รายงานวิจัยฉบับสมบูรณ์

โครงการ เชื้อเพลิงชีวภาพจากน้ำมันพืชด้วยกระบวนการไมโครอิมัลชัน โดยสารลดแรงตึงผิวที่เป็นมิตรต่อสิ่งแวดล้อม
BIOFUELS FROM VEGETABLE OIL-DIESEL BASED MICROEMULSIONS BY GREENER SURFACTANT SYSTEMS

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บทคัดย่อ:

การนำน้ำมันพืชมาใช้ในการผลิตเชื้อเพลิงเพื่อทดแทนการใช้น้ำมันดีเซลได้มีการพัฒนามาอย่างกว้างขวาง แต่เนื่องจากน้ำมันพืชมีค่าความหนืดสูงทำให้เมื่อนำมาใช้กับเครื่องยนต์โดยตรงมีข้อจำกัดหลายประการ กระบวนการไมโครอิมัลซิฟิเคชันเป็นหนึ่งในเทคโนโลยีที่สามารถลดค่าความหนืดของน้ำมันพืชได้ โดยไม่ต้องผ่านกระบวนการทางเคมีที่ซับซ้อนที่อาจเกิดของเสียที่ต้องการการบำบัดต่อ น้ำมันชีวภาพไมโครอิมัลชันเป็นน้ำมันที่ได้จากการผสมเชื้อเหลวต่างๆที่มีสมบัติความเป็นขั้วต่างกันให้สามารถรวมกันเป็นเนื้อเดียว มีความใส และเสถียรทางอุณหพลศาสตร์ การศึกษานี้มีวัตถุประสงค์เพื่อสังเคราะห์น้ำมันชีวภาพกระบวนการไมโครอิมัลชันที่ได้จากน้ำมันปาล์ม ซึ่งเป็นน้ำมันพืชที่ได้รับความนิยมใช้กันอย่างแพร่หลายในการนำมาผลิตเป็นเชื้อเพลิงชีวภาพในประเทศไทย โดยผสมร่วมกับดีเซล และแอลกอฮอล์ซึ่งทำหน้าที่เป็นสารลดค่าความหนืด และใช้สารลดแรงตึงผิวและสารลดแรงตึงผิวร่วมเป็นสารเชื่อมประสานให้เชื้อเพลิงเหลวรวมตัวเป็นเนื้อเดียวกัน ในการศึกษานี้ได้มีการนำใช้สารลดแรงตึงผิวที่เป็นมิตรต่อสิ่งแวดล้อมซึ่งผลิตมาจากพืช ได้แก่ เมทิลโอลิเอต เมทิลเอสเทอร์ และ แอลกอฮอล์อิทอกซิเลต โดยศึกษาผลของชนิดสารลดแรงตึงผิว อัตราส่วนสารแรงตึงผิวและสารลดแรงตึงผิวร่วม ที่เหมาะสมต่อการสังเคราะห์น้ำมันไมโครอิมัลชัน นอกจากนี้ยังศึกษาผลของชนิดและสมบัติน้ำมันปาล์ม และสัดส่วนและชนิดของแอลกอฮอล์ ต่อสมบัติการเกิดอิมัลชัน ได้แก่ การเกิดวัฏภาคของอิมัลชันที่เป็นเนื้อเดียวกัน ขนาดของอนุภาค ความเสถียร และสมบัติน้ำมันเชื้อเพลิงดีเซล ได้แก่ ค่าความหนืดจลนศาสตร์ ค่าพลังงานความร้อน จุดขุ่น จุดไหลเท และความหนาแน่น ผลจากการศึกษาพบว่า ปริมาณสารลดแรงตึงผิวที่ใช้ในการทำให้เกิดน้ำมันชีวภาพไมโครอิมัลชันขึ้นอยู่กับค่าความเป็นไฮโดรโฟบิกของสารลดแรงตึงผิว (HLB) ทั้งนี้สารที่มีสมบัติเป็นแอมโฟเทริกกลุ่มเอสเทอร์ที่มีความเป็นไฮโดรโฟบิกที่ใกล้เคียงกันสามารถนำมาใช้ทดแทนสารลดแรงตึงผิวได้ การใช้โครงสร้างของสารลดแรงตึงผิวร่วมที่มีโมเลกุลแบบโซ่ตรงและแบบกิ่งไม่มีผลต่อประมาณความต้องการสารลดแรงตึงผิวในการสังเคราะห์น้ำมันเชื้อเพลิงไมโครอิมัลชัน การใช้บิวทานอลผสมร่วมกันเอทานอลเพื่อเป็นสารลดค่าความหนืดช่วยลดปริมาณการใช้สารลดแรงตึงผิวและสารลดแรงตึงผิวร่วมได้อย่างมีนัยสำคัญ แต่อย่างไรก็ตามปริมาณของบิวทานอลส่งผลต่อค่าความหนืดของน้ำมันไมโครอิมัลชัน นอกจากนี้ชนิดของน้ำมันปาล์มจะส่งผลต่อการเกิดอิมัลชันและสมบัติของเชื้อเพลิงโดยตรงแม้ว่าน้ำปาล์มที่ยังไม่ได้ผ่านการแยกไข จะสามารถนำมาใช้ในการผลิตเชื้อเพลิงชีวภาพได้แต่ในมีสมบัติเชื้อเพลิงบางประการที่ไม่เหมาะสมสำหรับการนำไปใช้กับเครื่องยนต์ได้โดยตรง และจากการศึกษาน้ำมันชีวภาพตลอดวงจรชีวิตผลิตภัณฑ์พบว่าการน้ำมันไมโครอิมัลชันก่อให้เกิดผลกระทบสิ่งแวดล้อมน้อยกว่าการใช้น้ำมันชีวภาพที่ผลิตมาจากกระบวนการทางเคมี ผลการศึกษานี้แสดงให้เห็นว่าการปรับปรุงสัดส่วนที่เหมาะสมของน้ำมันพืช/น้ำมันดีเซล แอลกอฮอล์ และสารลดแรงตึงผิว ส่งผลต่อการสังเคราะห์น้ำมันไมโครอิมัลชัน ตลอดจนการลดการปลดปล่อยมลพิษทางสิ่งแวดล้อม ซึ่งองค์ความรู้จากการศึกษานี้เป็นข้อมูลในการพัฒนาการผลิตน้ำมันชีวภาพโมโครอิมัลชันที่สามารถนำไปใช้ทดแทนน้ำมันจากฟอสซิลได้อย่างยั่งยืน

คำหลัก : เชื้อเพลิงชีวภาพ ไมโครอิมัลชัน น้ำมันปาล์ม สารลดแรงตึงผิว วงจรชีวิตผลิตภัณฑ์

Abstract

Project Code : TRG5780163

Project Title : Biofuels from Vegetable Oil-Diesel based Microemulsions by Green Surfactant Systems

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Project Period : 2 years

Abstract:

The use of vegetable oils has been widely investigated with the aim to substitute diesel fuels. Due to the fact that vegetable oils have high viscosity, this limits their utilization in mechanical engines. Microemulsification is an emerging technology to reduce vegetable oil's viscosity without complex chemical processes and waste generation that need to be managed properly. Microemulsion biofuels are an isotropic, transparent and thermodynamically stable mixture of mixed immiscible liquid fuels that contains different polarity. Palm oil is intensively used for producing biofuels in Thailand. This study, palm oil based biofuels were formed through reverse micellar microemulsion formation using palm oil/diesel blends with alcohols as a viscosity reducer and stabilized by a surfactant/cosurfactant system as an emulsifying agent. The environmentally friendly nonionic surfactants derived from renewable resources comprising of methyl oleate, ester based and alkyl alcohol ethoxylate surfactants are selected for formulating microemulsion biofuels. The effects of surfactant types and structure and surfactant and cosurfactant blended ratios on the microemulsion biofuel formation were investigated. The effects of palm oil types and ratios of alcohol blended on microemulsion phase behaviors, droplet size and size distribution, and the emulsion stability were investigated as well as their fuel properties in terms of kinematic viscosity, heat of combustion, cloud point, pour point and density were determined. The results show that the amount of surfactant required to form a single phase microemulsion depends on the hydrophobic-hydrophilic property of the surfactant. The ester based amphiphile containing similar hydrophobic-lipohilic property, palm oil methyl ester-PME can be used as a surfactant in the microemulsion biofuel formation. The branch and straight chain in cosurfactant did not affect to the amount of surfactant used to form a single phase microemulsion. While adding butanol in to the polar phase, ethanol can significantly reduce the amount of surfactant system required to form a single phase microemulsion; however, the presence of butanol increased notably overall kinematic viscosity of the formulated fuels. The use of RBDPO did not affect the amount of surfactant required, due to the precipitation of semi-solid fats, the formulated fuels did not meet the fuel standards for engines in terms of cold flow properties. According to life cycle assessment, the microemulsion biofuels produced less environmental impacts than diesels and transesterification biodiesels. Thus these results show that the fuel properties as well as environmental performances of palm oil/diesel microemulsion biofuels can be optimized though formulation adjustment. The findings of this study provide the insight information for sustainable microemulsion biofuel production for replacing fossil fuels.

Keywords : 3-5 words Biofuel, Microemulsion, Palm oil, ethanol, surfactant

Biofuels from Vegetable Oil-Diesel based Microemulsions by Green Surfactant Systems

Executive summary

1. Introduction

Through supply chain business of bio-based production, the domestic industries together with local farming will be supported; therefore, using of biofuel provides sustainable energy production all over the country. Palm oil is one of the most valuable economic crops in South East Asia. This is because of the origin of palm oil - it grows well in different regions of tropical countries. Even more, palm oil is a highly efficient, high yielding source of food and non-food. Falling in place with sufficient supply, palm oil is a potential source for biofuel production.

Biofuel production technologies have been developed for many years. Among the commercialized technologies, ethanol and biodiesel are primary alternatives for gasoline and diesel engines, respectively. Recently, the blending of ethanol with diesel has been demonstrated as an alternative diesel in certain countries. In all cases, cost-effective and eco-friendly perspectives are the key challenges to satisfy future biodiesel technologies. Nevertheless, their high viscosity of vegetable oils is an important characteristic that limits their uses in vehicle engines. A number of biofuel production technologies for reducing vegetable oil viscosity have been developed, such as direct-blend, trans-esterification, pyrolysis and microemulsion. Direct blending of vegetable oil with diesel fuel can reduce total viscosity to a certain level; however, similar problems to with using pure vegetable oil still exist, especially for long-term use.

Although trans-esterification with basis catalyst is a common technology that widely used for biodiesel production, there are several environmental aspects to consider including by-products, spent toxic chemicals and wastewater. Therefore, waste treatment and disposal facilities are additionally required to ensure the environment quality, resulting in additional investment and operating costs of trans-esterification technology. Owing to ethanol can produce from renewable biomass materials (bio-ethanol), it also being considered to substitute petroleum based diesel fuel. Ethanol-Diesel blend (ED), or so called diesohol, is expected to provide positive benefits similar to using ethanol in gasoline engines. However, ethanol is insoluble in the diesel fuel over a wide range of conditions because of their difference in chemical properties (Rakopoulos et al., 2010).

Microemulsion-based biofuel is a promising technology, which could fulfill both environmental and economic competitiveness. The benefit of this technique is not only to reduce vegetable oil viscosity, but it also satisfies ethanol-diesel fuel homogeneity or prevent phase separation. Microemulsions are amphiphile stabilized transparent, iso-tropic and thermodynamically stable dispersions of otherwise immiscible liquid phase and oil. Therefore, an effective surfactant or emulsifier is needed. Selecting an appropriate surfactant system is a key challenge of stabilized

single phase microemulsion formation of vegetable oil/diesel blends with ethanol. Cosurfactants (i.e., long-chain alcohol), which can play a role of a lipophilic linker accumulating near the interface, are added to microemulsion system in order to enhance solubilization capacity. By varying compositions of the liquid biofuels, the tertiary mixtures of the ethanol-surfactants-oils or the quatertiary mixtures of the ethanol-surfactant/co-surfactant-oils can exhibit different phase behaviors. In addition, types and chemical structures of vegetable oil, surfactant, co-surfactant and fuel additives (i.e. ethanol) as well as temperature are significant factors affecting the microemulsion characteristics.

The goal of this study is to formulate palm oil based microemulsion fuels that will meet the basic requirements in terms of fuel performance and environmental aspects of next generation diesel fuels. The environmentally friendly surfactants derived from renewable based feedstock were selected as an emulsifying agent, methyl oleate, ester-based and alcohol ethoxylate surfactants. This study determined the effects of surfactant properties, oil types and ratio of ethanol/butanol blends as well as the appropriate composition of microemulsion-based biofuels through microemulsion phase behaviors, kinematic viscosity, microemulsion droplet size and other fuel properties. Consideration of environmental impacts, the life cycle of different formulations of microemulsion based biofuels was evaluated from raw materials production toward to the end of use. To our knowledge, this is the first time that the effects of surfactant structure and co-surfactant (alkanols) structures with varying chain length and butanol/ethanol ratios on formulating palm oil based microemulsion fuel are evaluated. The outcome of this study will provide valuable information on vegetable oil microemulsion fuel with regarding to their formulation and uses.

2. Theoretical background

Vegetable oils and palm oil

Palm oil plays an important role in consumer products, oleochemical industries as well as biodiesel production. The foremost advantages of palm oil are high yields and moderate world-market prices than the other crops. Therefore, palm oil has been promoted as renewable feedstock for biofuel production. Triglyceride oils, derived from plants and vegetable, are the primary composition of vegetable oils. Having high viscosity is the major limiting factor that renders the uses of vegetable oil in diesel engine. Table 1 represents the kinematic viscosity of different vegetable oils. It can be seen that the viscosities of vegetable oils are dramatically high ranging from 40-27 mm²/s at 38 °C and about 40 mm²/s for palm oil, when compared with those of the biodiesel standard ranging from 3.5-5.0 mm²/s at 40°C. The short-term diesel engine tests indicated that these vegetable oils could deliver power similar to those of neat diesel fuel did. The long-term durability tests, in contradictory, revealed serious problems from carbonization of the combustion chamber. Additionally, poor atomization, incomplete combustion, coking of injector nozzles and sticking of piston rings were the common problems found in many studies (Wang et al., 2006).

Microemulsions

Microemulsification is one of the potential technologies to reduce high viscosity of vegetable oil and immiscible phase separation of the liquid mixture with two opposite polarities (i.e., water-oil,

ethanol-diesel). Microemulsion technique, two renewable liquid fuels with different hydrophobicity such as vegetable oil-diesel blends and ethanol can be thermodynamically emulsified into a stable single phase dispersions of otherwise immiscible liquid phase and oil by low energy mechanical blending with appropriate surfactants. Microemulsions can form and transition among four basic types; Winsor Type I, Winsor Type III, Winsor Type II, and Winsor Type IV, is depending on the hydrophile-lipophile balance (HLB) of the surfactant (Childs et al., 2004; and Rosen, 2004). Microemulsion phase behaviors described in term of tuning parameter versus surfactant concentration, known as Winsor diagram is shown in Figure 1 (adapted from Goodwin, 2005).

Tuning Parameter (Electrolyte concentration for ionic surfactants or temperature for non-ionic surfactants)
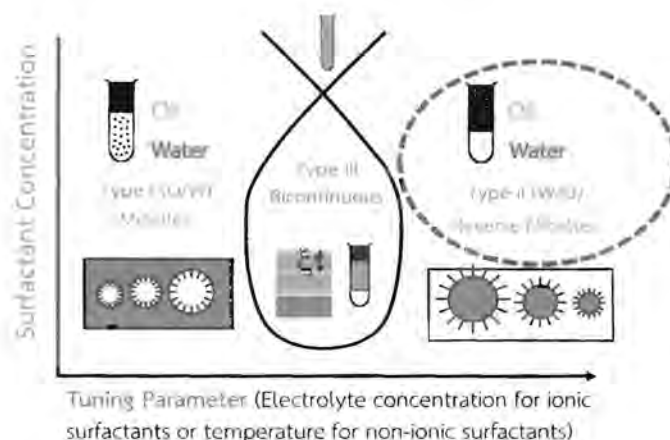
Adapted from Goodwin, 2005

Figure 1 Microemulsion formation

In one hand, when surfactant aggregates solubilize oil in aqueous phase, the normal micelles (surfactant aggregates having hydrophobic interiors and hydrophilic exteriors) are formed, resulting in Winsor Type I (oil-in-water, O/W) microemulsions. On the other hand, when the surfactant aggregates move into oil phase and solubilize aqueous or polar solvent, the aggregates transform into reverse micelles (surfactant aggregates having hydrophilic interiors and hydrophobic exteriors). The formation of reverse micelles are classified as Winsor Type II microemulsion (water in oil, W/O) which is typical microemulsion system to formulating biofuels. Figure 3 indicates the formations of microemulsion system.

Tertiary phase diagram

The tertiary phase diagram is classically used to determine phase behavior and miscibility of three multicomponent systems of microemulsion formation. A tertiary phase diagram is an equilateral triangle consisting of three vertices of three components. Two vertices at the base of triangle represent vegetable oil/diesel and ethanol mixtures at the left side and the right side, respectively, while the upper vertex represents the surfactant/co-surfactant mixture at a constant ratio for a given temperature. The composition at each point in a tertiary phase diagram demonstrates the volume percent of the three components (A, B, C) as follows

$$x\%A + y\%B + z\%C = 100\%$$

The miscibility curve is plotted as the boundary between two phase and single phase microemulsions. The regions above the curve are single phase systems where sufficient surfactant is added to solubilize all of components – this is a thermodynamically stable and transparent microemulsions. The curve, two visibly separate phases occur which in our case is a Winsor Type II.
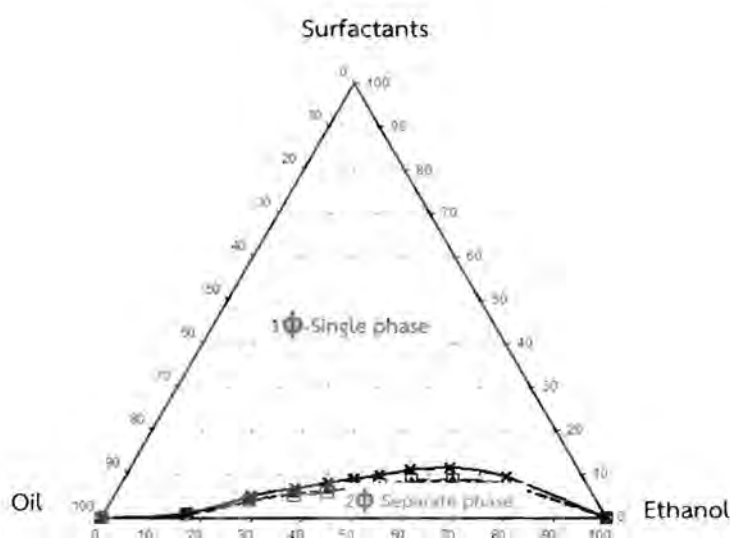

Figure 2   Tertiary phase diagram of Winsor Type II (water in oil) microemulsion

Castro and co-workers (2001) formulated a microemulsion system containing diesel and different percentages of vegetable oils. They constructed a pseudo-ternary phase diagram in order to determine the phase boundaries of the microemulsion regions. The main parameters that affect the microemulsion areas were the nature of the surfactant and the co-surfactant, and the co-surfactant-to-surfactant ratio (C/S ratio). They found that the addition of 20% of soy bean oil as a substitution for the pure diesel caused a change in the microemulsion area. There are many factors affecting phase behavior and the internal structure of a microemulsion including the chemical structure of oil (vegetable oil), surfactant type, carbon-chain length of the surfactants and co-surfactants molecules, co-surfactant–to-surfactant ratio, ionic strength of the solution, temperature, and pressure. (Rosen, 1980; Paul and Panda, 2011)

The Combustion and Fuel Properties

The kinematic viscosity (at 40 °C) is the main parameter required by biodiesel and petrodiesel standards. Many researchers have studied the influential parameters that affect the kinematic viscosity of biofuels (Knothe and Steidley, 2005; Rodrigues et al., 2006). Knothe and Steidley (2005) investigated the influence of a fatty compound structure including the chain length, acid and alcohol moieties of esters, number and configuration of double bonds, on kinematic viscosity of biodiesels. In their study, the kinematic viscosity of various saturated and unsaturated fatty compounds was reported. The results showed that the kinematic viscosity increased with the increasing chain length of either the fatty acid or alcohol moiety or in an aliphatic hydrocarbon. At the same number of carbon atoms, the unsaturated hydrocarbons have lower kinematic viscosity than that of saturated hydrocarbons.

Considerations of emission quality, Lif and Holmberg (2006) investigated the water-in-diesel emulsion properties in a regular diesel engine. The formulated emulsion fuel reduced emissions of nitrogen oxides (NO_x), particulate matter (PM), and fuel consumption due to its better burning efficiency. Their study focused on the influence of water addition on emissions and combustion efficiency. It was found that the emissions of NO_x and PM decreased as the water content of the emulsion increased. On the other hand, the emissions of hydrocarbons (HC) and carbon monoxide (CO) increased. In terms of combustion efficiency, it was found that the water content reduced the peak temperature in the cylinder, resulting in a lower level of NO_x formed. The presence of water-in-diesel can introduce to the micro-explosion phenomenon, enhancing the atomization of fuel.

Life cycle assessment

A microemulsion theoretically produces biofuel with 100 percent yield with less waste and emissions, the feedstock otherwise bio-based material production i.e., cultivation activities thru virgin oil extraction entail emissions to the environments. In order to accumulating environmental impacts, both direct and indirect emissions of microemulsion-based biofuel production need to be wisely addressed for each step of the product life-cycle. Life-cycle assessment (LCA) is an environmental tool to evaluate the potential impacts of a product on the environment over the entire period of its life: from the extraction of raw materials; through the production and packaging process (i.e. from cradle to gate); the use and maintenance of the product; and on to the recycling or disposal as waste at the end of its life (i.e. from cradle to grave). All materials and energy input and output of each step process are required as inventory data for LCA assessment. There is many research used a LCA technique to evaluate the environmental impacts of alternative fuels or biofuels (Papong and Pomthong, 2010; Papong et al., 2012). Throughout the material balance calculation, LCA can be a useful tool for industrial process by clarifying emission hotspots as well as prioritize alternative technology to mitigate impacts.

3. Objectives

The overall objective of this study is to formulate a palm oil based microemulsion fuel from vegetable oil using green surfactant system. The specific objectives of this study are:

1) To determine phase behavior and kinematic viscosity of reverse micelle microemulsion containing a surfactant, a co-surfactant, an ethanol/butanol, and a vegetable oil/diesel blends.

2) To study the effects of surfactant structure, palm oil type and alcohol blend and ratio of each component (vegetable oil, surfactant/co-surfactant and additives) on the microemulsion phase behavior and kinematic viscosity and microemulsion droplet size

3) To evaluate the environmental impacts of microemulsion biofuels and compare with those of biodiesels and regular diesel fuels

4. Methodology

Materials

Apart from having high solubilizing efficiency in microemulsion, surfactants will be selected based on environmentally friendly product produced form renewable resources such as sugar based or palm oil based from oleochemical production. Three types of surfactant, methyl oleate, methyl ester and alcohol ethoxylate were selected as a primary surfactant. For methyl ester based surfactant, palm oil methyl ester (PME) was selected because of its structure and hydrophobic-lipophilic balance. Co-surfactants, 1-butanol, 1-octanol, and 2-ethyl-1-hexanol were used to identify the effect of alkyl chain lengths. The properties of the surfactants and co-surfactants are summarized in Table 1.

Ethanol represented as the polar liquid phase in the biofuel was used as viscosity reducer in the system. Butanol which has a higher in cetane number was used as cetane enhancing additive. All chemical uses in this study are both analytical and commercial grade.

Palm oils as palm olein was selected as a vegetable oil used for blending with regular diesel. While refined bleached deodorized palm oil (RBDPO), a low cost palm oil, is a palm oil containing palm olein and stearin was evaluated the possibility for formulating microemulsion biofuels.

Table 1 Summary of chemical properties of surfactants and co-surfactants
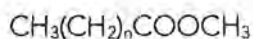
Surfactant
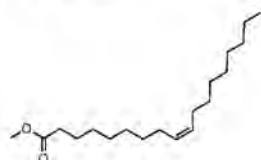
Methyl oleate

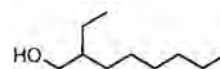Ethoxylate based surfactants
Alcohol ethoxylate LS1, LS3, LS5,LS7 TH

$CH_3(CH_2)_nCOOCH_3$

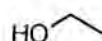Palm oil methyl ester (PME)

Co-surfactant

1-Octanol

2-ethyl-1-hexanol

Alcohols

ethanol

1-Butanol

Methods

Microemulsion fuel formation

Microemulsions are prepared on a weight basis for the surfactants and on a volumetric basis for the co-surfactants. The mixtures of the co-surfactant and the surfactant (C/S ratio) are prepared at fixed mole ratios and are gradually added into glass vials. Then, different amounts of ethanol and vegetable oil and diesel are added into the solution. The mixture of surfactant-cosurfactant/vegetable-diesel blend/ethanol is hand-shaken gently and kept at room temperature 25±2°C. Subsequently, phase behavior is determined by visual inspection with polarized light (Fernando and Hanna, 2004).

Tertiary Phase Diagram

In order to study the phase behavior and miscibility of the biofuel based-microemulsion, the principles of a tertiary phase diagram representing the three-component system are used. A tertiary phase diagram is an equilateral triangle, consisting of three vertices of three components by the method of phase volumes (Dunn and Bagby, 1994). Two vertices at the bottom of the triangle represent the vegetable oil-diesel blend and ethanol at the left side and the right side, respectively, while the upper vertex represents the co-surfactant/surfactant mixture at a constant ratio at a given temperature. Finally, the total volume of the C/S solution, vegetable/diesel blend, and ethanol are calculated to 100 percent for all components. The miscibility curve will be plotted as the boundary between the two-phase- and single-phase-microemulsions. The regions above the curve are single phase systems where a sufficient surfactant has been added to solubilize all of the components. The tertiary phase diagram is shown in Figure 2.

Biofuel property testing

Viscosity Measurement

The viscosity of microemulsion fuel is measured by a Canon-Fenske type viscometer. A minimum sample volume of 7.0 mL of the microemulsion fuel sample (as recommended by the manufacturer) is transferred into a viscometer chamber, and the time required for the fluid to flow between two specific points is measured. The effects of the fraction of vegetable oil to diesel, ethanol, and the C/S ratio on viscosity are then evaluated. The temperature is varied from 15°C to 40°C. Afterwards, the kinematic viscosity is calculated from Equation 1, which has been provided by the manufacturer of the viscometer:

$$\mu = Kt \qquad \text{Equation 1}$$

where μ is the kinematic viscosity (mm/s), K is the viscosity constant, t is the efflux time (in seconds) of the sample through the capillary tube.

Dynamic Light Scattering (DLS) Measurements

The size and size distribution of the microemulsion-based biofuels are investigated to determine the characteristics of the microemulsion. The measurement of microemulsion droplet size is indirect method for determine the stability and against coalescence of droplets. The effects of surfactants, co-surfactants, C/S ratio, and ethanol content are evaluated and compared with the kinematic viscosity results. The dynamic light scattering measurements are performed to obtain the mean diameter (DL) and size distribution of the W/O microemulsion droplets.

Fuel Properties of the Microemulsion fuel

The fuel properties of the microemulsion-based biofuel are tested to investigate its short-term and long-term effects on the diesel engine. The properties of microemulsion-based biofuels are investigated according to the ASTM standard. The parameters are in the kinematic viscosity, flash point (FP), cloud point (CP), pour point (PP), cetane number (CN), and water content. In addition, the fuel properties of these biofuels are compared with those of neat diesel fuel.

Life-cycle impact assessment (LCA)

The inventory data from each production stage were compiled in LCA support software SimaPro v. 7.1 to evaluate the environmental impacts of microemulsion-based biofuel production (cradle to gate) using CML 2 baseline 2000 method. The activity data used in this study were gathered from both primary and secondary data. Input data including raw materials and energy consumption in microemulsion production stage were collected as primary data from the results in laboratory experiment. The secondary data were used as necessary from literatures, calculation, US LCI database, and Ecoinvent database version 2.1 for certain items such as production of fertilizers, diesel, etc. The environmental impact categories investigated in detail are acidification (AP), eutrophication (EP), global warming (GWP), ozone layer depletion (ODP), and human toxicity (HTP). Figure 3 shows the experimental approaches of this study.
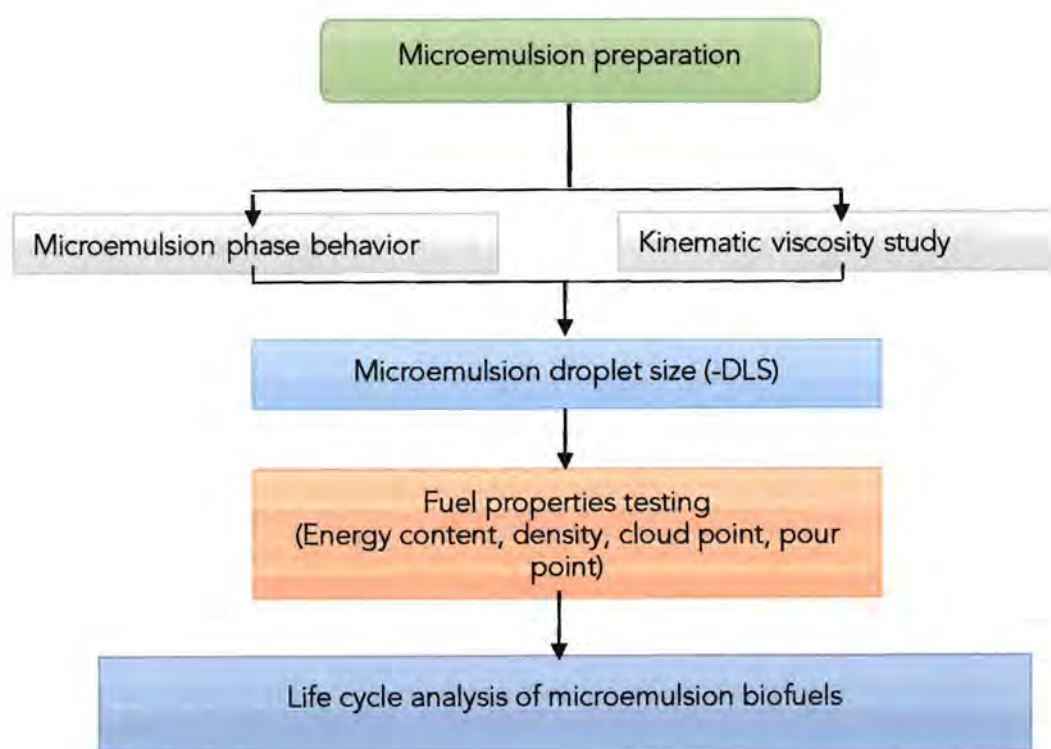

Figure 3 Experimental approach of the study

5. Research Tasks

This research is divided into the following four parts:

Part 1: Palm oil based Microemulsion Biofuels using Nonionic surfactant: the Effect of surfactant and cosurfactant structures

This work aims to formulate microemulsion biofuels of a palm oil/diesel and a refined bleached deodorized palm oil (RBDPO)/diesel blended with ethanol as a viscosity reducer. Three types of nonionic surfactant derived from renewable based feedstock, i.e., methyl oleate, sorbitan monoleate and palm oil methyl ester) and two type of cosurfactants with different structure, i.e., 1-octanol and 2-ethyl-1-hexanol were investigated. Their fuel properties in terms of kinematic viscosity, droplet size, turbidity, density and heat of combustion were investigated and compared with No.2 diesel fuel. It was found that nonionic surfactant and cosurfactant structures has no significant impact on their phase behaviors. The formulated microemulsion biofuels had higher kinematic viscosity than that of the diesel. The fuel properties of microemulsion biofuels are depended on the raw material selection. These results show that the microemulsion biofuels can form using renewable based surfactants which is an attractive option for environmentally friendly biofuel production.

Part 2: Palm oil based Microemulsion Biofuels using Renewable based Nonionic surfactants: The Effect of Ethanol/Butanol in Palm Oil/Diesel Blends

This work focused on the formation of microemulsion biofuels using two type of a palm oil/diesel and a refined bleached deodorized palm oil (RBDPO)/diesel blend as an oil phase with an ethanol and butanol blend as a viscosity reducer. The ester based surfactant with similar structure, Methyl oleate (MO) and palm oil methyl ester (POME) were used as a surfactant and 1-octanol was used as a cosurfactant at the mixing ratio of 1:8 M/M surfactant: cosurfactant by molar. The effects of surfactant structure, ethanol/butanol blending ratios, palm oil/diesel blending ratios on phase behavior, kinematic viscosity, microemulsion droplet size and fuel properties of formulated microemulsion fuels were investigated. The results show that the phase behaviors of different surfactant systems had similar trend of the miscibility curve. The microemulsion biofuels containing butanol in the mixture showed remarkably a decrease in the area of two-phase separation. Based on our findings, the blending ratios of ethanol/butanol is a major parameter for optimizing the viscosity and other fuel properties of microemulsion biofuels.

Part 3: Palm Oil based Biofuels by Reverse Micelle Microemulsion: The Effect of Palm oil Type and Property

This study aims to formulate microemulsion biofuels (MEs) containing RBDPO/diesel as a non-polar phase blended with ethanol as a polar phase and stabilized by surfactant/cosurfactant (S/C) system. The effects of nonionic surfactant structure and S/C ratio on the phase behavior of the ME system were investigated. The nonionic surfactants were alcohol ethoxylate surfactant with different EO groups (EO groups: n = 1, 3 and 5) and palm oil methyl ester. The MEs were formulated using a surfactant mixed with a cosurfactant (1-octanol) at a mole ratio of 1:4, 1:8 and 1:16, and blended with RBDPO/diesel (1:1 v/v) and ethanol to formulate ME. Pseudo-ternary phase diagram was conducted to determine the phase behavior of ME. In addition, the solid fats precipitated from RBDPO in the biofuel was observed. The results of this study indicated that the

formation of ME depends on surfactant structure, while the crystallization of the solid fats and their fuel properties were influenced by surfactant structure and mixing ratio of S/C.

Part 4: Environmental Life Cycle Assessment of Palm Oil based Microemulsion Biofuel Production from Renewable based Materials

The greenhouse gas emission and related environmental impacts of microemulsion based biofuel technology is evaluated through life Cycle Assessment (LCA) tools. This study focuses on evaluation of Greenhouse Gas (GHG) emissions and environmental impacts of microemulsion (ME) biofuels from different formulations based on life cycle assessment (LCA) approach. The functional unit is set to be one ton of ME biofuel. LCA system boundary was separated into four stages: cultivation, oil extraction, refining and ME stage. The ME biofuels with different formulations had been set for four different scenarios by varying the type and ratio of raw materials used. The GHG emissions results described that Scenario IV contributes to the lowest GHG emissions (1,017 kgCO2) and lowest environmental impacts as the result of using refined bleached deodorized palm oil (RBDPO) in the ME formulation. When RBDPO was used to formulate ME biofuel, the total GHG emission was significantly reduced comparing to base case (1,448 kgCO2). When the emissions of each scenario were compared based on the normalized results, the biobased case contributed significantly to some environmental impact categories such as fresh water aquatic ecotoxicity, terrestrial ecotoxicity and eutrophication.

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Output จากโครงการวิจัยที่ได้รับทุนจาก สกว.

1. ผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ

N. Arpornpong, D. A. Sabatini, S. Khaodhiar, A. Charoensaeng (2015), **Life cycle assessment of palm oil microemulsion-based biofuel**, The International Journal of Life Cycle Assessment, International Journal of Life Cycle Assessment, vol. 20 no. 7, p

2. การ นำเสนอผลงานในการประชุมวิชาการ
   ผลงานในงานประชุมวิชาการระดับนานาชาติ

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3) S. Manaphati, P. Malakul, D. A. Sabatini b, A. Charoensaeng, Reverse Micelle Microemulsion Biofuel using Palm oil/Diesel Ethanol with Renewable Nonionic Surfactant Systems, The 6th Research Symposium on Petrochemical and Materials Technology. and. The 21st PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand, 21 April 30, 2015

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6) A. Charoensaeng, S. Khaodhiar, P. Malakul Na Ayudhaya[1], D. Sabatini[2] Formation and phase behaviors of ethanol in palm oil/diesel blend reverse micelle microemulsions using nonionic surfactants for biofuel application, The 6th International Colloids Conference Berlin, Germany, 19 - 22 June 2016

Chapter 1:

Palm oil based Microemulsion Biofuels using Nonionic Surfactants: The Effect of Surfactant and Cosurfactant Structures

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Abstract

Biofuels are one of renewable fuels used in many vehicles and industries. Vegetable oils which are green and non-toxic nature derived from agricultural feedstock, have been used for biofuel's production for many years. Due to their high viscosity, the direct use of vegetable oil in diesel engines can lead to engine durability problems. Reverse micelle microemulsion as an alternative biofuel production has been intensively studied for formulating biofuel with desirable viscosity. This work aims to formulate microemulsion biofuels of a palm oil/diesel and a refined bleached deodorized palm oil (RBDPO)/diesel blended with ethanol as a viscosity reducer. Three types of nonionic surfactant derived from renewable based feedstock, i.e., methyl oleate, sorbitan monoleate and palm oil methyl ester) and two type of cosurfactants with different structure, i.e., 1-octanol and 2-ethyl-1-hexanol were investigated. Their fuel properties in terms of kinematic viscosity, droplet size, turbidity, density and heat of combustion were investigated and compared with No.2 diesel fuel. The results show that nonionic surfactant and cosurfactant structures has no significant impact on their phase behaviors. The formulated microemulsion biofuels had higher kinematic viscosity than that of the diesel. The fuel properties of microemulsion biofuels are depended on the raw material selection. These results show that the microemulsion biofuels can form using renewable based surfactants which is an attractive option for environmentally friendly biofuel production.

KEYWORKDS: Microemulsion Biofuel, Nonionic surfactants, Palm oil, Reverse micelles

1. Introduction

Nowadays, concerns of environmental quality drive people's effort in decreasing the use of petroleum energy resources and in the meantime increasing the use of renewable biofuels. Vegetable oils have been considered as such an alternative fuel source owing to its nontoxic and renewable nature. Several vegetable oils have been used to replace diesel fuels that typically used in engines for vehicles and industries. Among there, vegetable oils such as palm oil, canola oil and soybean oil, castor oil have received increased interests in several research studies. However, the utilization of vegetable oils in diesel fuels has a limitation due to high viscosity of vegetable oils. As a result, the technologies for reducing vegetable oil viscosity have been widely developed. Microemulsification is an emerging technology to reduce the vegetable oil's viscosity, so called vegetable oil based microemulsion biofuels. The advantages of this technology are that it is simple, less CO and NO_x emission, and burn more completely. A microemulsion biofuel is combination of liquid fuels, a diesel fuel and vegetable oil blend, alkanols and surfactants and cosurfactants as an emulsifier used to stabilized all immiscible liquids to be a single phase microemulsion.

