion biofuels at 60°C, using octanol as cosurfactant which surfactant/cosurfactant 1:8 mole ratio, palm oil/diesel 1:1 (v/v) with varying butanol contained in butanol and ethanol blends at 20% volume of alcohol.

Sample	**BuOH:EtOH**	**Time (sec)**			
		#1	**#2**	**#3**	**Average**
EO1/Octanol	10:90	195.00	203.40	203.40	200.60
	20:80	205.80	203.40	208.80	206.00
	30:70	210.00	210.60	212.40	211.00
	40:60	213.00	213.60	212.40	213.00
	50:50	240.60	215.40	215.40	223.80
EO5/Octanol	10:90	206.40	209.40	206.40	207.40
	20:80	214.80	214.20	213.00	214.00
	30:70	211.80	213.00	211.80	212.20
	40:60	240.60	213.60	213.00	222.40
	50:50	241.20	215.40	216.00	224.20
EO9/Octanol	10:90	213.00	210.00	212.40	211.80
	20:80	214.80	213.00	210.00	212.60
	30:70	215.40	214.20	210.60	213.40
	40:60	241.20	241.20	215.40	232.60
	50:50	243.00	240.60	244.20	242.60

Table D11 Kinematic viscosity of microemulsion biofuels at 60°C, using octanol as cosurfactant which surfactant/cosurfactant 1:8 mole ratio, palm oil/diesel 1:1 (v/v) with varying butanol contained in butanol and ethanol blends at 20% volume of alcohol.

Sample	**BuOH:EtOH**	**Kinematic viscosity at 60ºC (cSt)**				
		#1	**#2**	**#3**	**Average**	**SD**
EO1/Octanol	10:90	3.01	3.14	3.14	3.10	0.08
	20:80	3.18	3.14	3.23	3.18	0.05
	30:70	3.24	3.25	3.28	3.26	0.02
	40:60	3.29	3.30	3.28	3.29	0.01
	50:50	3.72	3.33	3.33	3.46	0.24
EO5/Octanol	10:90	3.19	3.24	3.19	3.20	0.03
	20:80	3.32	3.31	3.29	3.31	0.02
	30:70	3.27	3.29	3.27	3.28	0.01
	40:60	3.72	3.30	3.29	3.44	0.26
	50:50	3.73	3.33	3.34	3.46	0.25
EO9/Octanol	10:90	3.29	3.24	3.28	3.27	0.03
	20:80	3.32	3.29	3.24	3.29	0.04
	30:70	3.33	3.31	3.25	3.30	0.04
	40:60	3.73	3.73	3.33	3.59	0.25
	50:50	3.75	3.72	3.77	3.75	0.03

Appendix E Supplemental Materials for Droplet Size

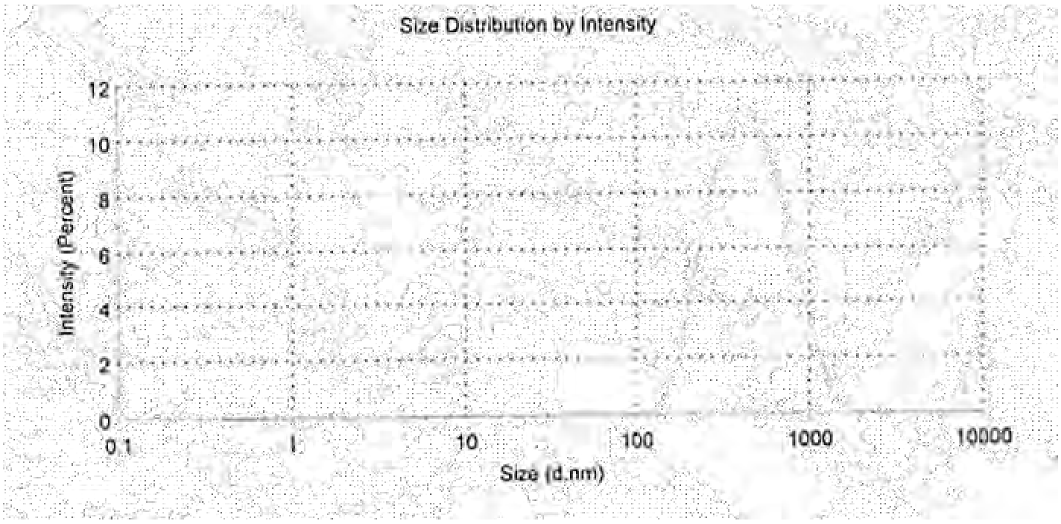


Figure E1 Droplet size and size distribution of EO3/1-octanol 1:8 mole ratio, neat Palm oil/diesel 1:1 (v/v) with 20 vol.% of ethanol.