Although, ethanol is a renewable energy source from agricultural feedstocks such as corn and sugar cane crops, the use of ethanol in diesel engines is limited due to the fact that ethanol/diesel blends (i.e., ED95) are immiscible at wider range of temperatures. In reverse micellar or water in oil microemulsion system, ethanol is used in place of water or polar phase which disperses as small size droplets (10 to 100 nm; Rosen, 2004) in oil phase; it can reduce viscosity of a vegetable oil and diesel mixture. Therefore, ethanol can be blended with a diesel and vegetable oil and then utilized in diesel engines without engine modification.

The aim of this research is to formulate microemulsion biofuels with palm oil/diesel blends using nonionic surfactant systems. Three types of nonionic surfactants with different structure and two cosurfactants deviated by branching are investigated. The Two types of palm oil are used as a vegetable oil in order to extend the range of oil's property to formulate microemulsion biofuels. The emulsion properties in terms of phase separation and droplet size are measured along with theirs fuel performance with the aim to compare with those of diesel fuel.

2. Literature review

Several type of surfactants and cosurfactants were used to form microemulsion fuels such as anionic carboxylate based extended surfactants, renewable based nonionic surfactants. Among them, a nonionic surfactant has better performance than an anionic surfactant system in cases of no salt required, more oil soluble, and no phase separation and precipitation at low surfactant concentrations. Many researchers studied the effects of surfactant types for formulating microemulsion fuels. Sabatini and co-worker (2012) studied phase behavior of microemulsion biofuels using carboxylate-based extended surfactants with a canola oil and diesel blend with ethanol. Their results showed that the branching of surfactant and the number of EO groups of this extended surfactants affect the amount of the surfactant required to form a single phase microemulsion. This is because the branching in surfactant molecule increases the performance of oil solubility. However, the increasing of EO group in the extended surfactant made poorly oil soluble which needs more surfactant to stabilize all components in the microemulsion fuels. For the effect of surfactant/cosurfactant ratio, they found that it did not significantly affect the

microemulsion fuel formation. Thus, they selected the ratio of surfactant/cosurfactant based on the cost-effective and limitation of surfactant preparation. The kinematic viscosity study indicated that the viscosity of diesel fraction over 50% by vol. of the oil phase closed to the standard viscosity of the ASTM No. 2 diesel fuel.

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

Thu and coworkers (2012) studied canola oil, diesel and alcohols in microemulsion fuel formulation. Ethanol and sec-butanol were used as a polarity phase and oleyl amine/1-octanol was used as a surfactant and cosurfactant. In their study, ethanol and sec-butanol ratios were varied, while other components were fixed at the same concentration. They demonstrated that at ethanol and sec-butanol ratio greater than 1:2, the phase separation of the biofuel occurred at lower than -10°C. On the other hand, at 30% by volume sec-butanol with no added ethanol, it can be stabilized to single phase microemulsion fuel. However, sec-butanol has a higher viscosity than ethanol, but it has higher heat of combustion than ethanol. When they considered the ethanol and sec-butanol concentration which was varied and fixed the ratio of ethanol to sec-butanol at 1:2, the result indicated that when amount of ethanol as a viscosity reducer in the mixture decreased, the overall viscosity of the microemulsion fuels increased and cetane number and decreased resulting a lower diesel engine's performance.

Sabatini et al. (2013) studied phase behaviors comparing five types of nonionic surfactants with anionic carboxylate-based extended surfactant. Three types of sugar-based surfactants, oleyl alcohol, and 2-ethyl-hexanol was selected as surfactant in this study. It was found that oleyl alcohol required the lowest amount of surfactant to formulate single phase microemulsion. For nonionic surfactants, the number of EO groups decreased as increasing hydrophobicity of the surfactants, the use of surfactant concentration was lower to form single phase. When temperature decreased, the fuel needed more added surfactants to form single phase. The systems of oleyl alcohol/2-ethyl-hexanol with canola oil/diesel mixture in ethanol with and without additives can formulate similarly microemulsion below 0°C, and both met closely kinematic viscosity standard of the No.2 diesel, and had heat of combustion comparably to the No.2 diesel.

Tohren and coworkers (2014) studied on the prediction of kinematic viscosity of reverse micelle microemulsion biofuels. They aimed to explore and develop viscosity prediction models. The

Chevron's models were used for calculation of viscosity depending on temperature for the fuel components, and used to predict the viscosity of reverse microemulsion fuels. Canola, algae and palm kernel oil as the vegetable oil, mixed with diesel and ethanol were investigated. They concluded that viscosity calculation of microemulsion fuels by the Chevron model can be used for prediction of kinematic viscosity of biofuels from the viscosity of each of the components. This model can calculate viscosity blending index for each component in the mixture. Their study could well predict from consideration of the microemulsion fuels to liquid mixtures.

3. Method

3.1 Materials

Surfactants

Three types of nonionic surfactant derived from renewable feedstock used in the research were 1) methyl oleate as a fatty ester 2) sorbitan monooleate, Span 80 and 3) biodiesel or palm oil methyl ester (PME). The properties and the structure of surfactants are showed in Table 1 and Figure 1, respectively. Methyl oleate, a methyl ester based surfactant, contains C-18 carbons chain length with a double bond in the structure. It was selected because of high solubilization form single phase microemulsion and microemulsion fuel with methyl oleate system indicating closely and suitably the properties to the standard No.2 diesel as reported elsewhere (Sabatini et al., 2014). Methyl oleate with 70% purity (technical grade) was purchased from Sigma-Aldrich (Thailand). Span 80 or sorbitane monoleate is renewable sugar based surfactant. Span80 (Rheodol SP-O10) was obtained from Kao Chemical Company (Thailand) Co., Ltd. Biodiesel based palm oil is fatty acid methyl ester (FAME) which is derived from palm oil. Biodiesel (B100) was received from biodiesel manufacture (Verasuwan Co., Ltd) with 98%

Cosurfactant

Two cosurfactants used in this study were 1-Octanol and 2-ethyl-1-hexanol; 1-Octanol at 99.0% of purity was purchased from Acros Organics (Italmar, Thailand) and 2-ethyl-1-hexanol at 99.6% of purity was purchased from Sigma-Aldrich (Thailand). In addition, two selected cosurfactants has same carbon chain length, C8OH but differs in their branching structure. The properties and the structure of cosurfactants are showed in Table 1 and Figure 2, respectively.

Methyl oleate

Palm oil methyl ester

Sorbitan monooleate (Span 80)
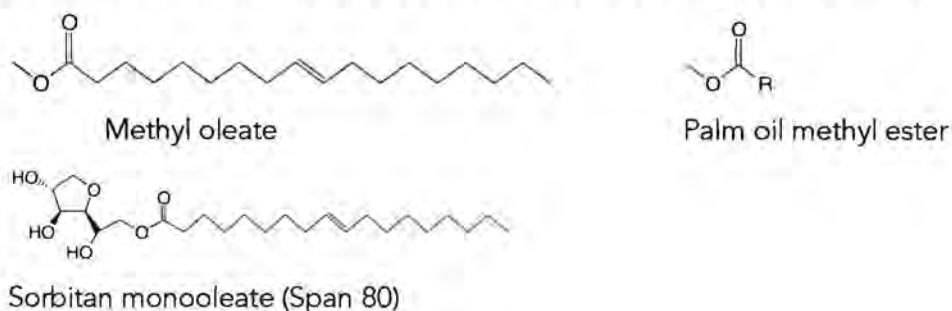
Figure 1 Structure of surfactants.

1-Octanol

2-Ethyl-1-Hexanol

Figure 2 Structure of cosurfactants.

Table 1 Properties of the studied surfactants and cosurfactants

Materials	Molecular Weight	Density (g/mL)	Purity (%)
Nonionic surfactants			
Metyl oleate	296	0.874	70.0
Span 80	428	0.985	99.0
PME	283	0.890	65.5
Cosurfactants			
1-Octanol	130	0.825	99.0
2-Ethyl-1-hexanol	130	0.833	99.6

Palm Oil, RBDPO and Diesel

Food-grade palm oil and commercial-grade diesel were purchased from Morakot industries PCL and PTT Public Company Limited, respectively. Refined bleached deodorized palm oil (RBDPO) was supported by Bangchak Biofuel Co., Ltd. Table 3.2 shows the fatty acid compositions of palm oil and RBDPO.

Ethanol

Ethanol (with 95%) was used as a viscosity reducer and a polar liquid phase in microemulsion system. Ethanol can dissolve completely in water and flash point of ethanol is 12-15°C (Hansen et al., 2005).

Table 2 Fatty acid compositions of palm oil and RBDPO

Materials	Fatty acid composition (%)	
	Palm oil	RBDPO
Myristic acid (C14:0)	0.89	0.92
Palmitic acid (C16:0)	41.54	46.30
Stearic acid (C18:0)	3.51	3.52
Oleic acid (C18:1)	43.63	39.58

Linoleic acid (C18:2)	10.43	9.68

The data from Che Man et al., 1999

3.2 Experimental Methods

Microemulsion Preparation

Composition of the microemulsion fuels contains surfactant/cosurfactant blended with ratio of 1:8 by molar, vegetable oil/diesel mixture at 1:1 by volume and ethanol. Each microemulsion fuel sample was prepared in a 15 mL glass vial. Amounts (1, 2, 3, 4 and 5 mL) of ethanol with 5 mL of the palm oil/diesel blend was added into the surfactant and cosurfactant mixture to formulate a reverse micelle microemulsion. The fixed amount of ethanol at 5 mL and varied palm oil/diesel blends in 1, 2, 3, 4 and 5 mL were conducted. Finally, all mixtures were then hand-shake and placed at the room temperature (25±2 °C) for 48 hours to observe phase separation.

Pseudo-ternary Phase Diagram

Pseudo-ternary phase diagram, a triangle diagram consists of at least three components in the mixing system, was conducted for phase behavior study of the microemulsion fuels (as can be seen from Figure 3). The upper vertex represents the surfactant and cosurfactant mixture at a constant ratio. The vertex at the bottom in the left hand side represents vegetable oil and diesel blend at a constant ratio, and the right hand side represents ethanol. Each point in a pseudo-ternary phase diagram was calculated based on three components in volume percentage.

Droplet Size

Droplet size and size distribution of the microemulsion fuels can be determined by dynamic light scattering (DLS). A 0.45 μm PTFE membrane filters was used to remove dust particles and impurity. Nano Zetasizer (Malvern) is performed the samples that are transferred to a cylindrical light-scattering cell of 10 mm outer diameter, set temperature at 25°C and a scattering angle of 173° and light source is a He-Ne laser (λ=633 nm; 4mW)

Fuel Properties Determination

- #### Kinematic Viscosity

The kinematic viscosity can be measured by Cannon-Fenske Routine viscometer follows ASTM D 445. The measurement requires a 10 mL of single phase microemulsion fuel sample. Next, count a time for finding flow rate in cSt/sec unit at constant temperature water bath of 40°C and then, the kinematic viscosity can be calculated by equation (2.1). In this study, the kinematic viscosity of the microemulsion fuels are compared with neat diesel fuel followed the ASTM No.2 diesel fuel at 40°C and the standard kinematic viscosity at 4 cSt.

- #### Turbidity

Turbidity of the microemulsion fuels is determined by UV spectroscopy using photometric mode. Acetone and the samples of microemulsion fuels are filled in reference and sample cell, respectively. The absorbance is recorded for comparison of the samples.

Cloud Point

Cloud point is the temperature at the fuel which is initial to form crystals. In this study, the cloud point can be measured by using cooling bath. The fuel was observed for the cloudiness as the temperature is decreased every in 2°C

Density

Density of the samples is measured using the weighing of mass per unit volume at 25°C. The fuel density was weighted 4-digit digital analytical balance.

Gross Heat of Combustion

Heating values can be measured by oxygen bomb calorimeter (model AC-350, LECO Corporaiton, USA) following to ASTM D 240. Biofuel is placed in a crucible inside calorimeter to the heating value and to collect carbon residuals after testing fuel. The heat of combustion was calculated by the measured temperature increase of the water bath surrounding the bomb.

4. Results and discussion

4.1 Phase Behavior Study

The goal of this study is to determine the effect of surfactant's and cosurfactant's structures on phase behavior of reverse micelle microemulsion fuels. The miscibility and phase behavior of microemulsion biofuels are formulated in Winsor type II microemulsion system using pseudo-ternary phase diagram as shown in Figure 3. The upper vertex of the diagram is a surfactant/cosurfactant mixture and the bottom of the triangle represents a vegetable oil/diesel mixture and an ethanol, respectively. The area above the miscibility curve is the composition of a single phase microemulsion. On the other hand, the area below the curve is the composition of a separate phase. The phase behavior study of microemulsion fuels was conducted at room temperature (25±2°C).

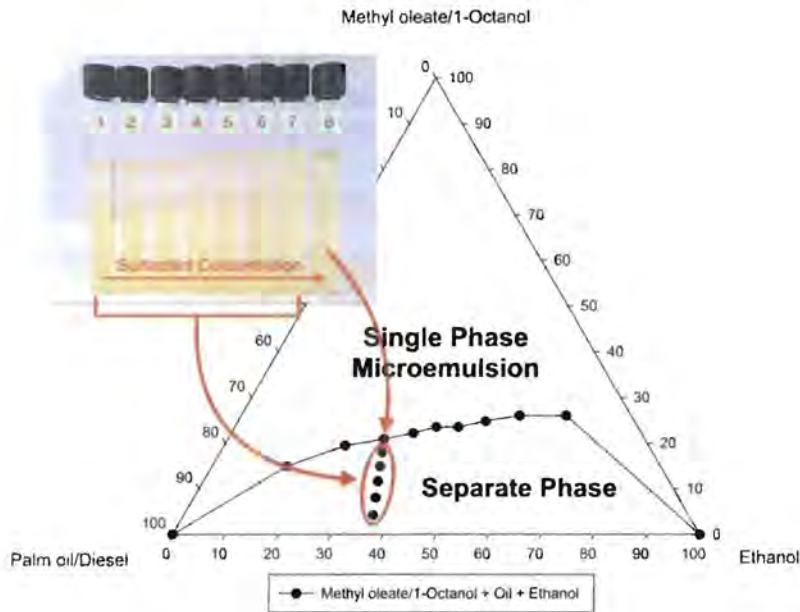**Figure 3** The pseudo ternary phase diagram of microemulsion biofuel using methyl oleate/1-octanol as surfactants at 1:8 molar ratio with palm oil/diesel blend at a ratio of 1:1 (v/v).

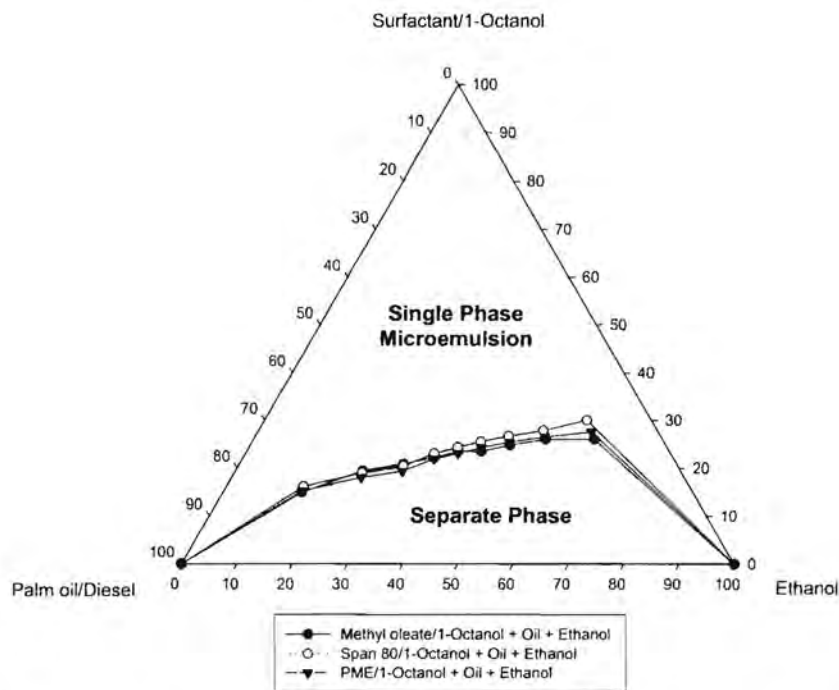**Figure 4** Pseudo ternary phase diagram of microemulsion biofuel systems using methyl oleate, Span 80 and PME as a surfactant at surfactant/1-octanol molar ratio of 1:8 with a palm oil/diesel at a ratio of 1:1 (v/v) at room temperature (25±2°C).
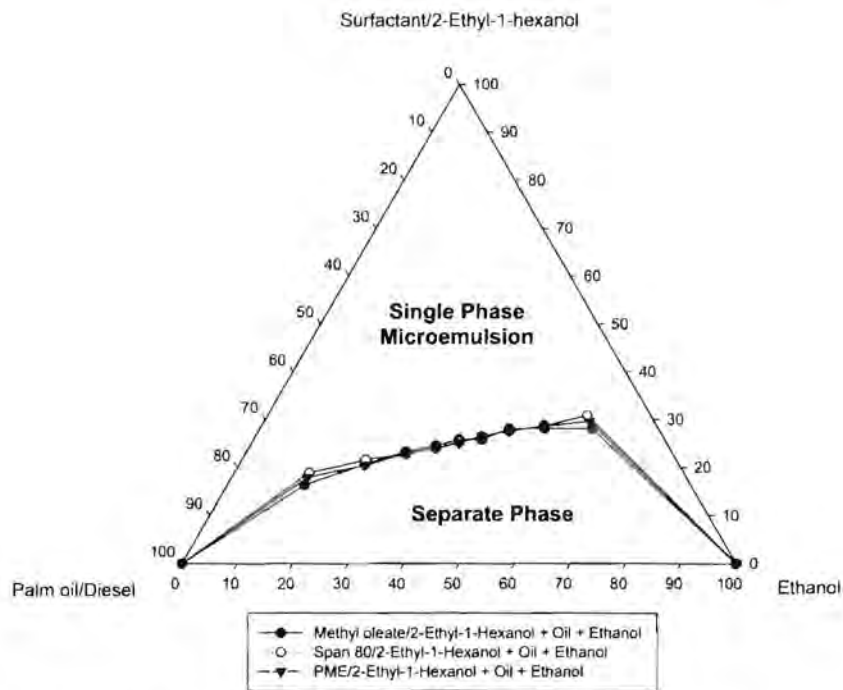
Figure 5 Pseudo ternary phase diagram of microemulsion biofuel systems using methyl oleate, Span 80 and PME as a surfactant at surfactant/2-Ethyl-1-hexanol molar ratio of 1:8 with a palm oil/diesel at ratio of 1:1 (v/v) at room temperature (25±2°C).

Effect of Surfactant's Structures

Figure 4 and Figure 5 present the pseudo ternary phase diagram of microemulsion fuel systems with palm oil/diesel blend at a ratio of 1:1 (v/v) using 1-octanol and 2-ethyl-1-hexanol as a cosurfactant at the molar ratio of 1:8; respectively. The plotted data reveal the miscibility curves of methyl oleate (black circle), Span 80 (white circle) and biodiesel or known as palm oil methyl ester (PME) (black triangle) systems.

Two pseudo ternary phase diagrams in Figure 4 and Figure 5 indicate that when amount of ethanol in biofuel solutions increased, the additional surfactant concentration was required to formulate a single phase microemulsion biofuel. At very high fraction of ethanol, surfactants used to form a single phase microemulsion biofuel decreased and then, no surfactant was required to solubilize at 100% of ethanol. This trend are followed the works of Attaphong et al. (2010) and Arpompong et al. (2014).

For the effects of surfactant's structure on the phase behavior, a minimum concentration of surfactants required to solubilize all components and form a single phase microemulsion were not different significantly. The reason for this could be due to the fact that the hydrophilic-lipophilic balance (HLB) value of these surfactants is almost similar. The HLB value of methyl oleate, Span 80 and biodiesel (PME) are 4.0, 4.3 and 4.2, respectively. Therefore, the polarity of surfactants interacted similarly to the oil and ethanol phase in microemulsion systems. This result is accordance with the work from Balcan et al. (2014).

Effects of Cosurfactant's Structures

Figures 6 to 7 show the effect of cosurfactant's structures on the phase behaviors of methyl oleate, Span 80 and PME systems, respectively. These fuel systems consist of palm oil/diesel blend at a ratio of 1:1 (v/v) with ethanol and surfactant/cosurfactant at a molar ratio of 1:8 at room temperature. 1-Octanol and 2-ethyl-1-hexanol were used as a cosurfactant for the comparison in this work. For 1-octanol, it is a medium chain alcohol (or alkanol) with linear structure but the structure of 2-ethyl-1hexanol is a branching isomer of octanol. When the amount of ethanol increases to 30 vol.% of methyl oleate's system, the added surfactant between using 1-octanol and 2-ethyl-1-hexanol as a cosurfactant was slightly different accounting for 1-2 vol.%. At higher fraction of ethanol, the amount of surfactant used to stabilize all components to become a single phase microemulsion biofuel was slightly increased by 2-3 vol.%.

For the pseudo ternary phase diagrams as shown in Figures 6 to 8, it was found that 2-ethyl-1hexanol system more slightly required about 1-4% of surfactant than that of 1-octanol system at lower ethanol fraction. These results can be explained that the cosurfactant structures did not affect to surfactant concentration to formulate a single phase microemulsion biofuel, since branching structure of cosurfactant has less influence on the phase behavior of microemulsion biofuel than the number of carbon chain length of cosurfactants. This result is in agreement with the studies of Attaphong et al. (2010) and Arpompong et al. (2014).

Figure 6 Pseudo ternary phase diagram of methyl olelate/1-octanol and methyl olelate/2-ethyl-1-hexanol at surfactant/cosurfactant molar ratio of 1:8 with a palm oil/diesel at ratio of 1:1 (v/v) at room temperature (25±2°C).
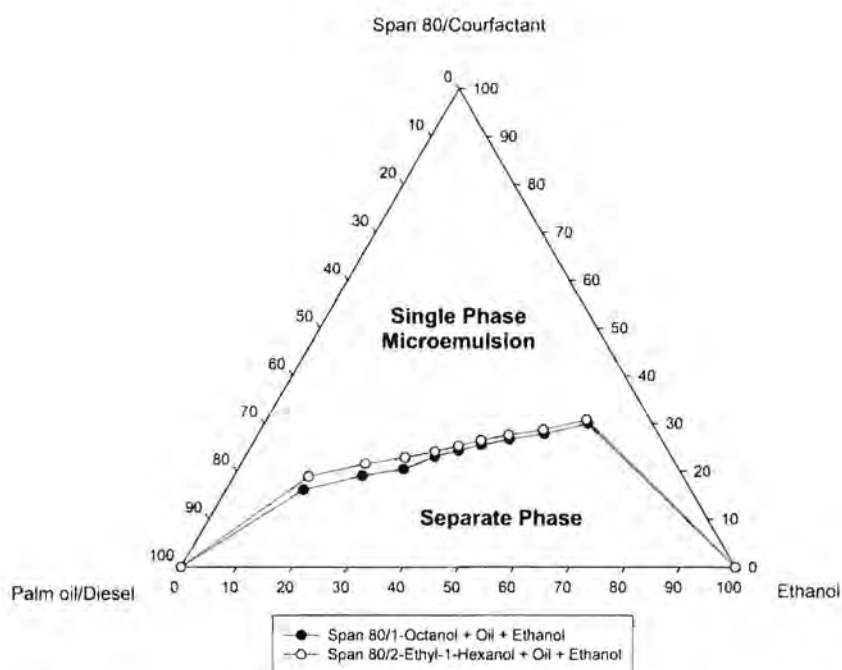
Figure 7 Ternary phase diagram of Span 80/1-octanol and Span 80/2-ethyl-1-hexanol at surfactant/cosurfactant molar ratio of 1:8 with a palm oil/diesel at ratio of 1:1 (v/v) at room temperature (25±2°C).
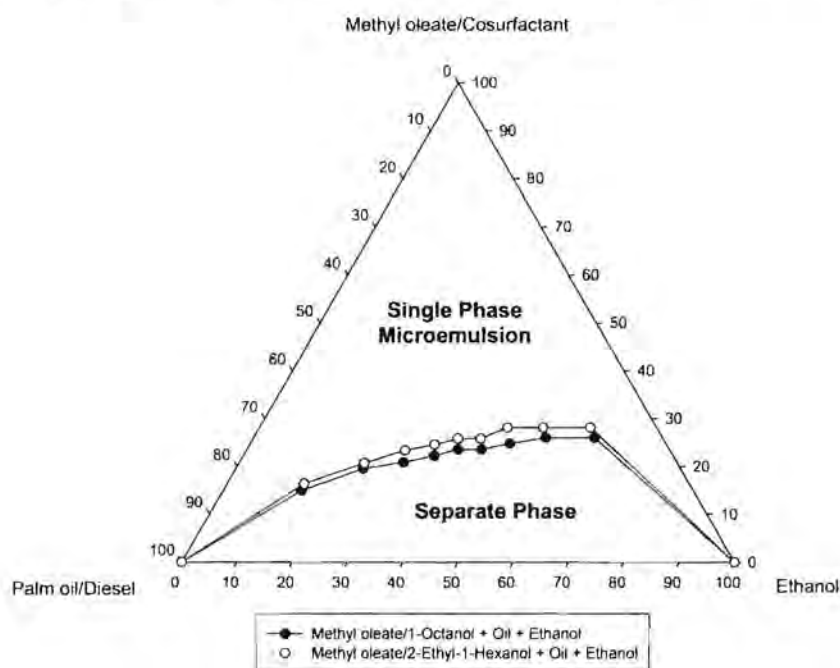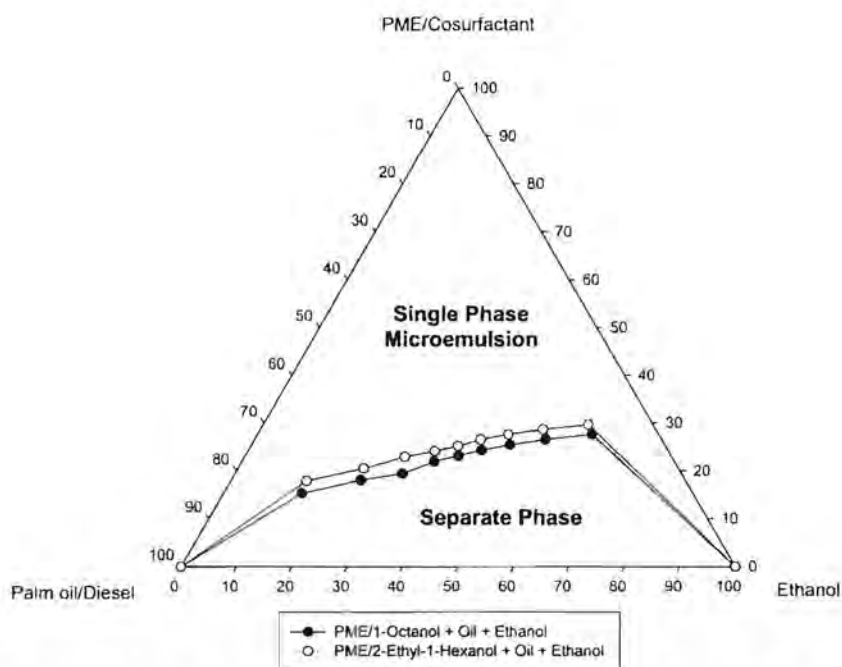

Figure 8 Ternary phase diagram of PME/1-octanol and PME/2-ethyl-1-hexanol at surfactant/cosurfactant molar ratio of 1:8 with a palm oil/diesel at ratio of 1:1 (v/v) at room temperature (25±2°C).

Effect of Types of Palm Oil

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

Amount of Surfactant Required to Formulate Single Phase Microemulsion Study

The effect of palm oil type, palm oil-olein (PO-olein) and palm oil – RBDPO, on minimum surfactant concentration required to formulate single phase microemulsion shown in Figure 9 and Figure 10 respectively. In comparison with same type of the surfactant, the RBDPO's systems used surfactant concentration slightly less than those of palm oil's system by 2 to 5 %. This could be the fact that RBDPO is a mixture of palm olein (65%) and palm stearin (35%) (Nusantoro, 2007) and/or perhaps the fatty acids in RBDPO can facilitate the surfactant to form a single phase microemulsion. Most types of fatty acid in palm oil are oleic acid (C18:1). For RBDPO, palmitic acid (C16:0) is the major fatty acid composition followed Table 2.
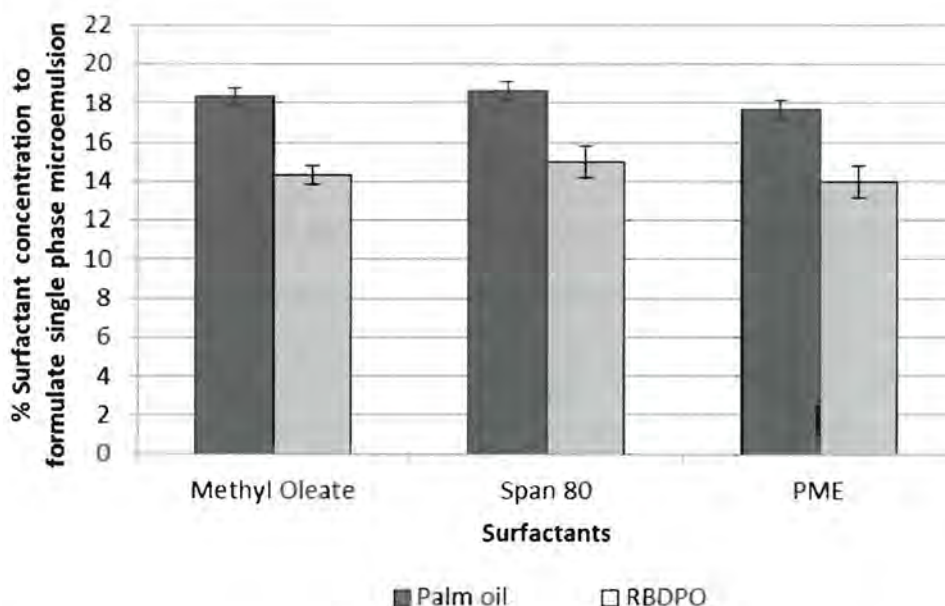
Figure 9 Minimum total surfactant concentration (%) to formulate single phase microemulsion versus types of surfactant and 1-octanol as a cosurfactant at a molar ratio of 1:8 compared with a palm oil/diesel and RBDPO/diesel blends at a ratio of 1:1 (v/v) with 20 vol.% of ethanol at room temperature (25±2°C).
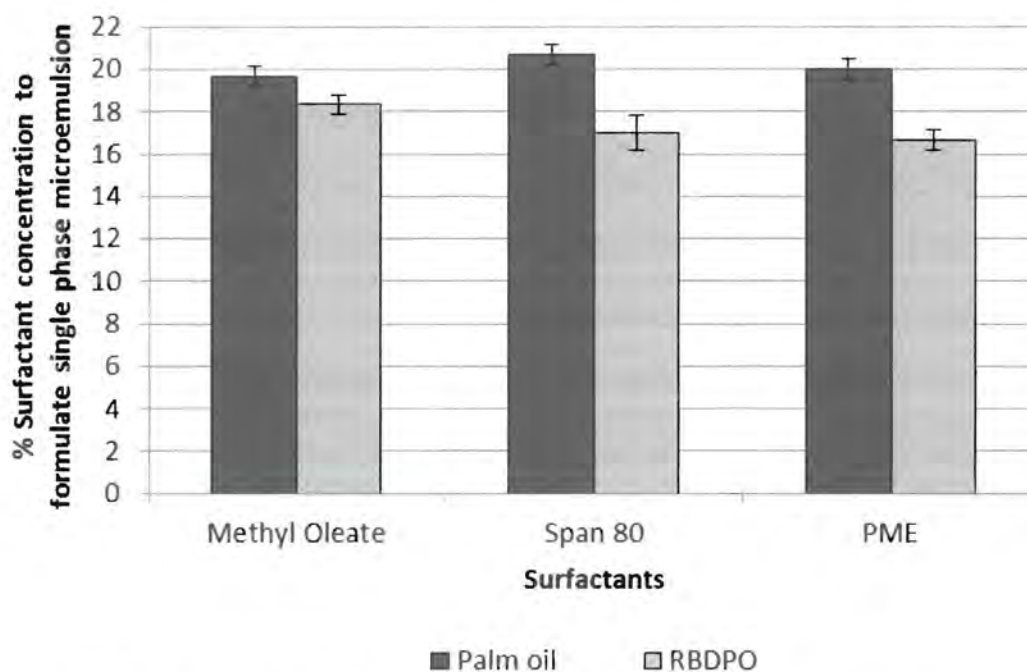
Figure 4.10 Minimum total surfactant concentration (%) to formulate single phase microemulsion versus types of surfactant and 2-ethyl-1-hexanol as a cosurfactant at a molar ratio of 1:8 compared with a palm oil/diesel and RBDPO/diesel blends at a ratio of 1:1 (v/v) with 20 vol.%. of ethanol at room temperature (25±2°C).

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

Table 2 Fatty acid compositions of palm oil and RBDPO

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

The data from Che Man et al., 1999

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

The results in Figures 12 to 13 show the effect of cosurfactant's structures in various surfactant systems; methyl oleate, Span 80 and PME, the surfactant concentration with 1-octanol systems as a cosurfactant required to produce to a single phase microemulsion was less than those of 2-ethyl-1-hexanol system for both palm oil olein and RBDPO systems. Furthermore, the RBDPO systems needed lower surfactant concentration than those of palm oil olein systems (16% for 2-ethyl-1-hexanol system and 15% for 1-octanol system).

Even though, there are evidences that palm oil - RBDPO has a remarkable benefit in terms of surfactant loading, it can be a potential option to replaced palm oil olein. However, the limitation of RBDPO is the phase separation due to wax or solid fat formation at its below melting point. The RBDPO generally contains palm stearin fraction (35%) (Nusantoro, 2007) which could form a crystalline semi-solid fat at low temperature.
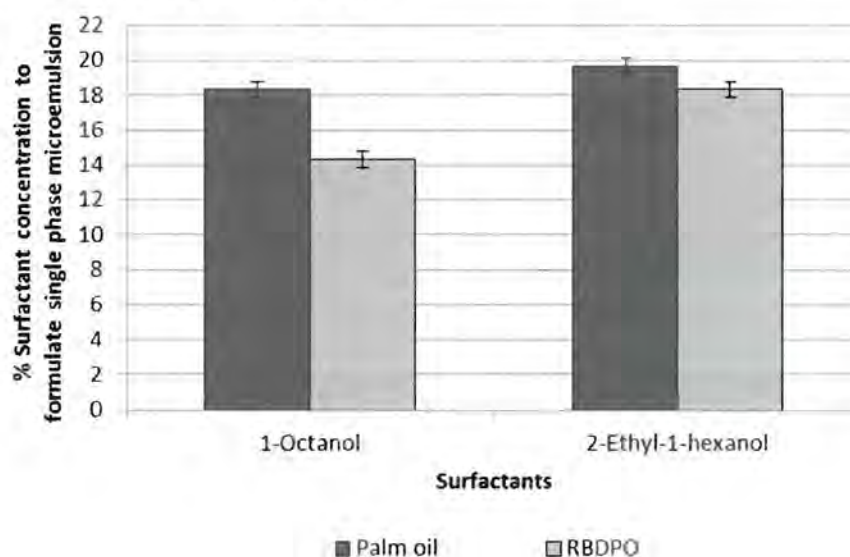
Figure 12 Minimum total surfactant concentration (%) to formulate single phase microemulsion of methyl oleate systems versus types of cosurfactant at a molar ratio of 1:8 with a palm oil/diesel blends at a ratio of 1:1 (v/v) and 20 vol.%. of ethanol at room temperature (25±2°C).
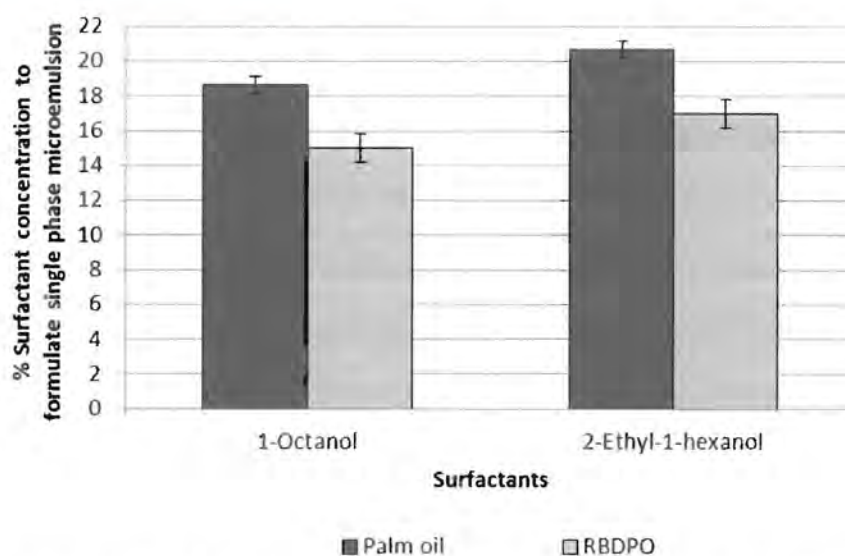
Figure 13 Minimum total surfactant concentration (%) to formulate single phase microemulsion of Span 80 systems versus types of cosurfactant at a molar ratio of 1:8 with a palm oil/diesel blends at a ratio of 1:1 (v/v) and 20 vol.%. of ethanol at room temperature (25±2°C).
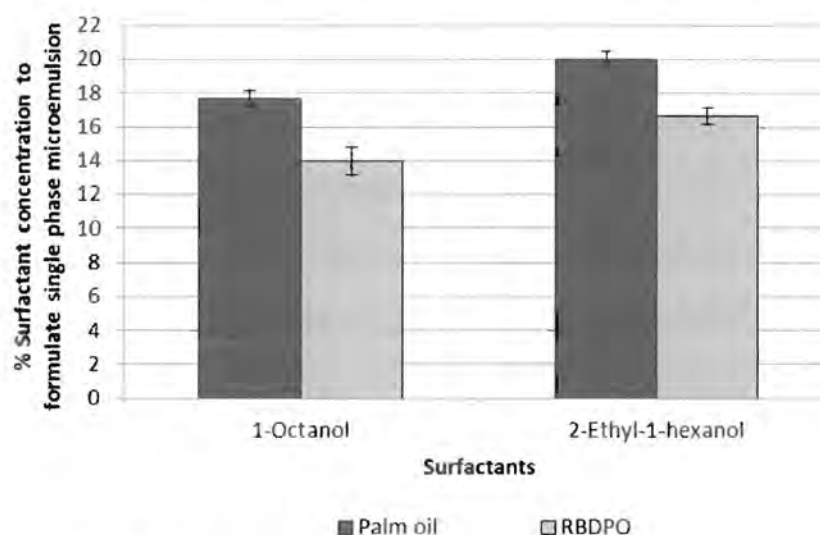
Figure 14 Minimum total surfactant concentration (%) to formulate single phase microemulsion of Span 80 systems versus types of cosurfactant at a molar ratio of 1:8 with a palm oil/diesel blends at a ratio of 1:1 (v/v) and 20 vol.%. of ethanol at room temperature (25±2°C).

4.3 Droplet Size and Size Distribution measurement

Microemulsion droplet size and size distribution of the biofuels was analyzed by monomodal or multimodal between intensity versus diameter of droplet from dynamic light scattering (DLS), Nano Zetasizer 3600 (Malvem). The scattering intensity from measuring by DLS can be used to define the amount of microemulsion droplets (percentage) of each mean droplet size. Microemulsion droplet size was studied to determine the correlation of kinematic viscosity

of biofuels with other biofuel's properties. This section, the effects of surfactant's and cosurfactant's structures on droplet size in palm oil/diesel blend with ethanol were study.

Effect of surfactant's structures

From Table 3, the microemulsion biofuel systems were prepared at 25±2°C, with surfactant/cosurfactant molar ratio of 1:8. Surfactant and cosurfactant were added in palm oil/diesel blend at a ratio of 1:1 (v/v) with 20 vol.% ethanol. For the effect of surfactant's structure on droplet size, the results showed that methyl oleate's and PME's systems had microemulsion droplet size ranging from 5,228-5,495 nm with 100% intensity, the proximity of droplet size and distribution of those affected from the similarity of methyl ester group in the head group (hydrophilic group) of both surfactants. Most droplet size of Span 80's systems ranging from 16.16-20.31 nm at 91-97% and another size ranging from 4,925-5,207 nm had about 3-9% which was much smaller than methyl ester surfactants. It could be due to the fact that head group of Span 80 comprising of hydroxyl groups that has more hydrogen bond than the other surfactant systems. Therefore, Span 80 can stabilize ethanol in oil phase less than methyl oleate and PME, the microemulsion droplet size of Span 80's system was smaller than other systems. Note that palm oil/diesel blend without surfactant system, the droplet size of palm oil /diesel blend was about 4.32 with 100% intensity which was lower than those of all microemulsion fuel performed in this study.

Table 3 Comparison of the droplet size and distribution of microemulsion biofuels with palm oil/diesel blend (1:1 v/v) at room temperature (25±2°C)

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

Table 4 Comparison the time that the sample of Span 80's systems with palm oil/diesel blend (1:1 v/v) and 20 vol.% ethanol was placed before measured droplet size and distribution at 25±2°C

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

Effect of Cosurfactant's Structures

The effect of cosurfactant's structure on microemulsion droplet size can be explained by Table 4 that the droplet size of 1-octanol's systems was in proportion to 2-ethyl-1-hexanol's system. Therefore, it can be concluded that cosurfactant's structures in terms of branch and linear structure did not affect to the size of reverse micelle microemulsion.

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

Considering the microemulsion samples which placed at room temperature of 25±2°C for 7 days before measurement, the droplet size distribution of 1-octanol's and 2-ethyl-1-hexanol's system ranging from 2,500-5,500 nm decreased by 3-9 % intensity. On the other hand, the droplet size of both cosurfactant systems ranging from 15-25 nm increased after holding the sample for 7 days. This fact indicates a time evolution in microemulsion stability of microemulsion droplet and size distribution. This can be concluded that much smaller size of microemulsion droplet affect to their stability due to very large entropy of dispersion (Akhtar ,1996).

Relation of Droplet Size Distribution with Kinematic Viscosity

Stokes–Einstein's equation (2) can be used to explain the correlation between droplet size and kinematic viscosity of microemulsion biofuels. Hydrodynamic radius (R_h) or referred as microemulsion droplet size is inversely proportional to viscosity of biofuels.

The results from Table 7 show that the droplet size of Span 80's systems were smaller than those of methyl oleate's and PME's systems. Span 80's systems had higher viscosity than

those of the other fuel systems. This results are followed the Stokes–Einstein's equation and in accordance with Arpornpong *et al.* (2014). In comparison with droplet size distribution and kinematic viscosity, there was no significant trend observed between two microemulsion biofuels with different types of cosurfactant.

Table 5 Comparing relation of droplet size with kinematic viscosity of palm oil/diesel blend (1:1 v/v) and 20 vol.% ethanol with surfactant/cosurfactant at molar ratio of 1:8 at 25±2°C

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

Fuel Properties Determination

Property of biofuels is an important factor to utilize for many applications such as vehicles and industries. In this section, the effect of surfactant's and cosurfactant's structures and types of palm oil on their fuel properties including kinematic viscosity, droplet size, turbidity, cloud point, density and heat of combustion were evaluated. The microemulsion biofuel systems were palm oil/diesel and RBDPO/diesel blends with 20 vol.% of ethanol. In addition, the appropriate surfactant concentration of each system to formulate all microemulsion biofuels was selected at 5% (v/v) of upper miscibility curve.

Table 6 and Table 7 show the composition of microemulsion biofuels of palm oil's and RBDPO's system with 20 vol.% of ethanol, respectively. Surfactant and cosurfactant of a molar ratio of 1:8 was prepared and blended with oil phase, a ratio of palm oil/diesel and RBDPO/diesel blends 1:1 (v/v).

Table 6 Composition of microemulsion biofuels in palm oil - olein system with 20 vol.% of ethanol used for fuel property determination

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

Table 7 Composition of microemulsion biofuels in RBDPO's system with 20 vol.% of ethanol used for studied fuel properties determination

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

Kinematic Viscosity Measurement

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

- Effect of Types of Palm Oil

Comparing with types of palm oil from Figure 15 and Figure 16, the palm oil olein/diesel and RBDPO/diesel blends with the same type of surfactants/cosurfactants system had no difference in kinematic viscosity at 40°C. The kinematic viscosity of neat palm oil and RBDPO are 40.88 (Anantarakitti et al., 2014) and 38.9 cSt (Sukimo et al., 2010), respectively.

Figure 15 Kinematic viscosity (cSt) at 40°C versus types of surfactant and 1-octanol as a cosurfactant at a molar ratio of 1:8 compared with a palm oil/diesel and RBDPO/diesel blends at a ratio of 1:1 (v/v) with 20 vol.% of ethanol.

- **Effect of Surfactant's Structures**

To study the effect of surfactant's structures on kinematic viscosity at 40°C, the various surfactants including methyl oleate, Span 80 and biodiesel (PME) were selected as a surfactant which was mixed with 1-octanol and 2-ethyl-1-hexanol at a ratio of 1:8 as shown in Figure 12 and Figure 13; respectively. It was found that, the kinematic viscosity of each of microemulsion biofuel was ranging from 5.0-7.0 cSt and the viscosity of Span 80 systems was higher than those of methyl oleate and PME systems, respectively. This is due to the fact that the larger head (hydrophilic part) of Span 80 surfactant and more hydrogen bond between the molecules than methyl oleate and PME, resulting in the Span 80 has higher viscosity than those of the other surfactants, therefore, the kinematic viscosity of Span 80's system was higher than that of both methyl oleate and PME systems. Because of the similar structures between methyl oleate and PME, their kinematic viscosities were not significantly different in figure.
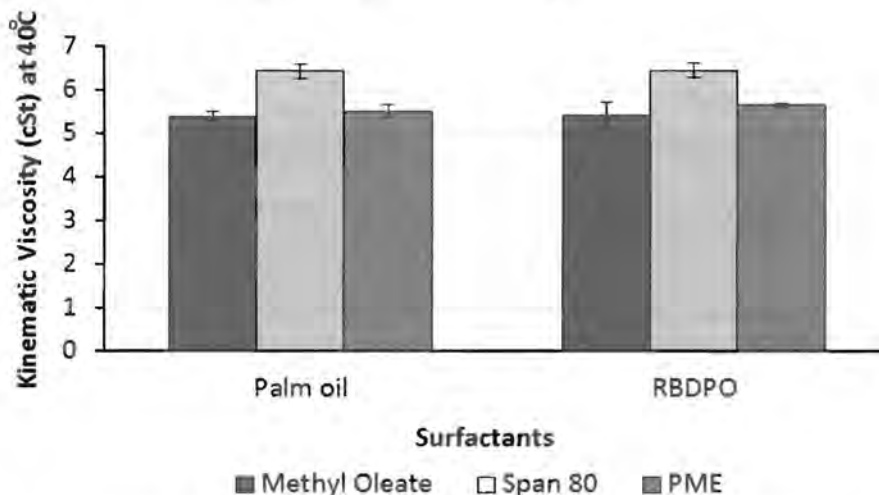
Figure 16 Kinematic viscosity (cSt) at 40°C versus types of surfactant and 2-ethyl-1-hexanol as a cosurfactant at a molar ratio of 1:8 compared with a palm oil/diesel and RBDPO/diesel blends at a ratio of 1:1 (v/v) with 20 vol.% of ethanol.

Effect of Cosurfactant's Structures

The results from Figure 4.14 and Figure 4.15 display the kinematic viscosities of palm oil/diesel and RBDPO/diesel blended with 20 vol.% of ethanol. In comparison between types of surfactant and cosurfactant, the kinematic viscosity of 2-ethyl-1-hexanol's systems was less than those of 1-octanol's systems. It can be in line with previous study (Anantarakitti et al., 2014) that the different structures of straight chain (1-octanol) and branching chain alcohol (2-ethyl-1-hexanol) were not affected to kinematic viscosity of microemulsion biofuels.
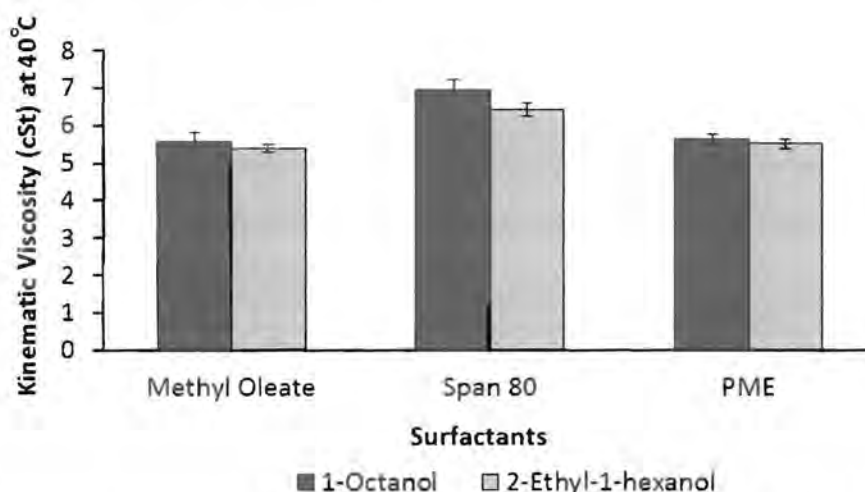
Figure 17 Kinematic viscosity (cSt) at 40°C versus types of surfactant and cosurfactant at a molar ratio of 1:8 with a palm oil/diesel blends at a ratio of 1:1 (v/v) and 20 vol.%. of ethanol.

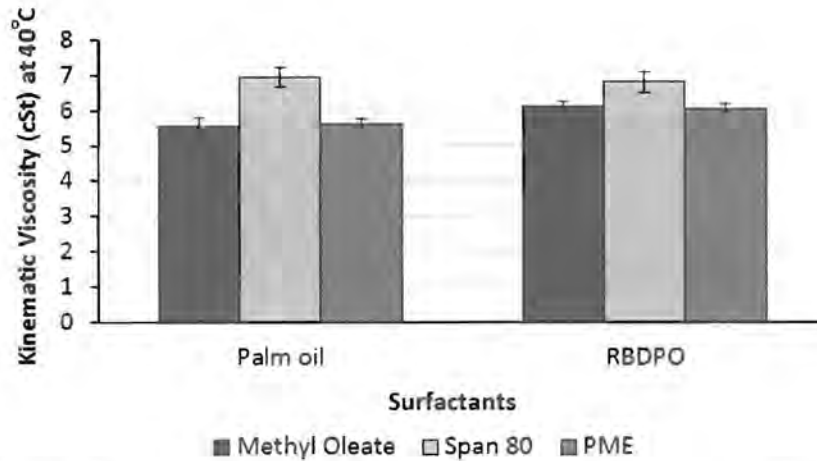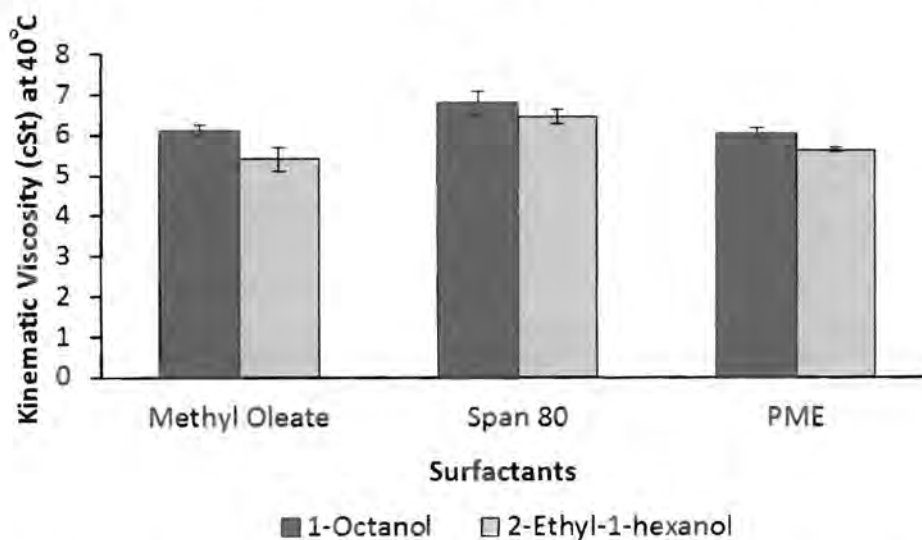**Figure 4.18** Kinematic viscosity (cSt) at 40°C versus types of surfactant and cosurfactant at a molar ratio of 1:8 with a RBDPO/diesel blends at a ratio of 1:1 (v/v) and 20 vol.%. of ethanol.

Turbidity

For turbidity of microemulsion biofuels, the measurement was carried out using by UV spectroscopy. Due to the limit of detection, however, the absorbance of microemulsion biofuels

could not be observed in which the appeared noise peaks ranging in 200-500 nm were overlapped with interesting peak. The turbid solution was then observed by visual observation.

Figure 16 shows the phase behavior of palm oil/diesel blend with ethanol with methyl oleate/1-octanol as surfactants. It can be noted that the vial No. 1 to No. 7 depicted a separate phase. When added more surfactants, the mixture of liquid fuels can form a single phase microemulsion as illustrated in vial No. 8.

In addition, it can be explained according Figure 16 that when increased the surfactant concentration, the phase behavior of microemulsion biofuels had changed from Winsor Type II to a single phase microemulsion as it can be seen from that the phase behavior and turbidity between RBDPO and palm oil olein systems when using Span 80/1-octanol as a surfactant system. This trend was also observed in Figure 17. However, based on Figure 17, it is interesting to note that there was solid fat precipitates in RBDPO's system after placed the sample at room temperature (25±2°C) for 48 hours. The melting point of RBDPO was reported ranging from 33-39°C (Morad et al., 2006). This precipitate could be a solid fat from crystallization of fatty acids in vegetable oil.

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

Figure 16 Phase behavior and turbidity varying surfactant concentration of methyl oleate/1-octanol with a palm oil/diesel blends at a ratio of 1:1 (v/v) and ethanol.

Figure 17 Phase behavior and turbidity compassion of Span 80/1-octanol system in RBDPO/diesel blend and palm oil/diesel blend at a ratio of 1:1 (v/v) with ethanol.

The comparison of turbidity for all microemulsion biofuels with regular diesel fuel is shown in Figure 18, there is no significant difference through visual observation. The appearance of microemulsion solutions were clear and transparent and their color were naturally yellow. Additionally, the color intensity of the biofuels depending on fraction of vegetable oil and diesel used for forming microemulsion biofuels and natural color of raw materials.

Figure 18 Turbidity of all of palm oil/diesel blend with 20 vol.% of ethanol systems after held at room temperature (25±2°C) for 48 hours.

Cloud Point

Cloud point is the temperature of the fuel in which starting to form crystals or cloud solution. In typical, petroleum industries substantially concerned about operating temperature because at temperature lower cloud point, solidified wax from the oil clogs injectors and filters in diesel engines and makes fouling's problem in pipeline and heat exchanger (Mittelbach, 2004). In this study, the cloud point of microemulsion biofuels was measured using cooling bath

following to ASTM D 2500. The effects of types of surfactant and cosurfactant on cloud point of palm oil/diesel blend (1:1 v/v) with ethanol 20 vol. % systems were evaluated. The fuel was observed to be the cloudiness when the temperature decreased in every 2°C.

The result from Table 8 demonstrates the phase change of the microemulsion biofuels with methyl oleate and PME. The cloud phases were appeared at both methyl oleate and PME systems at 5°C, but the cloud phase of Span 80 systems was 3°C which slightly lower than those of methyl oleate and PME systems. However, these biofuels' cloud point were similar to cloud point of biodiesel (B100) while these were higher than that of diesel standard (-15°C) while these were close. In comparison with palm oil/diesel blend and regular diesel, it can be seen that the cloud point of the microemulsion fuel was substantially higher than that of regular diesel standard. This could be because the cloud point of vegetable oil/diesel blend depends on the nature of vegetable oils such as cloud point of palm oil (15°C) and rapeseed oil (-4°C) (Balat et al., 2008).

Table 8 Cloud point, density and heat of combustion of microemulsion biofuels compared with diesel and palm oil/diesel blend and 20 vol.% of ethanol

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

[a] The data from Arpompong et al., 2014

Density

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

Heat of Combustion

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

5. Conclusions

For phase behavior study, surfactant structures were not affected to concentration of surfactants in palm oil/diesel blend with ethanol to formulate a single phase microemulsion. For microemulsion droplet size and size distribution study, droplet size of Span 80 system was smaller than that of methyl oleate and PME systems. This led to the kinematic viscosity of Span 80 systems was higher than those of the other systems. However, cloud point, density and heat of combustion of each microemulsion systems have no significant difference. For the effect of cosurfactant structures in which branching chain of 2-ethyl-1-hexanol was compared with 1-octanol, types of cosurfactant did not affect to phase behavior, kinematic viscosity, droplet size, turbidity, cloud point, density and heat of combustion. In comparison, palm oil and RBDPO systems were observed their phase behavior and kinematic viscosity, the fatty acid composition of palm oil and RBDPO was differrent. As a result, minimum amount of surfactant required to formulate a single phase microemulsion of RBDPO system were slightly less than that of palm oil system but their kinematic viscosity and turbidity have no difference significantly.

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Chapter 2:

Palm oil based Microemulsion Biofuels using Renewable based Nonionic surfactants: The Effect of Ethanol/Butanol in Palm Oil/Diesel Blends

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Abstract

Vegetable oil is an option for renewable fuels production to replace the diesel oils. Because vegetable oils have higher viscosity than diesel oils, the usability of neat vegetable oils can lead to engine stability problems such as poor atomization of the fuel. However, vegetable oil viscosity can be reduced by blending with diesel fuel in thermodynamically stable mixtures using microemulsion formulation. This work focused on the formation of microemulsion biofuels using two type of a palm oil/diesel and a refined bleached deodorized palm oil (RBDPO)/diesel blend as an oil phase with an ethanol and butanol blend as a viscosity reducer. The ester based surfactant with similar structure, Methyl oleate (MO) and palm oil methyl ester (PME) were used as a surfactant and 1-octanol was used as a cosurfactant at the mixing ratio of 1:8 M/M surfactant: cosurfactant by molar. This work studied the effects of surfactant structure, ethanol/butanol blending ratios, palm oil/diesel blending ratios on phase behavior, kinematic viscosity, microemulsion droplet size and fuel properties of formulated microemulsion fuels and compared their fuel properties to a regular biodiesel (B100) and diesel (No.2). The results show that the phase behaviors of different surfactant systems had similar trend of the miscibility curve. The microemulsion biofuels containing butanol in the mixture showed remarkably a decrease in the area of two-phase separation. Based on our findings, the blending ratios of ethanol/butanol is a major parameter for optimizing the viscosity and other fuel properties of microemulsion biofuels.

KEYWORDS: Microemulsion Biofuel, Ethanol, Butanol, Palm oil, Nonionic surfactant, Kinematic viscosity

1. Introduction

The alternative fuels from vegetable oils are an option for renewable fuels production to replace or partial substitute diesel oils. The vegetable oils have the same comparable physical and chemical properties to those of diesel oils thus they have comparable performance to utilize in diesel engines (Pryde, 1983; Ryan et al., 1984; Altin et al., 2001). However, usability of neat vegetable oils can lead to engine stability problems because of their viscosity being higher than that of diesel such as a poor atomization of fuel. There are four methods that can reduce viscosity of vegetable oils: (1) vegetable oil/diesel blends, (2) pyrolysis, (3) vegetable oil transesterification to fatty alkyl esters or biodiesel, and (4) vegetable oil-based microemulsification (Balat, 2008). Transesterification is widely used method to produce biofuel, known as biodiesel. Transesterification reaction of triglycerides with an alcohol in the presence of a catalyst produces fatty acid methyl ester (FAME) as a main product and glycerol as a co-product. In addition, a by-product, glycerol requires a complex process to purify, resulting in additional energy consumption and environmental problems. (Galan et al., 2009; Pagliaro et al., 2007).

Due to the disadvantages of the transesterification process, microemulsions of vegetable oils can be considered as an alternative method to omit environmental burdens. Microemulsion biofuels can formulate with supplementary viscosity reducers such as methanol, ethanol or butanol (Goering et al., 1984; Ma et al., 1999, Sabatini et al., 2012). This biofuel is a transparent and thermodynamically stable of mixed liquid fuels classified into Winsor Type II microemulsion (W/O) where the polar alcohol phase is solubilized in reverse micelles occurring in the non-polar phase (oil). Ethanol has been used as a polar phase to produce microemulsion fuels. The benefit of the use of ethanol is that it is a renewable energy source which produces from very common crops such as sugar cane and corn. However, ethanol has an extremely low cetane number whereas diesel engines prefer high cetane number fuels. Therefore, butanol has been observed due to its comparable fuel property. Butanol is a renewable biofuel similar to ethanol but it has higher heating value and cetane number, more miscibility with diesel and less hydrophilic moiety compared to those of methanol and ethanol (Altun et al., 2011; Sukjit et al., 2013; Yoshimoto et al., 2013).

Since alcohol-diesel blends are limited because they are immiscible at wide range of temperature. This study, nonionic surfactant is used as an emulsifier to stabilize the miscibility of ethanol and diesel by Winsor Type II microemulsion. The nonionic surfactants have been found as an appropriate system for microemulsion formation or many reasons (Arpornpong et al., 2014). Methyl oleate (MO) has been used as a nonionic surfactant in microemulsion biofuel formation due to the fact that it can dramatically decrease the bulk viscosity and produce uniformly size of microemulsion droplets while the least amount of surfactant is required for solubilizing ethanol-in-oil in the microemulsion system. Octanol has been used as a cosurfactant because it can work well with methyl oleate (Arpornpong et al., 2014) resulting lower amount of surfactant and cosurfactant added to the system. For more practical usability of chemicals as raw material selection that can reduce viscosity by microemulsion technique, palm oil methyl ester (POME) known as biodiesel can be used as a surfactant for reverse micelle microemulsion. Because POME is an amphiphile molecule contained hydrophilic group of ester and hydrophobic group of alkyl chain length. Evenmore, it is naturally derived products which can help reduce dependency on foreign oil. Therefore, the use of POME or biodiesel as an emulsifier in microemulsion biofuel can directly use with less engine problems.

The objective of this research is to formulate single phase reverse micelle microemulsion consisting of palm oil/diesel blend for stabilizing alcohol in the oil phase. This work is divided in four topics including;

1) To study the effect of surfactant structure on phase behavior of palm oil/diesel blends.
2) To study the effect of palm oil/diesel and ethanol/butanol blending ratios) that appropriate for form a single phase reverse micelle microemulsion of palm oil/diesel blends.
3) To study the use of refined bleached deodorized palm oil (RBDPO)/diesel blends as an oil phase on the minimum surfactant used to formulate single phase microemulsion and kinematic viscosity study compare to palm olein/diesel blends.
4) To determine the fuel properties of the microemulsion biofuels including; kinematic viscosity at 40 °C, gross heat of combustion, cloud point, flash point, in comparison to those of the No.2 diesel fuel.

2. Theoretical Background

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

Palm Oil

Several types of vegetable oil have been utilized as a biofuel. Among them, palm oil is one of the high potential feedstock. Rupilius and coworker (2007) showed palm oil has the lowest cost for biodiesel production and needs far less agricultural land for production compared with soya bean, rapeseed, sun-flower seed and coconut (Table 2.1). The production and export trends in 2012 of palm oil in Thailand are 1,700 and 520, respectively. The volume of production and exports increased in every year at high rate of production (Mukherjee and Sovacool, 2014). This can be implied that palm oil is an appropriate vegetable oil for producing biofuel in Thailand.

Refined Bleached Deodorized Palm Oil (RBDPO)

Palm oil are made using milling and refining process, the oil is filtered and bleached to remove impurities. Finally, physical refining removes smell and color of oil to produce refined bleached deodorized palm oil (RBDPO). Because of the lower price of RBDPO than refined bleached deodorized palm olein (RBDPOL), 520 and 615 USD/tones, respectively (http://www.palmoilanalytics.com, retired at Jan 2015) . Due to economical perspective RBDPO

is selected to formulate as an alternative vegetable oil for producing microemulsion biofuels in this study.

Vegetable Oil based Microemulsification

Microemulsions are thermodynamically stable emulsions that include water and oil domains separated by surfactant film (Rosen, 1989). Microemulsions can exist in four Winsor Type microemulsion phases. Winsor Type I (oil-in-water or O/W) microemulsions are normal micelles in equilibrium with an excess oil phase, while Winsor Type II (water-in-oil or W/O) microemulsions are reverse micelles in equilibrium with an excess water. Winsor Type III microemulsions exhibit three phases, excess oil and water phases in equilibrium with a middle phase containing oil, water, and surfactant. In a middle phase microemulsion, increasing surfactant concentration causes the amount of the middle phase to increase until all of the oil and water coexists in a Winsor Type IV single phase microemulsion (Rosen, 1989). Microemulsion-based biofuels, or hybrid fuels, are transparent and thermodynamically stable of Winsor Type II microemulsions (See Figure 1) which the polar phase is solubilized in the reverse micelles occurring in the non-polar phase (vegetable oil/diesel blended). Alcohol is used in place of water as the polar phase which disperses in the vegetable oil/diesel blend.
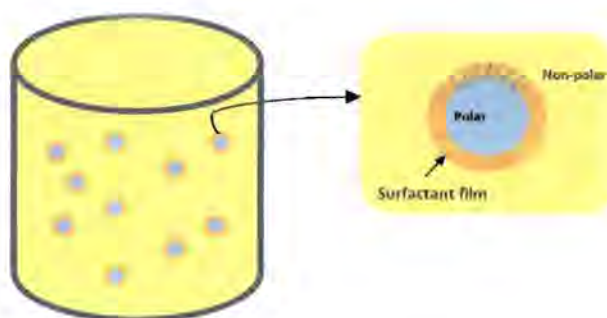
Figure 1 Schematic diagram of Winsor Type II microemulsions and their reverse micelle structure.

Alcohol Blended

The utilization of ethanol in diesel fuel can yield a significant reduction of exhaust emissions in terms of CO and NO_x (Ajav et al., 1999) and particulate matter (PM) emissions for motor vehicle. However, there are many hindrances in using ethanol in diesel engine (Xing-cai et al., 2004); Ethanol has limited solubility in diesel fuel, ethanol fuel has an substantially low cetane number, whereas diesel engines prefer high cetane number fuels, which makes auto-ignition easy and gives a short ignition delay; the dynamic viscosity of ethanol is much lower than that of diesel fuel, so that the lubricity, as a result is a potential concern of ethanol-diesel blend fuel; and ethanol has low flash point

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

Among alcohols, butanol has recently drawn particular attention as a renewable biofuel for diesel engines due to its higher heating value and cetane number and less hydrophilicity

compare to diesel, and more miscibility compared to methanol and ethanol (Altun et al., 2011; Sukjit et al., 2013; Yoshimoto et al., 2013). Recent studies recommended that butanol can be a better alternative biofuel than ethanol for using in diesel engine (Sukjit et al., 2012). However, there is a lack of detailed examinations on the effects of butanol addition to diesel blends on engine performance and particulate emissions.

Although ethanol is generally used for blending in diesohol (i.e., ED95), butanol is an alcohol which has higher solubility in diesel than ethanol. Areerat and coworkers (2009) investigated on the utilization of biodiesel as an additive in diesohol preparation, three types of biodiesel-methyl, ethyl, and butyl esters-were prepared from palm oil through transesterification using a conventional based catalyst. They found that the use of butanol in diesohol could solve the problem of fuel instability at low temperatures because of its higher solubility in diesel fuel. The fuel property study showed that the blends containing butanol have better properties than those of the blends containing ethanol (properties closer to diesel).

Surfactants and Cosurfactants

To overcome the immiscibility of alcohol and diesel, surface active agents or surfactants are used as emulsifiers to stabilize the miscibility phases of alcohol and diesel through microemulsification process. Surfactants are typically divided into four types anionic, cationic, nonionic and zwitterionic surfactants. Among them, nonionic surfactants have been found to be an appropriate surfactant for microemulsion formation of vegetable oil/diesel and ethanol blends from many reasons (Arpornpong et al. 2014) such as it has low HLB or it can work well with oil systems; nonionic surfactants can work without salt and they are no SO_x and NO_x emissions; and some special types of nonionic surfactant are biodegradable because it can derived from renewable feedstocks.

Alcohol Ethoxylates Surfactant

Alcohol ethoxylates are classified as a nonionic surfactant that can be derived from a bio-based product through oleochemical process. In petrochemical process, however, alcohol extoxylate is produced through ethoxylation. An alcohol is treated with ethylene oxide and potassium hydroxide (KOH), which serves as a catalyst. The reactor is pressurised with nitrogen and heated to about 150 °C. Typically, 5 to 10 units of ethylene oxide (EO) are added to each surfactant molecule. The amount of ethylene oxide group and the reaction time determine the degree of ethoxylation (the value of n in the equation above), which in turn determines the surfactant properties of the ethoxylated product. The hydrophilicity of the surfactant increases with the value of ethylene oxide group.

Many researchers investigated on various types of surfactant for formulating microemulsion biofuels. Attaphong and coworkers (2012) used the extended-surfactants, which have the intermediate polar groups enclosed between the head and the tail of the surfactant molecule, for forming microemulsions. The extended-surfactants have ethylene oxide (EO) or propylene oxide (PO) groups enclosed between the hydrophilic head and hydrophobic tail to improve polar phase and non-polar phase interaction, respectively. They determined the phase behaviors of carboxylated-based extended surfactants on reverse micelle microemulsion formation with ethanol and canola oil/diesel blends. 1-octanol and 2-ethyl-1-hexanol were used as a cosurfactant. 2-ethyl-1-hexanol is an isomer of octanol with a branched eight-carbon alcohol. Mixtures of surfactant and cosurfactant at fixed molar ratios(1-8, 1-16, and 1-32) were investigated. Different amounts of ethanol (0.5, 1,2, 3, 4 and 5 mL) with 5 mL of the canola

oil/diesel blend were added into the surfactant/cosurfactant mixture to formulate reverse micelle microemulsions. The results showed that the linear chain extended surfactants required less amount of surfactant than branched chain extended surfactants to solubilize all components and produce a single phase microemulsion. When the number of EO groups decreased from 5 to 3 in the extended surfactants led to 3 % to 4 % reduction of the amount of surfactant used. Therefore, the linear surfactant which has the least number of EO groups was identified as the preferred surfactant due to the fact that it needs the least amount of surfactant to achieve the single phase microemulsion. Moreover, they studied the effect of surfactant to cosurfactant ratio, the resulted showed that the phase behavior of microemulsions does not significantly affect by adjusting the ratio of surfactant to cosurfactant.

Another research work of Attaphong and coworkers (2012), they studied the phase behaviors of microemulsion fuels using renewable surfactants (alcohol ethoxylate, and sugar-based surfactants) and compared their results to the surfactant systems used in their previous study (carboxylated-based extended surfactants). They studied three types of noninionic surfactant (linear $C_{10-12}3EO$ OH, linear $C_{12-16}1EO$ OH and linear $C_{12-16}3EO$ OH) and anionic carboxylated-based extended surfactant (linear C_{16-18} 4PO 2EO carboxylate surfactant) with 2-Ethyl-1-hexanol as a cosurfactant. The result from their study showed that salt-free single phase microemulsion fuels were formed with all the surfactants used in this research even at low temperatures. Moreover, they demonstrated that all sugar-based surfactants required higher concentrations than carboxylate-based extended, alcohol ethoxylate, and fatty alcohol surfactants to produce a single phase microemulsion. For alcohol ethoxylate surfactants, linear $C_{12-16}1EO$ OH (L16-1) required the lowest concentration of surfactant. This is because increasing alkyl groups and decreasing EO groups increase hydrophobicity of surfactants which can facilitate the polar phase to solubilize in the oil phase.

Methyl Oleate with Cosurfactants

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

Arpompong and coworkers (2014) studied the effects of surfactant structures including, surfactant saturation, unsaturation, and ethylene oxide groups on phase behavior, kinematic viscosity, and microemulsion-droplet size with the purpose of formulating and optimizing surfactant used in microemulsion biofuel systems. They used four types of nonionic surfactants namely, stearyl alcohol (saturated), oleyl alcohol (unsaturated), methyl oleate (unsaturated with ester groups), and Brij-010 (EO groups). They found that methyl oleate could dramatically reduce the bulk viscosity and produce uniformly size of microemulsion droplets while required the least amount of surfactant to achieve a single phase microemulsion. Its kinematic viscosity at 40 °C of the appropriate fuel condition was 4.0 mm^2/s, which is nearly compared to that of No.2 diesel (1.9-4.1 mm^2/s). They concluded that methyl oleate (MO) is the most appropriate surfactant for this system when compared to the others. The results showed that increasing the cosurfactant

chain length, decreased the amount of surfactant required to form a single phase because the long chain cosurfactant is more suitable for producing stable ethanol-in-oil. For fuel viscosity study, the increasing the carbon chain length of cosurfactants insignificantly increased the kinematic viscosity (from 4.4 to 4.8 mm^2/s at 40 °C). Because the van der Waals forces of the hydrocarbon bonds in cosurfactant or alkanol are likely to be a main factor in determining the overall viscosity of palm oil/ethanol-diesel (Dunn et al., 1994).

Fatty Acid Methyl Ester (FAME) or Biodiesel

Fatty acid methyl esters (FAME) are a type of fatty acid ester that can be produced by an alkali-catalyzed reaction between fats or fatty acids and methanol known as transesterification product. Absolute biodiesel is referred to B100. A biodiesel blend is absolute biodiesel blended with petrodiesel which is defined as BXX (XX indicates the amount of biodiesel in the blend such as a B85 blend is 85 % biodiesel and 15% petrodiesel). Biodiesel is environmental friendly because of lower hydrocarbon emissions, smoke and lampblack reductions, lower CO emissions, reduction of greenhouse gases. Biodiesel has many advantages as the fact that, it is derived from biodegradable and renewable resources. It helps to lubricate the diesel engine itself reducing diesel engine wear. Biodiesel can be used directly in compression ignition engines with no substantial modifications of the engine (Sarin, 2012). Babadagli and Ozum (2010) studied the use of biodiesels as a surfactant additive for reducing heavy oil/bitumen-water interfacial tension in steam assisted recovery processes. Advantages of using biodiesel as a surfactant additive are that biodiesel is chemically stable under the operating pressure and temperature of the reservoir, it causes no harm on bitumen quality and released water chemistry and its use is economically feasible.

Pseudo-Ternary Phase Diagram

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

$$x\%A + y\%B + z\%C = 100\%$$

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

3. Materials & Methods

3.1 Materials

Surfactants

Two types of nonionic surfactants were used in this work including; methyl oleate and palm oil methyl ester (POME). Their properties and structure are shown in Table 1. Methyl oleate (MO), methyl ester, has carbon 18 atoms and a double bond. It was chosen because of the lowest amount of surfactant in microemulsion biofuels formulation. MO with 70% purity (technical grade) was purchased from Sigma-Aldrich (Thailand). Palm oil methyl ester (POME) or biodiesel derived from palm oil was selected because it has ester group as same as MO. The POME as B100 was received from Werasuwan Co., Ltd. (Thailand)

Cosurfactant

1-octanol was used in the research because it can work well with nonionic surfactants. It was purchased from Acros Organics (italmar, Thailand). The properties of structure of surfactant and cosurfactant used in this study are shown in Table 1.
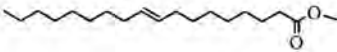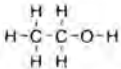
Polar Phase

Two types of alcohols, ethanol and butanol were used as a polar phase in the microemulsion formation. Their properties are shown in Table 1. Ethanol with 95 % purity was used as viscosity reducer in microemulsion biofuels. Butanol with 99 % purity was used together with ethanol for improving the microemulsion biofuel property. They were purchased from Sigma-Aldrich (Thailand).

Oil Phase

Palm oil, RBDPO and diesel were used in this work. Food-grade palm oil and commercial-grade diesel were purchased from Morakot industries Public Company Limited and SHELL (Thailand) Public Company Limited, respectively. Moreover, refined bleached deodorized palm oil (RBDPO) was supported by Bangchak Biofuel Co., Ltd.

Table 1 Properties and structures of materials

Chemical	Structure	Density (g/mL)	MW (g/mol)	Viscosity @40 °C (cSt)	Purity (%)
Surfactant and Cosurfactant					
Methyl Oleate (MO)		0.87	296.49	4.68	70
Palm oil methyl ester (POME)	$CH_3 - O - C - R_x$	0.89	283.37	4.76	96.5
1-Octanol	OH	0.83	130.23	6.06	99
Polar phase					
Ethanol	$H-C-C-O-H$	-	-	1.2	95
Butanol	OH	-	-	3.64	99
Oil phase					
Palm oil	-	0.90	-	45.34	-
RBDPO	-	0.90	-	37.95	-
Diesel oil	-	0.82	-	4.1	-
B100	-	0.87		6.0	-

Experimental Procedures

Microemulsion Biofuels Preparation

The compositions of microemulsion biofuels consist of surfactant/cosurfactant blend at a molar ratio of 1:8, vegetable oil/diesel mixture was fixed at 1:1 by volume and the amount of polar phase (alcohol) was varied in each sample to studying the phase behavior. The samples were prepared in a 15 mL glass vial. All mixtures were hand-shaken and placed at the room temperature for 48 hr to reach equilibration. Phase behavior is determined by visual inspection with polarized light. Different amounts of ethanol/butanol (vol.%, v/v) with palm oil/diesel blends (v/v) are added into surfactant-cosurfactant mixture to formulate reverse micelle microemulsions.