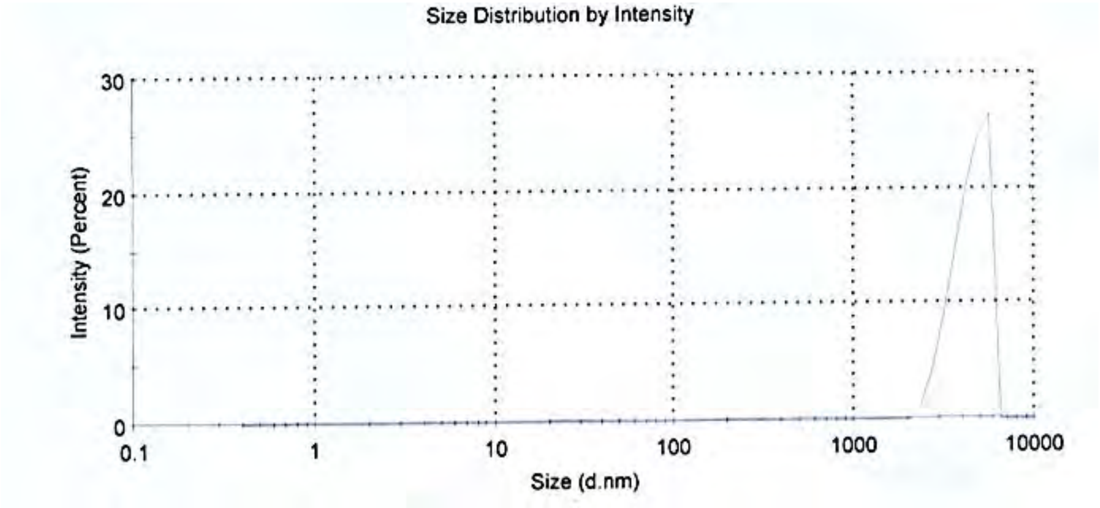


Figure E2 Droplet size and size distribution of EO5/1-octanol 1:8 mole ratio, neat Palm oil/diesel 1:1 (v/v) with 20 vol.% of ethanol.

Appendix F Supplemental Materials for Density Study

Table F1 Density of microemulsion biofuels, surfactant/cosurfactant 1:8 mole ratio, palm oil/diesel 1:1 (v/v) with 20 vol.% of ethanol

Sample	Density at 20°C (g/mL)				
	#1	#2	#3	Average	SD
EO1/Octanol	0.8495	0.8496	0.8497	0.8496	0.0001
EO3/Octanol	0.8504	0.8504	0.8506	0.8504	0.0001
EO5/Octanol	0.8507	0.8507	0.8504	0.8506	0.0001
EO9/Octanol	0.8520	0.8521	0.8521	0.8521	0.0001

Table F2 Density of microemulsion biofuels, surfactant/cosurfactant 1:8 mole ratio, palm oil/diesel 1:1 (v/v) with 20 vol.% of ethanol

Sample	Density at 20°C (g/mL)				
	#1	#2	#3	Average	SD
EO1/2-ethyl	0.8484	0.8484	0.8494	0.8487	0.0006
EO3/2-ethyl	0.8510	0.8516	0.8512	0.8513	0.0003
EO5/2-ethyl	0.8522	0.8537	0.8539	0.8533	0.0009
EO9/2-ethyl	0.8548	0.8548	0.8566	0.8554	0.0010

Table F3 Density of microemulsion biofuels, using octanol as cosurfactant which surfactant/cosurfactant 1:8 mole ratio, palm oil/diesel 1:1 (v/v) with varying butanol contained in butanol and ethanol blends at 20% volume of alcohol

Sample	BuOH:EtOH	Density at 20ºC (g/mL)				
		#1	#2	#3	Average	SD
EO1/Octanol	0:100	0.8495	0.8496	0.8497	0.8496	0.0001
	10:90	0.8499	0.8498	0.8502	0.8500	0.0002
	20:80	0.8503	0.8503	0.8505	0.8504	0.0001
	30:70	0.8511	0.8511	0.8512	0.8511	0.0001
	40:60	0.8518	0.8519	0.8517	0.8518	0.0001
	50:50	0.8519	0.8518	0.8519	0.8519	0.0000
EO5/Octanol	0:100	0.8507	0.8507	0.8504	0.8506	0.0001
	10:90	0.8523	0.8520	0.8520	0.8521	0.0002
	20:80	0.8529	0.8529	0.8529	0.8529	0.0000
	30:70	0.8534	0.8534	0.8535	0.8534	0.0000
	40:60	0.8536	0.8536	0.8534	0.8535	0.0001
	50:50	0.8542	0.8549	0.8550	0.8547	0.0004
EO9/Octanol	0:100	0.8520	0.8521	0.8521	0.8521	0.0001
	10:90	0.8525	0.8526	0.8527	0.8526	0.0001
	20:80	0.8525	0.8525	0.8543	0.8531	0.0010
	30:70	0.8532	0.8532	0.8538	0.8534	0.0003
	40:60	0.8539	0.8539	0.8541	0.8540	0.0001
	50:50	0.8549	0.8550	0.8551	0.8550	0.0001