Phase Behavior Study

To study the phase behavior and miscibility of the microemulsion biofuels, a pseudo-ternary phase diagram is created. Pseudo-ternary phase diagram, consisting of six components in the system is investigated. In order to show the variations of the six-component mixture on the pseudo-ternary phase diagram, the top vertex of the triangle represents the surfactant/cosurfactant mixture at a constant ratio, while the two vertices at the bottom of the triangle represent the palm oil-diesel blends and the ethanol/butanol at left side and right side respectively. Lastly, total volume of the surfactant/cosurfactant mixture, the palm oil-diesel blends, and the ethanol/butanol is calculated to 100 % for all components. The miscibility curves are plotted as the boundary between the separate-phase and single-phase are. Area above the curve indicate isotropic phase systems, where a sufficient amount of the surfactant has been added to solubilize all of the components. The pseudo –ternary phase diagram is shown in Figure 1.
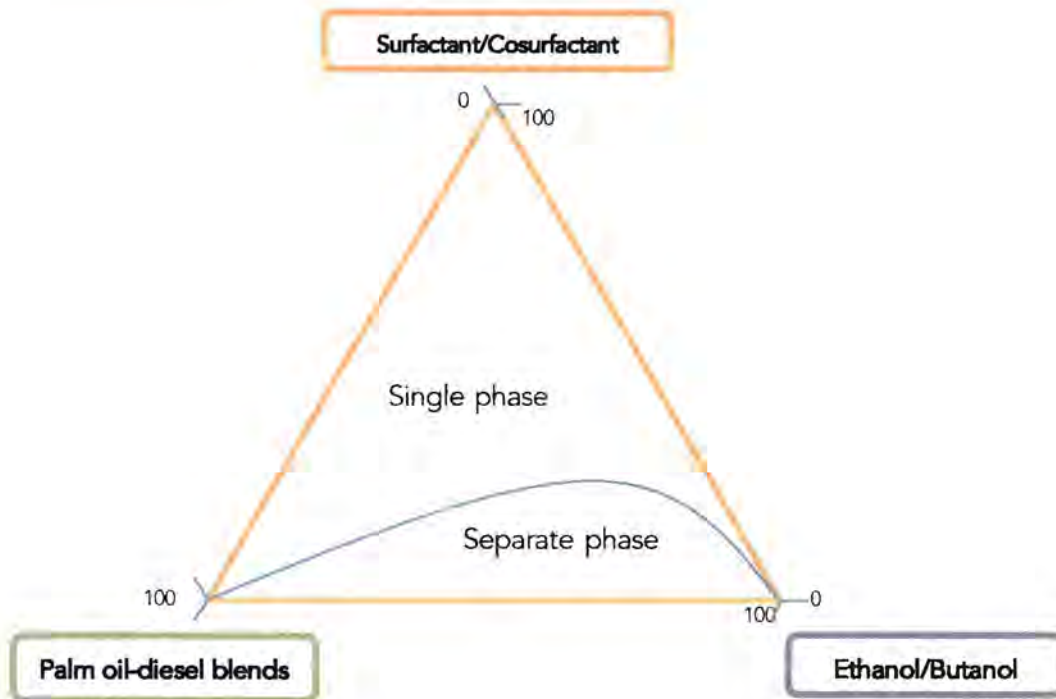
Figure 1 Pseudo-ternary phase diagram.

Kinematic Viscosity Measurement

The kinematic viscosity of microemulsion fuel was measured by Canon Fenske type viscometer followed ASTM D445. A minimum sample volume of 7.0 mL of (as recommended by the manufacturer) was then transferred into a viscometer chamber, and the time require for the fluid to flow between two specific points was measured. This study was measured at 40 °C. The kinematic viscosity was calculated using Equation (1), which is provided by the manufacturer of the viscometer:

$$ v = K_t T \qquad\qquad (Eq. 1) $$

where; v is the kinematic viscosity (mm^2/s)

K_t is the viscosity constant at test temperature.

K_t can be calculated and is described in manufacture manual.

T is the efflux time (s) of the sample through the capillary tube.

Droplet Size Determination

Mean diameter (d_m) and size distribution of the microemulsion droplets were performed through Dynamic light scattering (DLS). The measurements is performed at 25 °C at a fix angle of 173° (back scattering detection) by using a ZetasizerNano apparatus, Model ZEN 3600,

Malvem Instruments. The light source is a He-Ne laser (λ = 633 nm; 4mW) with a digital autocorrelation.

Fuel Properties of the Microemulsion Biofuel

The fuel properties of the microemulsion-based biofuel were determined to compare the properties between microemulsion biofuels and diesel No.2. The fuel properties were measured according to the American Standard Testing Methods (ASTMs). Table 2 shows the parameters and testing methods of the microemulsion-based biofuel. The parameters are the gross heat of combustion, cloud point, flash point, and kinematic viscosity. For this work, the fuel properties of the microemulsion-based biofuel were compared with those properties of No.2 diesel.

Gross Heat of Combustion

Gross heat of combustion was measured by an oxygen bomb calorimeter (model AC-350, LECO Corporation, USA) according to ASTM D 240. A crucible was used to place the fuels inside the calorimeter to test the heating value. The heat of combustion is calculated by the measured temperature increase of the water bath surrounding the bomb.

Cloud Point

In this study, the cloud point was determined following ASTM D 2500 by cooling bath, in which the test fuel was visually observed for the cloudiness and turbidity in cooling bath as the temperature is decreased for every 1 °C.

4. Results and discussion

Phase Behavior Study of Microemulsion Biofuels

This study aims to minimize amount of surfactant used while maintain the fuel properties of microemulsion biofuel. Pseudo ternary phase diagram represents phase behavior of microemulsion biofuel with varying surfactant concentration. The phase diagram divided into three main components, oil phase, surfactant phase, and alcohol phase; the top to the left bottom is the percentage of oil in the mixture, the left to the right is the percentage of alcohol, and the right bottom to the top is the percentage of surfactant as shown in Figure 3. The miscibility curve indicates the lowest composition for formulating single phase microemulsion. The upper area of miscibility curve is the single phase composition and the area lower is the separate phase composition.

Figure 3 Pseudo ternary phase diagram with single phase and separate phase example.

Comparisons of the System with Single and Mixed Alcohol System

Figure 3 and Figure 4 show pseudo ternary phase diagrams of microemulsion biofuel systems with three main components consisting of palm oil/diesel oil as an oil phase (palm oil/diesel oil blend at a ratio of 1:1 (v/v)), methyl oleate (MO) or palm oil methyl ester (POME or biodiesel) as a surfactant and 1-octanol as a cosurfactant (surfactant/cosurfactant at a molar ratio of 1:8), and ethanol and butanol blend at a ratio of 1:1 (v/v) as a polar phase. The experiment was done at room temperature (25±2 °C). The amounts of each component with the minimum amount of surfactant required to form a single phase microemulsion were plotted as shown in the Figure 4.2 and 4.3. It can be seen that the single phase microemulsion regions (above the immiscible curve) is larger with the addition of butanol compared with that of ethanol alone. This can be implied that the microemulsion biofuel system with butanol in the blend requires lower amount of surfactant to formulate the single phase microemulsion. Since butanol has less hydrophilic property than ethanol, the microemulsion tends to be more hydrophobic system which requires lower amount of surfactant used to be able to solubilize polar phase (i.e., ethanol in this case) into the hydrophobic oil phase. This can be concluded that the presence of butanol in the mixed liquid fuel of microemulsion biofuel remarkably gains a benefit in terms of reducing surfactant used.

Psuedo Ternary Phase Diagram
Surfactant/Cosurfactant
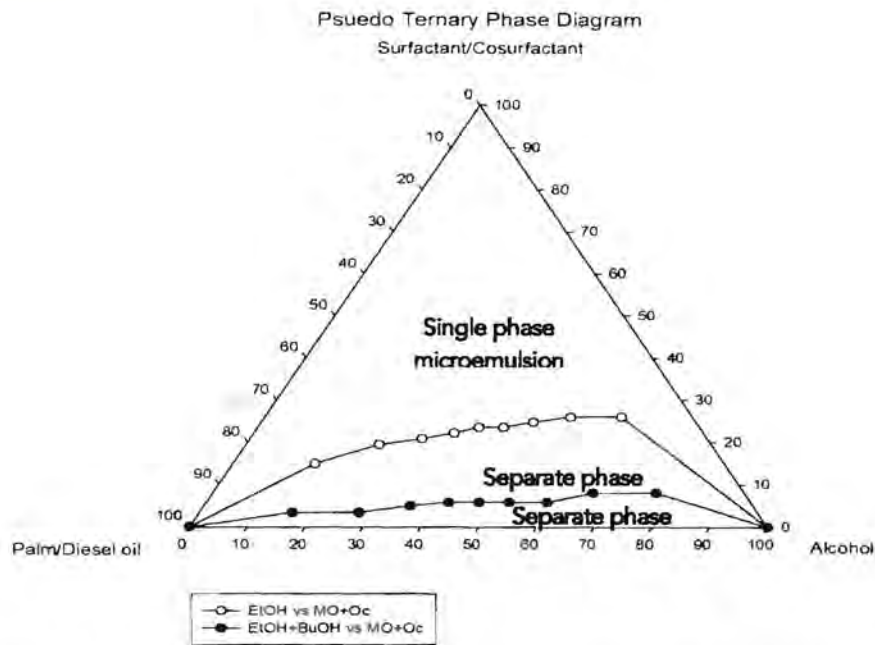
Figure 4 Comparison of microemulsion biofuel systems of methyl oleate (MO) surfactant at room temperature (25±2 °C) with palm oil/diesel oil ratio at 1:1 (v/v) with 1-octanol as a cosurfactant and a single and mixed ethanol-butanol blend system as a polar phase.

Psuedo Ternary Phase Diagram
Surfactant/Cosurfactant
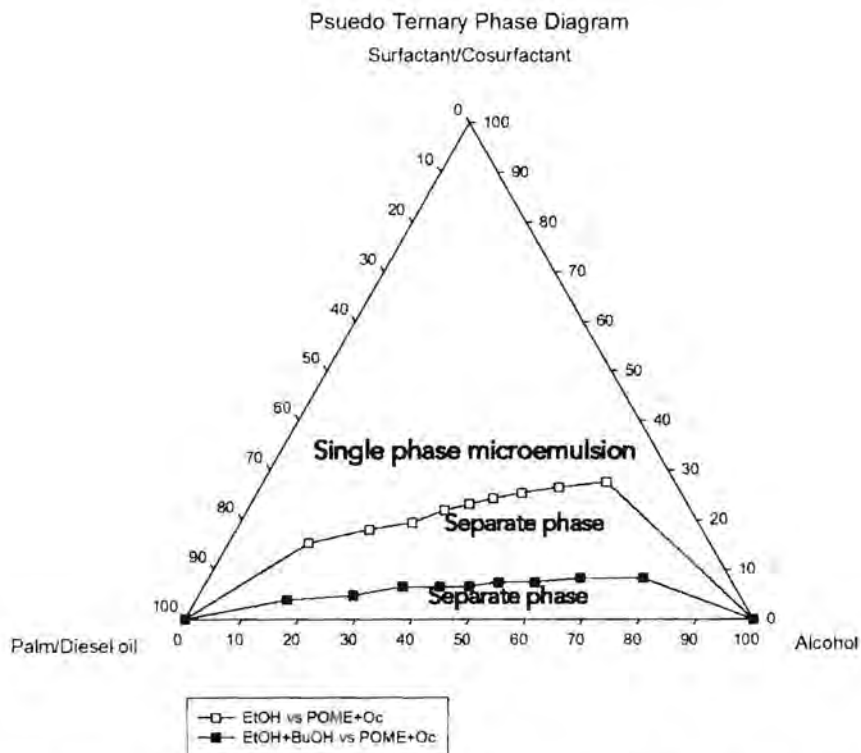
Figure 5 Comparison of microemulsion biofuel systems of biodiesel (POME) as a surfactant at room temperature (25±2 °C) with palm oil/diesel oil blend ratio at 1:1 (v/v), 1-octanol as a cosurfactant and a single and mixed ethanol-butanol blend system as a polar phase.

Comparisons of the System with Different Types of Surfactant

Figure 5 shows the comparison of the microemulsion biofuels system with different types of surfactant and 1-octanol as cosurfactant. Black circles and black squares represent methyl oleate (MO) and palm oil methyl ester (POME), respectively. The amount of surfactants required to formulate the ME have almost similar result, because hydrophilic-lipophilic balance (HLB) values of MO and POME are 4.0 and 4.2, respectively.

Pseudo Ternary Phase Diagram
Surfactant/Cosurfactant
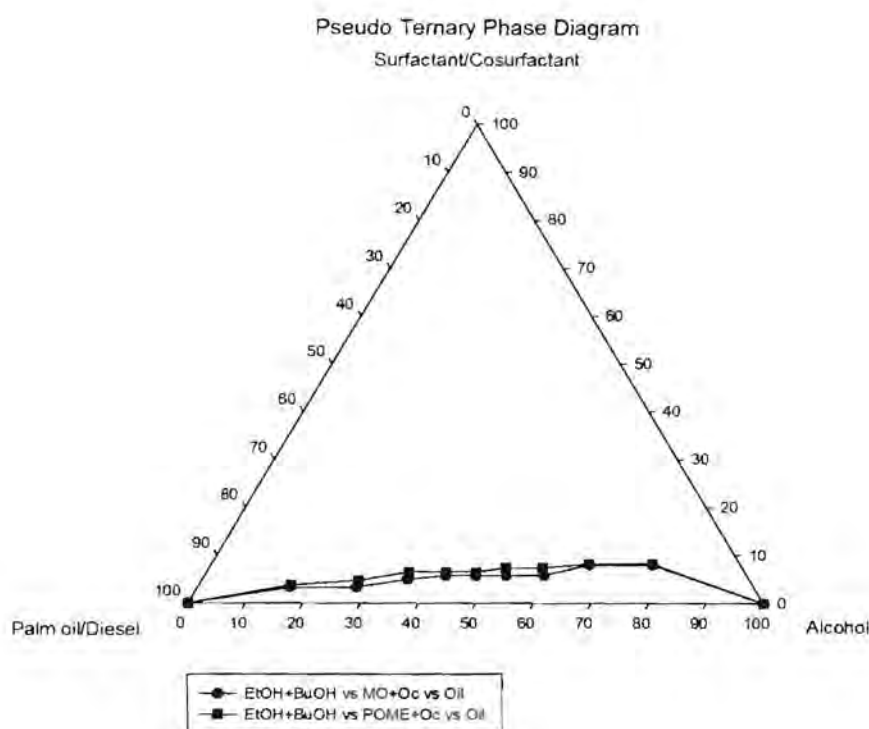
Figure 6 Comparison of the systems with methyl oleate (MO) and biodiesel (POME) at room temperature (25±2 °C) with palm oil/diesel oil ratio at 1:1(v/v) with EtOH/BuOH.

Palm Oil/Diesel Ratio Study

After the phase behavior study, the minimum surfactant concentration was obtained and used for palm oil/diesel ratio study. Alcohols (ethanol/butanol at a ratio of 1:1(v/v)) were fixed at 20 % of the mixture by volume and surfactant/cosurfactant was mixed at a molar ratio of 1:8. At low percentage of alcohols (20 %), the results showed that palm oil/diesel ratios did not significantly affect to minimum total surfactant concentration required to form a single phase microemulsion (Figure 6). The result is consistent with Attaphong and coworkers (2012), at high percentage of alcohol (more than 30 %), the amount of surfactant content increased with increasing of vegetable oil. While, at low percentage of alcohol, the amount of surfactant content was similar for different ratio of vegetable oil/diesel. Moreover, both types of surfactant, MO and POME, presented in similar results because of their similar HLB value.
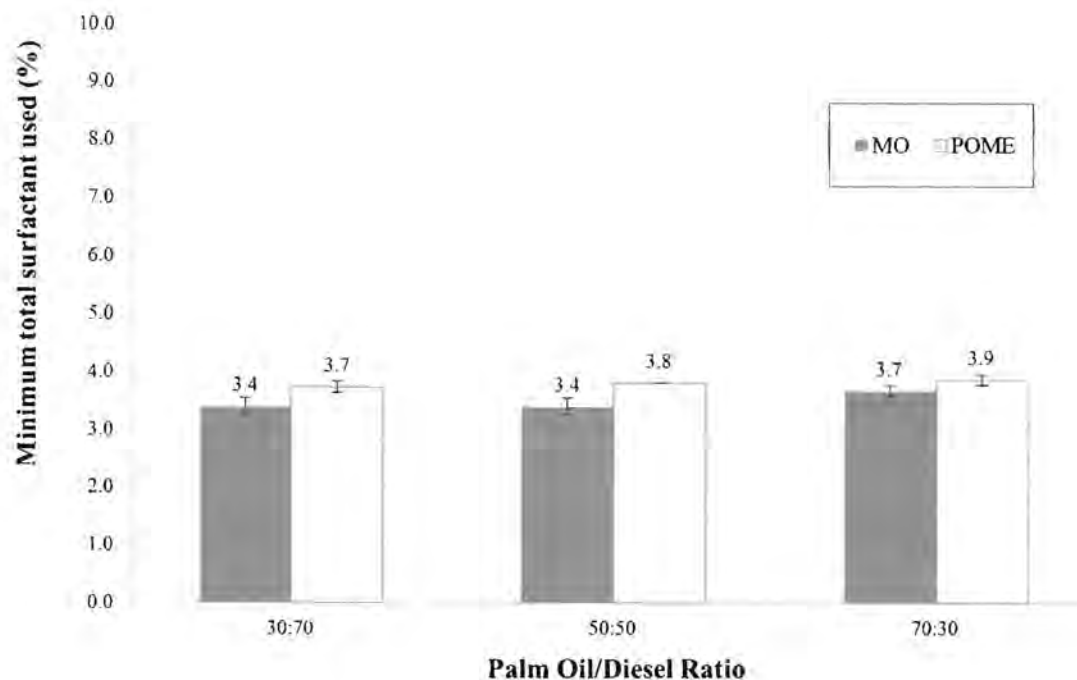
Figure 7 Minimum total surfactant concentration to formulate single phase microemulsion (%) versus palm oil/diesel ratio (v/v) compared with methyl oleate and POME (biodiesel) as surfactants and 1-octanol as a cosurfactant at a molar ratio of 1:8 by 20 vol.% of EtOH/BuOH at a ratio of 1:1(v/v).

EtOH/BuOH Ratio Study

Comparisons Minimum Total Surfactant Concentration to Formulate Single Phase Microemulsion over Effect of EtOH/BuOH Ratios of the System with Different Types of Surfactant

Figure 8 shows the minimum total surfactant concentration to formulate single phase microemulsion at five different EtOH/BuOH ratios. Both EtOH/BuOH ratios by percent volume of 0:100 and 30:70 in alcohol fraction do not need surfactant to formulate single phase microemulsion because at this range butanol can dissolve in all component. For EtOH/BuOH ratio of 50:50 or 1:1, the surfactant concentration was at the fraction of 5 % and 4.8 % for MO and POME surfactant, respectively. The similar results were observed for both type of surfactants, MO and POME (biodiesel). At the EtOH/BuOH ratio of 70:30, this system required higher amount of surfactant than that of the EtOH/BuOH ratio of 50:50. The comparison of five different EtOH/BuOH ratios, showed that amount of surfactant concentration to formulate single phase microemulsion increased when the composition of butanol decrease because butanol has less hydrophilic property than ethanol. Therefore, the presence of butanol can decrease the usability of surfactant to formulate single phase microemulsion.
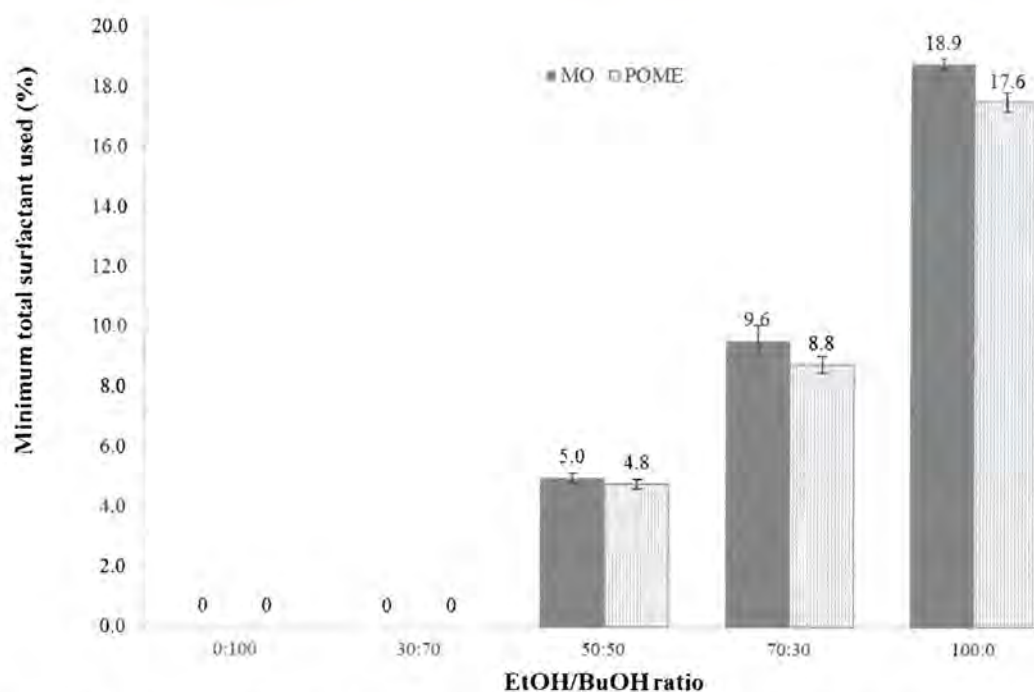
Figure 8 Minimum total surfactant concentration (%) versus EtOH/BuOH ratio (v/v) of ME with MO and POME as surfactants, 1-octanol as a cosurfactant at a molar ratio of 1:8 and palm oil/diesel ratio at 1:1 (v/v) in 20 vol.% of EtOH/BuOH.

Comparisons of Minimum Total Surfactant Concentration to Formulate Single Phase Microemulsion over Effect of EtOH/BuOH Ratios of the System with Different Types of Palm Oil

For this study food-grade palm oil (palm olein) and refined bleached deodorized palm oil (RBDPO) were selected to investigate as different types of palm oil. Because RBDPO has a benefit in terms of economic and environmental aspects, so it is selected. Figure 8 shows the minimum surfactant concentration to form a single phase microemulsion with varying three different EtOH/BuOH ratios. The result shows that amount of surfactant required increased significantly with decreasing the presence of butanol in systems for both types of palm oil. For comparison amount of surfactant required with different types of palm oil, the results showed that RBDPO systems required slightly lower surfactant concentration to form a single phase microemulsion than that of the palm olein system. Because the fatty acids in RBDPO (palmitic acid, C16:0) can facilitate the surfactant to form a single phase microemulsion. Palmitic acid was a major type fatty acid in the RBDPO accounting for 46.30 %, this figure is more than that of palm olein at amount of 41.54 % as shown in Table 3.
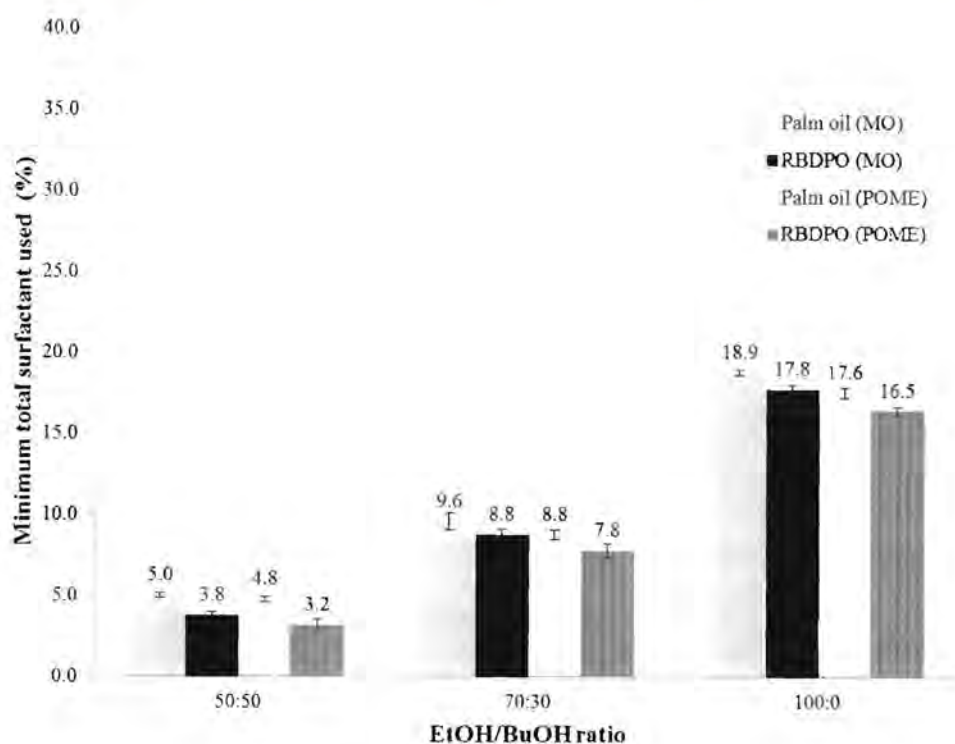
Figure 9 Minimum total surfactant concentration (%) versus EtOH/BuOH ratio (v/v) of microemulsion biofuel with MO and POME as surfactants with palm oil and RBDPO as oil phase, 1-octanol as a cosurfactant at molar ratio of 1:8 and palm oil/diesel ratio at 1:1 (v/v) in 20 vol.% of EtOH/BuOH.

Table 3 Fatty acid composition of palm oil and refined bleach deodorized palm oil (RBDPO) (Che Man et al., 1999).

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

Fuel Properties Determination

Fuel properties of microemulsion biofuels are the key factor to evaluate their performance close to those of diesel and biodiesel (B100) standard. For this part, we interested in the effects of surfactant's structure and type of palm oil and ratio of butanol in ethanol and butanol mixtures on their fuel properties, including kinematic viscosity, droplet size, cloud point, density, and heat of combustion. Microemulsion biofuels in this study were prepared by palm

oil/diesel and RBDPO/diesel blends with 20 vol.% of alcohols (ethanol/butanol) and the appropriate surfactant concentration was selected at 5 vol.% of above the miscibility curve.

Kinematic Viscosity Determination

In this research, the kinematic viscosity of microemulsion biofuels was measured by Cannon-Fenske viscometer followed the ASTM D445. The results were compared to neat diesel fuel and biodiesel (B100). The standard kinematic viscosity of No.2 diesel has been reported at 4.1 cSt (Arpompong et al., 2014) while kinematic viscosity of B100 has been reported at 6.0 cSt (Jan et al., 2010).

Effect of Surfactant Structures

Methyl oleate (MO) and palm oil methyl ester (POME) or known as biodiesel were selected as a surfactant mixed with 1-octanol as a cosurfactant at a constant molar ratio of 1:8. Figure 10 shows the kinematic viscosity of palm oil/diesel blend at a ratio of 1:1 (v/v) with 20 vol.% of alcohol at different blending ratios of ethanol and butanol mixture. For kinematic viscosity of both surfactants (MO and POME) showed the similar trends, decreased with decreasing of butanol fraction. This is because of their similar kinematic viscosity, 4.68 and 4.76 cSt for MO and POME, respectively. The kinematic viscosities of microemulsion biofuels with MO and POME gradually increase with increasing of butanol fraction in the ethanol and butanol mixture because the kinematic viscosity of butanol are higher than that of ethanol, 3.64 and 1.20 for butanol and ethanol, respectively (Rakhi et al., 2012). The result showed that the microemulsion systems with butanol alone presented the highest kinematic viscosity at 8 cSt. While kinematic viscosity of the microemulsion systems contained ethanol alone was about 5.5 cSt. At high percentage of ethanol fraction (70 % and 100 %) in ethanol and butanol mixture, the viscosity of microemulsion biofuels was close to that of the biodiesel (B100) standard ranging from 1.9 to 6.0 cSt (Jan et al., 2010).
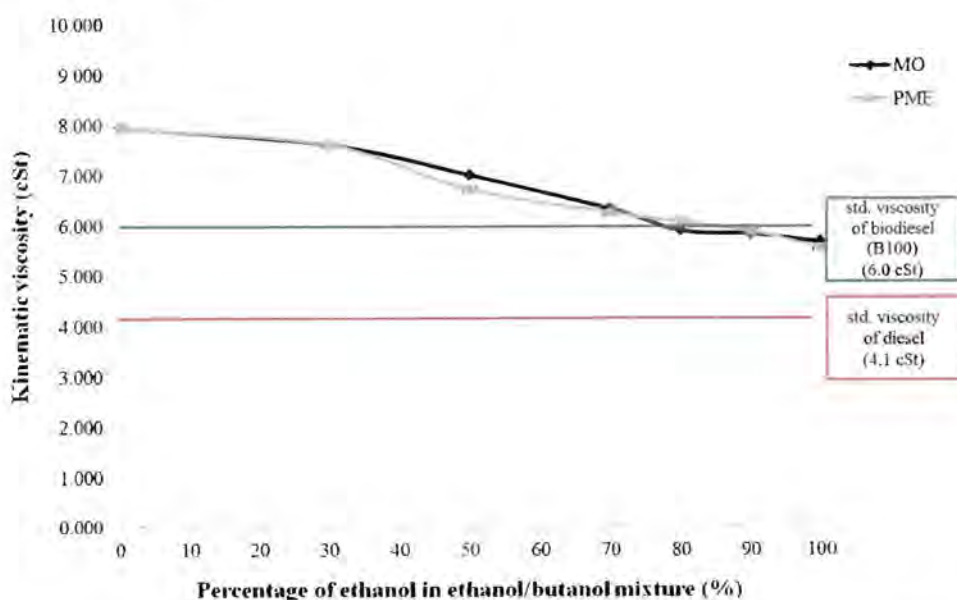
Figure 10 Kinematic viscosities (cSt) at 40°C of the microemulsion biofuels using MO and POME with 1-octanol at a molar ratio of 1:8 as surfactant systems with palm oil/diesel blend at a ratio of 1:1 (v/v) with varying butanol contained in ethanol and butanol blends at 20 vol.% of alcohol.

Effect of Different Types of Palm Oil

For this study, palm oil/diesel and RBDPO/diesel blended at a ratio of 1:1 (v/v) using MO and POME as a surfactant mixed with 1-octanol as a cosurfactant at a constant molar ratio of 1:8 with five different ethanol/butanol ratio (20 vol.% of ethanol and butanol mixture). The result in Figure 11 show that the kinematic viscosities of ME decrease with decreasing of butanol in ethanol and butanol mixture that is consistent with section 4.4.1.1. For effect of different types of palm oil, kinematic viscosities of RBDPO/diesel systems were slightly less than those of palm oil/diesel systems because RBDPO has kinematic viscosity lower than that of palm oil, 45.34 cSt (Bernat et al., 2012) and 37.95 cSt (Yusnida et al., 2013) for neat palm oil and RBDPO, respectively.
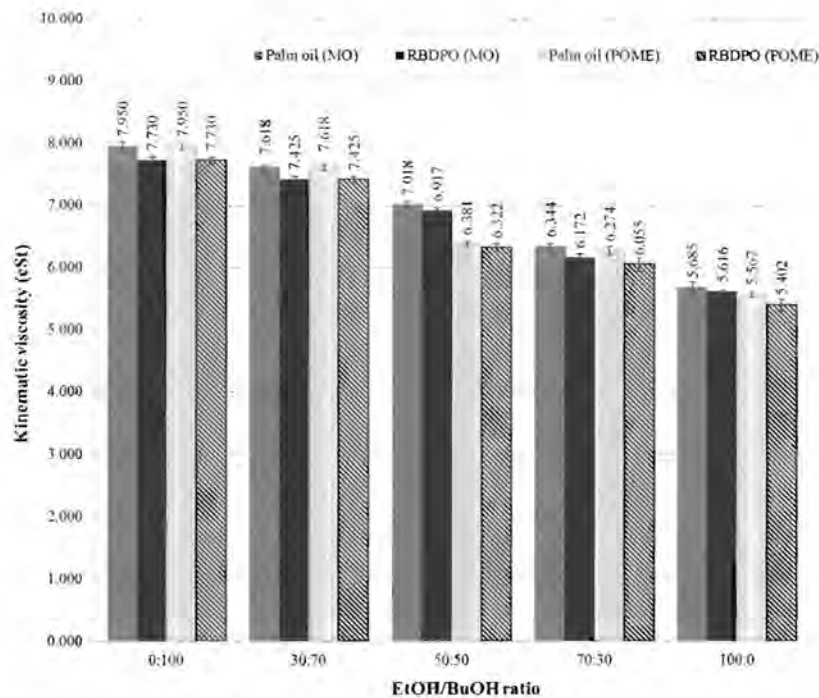
Figure 11 Kinematic viscosity (cSt) at 40 oC versus EtOH/BuOH ratio compared with palm oil and RBDPO as different palm oil with palm oil/diesel ratio at 1:1 (v/v) with MO and POME as surfactants with 1-octanol as a cosurfactant at a molar ratio of   1:8 with 20 vol.% of EtOH/BuOH mixture.

Effect of Adjustment Palm Oil/Diesel Ratio

Figure 12 represents the kinematic viscosity of palm oil/diesel blend at ratio of 30:70 (v/v) using MO and POME as a surfactant and mixed with 1-octanol as a cosurfactant at constant molar ratio of 1:8 with three different EtOH/BuOH ratios (20 vol.% of ethanol and butanol mixture). For the palm oil/diesel oil at ratio of 50:50 (v/v), the kinematic viscosity was not approach to standard viscosity of diesel. To reduce high viscosity of the microemulsion biofuels, palm oil/diesel ratios were adjusted to ratio of 30:70 (v/v). Result of adjusting palm oil/diesel ratios showed that the kinematic viscosities of palm oil/diesel blend (30:70) systems at three different ratios of ethanol and butanol mixture can be maintained to the kinematic viscosity standard of diesel.
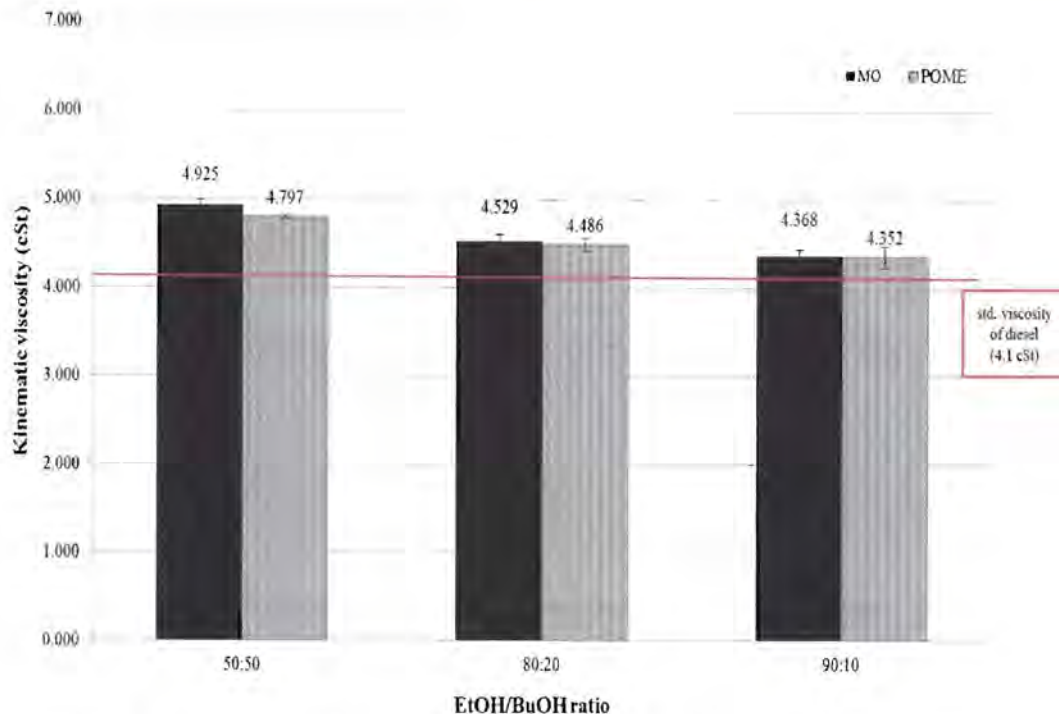
Figure 12 Kinematic viscosity (cSt) of palm oil/diesel blend at a ratio of 30:70 (v/v) systems at 40oC versus EtOH/BuOH ratio with MO and POME as surfactants and 1-octanol as a cosurfactant at molar ratio of 1:8 with 20 vol.% of EtOH/BuOH mixture.

Droplet Size Determination

Microemulsion biofuel droplet sizes and size distributions were measured by Zetasizer Nano apparatus (Model ZEN 3600, Malvern Instruments) with Dynamic Light Scattering technique (DLS). DLS technique measured the diffusion of particles moving undergo random motion known as Brownian motion, and converts this to size and a size distribution using the Stokes-Einstein equation (Noel et al., 1970). The sample were analyzed at room temperature (25±2 °C). The aim of microemulsion biofuel droplet size determination is to find the correlation of droplet size and kinematic viscosity of microemulsion biofuels. This study investigated the effect of surfactant structures and ethanol/butanol ratios on relation between droplet size and kinematic viscosity.

Effect of Surfactant Structures

Table 13 shows droplet sizes of microemulsion biofuels with palm oil/diesel blends at a ratio of 1:1 (v/v) using two types of surfactant, MO and POME mixed with 1-octanol as a cosurfactant at molar ratio of 1:8 at three different ratio of EtOH/BuOH. The result showed that the droplet sizes of microemulsion biofuel had no difference for MO and POME surfactants. The droplet size of microemulsion biofuels of MO systems ranged from 475.3-5,461 nm at monodipersion (100 % intensity). Similar figures were found for POME systems, the droplet size ranged from 475.3-5,560 nm. The droplet size of MO and POME systems were similar because both types of surfactant contain methyl ester group at their hydrophilic ends. For effect of ethanol/butanol ratio, the droplet sizes increased with decreasing of butanol in ethanol and butanol blends because of the stronger binding affinity between longer chain of butanol and surfactant structures than that of ethanol.

Table 4 Comparison of the droplet size and distribution of microemulsion biofuels with palm oil/diesel blend (1:1 v/v) with MO and POME as surfactants at room temperature (25±2 °C)

Sample	Size Distribution (nm)			
	MO/1-octanol		POME/1-octanol	
	$D_{1\ mean}$ (%intensity)	$D_{2\ mean}$ (%intensity)	$D_{1\ mean}$ (%intensity)	$D_{2\ mean}$ (%intensity)
EtOH:BuOH (0:100)	475.3 (100%)	- (0%)	475.3 (100%)	- (0%)
EtOH:BuOH (50:50)	5,361 (100%)	- (0%)	5,413 (100%)	- (0%)
EtOH:BuOH (100:0)	5,461 (100%)	- (0%)	5,560 (100%)	- (0%)

Relation between Droplet Size and Kinematic Viscosity of Microemulsion Biofuels

To describe the relationship between droplet size and kinematic viscosity of microemulsion biofuels, Stokes-Einstein's equation (Equation 2) was used in this calculation. For Stokes-Einstein's equation, microemulsion biofuel droplet size is explained in terms of D_h which is inversely proportion to kinematic viscosity (η).

$$D_h = \frac{k_B T}{3\pi\eta D_t} \qquad (2)$$

From Table 13, the kinematic viscosities of microemulsion biofuels system using MO as a surfactant were slightly higher than those of POME. While microemulsion droplet size using the MO system were less than those of POME system. So, we can conclude that these results were followed the Stokes-Einstein's equation and consistent with Arpompong and coworkers (2014).

Table 5 Kinematic viscosity and droplet size of palm oil/diesel blends at a ratio of 1:1 with 20 vol.% ethanol and butanol mixture with MO and POME as surfactants mixed with 1-octanol as a cosurfactant at a molar ratio of 1:8

Sample		Kinematic Viscosity (cSt)	Size Distribution $D_{1\ mean}$ (nm)
MO/1-Octanol Palm oil/Diesel oil)	EtOH:BuOH (0:100)	7.982	475.3
	EtOH:BuOH (50:50)	7.018	5,361
	EtOH:BuOH (100:0)	5.685	5,461
POME/1-Octanol (Palm oil/Diesel oil)	EtOH:BuOH (0:100)	7.982	475.3
	EtOH:BuOH (50:50)	6.381	5,413
	EtOH:BuOH (100:0)	5.567	5,560

Cloud Point Determination

Cloud point is the temperature that fuel becomes to form cloudy solution. When the temperature of fuel reaches to the cloud point, these wax crystals flowing with the fuel coat the filter element and suddenly decrease the fuel flow, making trouble the engine (Mittelbach, 2004). In this work, the cloud point of microemulsion biofuels were determined using temperature controlled water bath following to ASTM D 2500. Effect of ethanol/butanol ratios on the cloud points was investigated with palm oil/diesel blended at ratio of 1:1 (v/v) with 20 vol.% of ethanol and butanol mixture. The turbidness of the microemulsion biofuel is observed when the temperature is decreased every 1 °C.

The cloud points of microemulsion biofuel using MO and POME as a surfactant at the same ethanol/butanol ratio turned to be turbidness at the same temperature. This could be due to their similar functional group of surfactant as shown in Table 4.4. For EtOH/BuOH ratios of 0:100 and 30:70, the cloud point was observed at 5 °C. For other systems, the cloud point was observed at -3 °C. In comparison, the cloud points of microemulsion biofuels, the microemulsion biofuels were higher than that of diesel (-15 °C). This is because cloud point of palm oil is relatively high (13 °C) and similar to that of B100 (-3 °C) (Jan et al., 2010).

Table 6 Cloud point of MO and POME microemulsion biofuels
✓ means microemulsion biofuel forms cloudy
✗ means microemulsion biofuel was not form cloudy

Sample (EtOH:BuOH)	Temperature (°C)								
	5	4	3	2	1	0	-1	-2	-3
0:100	✓	✓	✓	✓	✓	✓	✓	✓	✓
30:70	✓	✓	✓	✓	✓	✓	✓	✓	✓
50:50	✗	✗	✗	✗	✗	✗	✗	✗	✓
70:30	✗	✗	✗	✗	✗	✗	✗	✗	✓
80:20	✗	✗	✗	✗	✗	✗	✗	✗	✓
90:10	✗	✗	✗	✗	✗	✗	✗	✗	✓
100:0	✗	✗	✗	✗	✗	✗	✗	✗	✓

Density Determination

Density of all sample were measured at room temperature (25±2 °C). Table 4.5 shows density of microemulsion biofuels, varying in range of 0.829-0.852 g/mL. the density of microemulsion biofuels were higher than diesel (0.828 g/mL) and less than biodiesel (B100) (0.876 g/mL).

Table 7 Density of microemulsion biofuels

Sample (Ethanol/Butanol Ratio)	Density (g/mL)	
	MO/1-octanol	POME/1-octanol
0:100	0.852	0.852
30:70	0.851	0.851
50:50	0.848	0.845
70:30	0.841	0.840
100:0	0.833	0.829
Diesel[a]	0.828	
Biodiesel (B100)[a]	0.876	

[a]Tha data form Bernat et al., 2012

Heat of Combustion

Heat of combustion is an important property of a fuel, describing the amount of energy released in terms of heat when ending of combustion of the fuels. The heat of combustion is commonly measured with a bomb calorimeter. For this study, heat of combustion was followed by ASTM D 240. Figure 4.11 shows the heat of combustion of palm oil/diesel blends at a ratio of 1:1 (v/v) with POME as surfactant mixed with 1-octanol at a molar ratio of 1:8 with different ratios of ethanol/butanol. The result indicated that the heating value decreased with amount of ethanol increased in the mixture of EtOH/BuOH blends. Microemulsion biofuel system contained high amount of ethanol, had high heating value vice versa that the lower amount of butanol had low heat of combustion. Microemulsion biofuels contained ethanol alone system had heat of combustion of 38.58 MJ/kg, while the system with ethanol/butanol at a ratio of 50:50 (v/v) had heat of combustion of 39.73 MJ/kg which higher than that of system with ethanol alone. Due to the fact that heat of combustion of butanol is originally higher than ethanol, accounting for 33 MJ/kg and 26.8 MJ/kg, respectively. However, heat of combustion of the microemulsion biofuels was slightly lower than diesel (43 MJ/kg) (Evangelos et al., 2013).
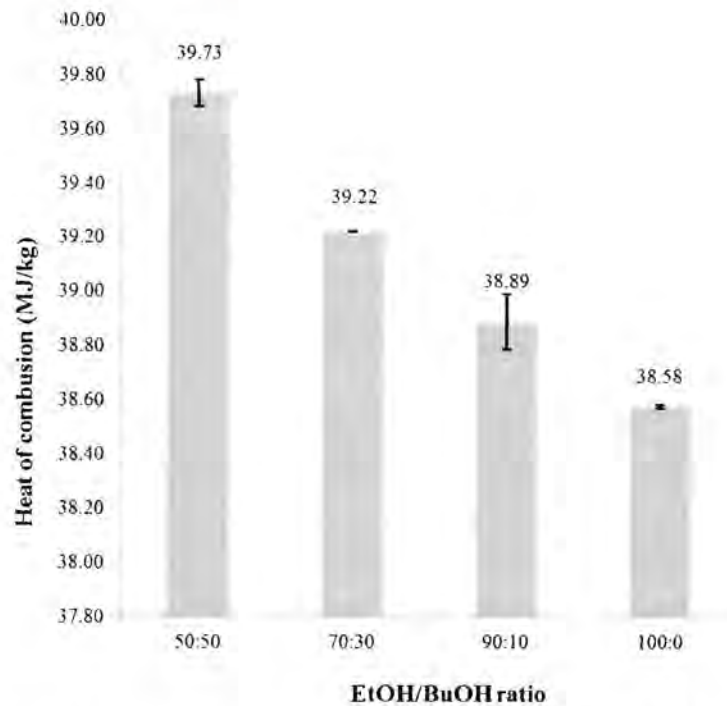
Figure 13 Heat of combustion of microemulsion biofuels with various EtOH/BuOH ratio using POME as a surfactant and 1-octanol as a cosurfactant at molar ratio of 1:8 with palm oil/diesel at ratio of 1:1 (v/v).

Based on this findings, it can be summarized that the use of butanol in microemulsion biofuels presents a benefit in terms of amount of surfactant used for formulate single phase microemulsion and heating value. While it causes high kinematic viscosity of microemulsion biofuels as a limitation. Therefore, using of butanol needs formula adjustment to optimize kinematic viscosity of system. In addition, the use of MO and POME for formulating microemulsion biofuel showed the similar results. According to the practical utilization in terms of economic and environment consideration, POME can be used as a surfactant instead of commercialized nonionic surfactant

5. Conclusions

This study aims to form single phase microemulsion biofuels with focusing on the effect of surfactant structure and ethanol/butanol ratio on phase behavior and fuel properties of microemulsion biofuels. Microemulsion biofuel system in this work used palm oil/diesel blends with ethanol and butanol mixture with two types of surfactant (MO and POME) and 1-octanol as a cosurfactant. From results, conclusions are made as follow:

For the effect of adding butanol, butanol can decrease the amount of surfactant used to formulate single phase microemulsion because butanol has higher hydrophilicity than ethanol. While the use of butanol causes the high kinematic viscosity of microemulsion biofuel because of the higher kinematic viscosity of butanol than that of ethanol. Moreover, at the palm oil/diesel ratio of 50:50 (v/v), the kinematic viscosity of ethanol/butanol blends systems were higher than that of diesel standard. Adjustment of palm oil/diesel ratio (30:70 (v/v)), the kinematic viscosity of microemulsion biofuel can approach to diesel standard. For the droplet size study, the droplet

size of ethanol/butanol systems were less than ethanol alone system because butanol has longer chain than that of ethanol. Therefore, it has high hydrophobicity (strong binding affinity between butanol and surfactant structure). The heating value of ethanol/butanol systems were higher ethanol alone systems because of higher heating value of butanol than that of ethanol. Therefore, using of butanol need formula adjustment to control the kinematic viscosity.

For the effect of types of surfactant (MO and POME), the amount of surfactant used to formulate single phase microemulsion biofuel of MO and POME systems were similar because of their similar in molecular structures (ester group) and HLB values. The kinematic viscosity of MO and POME systems were not significantly different due to their similar viscosity. For the droplet size study, the droplet size of MO and POME systems were not different. This could be due to their similar binding affinity of surfactant with oil and alcohols. For the effect of types of palm oil (palm olein and RBDPO), the amount of surfactant used to formulate single phase microemulsion of RBDPO systems were less than that of palm olein systems. Due to the fact that, fatty acids in RBDPO structure can help surfactant to formulate single phase microemulsion. The kinematic viscosities of RBDPO systems were less than that of palm olein systems because the viscosity of RBDPO are lower than palm olein. Note that, the using of RBDPO has limitation due to the wax precipitated in system. For the cloud point and the density measurements, the cloud point and the density of microemulsion biofuels were varied in ranging between diesel and biodiesel (B100).

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Chapter 4:

Environmental Life Cycle Assessment of Palm Oil based Microemulsion Biofuel Production from Renewable based Materials

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Abstract

This study focuses on evaluation of Greenhouse Gas (GHG) emissions and environmental impacts of microemulsion (ME) biofuels from different formulations based on life cycle assessment (LCA) approach. The functional unit is set to be one ton of ME biofuel. LCA system boundary was separated into four stages: cultivation, oil extraction, refining and ME stage. The ME biofuels with different formulations had been set for four different scenarios by varying the type and ratio of raw materials used. In addition, other potential environmental impact assessments of ME biofuel including global warming, acidification, eutrophication, ozone layer depletion, abiotic depletion, photochemical oxidation, land use, human toxicity, fresh water aquatic, marine aquatic and terrestrial ecotoxicity were also be evaluated by using commercial software, SimaPro version 7.1 with Eco-indicator 99 (H) and CML 2 baseline 2000 methods. Four different Scenarios evaluated in this study are Scenario I (base case), Scenario II (biobased case), Scenario III (butanol blend case) and Scenario IV (RBDPO case). The GHG emissions results described that Scenario IV contributes to the lowest GHG emissions (1,017 kgCO2) and lowest environmental impacts as the result of using refined bleached deodorized palm oil (RBDPO) in the ME formulation. When RBDPO was used to formulate ME biofuel, the total GHG emission was significantly reduced comparing to base case (1,448 kgCO2). When the emissions of each scenario were compared based on the normalized results, the biobased case contributed significantly to some environmental impact categories such as fresh water aquatic ecotoxicity, terrestrial ecotoxicity and eutrophication.

KEYWORDS: LCA, Environmental impact, Microemulsion Biofuel, Palm oil, Greenhouse gas, GHG

1. Introduction

Biofuels derived from renewable resources such as vegetable oils and agricultural feed stocks have been received much attention as alternative fuel which offers a benefit in terms of cleaner exhaust emissions. Nowadays, there are many plants which are grown for the newly alternative resource fuels such as Sunflower, rape seed, Jatropha, Canola, palm, Camellia Oleilifera, algae etc. Among them, palm oil is one of the most valuable economic crops in South East Asia. This is because of the origin of palm oil; it grows well in different regions of tropical countries. Even more, palm oil is a highly efficient, high yielding source of food and non-food. With sufficient supply, therefore, palm oil is a potential source for biofuel production.

Biofuel production technologies have been developed for many years. Transesterification method is the most common biodiesel production method to reduce the viscosity of vegetable oils. However, biodiesel also has many drawbacks which are old weather limitations due to relatively higher cloud point and pour point, and increasing nitrogen oxides (NOx) in the exhaust emissions. In addition, biodiesel is formed by the transesterification reaction of triglycerides with alcohols in the presence of a catalyst and produces glycerol as a co-product. However, glycerol requires energy intensive processes to purify or convert to a value-added product, which could cause not only direct emission from additional process, but also indirect impact to cover overall GHGs emission.

As an alternative approach, ethanol produced from agricultural feed stocks is a renewable energy source which can be made from very common crops such as sugar cane and corn. Therefore, ethanol–diesel blends, or E-diesel, are intensively studied for diesel engines without modification. However, ethanol–diesel blends are limited by the fact that they are immiscible over a wide range of temperatures. To overcome this problem, surface active agents or surfactants can be used as emulsifiers to stabilize the miscibility of ethanol and diesel. Due to the disadvantages of the transesterification process and ethanol blending process, microemulsification of vegetable oils have been considered as an alternative method to avoid the complex process of transesterification which generates a large amount of wastewater from purification of biodiesel and requires a large amount of energy for glycerol purification.

Microemulsions are amphiphile stabilized transparent, iso-tropic and thermodynamically stable dispersions of otherwise immiscible liquid phase and oil. In addition, the microemulsification approach helps to overcome the immiscibility of ethanol and diesel. Microemulsion-based biofuel is a promising technology, which could fulfill both environmetal and economic competitiveness. The benefit of this technique is not only to reduce vegetable oil viscosity, but it also satisfies ethanol-diesel fuel homogeneity or prevents phase separation.

In all cases, cost-effective and eco-friendly perspectives are the key challenges to satisfy future biodiesel technologies. The carbon label for community products has been rising as an approach to improve the product by reducing the used energy, wastes, and greenhouse gases emissions in a system. Many countries promote their manufactory which is friendly for environment. So, materials used in the process should be produced from renewable sources. Bio-based surfactant is prepared by using the long-chain fatty acids found in seed oil in the form of triglycerols (TAGs) for the lipophile. Typically, fatty acyl groups obtained from TAGs are converted into free fatty acids (FFA) or fatty acid methyl ester (FAME) or ethyl esters (FAEE) via hydrolysis and transesterification process. Feedstocks enriched in medium-chain saturates include palm, palm

kernel particularly palm stearin, a palmitic acyl-rich byproduct from the purification and fractionation of palm kernel oil. Other potentially valuable sources of fatty acyl groups for surfactants and detergents are inexpensive feed stocks such as tallow, used cooking oil and algal oils and oils from jatropha and soapnut.

Greenhouse gas emissions in a system are usually calculated by a tool for quantitative assessment of materials, energy flows and environmental impacts of products, services and technologies called Life Cycle Assessment (LCA). LCA is a methodology for evaluating the environmental load of processes and products (goods and services) during their life cycle from cradle to gate.

The goal of this research is to conduct Life Cycle Assessment of microemulsion biofuel production from palm oil. This study will determine greenhouse gas (GHG) emission process in which fatty acid methyl ester (FAME) will be used as surfactant and bioethanol will be substituted instead of ethanol as polar phase based on different raw materials, the microemulsion with low environmental emissions as well as water and energy will be formulated through life cycle analysis technique. Thus, all materials and energy consumption of microemulsion biofuel production process will be used as inventory data for life cycle inventory analysis to evaluate their environmental impacts using LCA software package Simapro version 7.1. The objectives of this study are;

1) To perform a life cycle assessment (LCA) of microemulsion biofuel production by varying the raw materials such as palm oil and crude palm oil, butanol, surfactant in microemulsion biofuel production stage

2) To compare the environmental impacts from microemulsion biodiesel production process in which fatty acid methyl ester (FAME) will be used as surfactant and bioethanol will be substituted instead of ethanol as polar phase

3) To evaluate the environmental impacts in terms of acidification, eutrophication, abiotic depletion, global warming (GWP 100), ozone layer depletion (ODP), human toxicity, fresh water aquatic ecotoxicity, marine aquatic ecotoxicity, terrestrial ecotoxicity and photochemical oxidation associated with the microemulsion biofuel production based on life cycle assessment approach

2. Theoretical Background

Biofuel

Biodiesel can be used as a fuel for vehicles in its pure form, but it is usually used as a diesel additive to reduce levels of particulates, carbon monoxides, and hydrocarbons from diesel-powered vehicles. Biodiesel is produced from oils or fats using transesterification process. Transesterification with alcohol to produce fatty acid methyl ester (FAME) known as biodiesel yields a fuel with lower viscosity and acceptable performance properties. However, the combustion of biodiesel in some cases slightly increases nitrogen oxides (NOx) in exhaust emissions (Kalam *et al.*, 2002). In terms of the environmental aspect, water washing process is typically used for biodiesel purification after the transesterification reaction. So, a large volume of wastewater stream is generated as well as the high energy consumption is used to remove crude glycerol byproduct, methanol, and catalyst (Sulaiman *et al.*, 2011).

Moreover, microemulsion biofuel production which is the concept of blending vegetable oil and/or diesel with ethanol, has been receiving interest in order to overcome the limitations of biodiesel production which uses transesterification process. Microemulsions are homogenous, transparent, thermodynamically stable colloidal dispersions of immiscible water and oil combination between surfactant with co-surfactant (Sabagh et al., 2012). It has been receiving increased attention for biofuel production since this technique can reduce the high viscosity of vegetable oil without large amount of wastewater (Balat et al., 2008). The life cycle of microemulsion biofuel beginning with the acquisition of raw materials, palm oil, and other raw materials including diesel, ethanol, surfactant and cosurfactant. In order to get palm oil, the palm oil cultivation, harvesting, oil extraction and oil refining processes are involved.

Palm Oil Production

Palm oil presents a better and attractive feedstock for biofuel production compared with other first and second generation feedstock. Because of its high oil yield (averagely 8.6 ton per hectare of land), it is almost three times more than that for coconut, 12 times more than soybean oil yield, and seven times more than that for rapeseed (Schmidt et al., 2007). Currently, palm oil is the second largest edible oil source after soybean oil, which forms approximately 34 % of the global oil supply. In 2009, both palm oil and palm kernel oil accounted for 5 % of the total cultivated land for vegetable oil production globally. In 2010, the global palm oil production was 47.9 million tons of which 11 % were used for biodiesel production (Schmidt et al., 2007). For the production in 2010, Malaysia and Indonesia together contributed about 87 % of the total palm oil produced in the world with about 19.5 and 22.5 million tones, respectively (MPOB, 2010). In Thailand, palm oil production has been accelerated in recent years.

Oil Palm Plantation

More than 70% of the oil palm plantations are located in the southern provinces of Thailand such as Krabi, Chumpom and Suratthani where the climate conditions are suited for growing oil palm. Cultivation of oil palm consists of two major stages i.e. growing at the nursery and planting in the field. In the nursery, the seeds are sown in small polyethylene bags until the seedlings are approximately three to four months old. After that, the seedlings are transferred to larger bags until they are 12 to13 months old and ready for planting. Oil palm starts bearing fruits after 2.5 to 3 years. The first harvest is possible after five years, and estimated plant lifetime is more than 30 years; however, it is generally replanted after 25 years because it starts getting to tall for convenient harvesting. The plantation has about 131 to137 trees per hectare. The average fresh fruit bunches (FFB) yield in Thailand is 17.5 ton /ha/yr. The seeds of oil palm are applied at 168 kg /ha/yr. The applied fertilizers are 151, 72 and 307 kg /ha/yr. for N, P_2O_5 and K_2O fertilizer, respectively. Herbicides such as glyphosate and paraquat are applied at 4.8 and 1.6 kg ha/yr, respectively. In addition, biomass residues such as fronds and trunks are also generated in the plantation. Each palm tree produces 20 to 30 fronds per year. The fronds cut down regularly from the palm trees over the service life of the plantation, are estimated to be around 12 ton of dry matter per hectare and year. However, the trunks will be available only one time (when cutting down for re-planting) over the 25 years; the total dry mass of these trunks was estimated to be around 57 ton / ha/yr.

(Silalertruksa et al., 2012).

The production of FFB involves six main processes. The planning stage involves the feasibility studies of the proposed area for plantation. Oil palm nursery proceeds after confirmation of the suitability of area for plantation which is normally endorsed by respective bodies for development. The seedlings are raised in polybags as nursery for about a year with adequate irrigation with manuring. Other field maintenance practices include pruning, pest and disease control, and mulching. After 24–30 months of transplanting depending on the nutritious value of the soil, harvesting of FFB may be due. Normally, harvesting is done manually with chisels and sickles mounted on bamboo or aluminum poles. The FFB are then sent to the oil mill for oil extraction. In order to ensure the amount of free fatty acid (FFA) content of the oil, handling of FFB after harvesting must be done in a way to reduce bruises on the fruits. Also, since the quality of the oil produced depends on the time interval between harvesting and sterilization (the first stage of milling), FFB must be transported as soon as possible after harvesting and the distance from plantation to milling site must be close. Therefore, most oil mills are located near the cultivation area to minimize the cost of transportation (Anoop et al, 2013).

Palm Oil Extraction

The main processes involved in the milling or extraction of palm oil from fresh fruit bunches (FFB). Sterilization of FFB is done in a steamer (pressurized cages) at about 2–3 bars to ameliorate the content of free fatty acid (FFA) which could reduce the quality of the oil. Therefore, this process requires the large amount of energy and water to make hot steam. A rotation drum stripper is used to thresh the fruitlets from the sterilized bunches and the fruitlets sent to the digester. The empty fruit bunches (EFB) are also used as mulch in the oil palm plantation.

The digester then removes the fruits' mesocarp from the nuts by continuous heating the fruits with steam which helps to open the oil cells in the mesocarp for effective oil extraction. The oil extraction is done with the help of screw press where the press cake and nuts are conveyed to the palm kernel crushing (PKC) plant and the pressed liquid oil also sent to a vibrating screen where it is diluted. The oil is then clarified and purified to remove dirt and moisture. The sludge from clarifier consists of mainly water soluble parts of the palm fruits and suspended materials. Then, it is desalted and further sent to the centrifuge to recover the excess oil which is recycled and return into the clarifier. The water–sludge mixture (palm oil mill effluent, POME) is then sent to the effluent treatment plant (ETP). Then, the crude palm oil (CPO) from the oil extraction process is then stored and transported to oil refinery. The palm kernel nuts are also cracked to separate the kernel from the shells. The oil palm fiber and kernel shells from the PKC plant are used as biomass fuel in the boiler which generates steam for the oil milling processes.

Palm Oil Refining

In the refining process, palm oil can be separated in fractions of liquid and higher melting-point (at room temperature) substances. Different grades of olein and stearin are commercially usable. CPO from extraction mills has to be refined in order to obtain pure palm oil that is suitable for consumption or for use as raw material by down- stream industries. The main product is pure palm oil and the co-product is palm stearin. The pure palm oil yield is 0.71 kg/kg CPO and palm stearin yield is 0.29 kg/kg CPO. (Papong S. et al., 2009)

Palm and palm kernel oils consist mainly of glyceride and, like other oils in their crude form may consist of small and variable portions of non-glyceride components as well. In order to render the oils to an edible form, some of these non-glycerides need to be either removed or reduced

to an acceptable level. The refining routes of palm oil and palm kernel oil are quite identical. There are two routes which can be taken to process crude oil into refined oil

Chemical refining, which has a higher cost of refining and generally found in older refineries, utilizes an alkali to neutralize most of the fatty acids which are removed as soap. Physical refining, which eliminates the need for an effluent plant for the soap stock, involves subjecting the oil to steam distillation under high temperature and vacuum for removal of the free fatty acids.

Microemulsion Biofuels

Microemulsion-based biofuel is an emerging biofuel production technology, produced by microemulsification of mixed liquid fuels such as vegetable oils and bio-alcohols which are derived from renewable and locally agricultural based feedstocks. Therefore, the microemulsion fuels have been considerable interest in an alternative fuel to replace petroleum-based transportation fuels. Microemulsion biofuels can be typically formulated by stabilizing polar phase (e.g., ethanol) in reverse micelles which all disperse in non-polar phase (vegetable oil and/or diesel blend) which known as water in oil microemulsion formation. The unique characteristics of microemulsion fuel are isotropic, transparent, thermodynamically stable mixtures consisting of non-polar phase, polar phase and stabilized by an appropriate surfactant system in sufficient concentration. Furthermore, microemulsion biofuel contains about five components (vegetable oil/diesel, ethanol and surfactant and/or cosurfactant). So, surfactant is one of the key parameters to formulate the optimum microemulsion fuel. Several surfactants have been used to formulating of microemulsion based biofuel from vegetable oil feedstock. Selecting an appropriate surfactant is a challenge for formulating thermodynamically stable mixtures of microemulsion fuel (Arponpong et al., 2014).

Surfactants

Theoretically, surfactants (*Surface active agent*) contain two parts (hydrophilic and hydrophobic part) in a molecule or known as an amphiphile molecule; hydrophilic part soluble in polar phase (e.g. water, ethanol) and hydrophobic part soluble in the non-polar phase (e.g. oil) (Charoensaeng A., 2014). The polar part of the surfactant molecule (e.g., SO_4 -, COOH-, EO-ethylene oxide group) is referred as head, and the non-polar part of the molecule is referred as tail. The polar nature of the head group of surfactants varies from non-ionic to ionic character. Depending on the nature of this part, the surfactants are classified into four types; anionic, cationic, non-ionic, and zwitterionic surfactants. Surfactant monomer and micelle structures are shown in Figure 2.5 (Arponpong et al., 2014).

Cosurfactants

Short-chain alcohols act as cosurfactants, directly influencing the properties of the aggregates, while alcohols with longer hydrocarbon chains perform as cosolvents, altering the properties of the solvent. (Naresh et al., 2005). The impact of alcohol additives on the self-assembly of surfactants in supercritical carbon dioxide was investigated using lattice Monte Carlo simulations. The result showed that the present of alcohols reduce the critical micelle concentration (CMC). The CMC was greater when the number of hydrocarbon chain and the concentration of alcohol increased. Short-chain alcohols were found to concentrate in the surfactant layer of the aggregates, replacing surfactant molecules and leading to a strong decrease of the aggregation number. On the other hand, only a small number of alcohol molecules with longer chain length were found in the aggregates, leading to a slight increase in the aggregation number.

Alkanols as fuel additives

The use of ethanol in bio-based fuel has been receiving much attention since ethanol can be converted from renewable resources. In general, ethanol can be produced from petrochemical based process with low cost. Bioethanol, on the other root, can be produced from sugar-based alcoholic fermentation derived from plant or biomass materials (e.g., corn, cassava, sugar cane, molasses and agricultural residuals). Because of its high octane number, ethanol is a good spark-ignition in a gasoline engine, while vegetable oils have high cetane number resulting good combustion in diesel engine. The works on blending an ethanol with a diesel so called diesohol. Although blending diesel fuel with ethanol has notable advantages in terms of renewable nature as well as emission reduction, the major problem is that ethanol is insoluble in diesel over a wide range of temperatures. Therefore, a suitable emulsifying agent or surfactant is required to formulate an emulsion of homogeneous mixture.

The critical issues of using ethanol in the diesel blend have been debating. Because ethanol has lower heating value than those of regular diesel as well as possess a very low cetane number that can reduce overall cetane level in ethanol-diesel blends. To overcome this problem, cetane boosters are normally required in order to improve energy content. Due to butanol having higher energy configuration and higher immiscibility than ethanol, it has been being an interest for cetane enhancing additives in diesel fuel. Furthermore, similar to bio-ethanol, butanol can be derived from biomass or agricultural crop. (Charoensaeng et al., 2014)

Life Cycle Assessment (LCA)

LCA is defined as the "compilation and evaluation of the inputs, outputs and potential environmental impacts of a product system throughout its life cycle". Thus, LCA is a tool for the analysis of the environmental burden of products at all stages in their life cycle – from the extraction of resources, production of materials and use of the product to the management after it is discarded, either by reuse, recycling or final disposal. The total system of unit processes involved in the life cycle of a product is called the "product system". The environmental burden covers all types of impacts upon the environment, including extraction of different types of resources, emission of hazardous substances and different types of land use (Dr. Amold T. et al., 2004).

LCA methodology used in this study followed the principles and framework of the International Organization for Standardization, ISO 14040 and 14044. The steps of LCA framework are 1) Goal and Scope Definition 2) Inventory Analysis (LCI) 3) Impact Assessment or LCIA 4) Interpretation

Many LCA studies have been carried out on biodiesel and microemulsion biofuel production. In one of the LCA studies, Thapat et al. (2012) carried out the LCA to evaluate the potential environmental impacts associated with biodiesel production. The functional unit of the study is the production of 1000 L of palm biodiesel. In this study, oil palm plantation and palm oil milling are the two major contributors to global warming. N-fertilizer production and its application which induces N_2O emissions is the main source for agricultural stage. For milling stage, methane generated from the treatment of POME in open ponds is the biggest source of global warming potential (GWP). It contributes almost 100% of GWP in the milling stage.

Wibul (2012) provided a cradle to gate LCA of biofuel production from microalgae. According to impact assessment results, $NaNO_3$ becomes a main contributor in terms of energy consumption and environmental impact in cultivation process. However, decrease in $NaNO_3$ may

have an adverse effect on the growth rate of microalgae. (Quan, 2006) studied the effects of sodium nitrate on the growth rate of microalgae *Nannochloropsis* and concluded that microalgae productivity increased when concentration of sodium nitrate was increased. In the study of Chisti (2007), lipid content in microalgae was found to be in the range of 15 to 80 % by weight. Freshwater green microalgae *Scenedesmus armatus* contains a lipid content of 40 % by weight. When the lipid content of microalgae was increased from 40% to 80% by weight, GWP decreased significantly. Furthermore, algae biomass concentration can be as high as 4g/L for photobioreactor facility. According to the result, it can be obviously seen that global warming potential (GWP) decreases sharply for biomass concentration in the range of 0.5-2.0 g/L. Beyond this concentration, GWP decreases slightly.

3. Methodology

Goal, Scope, Functional Unit, and System Boundary

The goal of this study was to assess the environmental impacts of the microemulsion biofuel production from palm, soybean and algae oil. The process of biofuel production is divided into four stages: cultivation, oil extraction, refining and microemulsion production. In microemulsion biofuel production stage, it will differ in two different production processes. They are ordinary microemulsion process and bio-based microemulsion process. Moreover, the environmental impacts from production of microemulsion biofuel from each different oil source will be compared. All together six scenarios will be investigated under this study. The methodology used in this study was based on ISO14040 series. The life cycle inventory data were collected from secondary data sources (National Thai LCI database, previous works on LCA of palm oil microemulsion-based biofuel, and selected references). Commercial LCA software, SimaPro 7.1, with CML 2 baseline 2000 methods was applied to evaluate the ten potential environmental impact categories such as acidification, eutrophication, abiotic depletion, global warming (GWP 100), ozone layer depletion (ODP), human toxicity, fresh water aquatic ecotoxicity, marine aquatic ecotoxicity, terrestrial ecotoxicity and photochemical oxidation. Production of capital goods, risk, facilities construction, human labor and transportation at all stages of the system boundary are excluded in this study. In this research, functional unit which provides a reference to which the inputs and outputs are related is set to be one ton of microemulsion biofuel production.

System boundary of the study The system boundary which covers cultivation, oil extraction, refining and microemulsion production was illustrated in Figure 1. The capacity of microemulsion biofuel production is 1 ton/day. Commercial software, SimaPro version 7.1, with CML 2 baseline 2000 method was used to calculate impact potentials based on the LCI results. The impacts on human health and the environmental burdens associated with raw material inputs quantified by the inventory are analyzed and compared. Potential impact categories included in this study are as follows; acidification,fresh water aquatic ecotoxicity, human toxicity, terrestrial ecotoxicity, marine aquatic ecotoxicity, ozone layer depletion, eutrophication, abiotic depletion, photochemical oxidation, global warming potential,
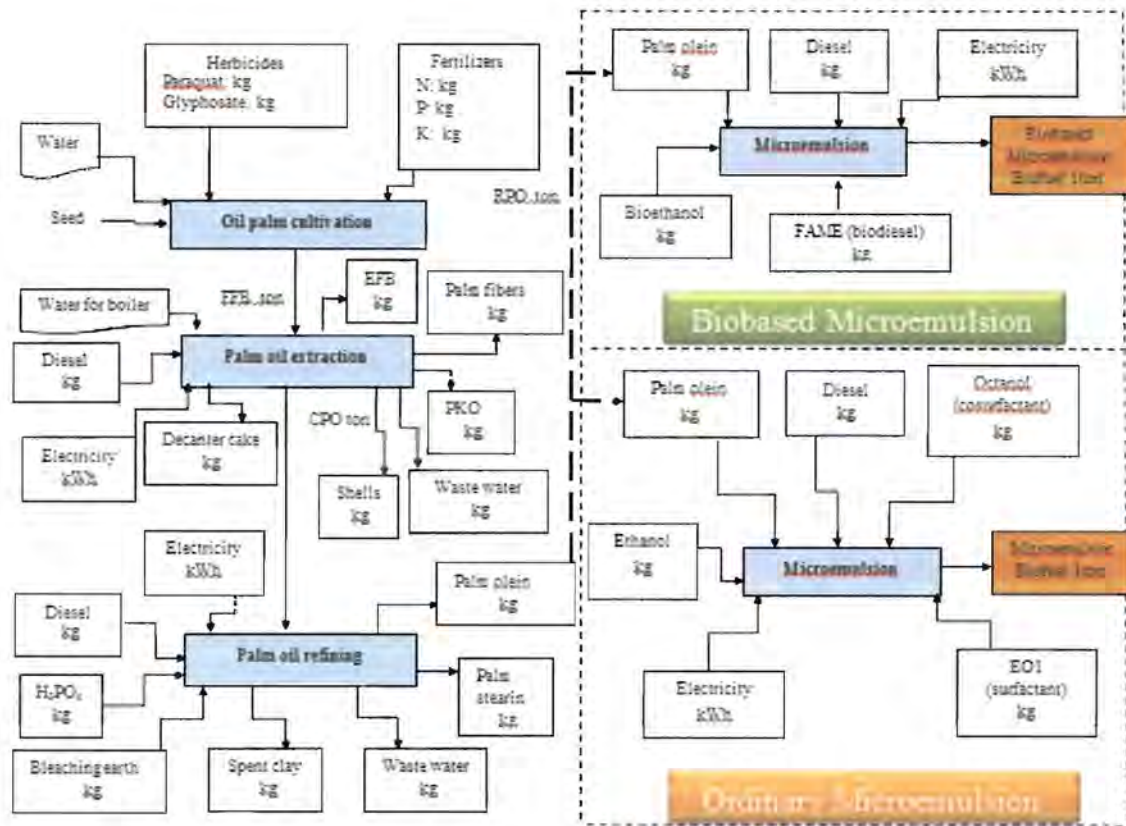
Figure 1 The system boundary of microemulsion biofuel production from palm oil

Palm oil production

Cultivation

Oil palm normally takes two and a half to three years to start bearing bunches and continues bearing until the end of its lifetime, approximately 25 years. It yields about 3.6 tons of fresh fruit bunch (FFB) per rai per year (23 tons of FFB per hectare per year). The oil palms are planted with the density ranging from 128 to 148 trees per hectare, depending on the planting material, soil and climate (Papong et al., 2009). The fertilizers used are 7.79 kg/ton FFB for N fertilizer from ammonium sulphate , 0.05 kg/ton of FFB for P2O5 fertilizer from ground rock phosphate and 14.41 kg/ton FFB for K2O fertilizer from potassium chloride . Moreover, 0.28kg/ ton of FFB and 0.10kg/ton FFB of glyphosate and paraquat respectively are used as herbicide at an average of 1-3 times per year. They are used every year, but the rates of application are different depending on the age of the plants. The usual frequency of a harvesting cycle of FFB is 10-15 days or 2-3 times a month. Water requirement for the oil palm plantation is mostly from rain water since most of the plantations are located in the tropical region. Young palms are harvested with a chisel whereas old and tall palms are harvested with a long-handled sickle. As they are harvested only by manual labor, there is no fossil energy input to harvesting. In this study, the representative oil palm plantation and crude palm oil mill are located in the Krabi province, in the southern part of Thailand. The palm oil mill is located close to the palm field; it is 34 km for round trip with 3-ton truck in the assumption. The fuel consumption for the heavy diesel vehicles used for transportation of FFB was 1.6 km/L of diesel (Pleanjai, 2009).

Table 1 Raw materials used in cultivation stage (base case)

Input		References
N- fertilizer(kg)	21.26	Pleanjai, 2009
P_2O_5 -fertilizer(kg)	0.14	
K_2O-fertilizer (kg)	39.34	
Glyphosate (kg)	0.75	
Paraquate (kg)*	0.27	
Diesel used (for transport FFB) (kg)	18.12	
Output		
Product FFB (kg)	2726.13	Pleanjai , 2009

*Bipyridylium has been substituted in the calculation.

Oil Extraction

Typically, the fresh fruit bunches (FFB) are directly transported to palm oil mills and extracted within 24 hours to ensure the desired quality. The outputs from palm oil mill include crude palm oil (15-18 %), shells (5-6%), kernels (5-6%), palm fiber (12-14%), and empty fruit bunches (25-27%) (Papong, 2009). The primary product is crude palm oil (CPO) which is approximately 0.163 ton/ ton FFB (Pleanjai, 2009). Fiber residues and empty fruit bunches (EFB) are used as a biomass fuel to generate internal power in the form of heat and electricity, which are integrated to the palm oil mill. Diesel oil used in the production process is approximately 1.62 liter /ton FFB which is used for the diesel generator and other diesel machines in the plant. In addition, palm oil mill effluent (POME) contains high COD loading (above 100,000 mg/L) (Kaewmai, 2012).

Table 2 Input and output in extraction stage (base case)

Input		References
FFB(kg)	2,726	Pleanjai, 2009
Water(completely softened at plant)(kg)	2,269	Kaewmai, 2012
Diesel for machine (low sulphur,at refinery)(kg)	1.08	Kaewmai, 2012
Electricity from grid (kWh)	6.96	Kaewmai, 2012
Output		
Product	444.36	Pleanjai, 2009
CPO(kg)	142.08	Kaewmai, 2012
Co-product	581.64	Kaewmai, 2012
Palm kernel(kg)	93.24	Kaewmai, 2012
Solid waste	168.72	Kaewmai, 2012
EFB(kg) Decanter cake(kg) Fiber(kg) Shell(kg) Liquid	159.84	Kaewmai, 2012
waste Palm oil mill effluent (m3)	1.52	Kaewmai, 2012

Oil Refining

In crude palm oil refining process, main product is palm olein and the co-product is palm stearin. The neat palm oil yield is 0.71 kg/kg of crude palm oil (CPO) and palm stearin yield is 0.29 kg/kg CPO (Papong et al., 2009). As an assumption, microemulsion biofuel production is carried out near the palm oil mill.

Table 3 Input and output for refining stage (base case)

Input		Reference
CPO (kg)	444.36	Arpornpong , 2013
Water (kg)	52.58	Arpornpong , 2013
Phosphoric acid (85% in H2O) (kg)	0.41	Arpornpong , 2013
Bentonite (kg)	4.14	Arpornpong , 2013
Electricity from grid (kWh)	369.1	Arpornpong , 2013
Output		
Product		Papong et al., 2009
palm olein (kg)	315.5	Papong et al., 2009
Co-product		
palm stearin (kg)	128.86	

The green scenarios for microemulsion biofuel formulation

The life cycle inventory data were collected from secondary data sources (National Thai LCI database, previous works on LCA of palm oil based microemulsion biofuel, and selected references) based on the functional unit (one ton) of microemulsion biofuel production and the boundary of biofuel production. In this study, the boundary of ME biofuel production consists of four stages: cultivation, oil extraction, refining and microemulsion production. In microemulsion biofuel production stage, four different formulations such as scenario I, II, III and IV have been assessed and compared.