Appendix G HLB Calculation of Nonionic Surfactants

HLB calculation for nonionic products is obtained with the Griffin formula:

$$\mathbf{2} \quad \frac{\mathbf{M}}{\mathbf{M} \qquad \mathbf{M}} \quad \mathbf{2} \quad \frac{\mathbf{M}}{\mathbf{M}}$$

where MW_H = Molecular weight of hydrophilic part

MW_L = Molecular weight of hydrophobic part

MW = Molecular weight of surfactant

For HLB calculation of Linear alkyl alcohol ethoxylate, EO1

$MW_H = 44$

$MW = MW_H + MW_L = 244$

$$\text{HLB} = 20 \times \frac{\text{MW}_\text{H}}{\text{MW}}$$

$$\text{HLB} = 20 \times \frac{44}{244}$$

$$\text{HLB} = 3.6$$

For HLB calculation of Linear alkyl alcohol ethoxylate, EO3

$MW_H = 132$

$MW = MW_H + MW_L = 332$

$$\text{HLB} = 20 \quad \frac{\text{MW}_\text{H}}{\text{MW}}$$

$$\text{HLB} = 20 \quad \frac{132}{332}$$

$$\text{HLB} = 7.95$$

For HLB calculation of Linear alkyl alcohol ethoxylate, EO5

$MW_H = 220$

$MW = MW_H + MW_L = 420$

$$HLB = 20 \quad \frac{MW_H}{MW}$$

$$HLB = 20 \quad \frac{220}{420}$$

$$HLB = 10.48$$

For HLB calculation of linear alkyl alcohol ethoxylate, EO9

$MW_H = 369$

$MW = MW_H + MW_L = 569$

$$HLB = 20 \times \frac{MW_H}{MW}$$

$$HLB = 20 \times \frac{369}{569}$$

$$HLB = 12.97$$

Appendix H The amount of surfactant used in gram to formulate microemulsion biofuel systems in various BuOH/EtOH blending ratios using the nonionic surfactant with different EO groups (n= 1, 5 and 9)

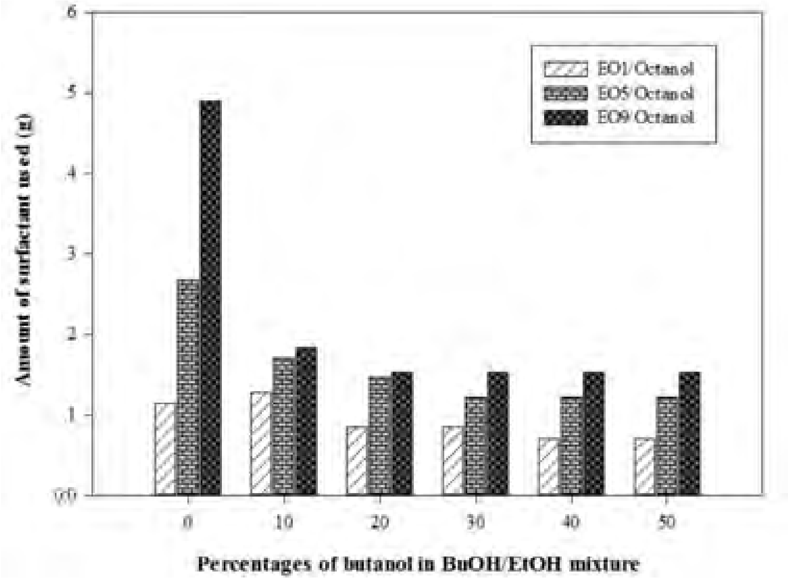


Figure H.1 The amount of surfactant used in gram to formulate microemulsion biofuel systems in various BuOH/EtOH blending ratios using the nonionic surfactant with different EO groups (n = 1, 5 and 9) as a surfactant at room temperature (25 ± 2ºC).

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Proceedings:

1. Peson, U.; Khaodhiar, S. and Charoensaeng, A. (2017, May 23) Influence of Butanol/Ethanol Blend Ratios in Palm Oil/Diesel based Microemulsion Biofuels using Alcohol Ethoxylate Surfactant - Phase Behaviors and Fuel Characteristics. Paper presented at The 8th Research Symposium on Petrochemical and Materials Technology and The 23rd PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.

Presentations:

1. Peson, U.; Khaodhiar, S. and Charoensaeng, A. (2017, June 18-21) Reverse Micellar Microemulsion of Palm oil/Diesel blends with Ethanol using Alcohol Exthylate based Surfactant Systems for Biofuel Applications. Paper presented at The 7th International Colloids Conference, 2017, Sitges, Barcelona, Spain.