Scenario I (Base Case)

Formulation of microemulsion-based biofuel (ME50) was the mixture of methyl oleate /1-octanol (22 vol. %), ethanol (20 vol. %), and the palm oil/diesel blend (58 vol. %). Methyl oleate and 1-octanol were used as nonionic surfactant and cosurfactant, respectively. Ethanol was used as polar phase In this study, palm olein was employed to formulate microemulsion fuels. Materials applied in the microemulsion biofuel production were the palm olein/diesel (1:1) by volume, ethanol and methyl oleate/1-octanol (1:8) by molar (Arpornpong et al., 2014). Palm olein (0.321 ton/ton of ME50) and diesel (0.289ton/ton of ME50) were directly mixed for ME biofuel production. Electrical energy consumption required for the mixing process only was approximately 7.46 kWh/ton of ME50. Particularly, biofuel microemulsion contributes ME50 with an absolute 100 percent yield without any waste or byproduct generation during the microemulsification (Arpornpong , 2013).

Table 4 Inventory data for Scenario I (Base Case)

Input		References
Palm olein(kg)	315.5 184.6	Arpornpong, 2013
Ethanol from ethylene(kg)	75.2	Arpornpong, 2013
Surfactant(kg)*	139.6	Arpornpong , 2013
Cosurfactant (kg)**	285	Arpornpong , 2013
Diesel, low sulphur, at refinery(kg)	7.46	Arpornpong , 2013
Electricity Thailand base 2007 (kWh)		Arpornpong , 2013
Output		
Product		Arpornpong , 2013
Microemulsion biofuel (ton)	1	

*Ethoxylated alcohol has been substituted in the calculation **1-butanol has been substituted in the calculation

Scenario II (Biobased Case)

In Scenario II, formulation of ME was conducted from renewable based component. Biobased case was simulated by fatty acid methyl ester (FAME) and bioethanol produced from biomass substituting instead of methyl oleate and ethanol produced from petrochemical process. Composition of microemulsion fuel are surfactant/cosurfactant blend (1:8) by molar, vegetable oil/diesel mixture (1:1) by volume and ethanol. Palm olein (0.301 ton/ton of ME biofuel) and diesel (0.284ton/ton of ME biofuel) were directly mixed for ME biofuel production. Electrical energy consumption required for the mixing process only was approximately 7.46 kWh/ton of ME biofuel. This inventory data were collected from laboratory research (Manaphati, 2015).

Table 5 Inventory data for Scenario II

Input		Reference
Palm olein(kg)	305.54	Manaphati, 2015
Bioethanol (kg)	189.76	Manaphati, 2015
Palm methyl ester(kg) (Surfactant)	47.11	Manaphati, 2015
1-octanol,propylene hydroformylation(kg)*	168.89	Manaphati, 2015
Diesel, low sulphur (kg)	288.7	Manaphati, 2015
Electricity thailand base 2007 (kWh)	7.46	Arpornpong, 2013
Output		
Product		
Microemulsion biofuel (ton)	1	

*1-butanol has been substituted in the calculation

Scenario III (Butanol Blend Case)

Formulation of Scenario III was the blending of butanol and ethanol as polar phase. Based on Arpornpong and coworkers' study (2013), the key factor which contributes to environmental impacts of ME came from raw materials including surfactant and cosurfactant. In this study, microemulsion biofuel with buthanol blend could reduce the amount of surfactant used in ME formulation. Composition of microemulsion fuel were surfactant/cosurfactant blend (1:8) by

molar, vegetable oil/diesel mixture (3:7) by volume and ethanol/butanol blend (9:1) by molar. Palm olein (0.183 ton/ton of ME biofuel) and diesel (0.404 ton/ton of ME biofuel) were directly mixed for ME biofuel production. Electrical energy consumption required for the mixing process only was approximately 7.46 kWh/ton of ME biofuel. This inventory data were collected from laboratory research (Apichatyothin, 2015).

Table 6 Inventory data for Scenario III

Input		References	
Palm olein(kg)	186.3 171.92	Apichatyothin,	2015
Ethanol from ethylene (kg)	60.84 150.93	Apichatyothin,	2015
Methyl oleate*(kg)	410.93 19.08	Apichatyothin,	2015
1-octanol(kg)**	7.46	Apichatyothin,	2015
Diesel, low sulphur (kg)		Apichatyothin,	2015
1-butanol, propylene hydroformaltion(kg) Electricity Thailand base 2007 (kWh)		Apichatyothin, Arpornpong, 2013	2015
Output			
Product Microemulsion biofuel (ton)	1		

*Ethoxylated alcohol has been substituted in the calculation **1-butanol has been substituted in the calculation

Scenario IV (RDBPO Case)

In Scenario IV, refined deodorized and bleached palm oil (RDBPO) was applied instead of refined palm oil. In order to reduce the emissions from palm oil production, scenario IV was simulated by bypassing the step of oil refinery In refining stage, distillation process which is used to separate palm olein and palm stearin required extensive energy. Composition of microemulsion fuel are surfactant/cosurfactant blend (1:8) by molar, RDBPO/diesel mixture (1:1) by volume and ethanol. RDBPO (0.319 ton/ton of ME biofuel) and diesel (0.296 ton/ton of ME biofuel) were directly mixed for ME biofuel production. Electrical energy consumption required for the mixing process only was approximately 7.46 kWh/ton of ME biofuel. This inventory data were collected from laboratory research (Manaphati, 2015).

Table 7 Inventory data for Scenario IV (RBDPO case)

Input		References	
RDBPO(kg)	324.68	Manaphati, 2015 Manaphati,	
Ethanol from ethylene(kg)	188.52	2015 Manaphati, 2015	
Methyl oleate(kg)*	53.19 132.2	Manaphati, 2015 Manaphati,	
1-octanol(kg)**	301.4	2015 Arpornpong, 2013	
Diesel, low sulphur, at refinery(kg)	7.46		
Electricity thailand base 2007 (kWh)			
Output			
Product Microemulsion biofuel (ton)	1		

RDBPO- Refined Deodorized Bleached Palm Oil *Ethoxylated alcohol has been substituted in the calculation **1-butanol has been substituted in the calculation

Comparison of the Properties of ME Biofuels

Table 4.8 Comparison of the Properties of ME biofuels and neat diesel

Properties of ME biofuel	SI *	SII **	SIII ***	SIV **	Neat diesel ****
Density , kg/cm³ @ 20° C	0.85	0.85	-	0.87	0.83
Kinematic viscosity, cst @ 40° C	4	6	4	6	3
Heat of combustion, MJ/kg	39	39	39	39	50
Flash point (° C)	15	-	-	-	1
Cloud point (°C)	-	5	-3	5	-

* (Arpompong, 2013) ** (Manaphati , 2015) ***(Apichatyothin , 2015) ****(Sivaramakrishnan , 2011)

4. Results and discussion

Greenhouse Gas Emissions

The total GHG emissions of the ME production for different scenarios described in the unit of CO_2-equivalent (CO2eq) are illustrated in Figure 1. Among them, scenario IV represents the lowest GHG emissions (1,017 kgCO2) as a result of using RBDPO instead of palm olein in the ME formulation. When RBDPO was used to formulate ME biofuel, the total GHG emission was significantly reduced by 40 percent compared to base case (1,448 kgCO2).
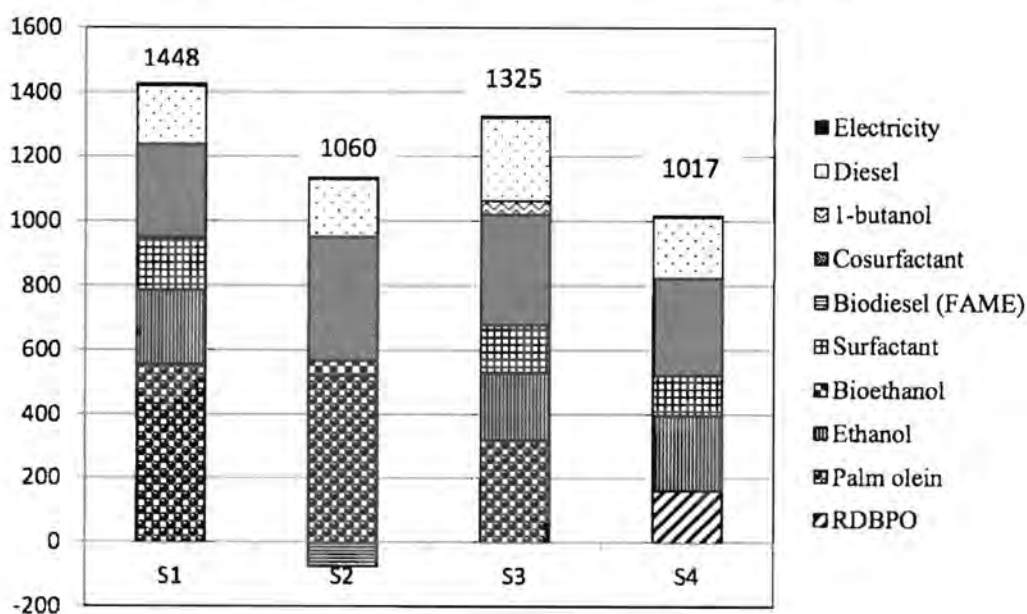
Figure 1 GHG emissions (kg of CO2 eq.) per 39,000 MJ of ME biofuel

Comparing GHG emissions of ME production process, it can be seen that the GHG emissions from raw material preparation accounted for 99% of all GHG emissions. In contrast, the production process accounted for only 1% in the case of electrical mixing. It can be noted that a GHG emission generated from production of palm olein was remarkably high relative to other raw materials. In palm olein production process, energy used in refining stage contributes more than other cultivation and extraction stages. In scenario IV, the GHG emissions of RBDPO production was lower than that of neat palm olein due to bypass the emissions from oil refining process which requires high energy supply.

According to the Figure 2, palm olein production; especially from N fertilizer loading during cultivation, was the highest GHG emission potential about at Scenario I and Scenario II. Furthermore, cosurfactant used in formulation of Scenario III and IV significantly accounted about 30 percent of GHG emission. In addition, the reverse impact was observed in Scenario II (biobased case) when using biodiesel instead of surfactant. The result is mainly influenced by the biodiesel production process.
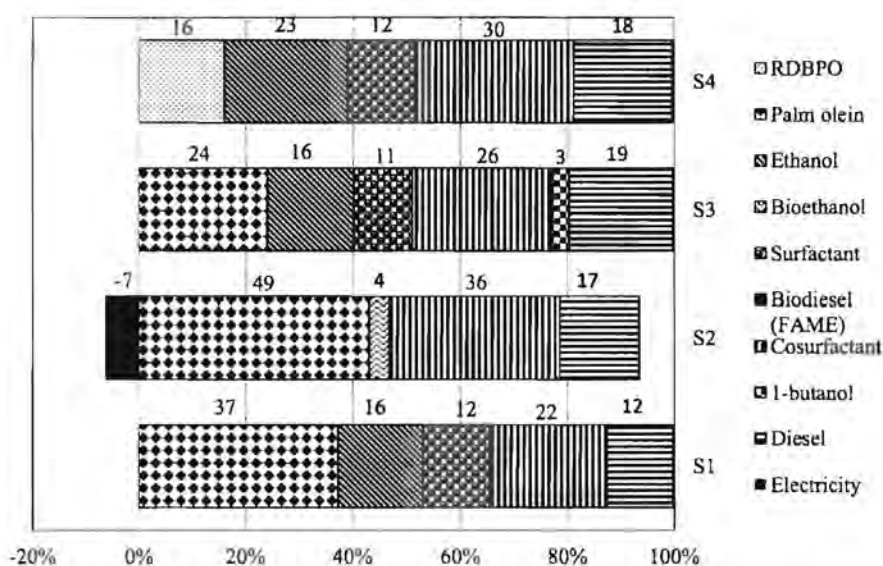
Figure 2. Comparison of the GHG emissions per 39,000 MJ of ME biofuels.

Life Cycle Impact Assessment (LCIA)

Environmental impacts of microemulsion biofuel production process were assessed by CML 2 baseline 2000 method. In this study, eleven potential environmental impact categories including acidification, eutrophication, abiotic depletion, greenhouse gas (GHG) emission, ozone layer depletion (ODP), human toxicity, fresh water aquatic ecotoxicity, marine aquatic ecotoxicity, terrestrial ecotoxicity, land use and photochemical oxidation were evaluated.

Global Warming Potential

The greenhouse gases considered in this study are carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). The greenhouse gas emission (GHG) is expressed in terms of kilogram equivalent of CO_2. (Wibul, 2012). According to the Figure 3, the lowest GHG emission was

observed from formulation of ME biofuel Scenario IV with RBDPO as a based vegetable oil instead of palm olein. In contrast, highest GHG emission formulation was Scenario I in which palm olein production contributed significant impact more than other materials used.

	S1	S2	S3	S4
≡ Bioethanol		45.94		
⊠ Electricity	4.85	4.85	4.85	4.85
⊠ Diesel	177.67	179.98	256.18	187.90
◘ 1-butanol			43.38	
ⅲ Cosurfactant	317.40	383.99	343.16	300.57
⊠ FAME		-75.87		
▢ Surfactant	179.32		145.08	126.84
⊠ Ethanol	230.03		214.23	234.91
■ Palm olein	538.59	521.59	318.03	
⊠ RDBPO				162.33
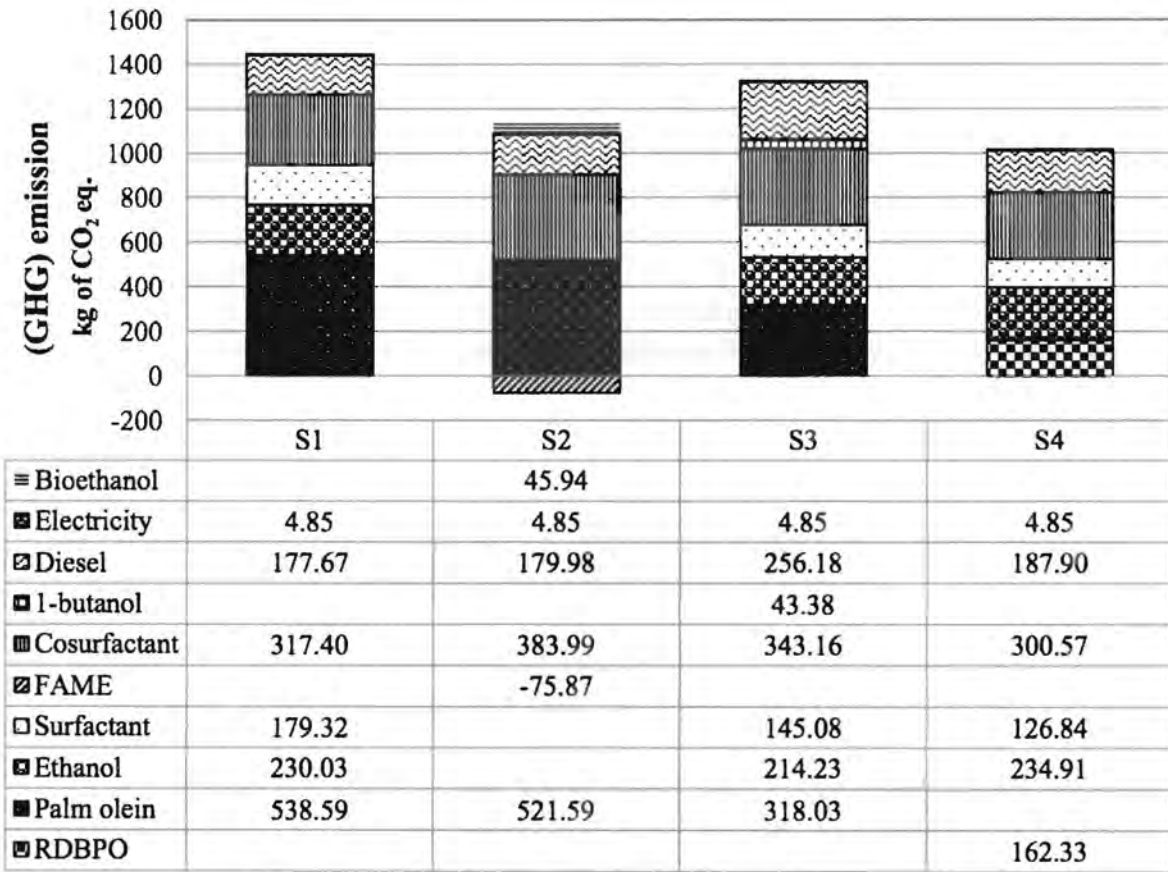
Figure 3 Greenhouse Gas (GHG) emission based on 1 ton of ME biofuel.

Acidification

Acidification is caused by acid deposition which is occured from emission of three main acidic substances. They are sulphur oxides (SOx), nitrogen oxides (NOx) and ammonia (NH_3). Other organic and inorganic acids can also contribute to the acidification and increase the acidity of water, soil and air. Sulphur dioxide is chosen as a reference acidic gas, and the impact of other emissions is also computed by means of equivalent factors based on relative acidity. Acidification potential is expressed as kilogram equivalent of SO_2. (Wibul, 2012) Figure 4 shows the results of acidification impact from each ME formulation. Among them, Scenario II (biobase case) contributed the highest acidification impact from

	S1	S2	S3	S4
⊟ Bioethanol		2.43		
⊗ Electricity	0.01	0.01	0.01	0.01
⊠ Diesel	0.58	0.59	0.84	0.61
⊞ 1-butanol			0.13	
▥ Cosurfactant	0.94	1.13	1.01	0.89
⊠ FAME		0.42		
☐ Surfactant	0.68		0.55	0.48
▣ Ethanol	0.67		0.62	0.68
■ Palm olein	1.56	1.51	0.92	
⊡ RDBPO				0.47
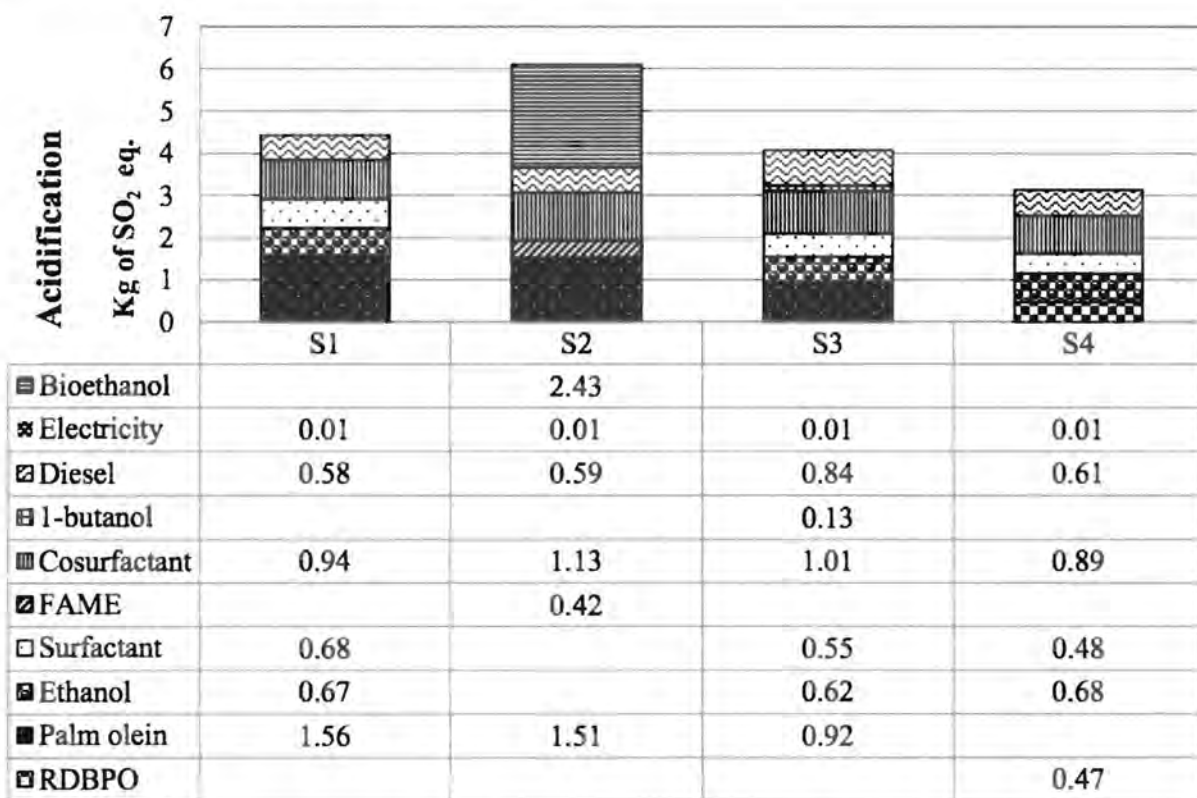
Figure 4 Acidification potential based on 1 ton of ME biofuel.

Ozone Layer Depletion

Ozone layer depletion is occurred by high level of chlorine and bromine compounds such as chlorofluorocarbons (CFCs), carbon tetrachloride (CCL_4), methyl bromide (CH_3Br), methyl chloroform (CH_3CCl_3), and halons (EPA 2010) in the stratosphere. The typical indicator for ozone layer depletion is chlorofluorocarbon (CFC). Ozone layer depletion potential of different gases is measured as kilogram equivalent of trichlorofluoromethane (CFC-11) (Wibul, 2012) Figure 5 shows the results of ozone layer depletion impact from each ME formulation. Especially, diesel usage in all four scenarios contributed the significant ozone layer depletion impact on the environment.

	S1	S2	S3	S4
▤ Bioethanol		2.82E-05		
✻ Electricity	3.25E-11	3.25E-11	3.25E-11	3.25E-11
▨ Diesel	2.09E-04	2.12E-04	3.02E-04	2.21E-04
⊞ 1-butanol			4.28E-06	
▥ Cosurfactant	3.13E-05	3.79E-05	3.38E-05	2.96E-05
▧ FAME		3.84E-06		
☐ Surfactant	7.56E-06		6.12E-06	5.35E-06
▣ Ethanol	6.71E-06		6.25E-06	6.85E-06
▪ Palm olein	1.66E-06	1.61E-06	9.80E-07	
⤴ RDBPO				4.12E-07
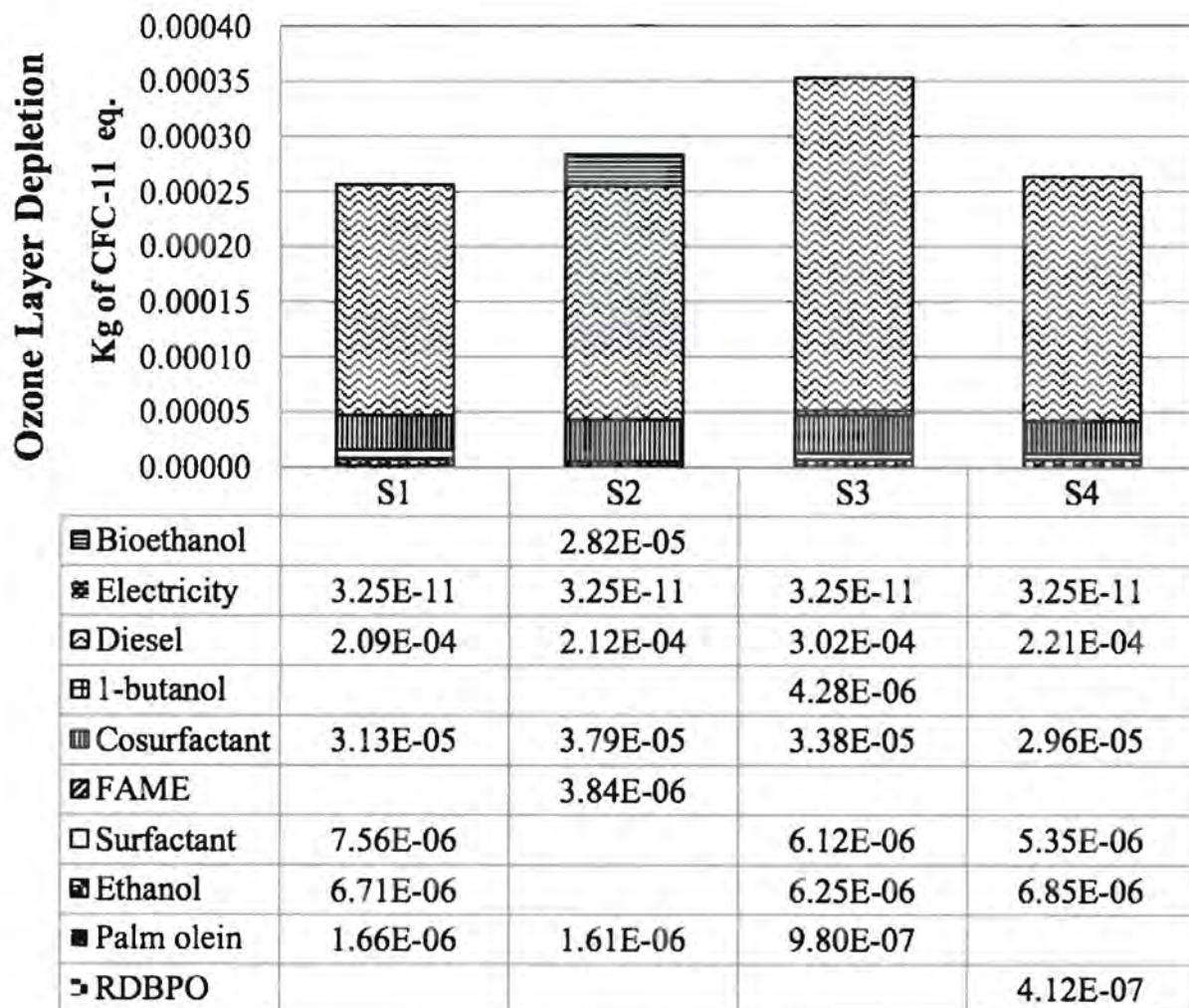
Figure 5 Ozone layer depletion potential based on 1 ton of ME biofuel.

Eutrophication

Eutrophication is primarily considered as the effect of releasing excessive amount of nutrients, especially nitrate and phosphate. The main contribution to this impact category is expressed in terms of kilogram equivalent of phosphate (PO_4) (Wibul, 2012). Figure 6 shows the results of eutrophication impact from each ME formulation. Among them, scenario II caused the highest eutrophication impact due to the production of bioethanol. Especially, application of nitrogen and phosphorus fertilizers from feedstocks cultivation was the main contributor (Gonzalez-Garcia et al., 2012).

	S1	S2	S3	S4
▤ Bioethanol		1.68		
✸ Electricity	0.00	0.00	0.00	0.00
▨ Diesel	0.09	0.09	0.13	0.09
⊞ 1-butanol			0.02	
▥ Cosurfactant	0.18	0.22	0.20	0.17
▧ FAME		0.19		
▢ Surfactant	0.06		0.05	0.04
▨ Ethanol	0.26		0.24	0.27
■ Palm olein	0.21	0.20	0.12	
▣ RDBPO				0.08
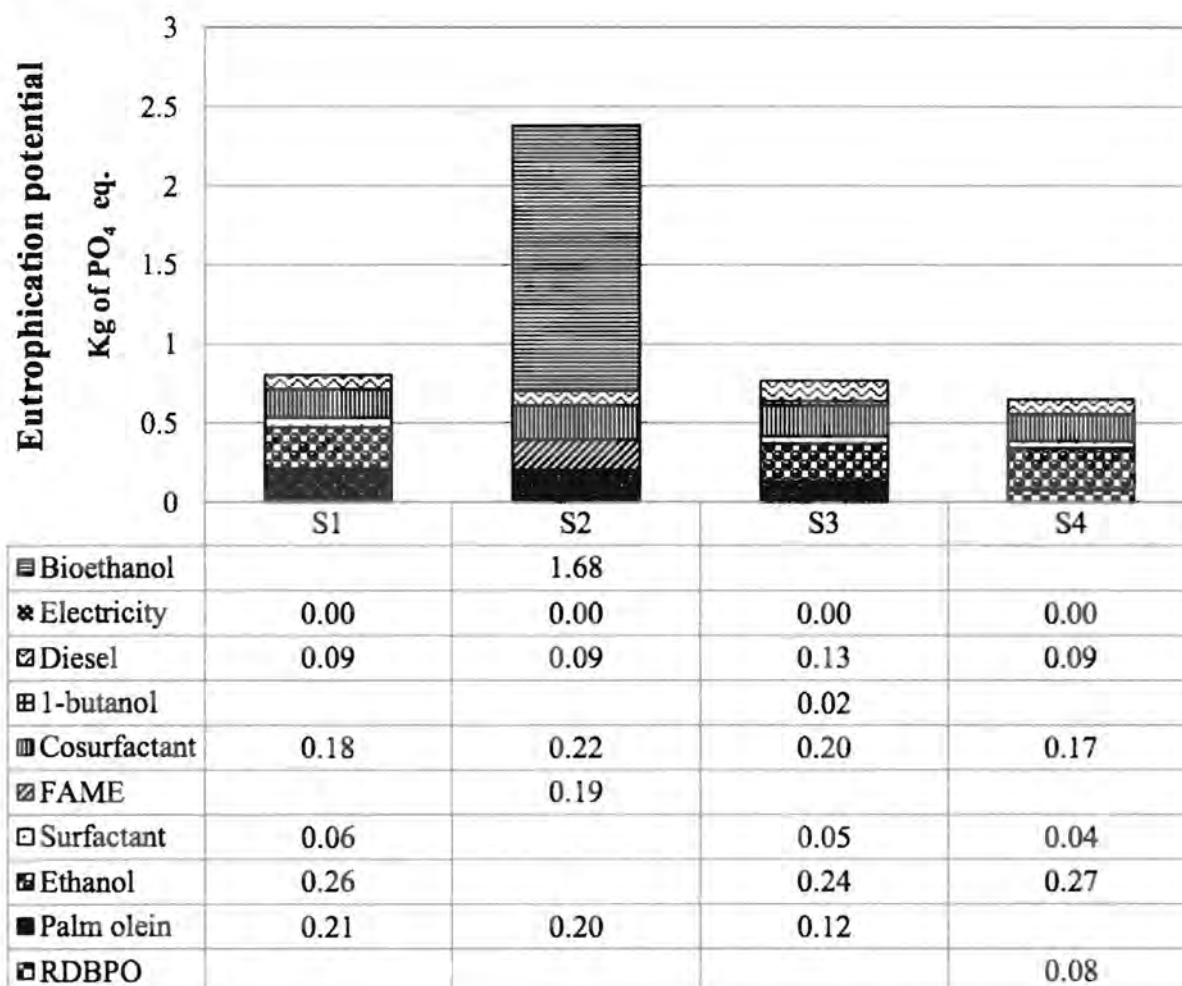
Figure 6 Eutrophication potential based on 1 ton of ME biofuel.

Land Use

The land use (either land occupation or land transformation) is mainly caused by continuous use of land area for a certain human-controlled purposes such as agriculture, raw material production and production processes. The contribution in this impact category is expressed in terms of PDF m^2yr. (Arpompong *et al.*, 2013) Figure 7 shows the results of land use impact from each ME formulation. Among them, scenario II caused the highest land use change impact because of the production of bioethanol. Especially, the bio-based feedstock cultivation was the main contributor of land use impact because a large area is

	S1	S2	S3	S4
⊟ Bioethanol		3738.06		
⊠ Electricity	0.00	0.00	0.00	0.00
☑ Diesel	3.28	3.32	4.73	3.47
⊞ 1-butanol			0.31	
▥ Cosurfactant	2.29	2.77	2.47	2.17
▨ FAME		170.43		
☐ Surfactant	1.23		1.00	0.87
▨ Ethanol	0.93		0.86	0.95
▪ Palm olein	0.42	0.41	0.25	
▣ RDBPO				0.07
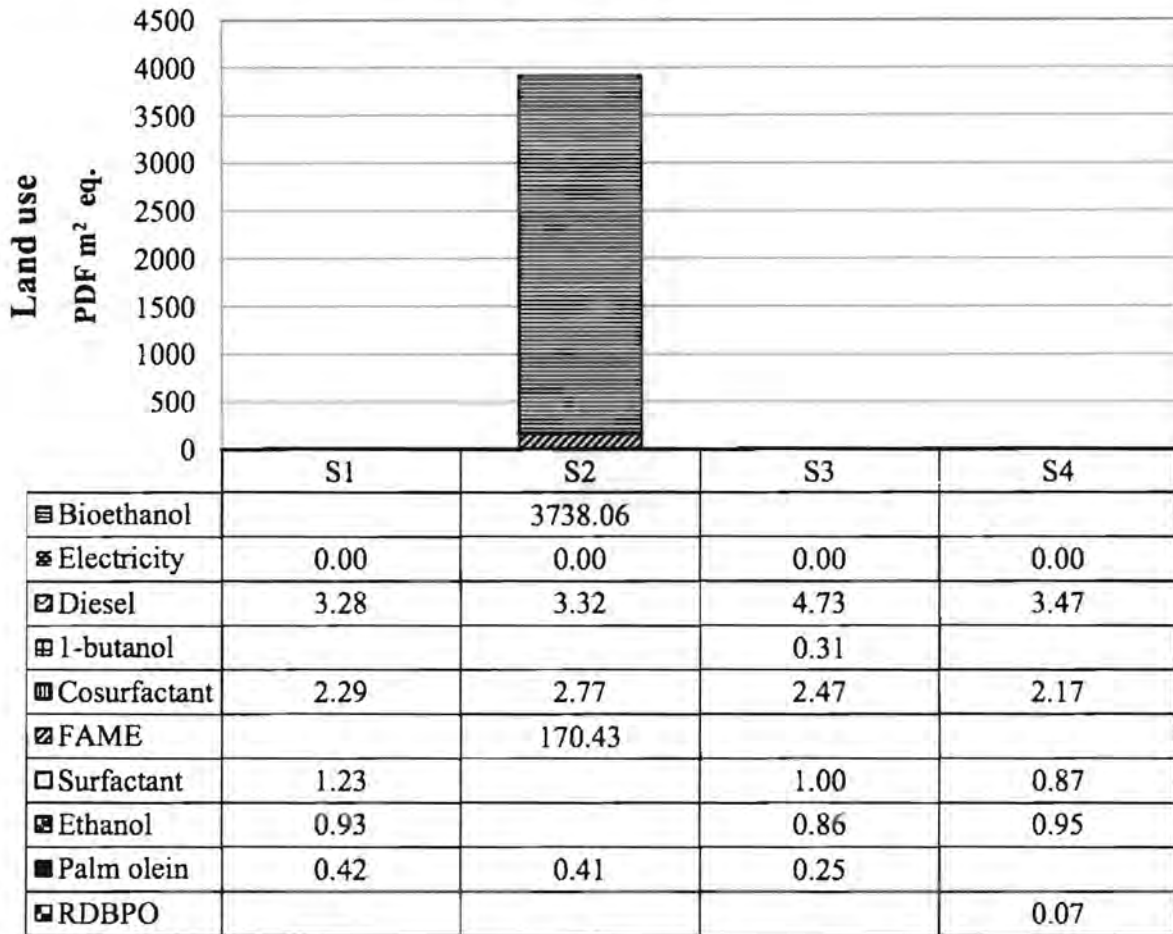
Figure 7 Land use potential based on 1 ton of ME biofuel.

Comparison of Environmental Impacts from raw material selection

The emissions of each impact category from four scenarios were compared based on the normalized results of each impact obtained from the SigmaPro software. According to the Figure 8, main contributor to most of the impacts was microemulsion stage more than 60 percent contribution. According to the results from SimaPro's impact assessment methods, cosurfactant causes significant toxic effects on environment and contributes to some impact categories such as photochemical oxidation, marine aquatic ecotoxicity, fresh water aquatic ecotoxicity, human toxicity and eutrophication. Among other materials used in ME formulation, diesel usage imparts highest contribution for land use change and abiotic depletion impact categories.
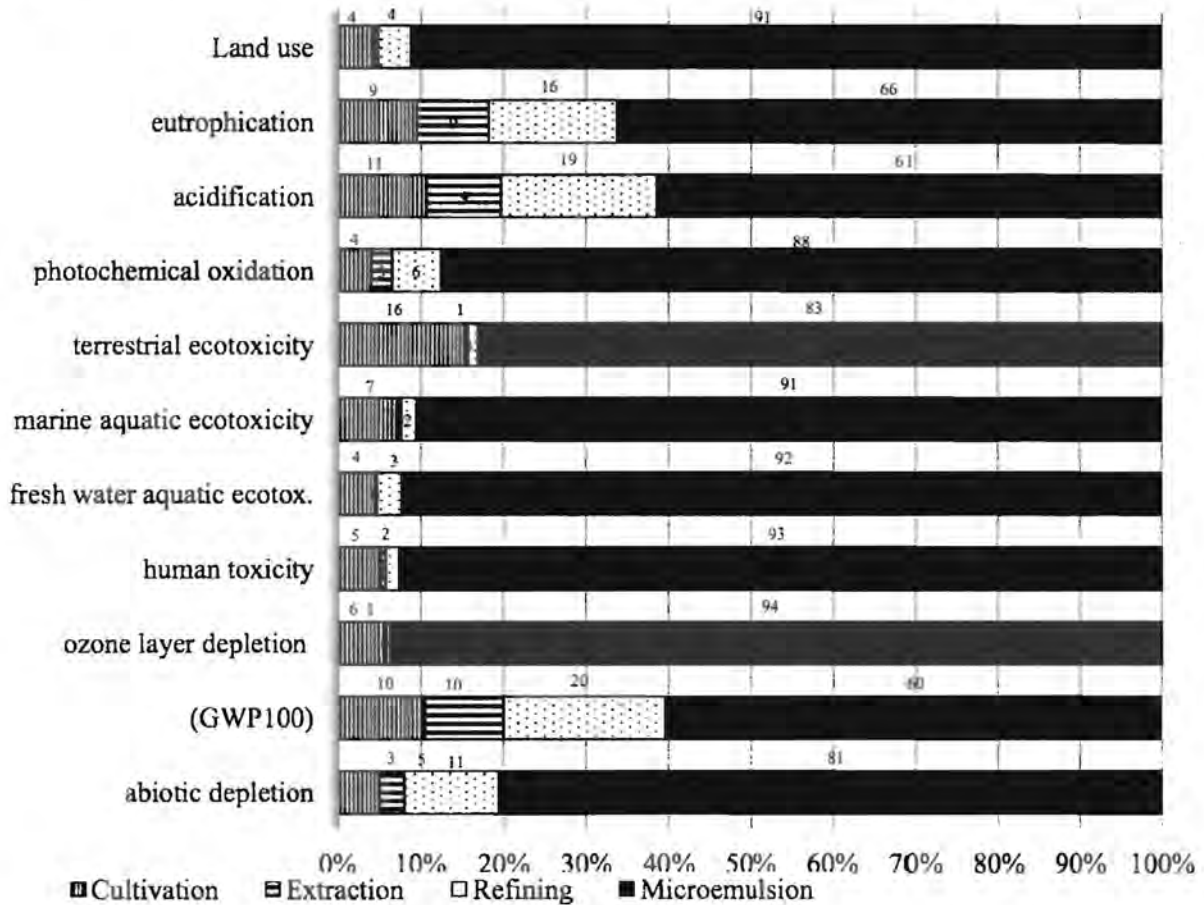
Figure 7 Comparison of environmental impacts related to cultivation (base case), extraction (base case), refining (base case) and microemulsion (scenario IV).
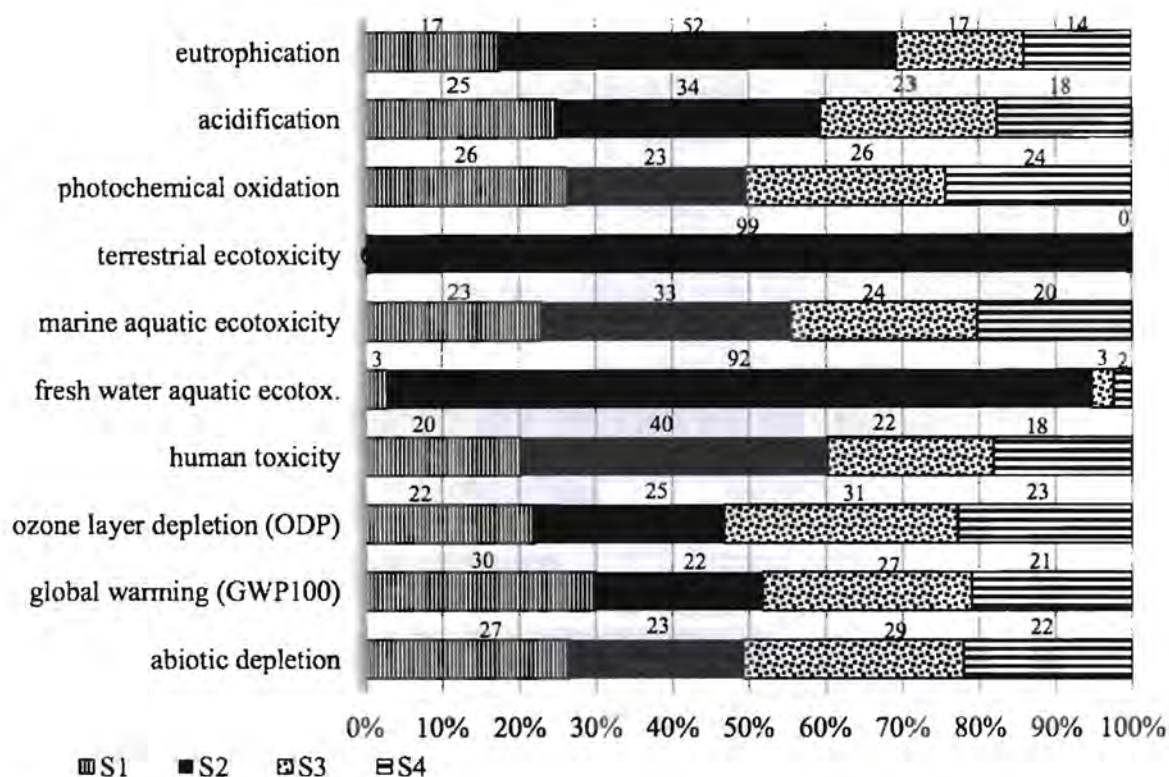
Figure 8 Comparison of environmental impacts related to different ME formulation.

According to Figure 8, Scenario IV (RBDPO case) contributed minimum GHG emission among other scenarios. In addition, Scenario II imparted significant effect to most impact categories such as eutrophication, acidification, fresh water aquatic ecotoxicity and terrestrial ecotoxicity. In Scenario II (biobased case), production of bioethanol is the major cause to some impact categories, such as eutrophication, terrestrial ecotoxicity and fresh water aquatic ecotoxicity. According to the results of the formulation of Scenario I (base case), palm olein production contributes a significant GHG emission potential to the environment.

5. Conclusions

This study provides the GHG emission and environmental impacts of palm oil based microemulsion biofuel production by means of the life cycle assessment (LCA) approach. The production of microemulsion biofuel data was collected from laboratory research works and secondary data sources based on its functional unit, one ton of microemulsion biofuel production. The life cycle environmental impact assessment (LCIA) evaluated in this study were GHG emission, acidification, eutrophication, ozone layer depletion, abiotic depletion, photochemical oxidation, land use, human toxicity, fresh water aquatic, marine aquatic and terrestrial ecotoxicity. Four different scenarios such as Scenario I (base case), Scenario II (biobased case), Scenario III (butanol blend case) and Scenario IV (RBDPO case) were created by varying the formulation of microemulsion biofuel production.

When GHG emissions from all four Scenarios were compared, formulation with RBDPO (Scenario IV) contributed only 1,017 kg CO_2 eq. per ton of ME biofuel production. From this result, the appropriate ME biofuel formulation with crude palm oil (RBDPO) can be achieved with 30 percent lower GHG emission than Scenario I (base case) which contributed 1,447 kg CO_2 eq. per ton of ME biofuel.

According to impact assessment methods' results, the highest contribution of Scenario IV (RBDPO case) was observed in only 24 percent contribution to the photochemical oxidation impact category and there was zero percent contribution to terrestrial ecotoxicity .In this study, major cause of terrestrial ecotoxicity potential was due to the usage of bioethanol and biodiesel in the formulation of Scenario II. When all environmental impact categories of four Scenarios were compared, Scenario II (biobase case), especially from utilization of bioethanol in the ME biofuel formulation contributed significant impacts on some impact categories than other Scenario I, III and IV. These impact categories were fresh water aquatic ecotoxicity, terrestrial ecotoxicity and eutrophication.

Based on the life cycle analysis results, appropriate raw material selection could parameter to optimize its emissions. Life cycle analysis revealed significant environmental hotspots of product, process or service to develop the environmental performance in real life by managing the processes carried out in the boundary of assessment.

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LCA FOR ENERGY SYSTEMS AND FOOD PRODUCTS

Life cycle assessment of palm oil microemulsion-based biofuel

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Ampira Charoensaeng[5]

Abstract

Purpose Microemulsion-based biofuel (ME50) is considered
a promising renewable transportation fuel as well as a feasible
substitute for diesel fuel. This study investigated the life cycle
environmental assessment (LCA) of ME50 production from
palm oil-diesel blends with ethanol and compared it with al-
ternative biofuels, neat biodiesel (B100) and biodiesel-diesel
blends (B50).
Methods The LCA system boundary was separated into five
stages: the oil palm cultivation stage, the palm oil production
stage, the microemulsion production stage, the transportation
stage, and the exhaust emissions in the use stage. Ten potential
environmental impacts of the ME50 were evaluated, namely,
acidification, eutrophication, global warming, ozone layer deple-
tion, human toxicity, aquatic ecotoxicity, terrestrial ecotoxicity,
land use, water depletion, and fossil depletion, by combining the
CML 2000, IPCC 2007, Ecoindicator 99, and ReCipe methods
in SimaPro (v. 7.1). Further, greenhouse gas (GHG) emissions
from the microemulsion fuel production stage were calculated
following the product carbon footprint (CFP) methodology.
Results and discussion It was estimated that 1.17 t or 45,800
MJ of microemulsion biofuel emits 3142 kg of CO_2eq through
its life cycle. Refined palm oil and co-surfactant are crucial
materials for the environmental performance of the
microemulsion-based biofuel. Based on the environmental
impact analyses, palm oil production from cultivation through
the oil refinery exhibited the greatest environmental impacts
in terms of eutrophication and water depletion. Surfactant
use—a key element in the microemulsion formation—has a
significant impact on land use and ecotoxicity-related impact
categories. In comparing the impacts among ME50, B100,
and B50, it was found that microemulsion fuel production
has lower environmental impact than B100 and B50, except
in terms of land use and fossil depletion.
Conclusions Based on this analysis, the major environmental
impact during the microemulsion biofuel production stage re-
sults from the raw materials used. The selection of appropriate
materials and formula adjustment in the microemulsion fuel
formulation are key in minimizing the potential impacts from
biofuel production. Therefore, microemulsion biofuel is
shown to be an environmentally sound technology for green
production of biofuel.

Keywords Biodiesel · Diesel · Greenhouse gases ·
Life cycle assessment · Microemulsion biofuel · Surfactant

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1 Introduction

Novel biofuel technologies capable of reducing the adverse
environmental impacts common to a variety of oil conversion
processes are receiving increased attention. One limitation for
vegetable oil-based biofuel is their naturally high viscosity

(ranging from 30 to 45 mm²/s at 40 °C), especially palm oil, which is ten times more viscous than the regular no. 2 diesel fuel. Numerous methods have emerged to reduce the viscosity of vegetable oils, for instance, direct blending, transesterification, fast pyrolysis, and microemulsification. Vegetable oil transesterification using alkaline catalysts is a widely utilized approach for producing methyl esters—widely known as biodiesel—with suitable viscosity. The methyl esters or neat biodiesel is commercially utilized in two ways: They can be directly used as B100 in modified engines or blended with regular diesel fuels with the bio-based oil fraction ranging from 5 to 50 % volume (B5 to B50) to be utilized in flexible fuel vehicles (FFV). However, life cycle analysis has highlighted the environmental consequences of transesterification, including toxic chemical handling, by-product, and waste management (Choo et al. 2011; Sander and Murthy 2010). Furthermore, the production of biodiesel requires intensive energy and wastewater treatment making the entire technology expensive.

Microemulsification of vegetable oils makes possible a mixture of liquid fuels such as water-diesel and ethanol-diesel blends. The resulting microemulsified fuel is an isotropic, transparent, and thermodynamically stable solution. Recently, microemulsion-based biofuel (Attaphong et al. 2012; Do et al. 2011; Nguyen et al. 2012) has been achieved by the microemulsification of renewable based liquid fuels such as vegetable oils and bio-alcohols. The fuel properties of the new hybrid biofuels were found to be very similar to those of petrol-derived fuels (Arpornpong et al. 2014; Attaphong et al. 2012; Do et al. 2011; Nguyen et al. 2012). Microemulsion biofuel basically consists of three main components: diesel/vegetable oil blends (non-polar phase), ethanol (polar phase), and surfactant/co-surfactant or the emulsifying agent. The microemulsion is a combination of the stabilizing polar phase (e.g., ethanol) in surfactant reverse micelles dispersed in the non-polar phase (vegetable oil and/or diesel blend) (Attaphong et al. 2012; Do et al. 2011; Kibbey et al. 2014). Suitable conditions of microemulsion fuel formation are obtained as type II microemulsions when a mixture of liquid fuels is well solubilized and produces a homogenous isotropic solution with desirable stability.

Relative to raw material selection, neat vegetable oil from renewable and local agriculture-based feedstocks (e.g., canola oil and palm oil) substitutes for a portion of diesel in the mixture. Further, ethanol is used as a viscosity reducer of the vegetable oil. Surfactant or amphiphile molecules—a crucial component in formulating microemulsion fuel—is employed to stabilize all of the immiscible phases in the liquid fuel, particularly by causing the vegetable oil blend to form a single-phase solution. A number of microemulsion biofuel formulations have been produced from the bio-based surfactant system (e.g., palm oil-derived alcohol ethoxylate-based surfactants, ester-based surfactants and sugar-based surfactants). Given that vegetable oil is made up of triglyceride, the vegetable oil-based

microemulsion necessarily requires a co-surfactant (such as alkanols) in combination with a primary surfactant as a bridging agent for stabilizing the homogeneous mixture of liquid fuels. Alkanol or short-to-medium-chain alcohols, including butanol, hexanol, octanol, and decanol, have been studied in the biofuel microemulsion formation. Unfortunately, many medium-chain alcohols are produced from a petroleum-based process and are thus not bio-renewable.

In comparison with petroleum-derived fuel, microemulsion fuel has a more environmentally favourable combustion performance due to lower exhaust emissions, such as low emissions of nitrogen oxides (NO_x), sulphur oxides (SO_x), particulate matters (PM), and unburned hydrocarbons (Do et al. 2011; Dunn and Bagby 2000; Lif and Holmberg 2006). The environmental advantage of microemulsion fuel technology is that it can be formulated with a selection of renewably based materials, which can substitute the use of fossil-based fuels (in addition to reducing the impact of abiotic depletion). Although bio-derived microemulsification seems to produce a biofuel yield with less waste and emissions relative to biodiesel from transesterification and conventional diesel, the raw material acquisition of palm oil and certain chemical productions in use could entail significantly adverse impacts on the environment. Hence, the direct and indirect impacts of microemulsion-based biofuel production on environmental resources need to be addressed for each step of its production.

To our knowledge, this is the first time that the life cycle assessment of the microemulsion biofuel derived from neat palm oil has been studied. The purpose of this paper is to evaluate the environmental benefits and impacts of microemulsion biofuel produced from palm oil for future renewably based fuel. In this study, microemulsion biofuel production from neat palm oil/diesel blend (ratio 50:50 v/v%) with ethanol stabilized by a non-ionic surfactant (ME50) was evaluated through well-to-wheel (WTW) analysis. Finally, the potential impacts were compared with biodiesel applications for B100 (neat transesterification-based biodiesel) and B50 (blend with 50 % biodiesel and 50 % diesel) fuels.

2 Methods

Using the life cycle assessment method, a comprehensive evaluation of the environmental impact categories was conducted for all stages of the microemulsion-based biofuel's life cycle. The environmental impacts from the life cycle inventory analysis (LCIA) were compiled using SimaPro v. 7.1 (LCA software) which contains the Ecoinvent (version 2.1) life cycle inventory (LCI) database for commercially available processing technologies. The scenarios of individual biofuel technology options were examined through well-to-pump (WTP), tank-to-wheel (TTW), and WTW analysis, and the results were compared for each case: microemulsion-based biofuel

(ME50), neat transesterification-based biodiesel (B100), and transesterification-based diesel blend (B50).

Ten environmental midpoint indicators were studied to determine the potential environmental impacts selected on the basis of their importance to their production and emissions. A classical characterization method, namely, CML 2000 (Center of Environmental Science of Leiden University) available in the SimaPro software, was used to consider the following categories: acidification (AP), eutrophication (EP), ozone layer depletion (ODP), human toxicity (HT), aquatic ecotoxicity (AET), and terrestrial ecotoxicity (TET). Moreover, the Intergovernmental Panel on Climate Change (IPCC) method, which lists the climate change factors of IPCC with a timeframe of 100 years (GWP 100), was used. Since the CML 2000 method does not address land use and natural depletion impacts, in this study, the impacts on land use (LU) and natural depletion (water and fossil) were included in the assessment by combining CML 2000 with the Eco-indicator 99 and ReCipe methods, respectively. However, the impacts from land use change did not account for the damage factors of land occupation and transformation from forest to oil palm plantation in this study. The methods and indicators carried out are reported in Table 1.

Additionally, GHG emissions in the microemulsion production stage were also calculated by following the product carbon footprint (CF) guidelines (PAS). Using this method, GHGs including CO_2, CH_4, and N_2O were converted into units of CO_2 equivalent (CO_2eq.) according to their GWP (CH_4=21 and N_2O=310) for over 100 years (IPCC 2006). The emission factors (EF) were mainly obtained from the publicly available databases of Thailand's agencies (TGO 2011). The EF, obtained from international agencies' databases (IPCC 2006), were used when local information was insufficient.

3 Goals and scope

The two goals of this study were (1) to evaluate the potential environmental impacts and activity hotspots of microemulsion-based biofuel (ME50) and (2) to compare these impacts with the comparative fuels of neat biodiesel (B100), biodiesel-diesel blends (B50, 50 vol % of neat biodiesel and 50 vol % of diesel), and diesel fuel. The system boundary for the life cycle of different biofuel technologies was classified into four stages as illustrated in Fig. 1.

4 Life cycle inventory

The inventory data of microemulsion fuel was calculated and analyzed in accordance with the methodology of ISO 14040/44 (ISO 2006), ISO/TS 14067 (ISO 2013), and PAS 2050

(PAS 2008). The activity data used in this study were gathered from both primary and secondary sources. Raw materials and energy consumption in the microemulsion production stage as well as the exhaust gases from engine tests were collected as primary data from laboratory-scale experiments in our previous research work (Arpornpong et al. 2014). The details of the fuel formulation and fuel properties of ME50 can be seen elsewhere (Arpornpong et al. 2014). The secondary information for certain items such as the production of chemical fertilizers and diesel was selected from the available literature, calculations, the Thai and international LCI database (USLCI 2013), and the Ecoinvent database version 2.1 for certain items such as the production of chemical fertilizers and diesel. The inventory data were divided into five parts: oil palm cultivation, palm oil extraction and refinery, biofuel production, transportation, and exhaust emissions.

4.1 Oil palm cultivation

Oil palm starts bearing bunches 2.5 to 3 years after being planted and continues until the end of its lifetime, which is approximately 25 years. It yields approximately 23 t of fresh fruit bunches (FFBs) per hectare per year, depending on the cultural materials, soil, territory, and climate conditions (SPORC 2008). Growing supply materials (e.g., nutrient supplements, fertilizers, and herbicides) are utilized in the cultivation of FFBs in palm cultivation. These supplements are preferably applied every year, but each dose is different depending on the age of the oil palm tree. In accordance with the data obtained from the literature (Pleanjai and Gheewala 2009), the plant nutrients were applied at 44 kg/t of FFBs for N fertilizer (21-0-0), 12 kg/t of FFBs for P_2O_5 fertilizer (0-3-0), and 31 kg/t of FFBs for K_2O fertilizer (0-0-60). Paraquat and glyphosate are used as common herbicides and applied at an average of one to three times per year or at 0.10 kg/t of FFBs for paraquat and 0.28 kg/t of FFBs for glyphosate (Pleanjai et al. 2007). Natural rainwater is the main water source for oil palm cultivation since most of the plantations are located in tropical regions. A common method for harvesting fresh fruit branches from young palm trees is through intensive labour with a chisel, while manual harvesting with a long-handled sickle is specifically used for old and tall palm trees. Thus, no conventional fuel input is required for harvesting activities in the assumption.

4.2 Crude palm oil extraction and palm oil refining

Typically, FFBs are directly transported to palm oil mills, where crude palm oil (CPO) has to be extracted within 24 h to ensure the desired quality. The benefits of the palm oil mill being located close to the palm field (within 5–10-km round trip) are not only that the yield quality can be maintained (Pleanjai and Gheewala 2009) but also that it reduces the cost

Table 1 Designated methodology for life cycle assessment under SimaPro v. 7.1

Indicators	Methodology	Abbreviation	Unit
Acidification	CML 2000	AP	kg SO$_2$ eq.
Eutrophication	CML 2000	EP	kg PO$_4$ eq.
GWP 100a	IPCC 2007	GWP	kg CO$_2$ eq.
Ozone layer depletion	CML 2000	ODP	kg CFC-11 eq.
Human toxicity	CML 2000	HT	kg 1,4-DB eq.
Aquatic ecotoxicity	CML 2000	AET	kg 1,4-DB eq.
Terrestrial ecotoxicity	CML 2000	TET	kg 1,4-DB eq.
Land use	Eco-indicator 99 (H)	LU	PDF m^2 year
Water depletion	ReCipe midpoint (H)	WD	m^3
Fossil depletion	ReCipe midpoint (H)	FD	kg oil eq.

PDF m^2 year indicates potentially disappeared fraction of species (PAF) over a certain amount of square metre during a certain amount of year

1,4-DB eq. is 1,4 dichlorobenzene equivalent

of transportation. The various outputs from the FFB milling are crude palm oil (15–18 %), palm kernel oil (5–6 %), shells (5–6 %), palm fibres (12–14 %), and empty bunches (25–27 %) (DOA 2008).

For the palm oil mill, the primary product is CPO (approximately 0.18 t/t FFB) and the co-product is palm kernel oil (PKO) (approximately 0.06 t/t FFB). In this study, energy inputs were allocated between CPO and PKO based on the oil yield of each product. The electricity consumption of all machinery used in palm oil production was estimated at 17.99 kWh per ton FFB (Pleanjai et al. 2007). Therefore, CPO accounted for 82 % of the total energy and PKO the remaining 18 % (Papong et al. 2010). Palm fibre residues were used as a biomass fuel to generate internal power in the form

of heat and electricity, which are integrated into the palm oil mill. The emissions of biomass production and combustion were assumed to be offset because the process utilized its internal waste (palm fibres, shells and empty branches) and is a biogenic fuel feed. The diesel oil used for generators and mechanical engines in the plant was approximately 1.62 L per ton of FFBs. The water used for the palm oil mill (POME) process and its effluent (POME), which typically contains extremely high chemical oxygen demand (COD) loading (above 100,000 mg/L) (Kaewmai et al. 2012), were accounted for as input and output, respectively. In the milling operation, the POME requires a treatment facility and an anaerobic process to reduce organic content before discharge (Crabbe et al. 2001; Oswal et al. 2002).
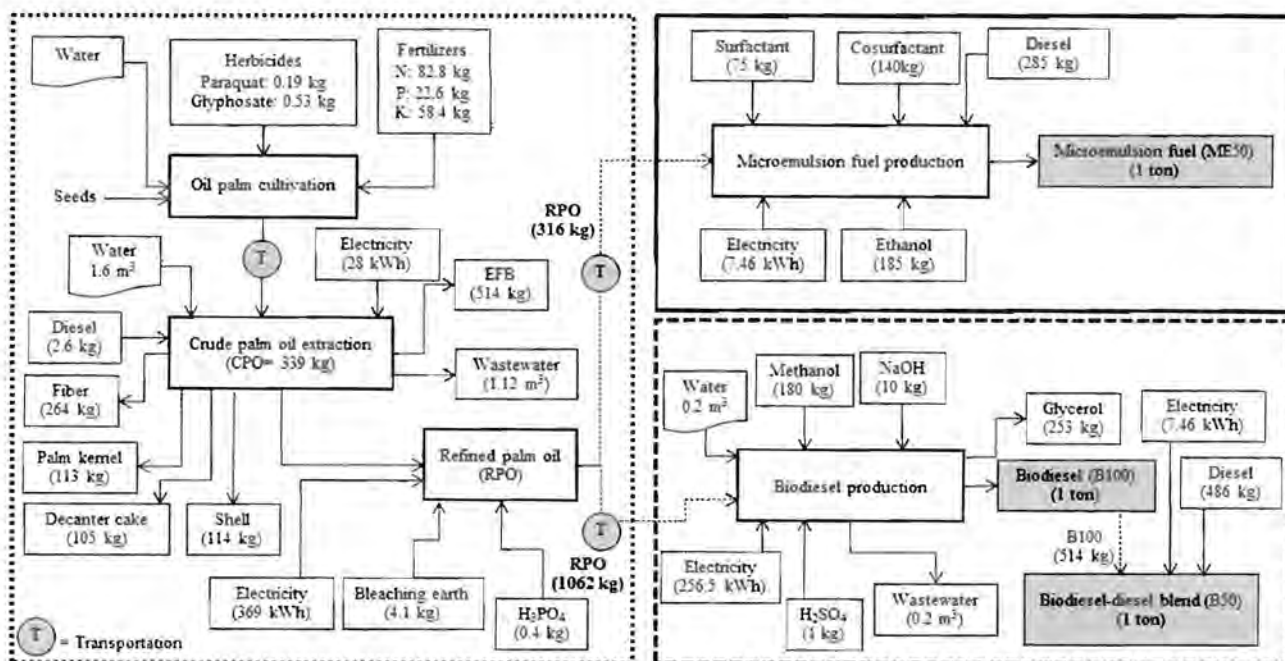

Fig. 1 The system boundary of the microemulsion fuel and biodiesel (well-to-pump approach)

For the refining process, crude palm oil is treated in the neutralization, degumming, bleaching and deodorization processes to get rid of the gum and impurities. The amount of refined palm oil (RPO) was 0.932 t/t of CPO (Kittithammavong 2014). The electricity consumed from the power grid for RPO refining was about 1.17 kWh/t of RPO. In this process, spent clays were obtained as residual wastes.

4.3 Microemulsion production

The microemulsion-based biofuel (ME50) was formulated from the mixture of methyl oleate/1-octanol (22 vol%), ethanol (20 vol%), and the palm oil/diesel blend (58 vol%). Methyl oleate and 1-octanol were used as nonionic surfactant and co-surfactant, respectively. Ethanol was stabilized by reverse micelles and dispersed in the palm oil/diesel blend or non-polar phase. The fuel formula is simplified and shown in Table 2. Neat palm oil typically consists of several fatty acid compositions, palmitic acid (C16:0) 43 %, steric acid (C18:0) 4 %, oleic acid (18:1) 41 %, and others 12 % (Balat 2008). In this study, RPO, which is employed to formulate microemulsion fuels, accounted for the raw material used in the microemulsion production stage. The conditions and details of the microemulsion fuel production technique have been described elsewhere (Arpompong et al. 2014).The surfactant is an emulsifying agent for formulating microemulsion biofuel. The surfactant derived from a bio-based feedstock, PKO, was selected from a dataset (Ecoinvent 2.1 dataset for PKO-derived surfactant production) for this study. The PKO-surfactant is mainly produced from fatty acid splitting, esterification of refined PKO and esterification of crude PKO processes with methanol, energy, natural gas and hydrogen as supplement raw materials.

Table 2 The formulation and properties of ME50

Properties	
Oil used	Palm oil-diesel blends (1:1 v/v)
Chemical composition of palm oil	C16:0, C16:1, C18:0, C18:1, C18:2
Surfactant used	Methyl ester of oleic acid (Methyl oleate)
Co-surfactant used	1-octanol ($C_8H_{17}O$)
Surfactant to co-surfactant mole ratio	1:8
Alcohol used	Ethanol (C_2H_5O) 20 vol%
Microemulsion droplet size, nm	21.86
Density at 25 °C, kg/m³	0.85
Kinematic viscosity at 40 °C, mm²/s	4.0
Heat of combustion, MJ	39.2
Flash point (°C)	15

Following the appropriate formulation, the materials used include palm oil/diesel blends, ethanol, methyl oleate, and 1-octanol. For the fuel production, RPO (0.316 t/t of ME50) and diesel (0.285 t/t of ME50) were directly mixed and were used as the main raw materials. The reactor time operated for 2 h per batch to allow the system to reach equilibrium in the homogenous solution. Next, the liquid fuel mixture was allowed to settle to check the phase stability of ME50 (without miscible phase separation). The operating temperature was controlled at room temperature (25±2 °C). Electrical energy consumption was required for the mixing process only, which was approximately 7.46 kWh/t of ME50. The biofuel microemulsion in particular produces ME50 with an absolute 100 % yield without any waste generation (Arpompong et al. 2014; Attaphong et al. 2012; Do et al. 2011). For the material used in ME50 production, the process mass and energy consumption balances were assessed only from a limited laboratory scale, which may not reflect normal commercial operations. Unlike BD production, the inventory data are readily available from commercial plant processes. In addition, the mixing process of the microemulsion fuel is very similar to that of the commercial fuel blending process in petrol production. The electricity consumption during the blending process of the biofuels, therefore, is fairly assumed to be equal for each case.

4.4 Transportation

In this study, the representative oil palm plantation and crude palm oil production were located in the southern part of Thailand. The oil palm field was located close to the oil palm mill, whereas the biodiesel plant was located in the central part of Thailand. The transport capacity and distance travelled from oil palm field to mill (56-km round trip in this study) and mill to biodiesel plant (1628 km for round trip) were retrieved from Pleanjai and Gheewala (2009). Three-ton trucks transport FFBs from the oil palm field to the palm oil mill, and 20-ton trucks transport RPO from the oil refinery plant to the biodiesel plant. It was assumed that the microemulsion plant was at the same place as the biodiesel plant. The fuel consumption for the heavy diesel vehicles was 1.628 km/L of diesel (DIESEL Status Report 2004). Air emissions from the transportation stage were taken from the Ecoinvent database.

4.5 Exhaust emissions

To evaluate the life cycle of microemulsion-based biofuel, the exhaust emissions including carbon dioxide (CO_2), carbon monoxide (CO), and nitrous oxide (N_2O) should be considered. A direct-injection diesel engine (single cylinder, air cooled, and four stroke) was used to assess the exhaust gas emissions from the engine. The engine was operated at 1200± 12-rpm engine speed with 1.0-kW engine load.

5 Comparison with biodiesel system

Biodiesel (B100) is generally produced from the transesterification process, whereby triglycerides in vegetable oil are converted to ethyl or methyl ester by reacting with alcohol (i.e. ethanol or methanol) in the presence of an alkaline catalyst (i.e. NaOH or KOH), with glycerol as a co-product. Crude glycerol can be converted into higher value products (Sanz Requena et al. 2011), used as a feed ingredient in the pig industry (Pluske 2007), and used for composting. In this study, biodiesel and glycerol were allocated based on weight at a ratio of 80:20. The system boundary of B100 comprises four main stages consisting of oil palm cultivation, crude palm oil production, transesterification, and transportation, whereas the system boundary allocated for B50 has fuel blending as an additional stage at the end of the process, as illustrated in Fig. 1. For the comparative study, the inventory inputs of B100 were adjusted from other studies (Pleanjai and Gheewala 2009; Pleanjai et al. 2007), while the inventory inputs of B50 were calculated by volume as 50 % of B100 blended with 50 % of diesel together with equal energy used in the microemulsion stage.

6 Results and discussion

6.1 Results from inventory analysis

All inventory data from WTP analysis for each biofuel are presented in Table 3. Note that the inventory data were calculated based on 1 t of biofuel produced (ME50, B100, and B50). The ME50 system consisted of ethanol in oils emulsion with surfactant and additives, which were major contributions to the inventory, while the BD production required NaOH and the alkaline catalyst as raw materials for the transesterification reaction process. The BD also used fresh water for purifying biodiesel, which resulted in a significant amount of the effluent, whereas the water used during microemulsion biofuel production was zero. In manufacturing operations, the effluent from biodiesel production requires additional treatment specifically in an anaerobic process, resulting in a considerable contribution of CH_4 emissions into the atmosphere. Microemulsion biofuel also offers an energy-saving technology relative to the thermochemical conversion of biodiesel, due to the use of direct blending with neat vegetable oil. The energy consumption for ME50 production is only required for the mixture of liquid fuels to be a homogenized solution, which is similar to that of a blending terminal at a petrol station. Regarding the inventory analysis, the ME production presents a benefit in terms of emission reduction from wastewater discharge and energy consumption over the BD production process.

Table 4 lists the exhaust emissions of the test engine. Due to the lower heat of combustion of biofuels, they generally consume more fuel as compared to diesel fuel. However, the exhaust emissions for B100 were calculated from the fraction of exhaust emissions from B50 and diesel because the neat B100 cannot be utilized with unmodified direct-injection engines. As concerns the well-to-tank analysis, the inventory data were calculated based on the provided 45,800-MJ biofuel for the comparative energy efficiency purpose (heating value of diesel=45.8 MJ/kg).

6.2 Environmental impact assessment of microemulsion biofuel

The raw materials used in ME50 production associated with ten environmental impact categories from microemulsion biofuel production are summarized in Fig. 2. The ten impact categories considered are as follows: acidification, eutrophication, greenhouse gas emission, ozone layer depletion, human toxicity, aquatic ecotoxicity, terrestrial ecotoxicity, land use, water depletion and fossil depletion. These categories characterize the emissions of ME50 production.

According to the results, the production of RPO, which is a primary feedstock of biofuel production, has a considerable influence on almost all of the impact categories due to the production of vegetable oil feedstock involving fertilizers, chemical energy and water. It should be noted that the production of bio-based feedstock contributes the most to eutrophying emissions (91 %), which could be mainly driven by nitrogen- (NH_3 and NO_x) and phosphorus-related emissions (Siles et al. 2011) from the use and production of nutrient supplements and wastewater discharges. The feedstock production also contributes more than 50 % to water depletion. This could be a consequence of the large amount of fresh water used in palm oil production.

The use of surfactant, which is a key component in formulating microemulsion fuel, contributes greatly to several impact categories. Note that the surfactant (alcohol ethoxylate) present in this formula is a renewably based product derived from PKO through the oleochemical process. Emissions from surfactant also accounted for more than 70 % of all materials regarding terrestrial and aquatic ecotoxicity impacts. These impacts are mainly caused by emissions from the use of agrochemicals during cultivation of palm oil such as fertilizers, pesticides and herbicides, which normally consist of organic chemicals (chlorinated and polyaromatic hydrocarbon compound and solvent) and heavy metals. These pollutants are not only widespread and persistent in environmental media (i.e. land, soil, and water) for a long time but also can accumulate in terrestrial, aquatic tissues and finally pass on to humans through the food chain. For the environmental damage in the form of human toxicity, the greatest impact was caused by the production of bio-based materials about 33 %

Table 3 Life cycle inventory for the production of one ton of fuel (FU)

Life cycle biofuel production	ME50	B100	B50[a]	Sources of inventory data
Input				
(a) Oil palm plantation				
N fertilizer (kg)	82.82	278.9	143.4	Ammonium sulphate, as N, at regional storehouse/RER S (Pleanjai et al. 2007)
P_2O_5 fertilizer (kg)	22.59	76.06	39.12	Single superphosphate, as P_2O_5, at regional storehouse/RER S (Pleanjai et al. 2007)
K_2O fertilizer (kg)	58.35	196.5	101.1	Potassium chloride, as K_2O, at regional storehouse/RER S (Pleanjai et al. 2007)
Glyphosate (kg)	0.530	1.775	0.887	Glyphosate, at regional storehouse/CH S (Pleanjai et al. 2007)
Paraquat (kg)	0.190	0.634	0.326	Bipyridylium compounds, at regional storehouse/CH S (Pleanjai et al. 2007)
Diesel used (for transport FFB) (kg)	18.12	61.03	31.39	(Pleanjai and Gheewala 2009)
(b) Crude palm oil production				
(i) Crude palm oil extraction				
Electricity (kWh)	27.76	93.48	48.08	Electricity, low voltage, consumer mix, at grid/CH S (Papong et al. 2010; Pleanjai et al. 2007)
Water for boiler (m^3)	1.557	5.244	2.697	Water, lake (Pleanjai et al. 2007)
Diesel for starting turbine (kg)	2.559	8.618	4.432	Diesel, combusted in industrial boiler/US (Pleanjai et al. 2007)
(ii) Palm oil refining				
Water (kg)	52.58	177.1	91.07	Water, lake (Kittihammavong 2014)
H_3PO_4 (kg)	0.413	1.392	0.716	(Kittihammavong 2014)
Bleaching earth (kg)	4.139	13.94	7.169	(Kittihammavong 2014)
Electricity (kWh)	369.1	1,243	639.3	Electricity, low voltage, consumer mix, at grid/CH S (Pleanjai and Gheewala 2009)
Diesel for starting machinery (kg)	3.067	10.33	5.311	(Pleanjai et al. 2007)
Diesel used (for transport RPO) (kg)	13.25	44.62	22.95	(Pleanjai and Gheewala 2009)
(c) Biofuel production				
(i) Microemulsion fuel				
Refined palm oil (kg)	315.5	–	–	(Arpornpong et al. 2014)
Ethanol (kg)	184.6	–	–	Ethanol from ethylene, at plant/RER S (Arpornpong et al. 2014)
Surfactant (kg)	75.2	–	–	Ethoxylated alcohols (AE3), palm kernel oil, at plant/RER S (Arpornpong et al. 2014)
Co-surfactant (kg)	139.6	–	–	1-butanol, propylene hydroformylation, at plant/RER S (Arpornpong et al. 2014)
Diesel (kg)	285.0	–	–	Diesel, low sulphur, at refinery/CH S (Arpornpong et al. 2014)

Table 3 (continued)

Life cycle biofuel production	ME50	B100	B50[a]	Sources of inventory data
Electricity for mixing (kWh)	7.460	–	–	Electricity, low voltage, consumer mix, at grid/CH S
(ii) Biodiesel (transesterification)				
Refined palm oil (kg)	–	1062	546.4	Pleanjai and Gheewala (2009)
Methanol (kg)	–	180.0	92.61	Methanol, at plant/GLO S (Pleanjai and Gheewala 2009)
NaOH catalyst (kg)	–	10.0	5.2	Sodium hydroxide (concentrated) E (Pleanjai and Gheewala 2009)
H_2SO_4 (kg)	–	1.0	0.5	Sulphuric acid/GLO U
Electricity (kWh)	–	256.5	132.0	Electricity, low voltage, consumer mix, at grid/CH S (Pleanjai and Gheewala 2009)
Water for washing (m³)	–	0.2	0.1	Water, lake (Pleanjai et al. 2007)
Diesel for starting machinery (kg)	–	33.6	17.3	Kittithammavong (2014)
(iii) Biodiesel-diesel blends				
Diesel for blending (kg)	–	–	485.5	Diesel, low sulphur, at refinery/CH S
Electricity for mixing (kWh)	–	–	7.460	Electricity, low voltage, consumer mix, at grid/CH S
Output				
(b) Crude palm oil production				
(i) Crude palm oil extraction				
Palm oil mill effluent (m³)	1.117	3.762	1.935	Pleanjai et al. (2007)
Palm kernel (kg)	113.1	380.8	195.8	DOA (2008)
Shell (kg)	113.1	380.8	195.8	DOA (2008)
Fibre (kg)	263.5	887.4	456.4	DOA (2008)
Decanter cake (kg)	104.9	353.4	181.7	DOA (2008)
Empty bunches (kg)	508.2	1,711	880.1	DOA (2008)
(ii) Palm oil refining				
Wastewater (kg)	52.58	177.1	91.07	Kittithammavong (2014)
Spent clay (kg)	4.139	13.94	7.169	Kittithammavong (2014)
(c) Biofuel production				
(i) Microemulsion-based biofuel (kg)	1000	–	–	
(ii) B100/B50		1000	1000	
Glycerol (kg)	–	253.0	130.2	Adapted from Pleanjai and Gheewala (2009) and Pleanjai et al. (2007)
Wastewater (m³)	–	0.2	0.1	

[a] Data are calculated from B100

Table 4 Exhaust emissions of the test engine

Test engine	Unit	ME50	B50	Diesel
Gross heat of combustion	MJ/kg	39.2	39.4	45.8
Carbon dioxide (CO_2)	g/kg fuel	2634	2870	3049
Carbon monoxide (CO)	g/kg fuel	58.17	58.77	39.6
Nitrogen oxide (NO_x)	g/kg fuel	28.60	34.06	40.46

Test engine was evaluated at 1200-rpm engine speed and 1-kW engine load. The exhaust emissions from the engine were directly measured by using a Testo 350 XL fuel gas analyzer

from surfactant production and 28 % from RPO production. The air pollutants (e.g. NO_x and heavy metals) from the production of non-renewable materials are also a contributor. This can be inferred from the impacts of ethanol, diesel and electricity on human toxicity, each contributing about 10 %. However, the negative impact on humans (401 kg 1,4-DB eq.) from 45,800 MJ of ME50 production is higher than that on terrestrial (105 kg 1,4-DB eq.) and aquatic toxicity (243 kg 1,4-DB eq.)— see Table 5.

For the global warming impact (GWP), all input materials have the potential to emit greenhouse gases. For ME50, co-surfactant production contributed the most to equivalent CO_2 emissions (30 %), followed by surfactant production (21 %). The main source of carbon emissions is likely from the refining and purification processes. The GHG emissions of 45,800 MJ from three different biofuel production technologies were 1268, 1188, and 991 kg CO_2eq. for ME50, B100 and B50, respectively (Table 5).

The depletion of the ozone layer is specifically caused by chlorofluorocarbons (CFCs), carbon tetrachloride (CCl_4), methyl bromide (CH_3Br) , methyl chloroform (CH_3CCl_3), and halons

(EPA 2010), well known as ozone-depleting substances (ODSs). These gases not only produce significant impact at very low concentrations but also originate from anthropogenic sources and industrial activities. Note that diesel oil has an impact of 76 % in the category of ozone layer depletion, which could be due to the ozone-depleting substances, air pollutants from aliphatic and cyclic hydrocarbon and their derivatives during the crude petroleum extraction process, and the energy combustion used for electricity and hot steam generation.

As for the WTW approach, the exhaust emissions generated during diesel engine operation were accounted for based on their environmental impacts for the whole of the life cycle. According to Fig. 3 and Table 5, the result shows that ME50 had a great impact on acidification and GWP, with an increment of more than 50 % from the production process.

6.3 GHG emissions from the CF method

GHG emissions described as CO_2eq. from the microemulsion production stage are presented in Table 6. The total GHG emissions were 1403 kg CO_2eq. per 45,800 MJ of ME50 or 1201 kg CO_2eq. per ton of ME50. Based on the calculation, the sources of emissions were divided into two categories, which include emissions from the raw materials used for formulating ME50 and the process for mixing the biofuel. The GHG emissions associated with the ME50 were significantly released from the production of the raw materials including vegetable oil, diesel, surfactant, co-surfactant and ethanol. On the other hand, the mixing process, which is the only primary process in the microemulsion production stage, requires a certain amount of energy for the mixer. When comparing the
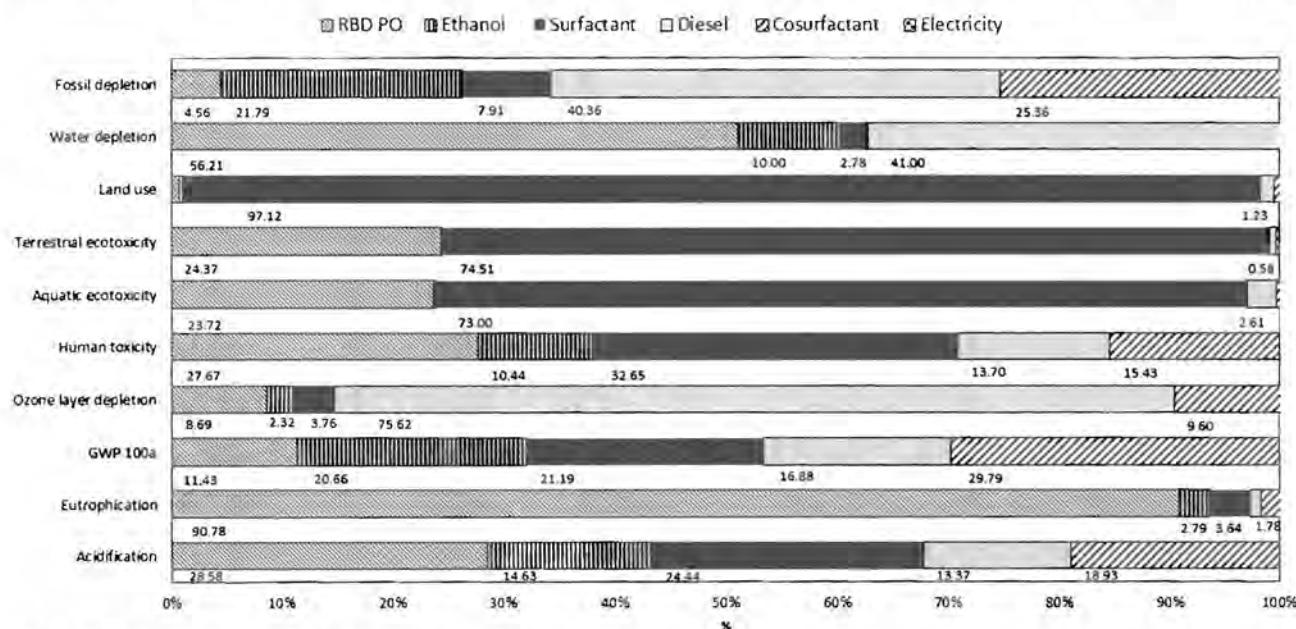
Fig. 2 Environmental impacts during the microemulsion production process

Table 5 Characterization of the LCA of microemulsion-based biofuel, B100, B50, and diesel providing 45,800-MJ energy content (well-to-wheel (WTW) analysis)

Impact categories	Unit	ME50[a]		B100[a]		B50[b]		Diesel[c,d]	
		Production	Emission	Production	Emission[e]	Production	Emission	Production	Emission
Acidification	kg SO$_2$ eq.	5.13E+00	1.67E+01	1.27E+01	1.94E+01	9.16E+00	1.98E+01	4.84E+00	2.02E+01
Eutrophication	kg PO$_4$ eq.	1.08E+01	4.34E+00	7.65E+01	5.03E+00	3.84E+01	5.15E+00	5.66E−01	5.26E+00
GWP 100a	kg CO$_2$ eq.	1.27E+03	1.87E+03	1.19E+03[f]	0.00E+00	9.91E+02	1.62E+03	6.11E+02	3.05E+03
Ozone layer depletion	kg CFC−11 eq.	3.27E−04	0.00E+00	3.20E−04	0.00E+00	4.92E−04	0.00E+00	5.72E−04	0.00E+00
Human toxicity	kg 1,4-DB eq.	4.01E+02	4.01E+01	2.89E+03	4.65E+01	1.61E+03	4.75E+01	2.89E+02	4.86E+01
Aquatic ecotoxicity	kg 1,4-DB eq.	2.43E+02	0.00E+00	4.19E+02	0.00E+00	2.56E+02	0.00E+00	2.13E+01	0.00E+00
Terrestrial ecotoxicity	kg 1,4-DB eq.	1.05E+02	0.00E+00	1.65E+02	0.00E+00	8.33E+01	0.00E+00	2.15E+00	0.00E+00
Land use	PDF m^2 yr.	3.15E+02	0.00E+00	1.88E+01	0.00E+00	2.61E+01	0.00E+00	2.89E+01	0.00E+00
Water depletion	m^3	9.49E+01	0.00E+00	4.15E+02	0.00E+00	2.09E+02	0.00E+00	4.50E+00	0.00E+00
Fossil depletion	kg oil eq.	1.06E+03	0.00E+00	6.67E+02	0.00E+00	1.08E+03	0.00E+00	1.29E+03	0.00E+00

[a] Heating value=39.2 MJ/kg; the amount of fuel for 45,800 MJ=1.17 t

[b] Heating value=39.4 MJ/kg; the amount of fuel for 45,800 MJ=1.16 t

[c] Heating value=45.8 MJ/kg; the amount of fuel for 45,800 MJ=1.0 t

[d] The impacts from diesel production were from the Ecoinvent 2.1 database for comparison purposes

[e] Because of lack of testing data for B100, the emissions were calculated from B50 and diesel

[f] B100 and glycerol were allocated based on weight at a ratio of 80:20
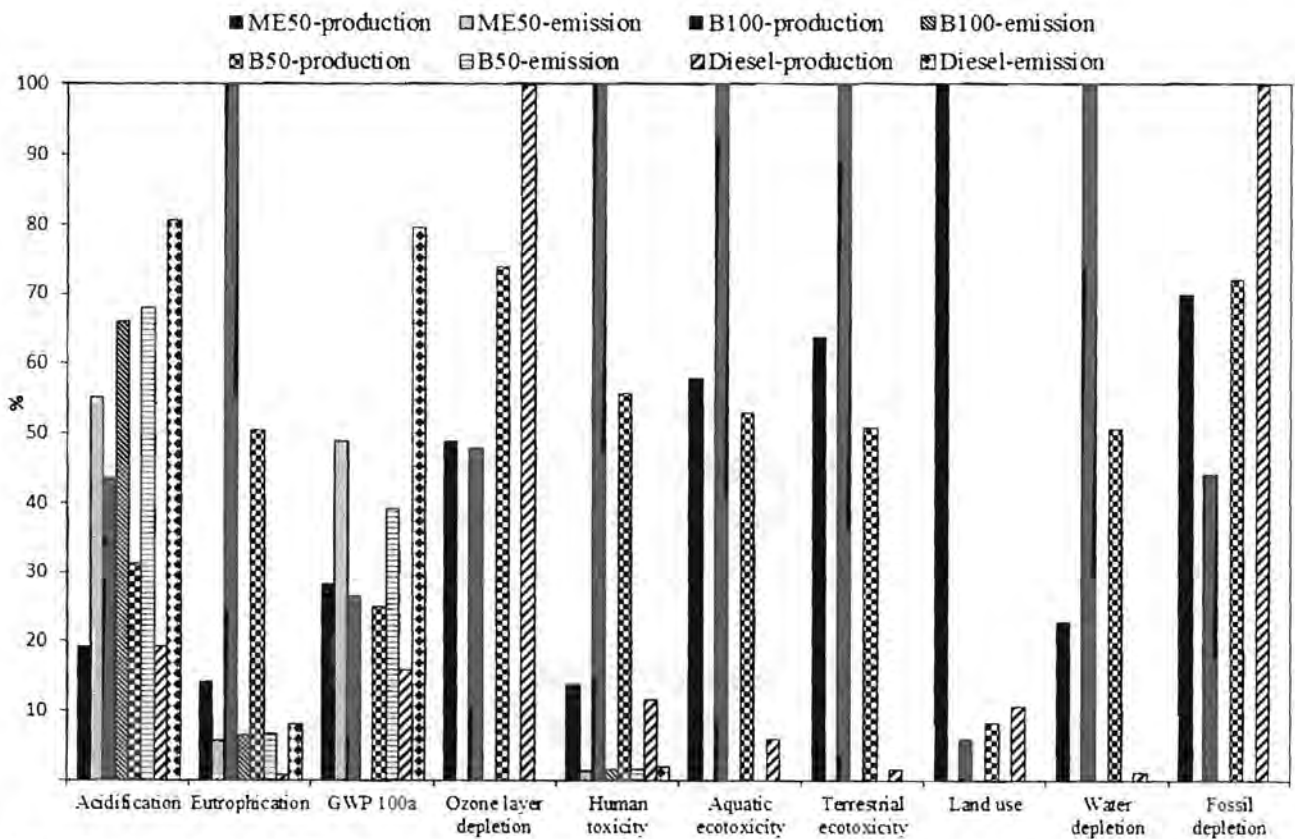
Fig. 3 The characterization of the life cycle impact assessment from well-to-wheel (WTW) analysis for microemulsion-based biofuel (ME50), biodiesel (B100), biodiesel-diesel blend (B50), and diesel

Table 6 Greenhouse gas emissions from biofuel production stage carbon footprint method

Activities	Emission factor		Data source	Emissions (kg/45,800-MJ biofuel)					
				ME50		B100		B50	
	Unit	Amount		CO_2 eq.	%	CO_2 eq.	%	CO_2 eq.	%
(a) Emissions from raw materials used									
Refined palm oil	kgCO$_2$ eq./kg	0.987	The project of developing GHG accounting for Thai palm oil industry (cradle to gate) (TGO 2011)	363.8	25.93	1225	69.85	626.9	54.88
Ethanol	kgCO$_2$ eq./kg	1.233	Ethanol from ethylene, at plant/RER S, Ecoinvent 2.0	258.8	18.45	–	–	–	–
Surfactant	kgCO$_2$ eq./kg	2.400	Ethoxylated alcohols (AE3), palm kernel oil, at plant/RER S, Ecoinvent 2.0	210.9	15.03	–	–	–	–
Co-surfactant	kgCO$_2$ eq./kg	2.589	1-butanol, propylene hydroformylation, at plant/RER S, Ecoinvent 2.0	422.3	30.10	–	-	-	-
Diesel (production)	kgCO$_2$ eq./L	0.429	IPCC 2007	143.0	10.19	–	–	242.3	21.21
Diesel for starting machinery (production)	kgCO$_2$ eq./L	0.429	IPCC 2007	–	–	16.85	0.961	8.633	0.756
Methanol	kgCO$_2$ eq./kg	0.268	Converted data from JEMAI Pro using Thai Electricity Grid (TGO 2011)	–	–	56.28	3.210	28.81	2.522
NaOH catalyst	kgCO$_2$ eq./kg	1.200	Sodium hydroxide (concentrated) E, Ecoinvent 2.0	–	–	14.02	0.800	7.254	0.635
Sulphuric acid	kgCO$_2$ eq./kg	0.138	Sulphuric acid, liquid, at plant/RER U, Ecoinvent 2.0	–	–	0.161	0.009	0.080	0.007
Water for washing	kgCO$_2$ eq./m^3	0.026	Metropolitan Waterworks Authority (Thailand)	–	–	0.006	<0.001	0.004	<0.001
Sub total				1399	99.70	1312	74.83	914.0	80.01
(b) Emissions from microemulsion/transesterification production process									
Electricity	kgCO$_2$ eq./kWh	0.561	TC common data	4.185	0.298	168.1	9.589	90.95	7.961
Diesel (combustion)	kgCO$_2$ eq./L	2.708	IPCC 2007	–	–	106.3	6.063	54.46	4.767
Wastewater [a,b]	kgCO$_2$ eq./L	4.20[c]	IPCC (2006)	–	–	166.8	9.516	83.00	7.265
Sub total				4.185	0.298	441.3	25.17	228.4	19.99
Total emissions (materials used + production process)				1403	100	1753	100	1142	100
Total emissions (with allocated product[d])				1403		1403		963	
Total GHGs (include exhaust from test engine)[e]				3280		1403[f]		2583	

[a] The amount of effluent is 0.2 m^3/t B100 and COD loading is 0.17 kg/L (Srirangsan 2008)

[b] GHGs were accounted from the indirect methane emissions generated from anaerobic reactor using 0.25 kg CH$_4$/kg COD (B$_o$), and methane recovery is not considered (MCF=0.8)

[c] EF=CH$_4$ impact potential × B$_o$ × MCF

[d] B100 and glycerol were allocated based on weight at a ratio of 80:20

[e] CO$_2$ emissions from the test engine were directly measured by using a Testo 350 XL fuel gas analyzer. The emissions from biofuels were accounted according to diesel in their composition

[f] B100 combustion is carbon neutral
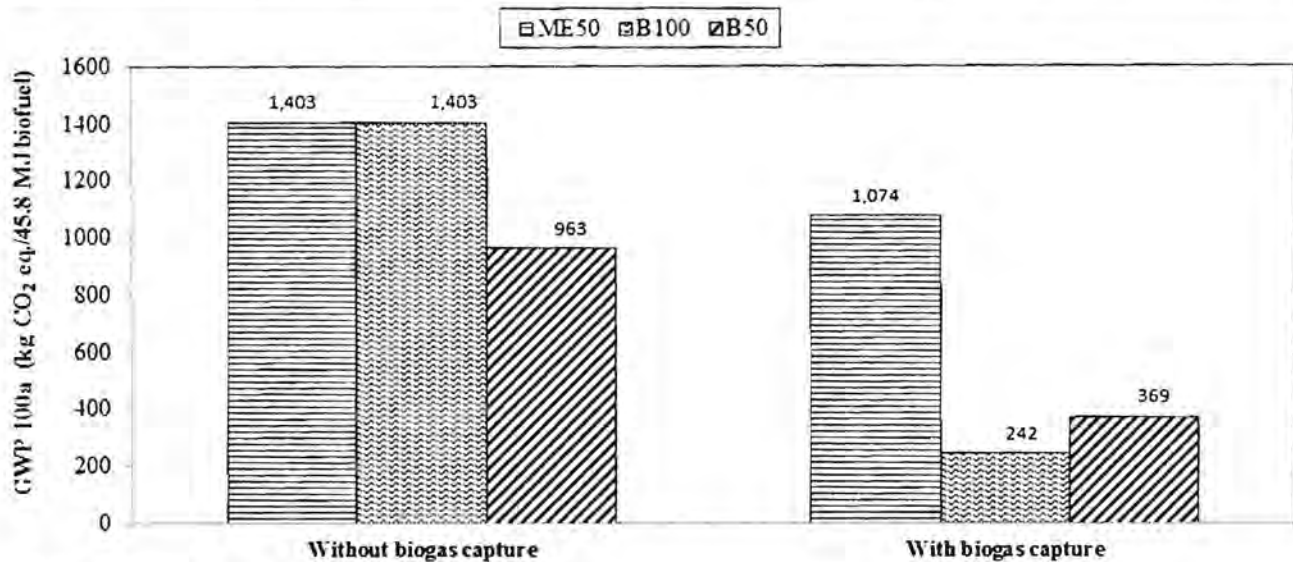
Fig. 4 GHG emission sensitivity analysis

GHG emissions from raw materials and the process, the emissions from the raw material production accounted for 99.7 % and therefore almost all of the total impact for this stage.

As regards the materials used, the co-surfactant (1-octanol) and palm oil feedstock (RPO) constituted a large share of GHG emissions, accounting for 30.1 and 25.9 % of a total 1403 kg CO_2eq. per 45,800 MJ of ME50, respectively, as shown in Table 6. According to the results, the potential measures to mitigate the GHG emissions of the production of the microemulsion biofuel are raw material selection and formula adjustment.

From the tank-to-wheel analysis, the CO_2 emission from the test engine was directly measured and accounted as shown in Table 4. According to diesel and non-bio-based materials in ME50, the CO_2 emission was allocated according to the GHG emission of ME50 combustion. During the microemulsion fuel combustion, 1877 kg CO_2 eq. was emitted to the atmosphere. Thus, the total GHG emissions from well-to-wheel analysis were 3280 kg CO_2eq. per 45,800 MJ of ME50.

6.4 Comparison with palm oil methyl ester (PME)

The comparison of the environmental impacts of microemulsion biofuel (ME50), palm oil methyl ester (B100), and palm oil methyl ester with the diesel blend (B50) with and without the exhaust emissions is shown in Fig. 3. The emission levels are converted to percentages for easier comparison of the impacts in the overview. It was found that both of the impacts from the production phase and the use phase of ME50 results tend towards better environmental performance than those of the B100 and B50 in terms of acidification, eutrophication, ecotoxicity related categories and water depletion. It should be noted that global warming impact and acidification are most affected by all biofuels, whereas the

other impacts do not differ significantly regarding exhaust emissions in the use phase (Fig. 3).

The acidification and eutrophication potential of the whole life cycle of the ME50 (both production and use phase) had the lowest impacts. The emission sources of acidification were mainly from the use of nitrogen-based fertilizers (i.e. ammonia to air and nitrates leaching to land and subsurface) at the stage of palm oil cultivation and the exhaust gas emissions from fossil fuel combustion during energy production. These results are consistent with other studies (Kaewcharoensombat et al. 2011). Kaewcharoensombat et al. (2011) studied the LCA of jatropha methyl ester using Eco-indicator, 99 and they reported that the main impacts on the acidification were from the transesterification production stage where various fuels are utilized to produce the energy. The transesterification of palm oil also generates a large-volume wastewater stream containing high COD and nutrient loadings, which are the primary sources of eutrophication. Based on the inventory analyses, the lack of wastewater could account for the lower eutrophication impact discharged from the ME50 production, while the B100 and its blends (B50) produced a large volume of effluent from biofuel purification. In addition, eutrophication results both from the direct and indirect emissions of nitrogen and phosphorus-based fertilizers leaching from crop farming to the watershed.

In the GHG emission results, the sources of emissions were derived from both production process and use phase. The significant contribution to a higher fraction of the GHG emissions from the use phase over the production process of microemulsion (ME50) was about 21 % of the total GHG emissions due to the diesel combustion in its composition. For B100 production, the GHG emissions from the transesterification production likely results from the effluent from biodiesel purification. The biodiesel effluent has

generally high COD loading (COD, 0.17 kg/L effluent) (Srirangsan 2008). This is conventionally treated using an anaerobic process in order to control the water pollution. In this study, the GHG emissions from the effluent were estimated from the amount of COD loaded in untreated wastewater. For indirect methane (CH_4), the emissions generated from an anaerobic reactor were calculated using a default value of 0.25 kg of CH_4/kg of COD conversion (IPCC 2006). Even though, the GHG emissions generated by transesterification process were higher than that by microemulsion process, B100 had lower GHG emissions than ME50. This is because it has a significant amount of co-product, glycerol (B100/glycerol weight ratio is 80:20). With the allocation analysis, it was found that the GHG emissions generated were 1.78 % lower in B100 and 3.32 % lower in B50 than that in ME50. Considering the GHG emissions from the use phase (tank to wheel analysis), it was found that ME50 had a comparable GHG emission with B50 and had much reduction in GHG emission relative to diesel fuel. The use of B100 instead of diesel fuel outperforms an environmental benefit in terms of carbon neutral consideration.

The land use or land occupation impact in this study refers to the damage as a result of the continuous use of a land area for a certain human-controlled purpose, i.e. agriculture, production of raw materials and processes. As mentioned, the land use impact of the ME50 production resulted largely from the surfactant derived from palm kernel oil. The results indicated that ME50 production (315 PDF m^2 year) caused more land occupation than B100 (19 PDF m^2 year), B50 (26 PDF m^2 year), and diesel as a reference (29 PDF m^2 year). The land use impact of ME50 production was mainly from bio-based feedstocks (i.e. palm oil and palm kernel oil) involving the higher land occupation for resource extraction through the purification process.

For water resource quality, the ME50 production is an enormous improvement due to the fact that there is no water used for production; thus, there is zero wastewater discharged from this process. Regarding the remaining categories, the ecotoxicity-related impact is highly influenced by the palm oil cultivation especially from the activities relating to agrochemical application. These biofuel production impact categories play a more dominant role in a high-level vegetable oil-diesel blend than in a low-level blend. The result of fossil depletion is straightforward as there was a higher reduction in fossil fuel consumption resulting in a substantially lower impact contributed from fossil resource.

In summary, the life cycle assessment results show that the use of ME50 can help reduce the depletion of fossil energy resources, acidification, and ozone layer depletion as compared to B100 and a reference diesel fuel. Additionally, the use of ME50 can reduce the GWP versus diesel fuel. However, there are also several adverse environmental burdens associated with the material acquisition process that need to be considered.

6.5 Sensitivity analysis

A sensitivity analysis was carried out on the biogas recovery from the palm oil mill effluent and B100 purification effluent (the effluent from B100 purification process) to evaluate the electricity used during the biofuel production in order to see its influence and the GHGs produced from wastewater effluent. For the B100 purification process, the effluent is used to solubilize free fatty acid and soap from methyl ester in order to eliminate contaminants from the product. Energy recovered from biogas, where CH_4 yield is 0.251 kg/kg COD (Wulfert et al. 2002), density of CH_4 is 0.656 kg/m^3 (Choo et al. 2011) and LHV of CH_4 is 23 MJ/m^3, was converted to electricity in the unit of kilowatt hour. The reduction of GHG emissions is due to the selling of generated electricity from biogas to Provincial Electricity Authority (PEA), Thailand through the grid connection. The results of the sensitivity analysis are presented in Fig. 4. The x-axis shows the two systems of wastewater treatment (with and without biogas capture), and the y-axis represents the GHG emissions variation. It is assumed that biogas could not be lost from the seal weld between plastic sheet and biogas recovery tank. It is clearly seen that the presence of biogas capture both form POME and B100 purification effluent reduced by 23 % from the GHG emissions of ME50 production, 83 % from the GHG emissions of B100 production and 62 % from the GHG emissions of B50 production. In case of the presence of biogas capture form POME, the GHG emissions of ME50, B100 and B50 production was reduced by 23, 79 and 59 % from the total GHG emissions, respectively. Therefore, the reduction of GHGs from biogas capture in the wastewater treatment of B100 purification effluent was considered as small when compared with that in palm oil mill effluent. However, in an ideal situation when the presence of biogas capturing from either POME or B100 purification effluent, GHG emissions of transesterification (B100 and B50) were less than that of microemulsion production (ME50).

7 Conclusions

The present study reports on the life cycle analysis performed on the novel microemulsion-based biofuel (ME50) production process. All production methods of ME50, namely, oil palm cultivation, palm oil processing, and microemulsion production, were evaluated based on 1 t of ME50. The production of microemulsion fuel data was gathered based on positive experimental results from our previous works. However, the results of the laboratory data provide a good estimate of the characteristics of the environmental impact and GHG emissions. The microemulsion fuel production had a significant environmental impact on land use, fossil depletion, and ecotoxicity due to the various processes of bio-based materials

from the oil palm cultivation through to the palm oil refinery, whereas there was only a minor impact on the eutrophication and human toxicity categories. The comparative results indicate that the impacts produced by transesterification, the B100, are greater than that produced by the ME50 and B50 in each of the impact categories except for those of global warming, fossil depletion and land use. Considering only the GHG emissions, the microemulsion fuel causes 3280 kg CO_2eq./45,800 MJ of ME50 (the carbon footprint method) with lower energy consumption and discharged wastewater. The dominant source of GHG emissions during the microemulsion production stage is the use of raw materials. It can be noted that the appropriate formulation of microemulsion fuel could reduce potential emissions such as GHG, acidification and ecotoxicology—related in both its production phase and use phase.

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Formation and phase behaviors of ethanol in palm oil/diesel blend reverse micelle microemulsions using nonionic surfactants for biofuel application

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Reverse micelle or water-in-oil microemulsion has attracted much attention for various potential applications including biofuels. A microemulsion is a thermodynamically stable, isotropic mixture of at least two-immiscible liquid stabilized by surfactant system. This study, the reverse micellar system was formulated using the mixture of palm oil/diesel blends as an oil phase and alcohols (i.e., ethanol and butanol) as a polar phase. The non-ionic surfactants derived from renewable based feedstock, were used to stabilize the oil phase and alcohol as a dispersed phase, including alcohol C_{12-14} fatty alcohol ethoxylate surfactants (AE), sorbitan monoleate (Span 80), methyl oleate (MO), and alkanols were used as a cosurfactant. Phase behavior of the microemulsions was conducted through pseudoternary phase diagram. In addition, the solubilisation mechanism of alcohols in palm oil/diesel blend as well as amount of surfactant required to formulate an isotropic area were systematically investigated to evaluate the solubilisation capacity of the alcohol in the oil phase under desired conditions. As the alcohol content increased, the minimum surfactant concentration required to obtain a single phase microemulsion increased, while the phase separation decreased with an increase in the butanol fraction in the ethanol/buthanol blends. The appropriate formulation for microemulsion biofuels were selected at minimum surfactant concentration that required to form a single phase at palm oil /diesel blended ratio of 1:1 (v/v) and alcohol of 20 % (wt). 1-octanol and 2 ethyl-1-hexanol were the appropriate co-surfactant with the optimal surfactant/cosurfactant (S/C) molar ratio of 1:8. The microemulsion properties including kinematic viscosity and microemulsion droplet size were determined and used to specify the potential application of the products.

Keywords: reverse micelle, biofuel, surfactant, microemulsion

Formation and Phase Behaviors of Ethanol in Palm Oil/Diesel Blend Reverse Micelle Microemulsions using Nonionic Surfactants for Biofuel Application

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Abstract

This study aims to formulate a single phase microemulsion of palm oil/diesel blended with ethanol known as Microemulsion Biofuels. The nonionic surfactants with different structures were used as an emulsifying agent. The effects of butanol in ethanol/butanol blends as an alcohol on microemulsion phase behavoir and its properties were investigated including the droplet size. The results indicated that the single phase formation depends strongly on hydrophilicity of the polar phase (alcohols). The ratio of the ethanol/butanol blended is the important key parameter for formulating ME in biofuel production.

Introduction

Vegetable oil based microemulsion biofuels have become more attractive for biofuel production technology due to environmental benefits of reducing energy and water uses in the production. Because of simple mixing process, it has no byproduct and waste that required additional treatment.

A microemulsion biofuel (ME) is a thermodynamically stable mixture of at least two-immiscible liquid fuels where a polar alcohol phase (i.e., ethanol, butanol) is dispersed in a non-polar oil phase (i.e. palm oil/diesel) stabilized by surfactant system, known as reverse micelles [1]. Appropriate surfactant and cosurfactant system and its formulation are key challenges to formulate a stable single-phase ME of various type of mixed liquid fuels especially with vegetable oils having high viscosity. This study, nonionic surfactants with different structure, methy oleate (MO), sorbitan monooleate (SM) and palm oil methyl ester (PME) were selected were selected. The effects of ethanol/butanol ratios on the microemulsion phase behavior, droplet size and viscosity were examined. Finally, The fuel properties of the formulated ME were determined to understand the parameter affecting microemulsion biofuel formation.

Goal & Objective

The goal are to formulate palm oil based microemulsion fuels using nonionic surfactant systems and examine the key parameter maintaining the emulsion and fuel property for biofuel application

Methodology

Nonionic surfactants

Methyl oleate (MO) HLB = 4.0

Palm oil methyl ester (PME) HLB = 4.2

Sorbitan molooleate (SM) HLB = 4.3

Cosurfactant: 1-octanol (99% purity)

Polar phase: Ethanol (95%) and Butanol/Ethanol blends

Oil phase: Palm oil/Diesel blended (50 vol.%)

Psuedo-ternary phase diagram

Surfactant/co-surfactant

Composition = 20% EtOH + 20% C/S + 60% Oil

Oil (palm oil/diesel)

Alcohol

Ternary phase diagrams of microemulsion biofuel :
palm oil/diesel blend (50 v:v%)- Ethanol - PME/octanol (1:8 M/M)

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Results

❖ Effect of surfactant structure

From the ME phase behaviors, structure of the surfactant did not significantly affect to the single phase formation of the palm oil/diesel blended. This could be due to the hydrophobicity described in terms of HLB play an important role in solubilizing of the oil phase in reverse micellar system.

❖ Effect of butanol blending

The addition of butanol in ethanol/butanol blended as a polar phase was found to reduce the concentration of the required surfactant to form a single phase microemulsion. The amount butanol in ethanol/butanol blended decreases with the increasing of the required surfactant. For the emulsion viscosity, it was found that the viscosity of the ME increases with increasing of butanol fraction in the blended.

❖ Fuel property of microemulsion biofuels

Fuel property of palm oil/diesel blend with ethanol

Sample (Ethanol 20%)	Formula (% vol.) S:O:AcOH	Properties of microemulsion biofuels			
		Viscosity (cSt 40°c)	Droplet size (nm)	Density (g/mL.)	Heat of combustion (MJ/kg)
MO-EtOH	18:62:20	5.57	5,342	0.874	38.9
PME-EtOH	23:57:20	5.64	5,495	0.854	38.6
PME-BtOH	0:80:20	7.98	475	0.852	41.0
PME-EtOH/BtOH.50:50	10:70:20	6.38	5,413	0.845	39.7
Palm oil/diesel blend	50:50	11.70	4	0.879	42.5

Conclusions

- The nonionic surfactants can be used for formulating palm oil/diesel blended (50:50 v%) with ethanol with high emulsion stability;
- The structure of surfactant is not effect to the amount of surfactant required to from the Mes, while
- Hydrophilicity of the polar phase (alcohol) is the influencing parameter for ME phase behaviors.
- The "Key Challenge" to adjusting emulsion and fuel property of the ME are surfactant structure, ratio of alcohols blended

Palm oil based biofuels by reverse micelle microemulsion formation using nonionic surfactant systems : The effect of ethylene oxide groups in the nonionic surfactants

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The direct use of vegetable oil as diesel fuel causes engine's efficiency due to theirs high viscosity. One of the biofuel technologies to reduce vegetable oil viscosity is microemulsification so called microemulsion biofuels. The reverse micelle microemulsion biofuel is thermodynamically stable emulsion of mixed liquid fuels which both a polar phase (i.e. ethanol) and a nonpolar phase (i.e. palm oil/diesel blend) are emulsified by surfactant film. The objectives of this research are to study the effects of surfactant structures, surfactant/cosurfactant ratios and to determine phase behaviors using a pseudo-ternary phase diagram of the biofuels with varying vegetable oil properties. This study, the biofuel microemulsion systems with refined bleached deodorized palm oil (RBDPO)/diesel blends at a ratio of 50:50 (v/v) with ethanol as a viscosity reducer and stabilized by surfactant/cosurfactant at a mole ratio of 1:8 were formulated. The nonionic alcohol ethoxylate surfactant with different number of EO groups (EO groups: n = 1, 3, and 5) was used as a surfactant to form reverse micellar system. 1-Octanol was chosen as a cosurfactant because it can maintain the single phase microemulsion formation with minimizing surfactant concentration. For the phase behaviors of microemulsion biofuel systems, the results showed that the amount of surfactant required to form a single phase was different significantly with different EO groups in the surfactants. The microemulsion systems with EO5 had the highest amount of surfactants required to form a single phase followed by EO3 and EO1, respectively. However, kinematic viscosity of the microemulsion biofuel that contains different EO groups in the surfactants was not significantly different.
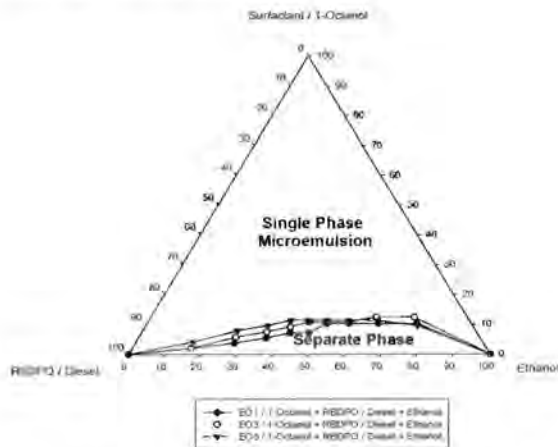

Figure A pseudo-ternary phase diagram of microemulsion biofuels using refined bleached

RBDPO/diesel blends at a ratio of 50:50 (v/v) with ethanol and surfactant/cosurfactant (1:8 M/M) with different number of EO groups (1, 3 and 5) in the alcohol ethoxylate surfactant

Keywords: Biofuels, Microemulsion, Palm oil, Nonionic surfactant

Palm Oil Based Biofuels by Reverse Micelle Microemulsion Formation : the Effects of Ethylene Oxide groups in the Nonionic Surfactants

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INTRODUCTION

Vegetable oils have been widely considered as such an alternative fuel source. Many vegetable oils have been used to replace diesel fuel. Due to high viscosity of vegetable oil, the direct use of vegetable oil can lead to engine's performance problem. Reverse micelle microemulsion has been studied to formulate biofuel with desirable viscosity. Microemulsion biofuel is direct mixture of vegetable oil and diesel fuel with ethanol stabilized by surfactant as an emulsifier to form a single phase microemulsion. In microemulsion system, ethanol is used as a polar phase and it can reduce viscosity of vegetable oil and diesel mixture.

OBJECTIVES

- To formulate microemulsion biofuels with refined bleached deodorized palm oil; RBDPO to diesel blends with ethanol using nonionic surfactant system.

- To study effects of the surfactant structure on phase behavior, kinematic viscosity in the microemulsion system and their properties.

METHODOLOGY

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ACKNOWLEDGEMENTS

RESULTS

Phase Behavior Study

For the effect of surfactant's structures on the phase behavior, the amount of needed surfactant increases with increasing the EO numbers to achieve a single phase microemulsion.
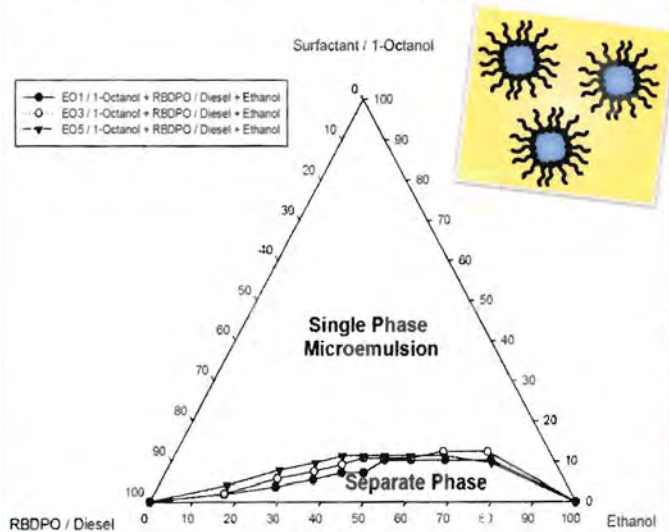

Figure 1 Pesudo-ternary phase diagrams of the ME systems using AE-EO1, AE-EO3 and AE-EO5 as a surfactant and 1-octanol as a cosurfactant with S/C at the molar ratio of 1:8, and the neat RBDPO/diesel blended at the ratio of 1:1 (v/v) under room temperature (25 ± 2°C).

Kinematic viscosity Measurement

The kinematic viscosity of microemulsion biofuels that contains different EO groups in the surfactants was not significantly different.

Table 1 The formula and properties of the ME prepared by various surfactant systems at the S/C molar ratio of 1:8 and the RBDPO/diesel blended at ratio of 1:1 (v/v) and 20 vol.% of ethanol under room temperature (25±2°C)

Sample	Formula (% vol.) (surfactant : Palm oil/diesel : ethanol)	Properties of microemulsion biofuels		
		Kinematic viscosity (cSt)	Density (g/mL)	Heat of combustion (MJ/kg)
EO1 / 1-octanol	2 : 78 :20	5.25	0.8196	39.49
EO3 / 1-octanol	3 : 77 : 20	5.26	0.8255	39.54
EO5 / 1-octanol	4 : 76 : 20	5.29	0.8271	39.24
Diesel*	-	4.10	0.8470	45.8

*The data obtained from Arpornpong et al., 2014

CONCLUSIONS

- The surfactant selection is one of the key parameters to formulate microemulsion biofuels. This study formulated microemulsion biofuels using RBDPO with diesel blend and ethanol
- Phase behavior study, the different types of surfactant were slightly affected to amount of surfactant to formulate single phase microemulsion. The structures of surfactant were not significantly different in kinematic viscosity.

Oral Sessions

30D1-4   10:00–10:20

Economic water productivity of polylactic acid (PLA) production chain in Thailand

Shinatiphkorn Pongpinyopap[1], Unchalee Suwanmanee[2], Thumrongrut Mungcharoen[1]

[1]Kasetsart University, [2]Srinakharinwirot University

30D2(Room 202) 10:40–12:00 October 30, Thursday

Water-2

Chair : A.-M. Boulay

30D2-1   10:40–11:00

Environmental life cycle emissions for vegetable oil microemulsion-based biofuels

Noulkamol Arpornpong[1], Ampira Charoensaeng[1], Virin Kittithammavong[1], David A. Sabatini[2], Sutha Khaodhiar[1]

[1]Chulalongkorn University, [2]The University of Oklahoma

30D2-2   11:00–11:20

Life cycle assessment of biofuels and the issue of indirect land use change

Liselotte Schebek, Yalda Cikovani

Technische Universität Darmstadt

30D2-3   11:20–11:40

Evaluation of uncertainty in for- and background systems: A case study of municipal wastewater treatment plant

Hiroko Yoshida, Charlotte Schuetz, Thomas H Christensen

Technical University of Denmark

30D2-4   11:40–12:00

Basin-scale multi-objective optimization of water and wastewater systems considering global and regional impacts

Seiya Maki, Jun Nakatani, Kiyo Kurisu, Keisuke Hanaki

The University of Tokyo

Surfactant, Separation and Environment	SE-O-2

Environmental Life Cycle Assessment of Palm oil based Microemulsion Biofuel Production

Chaw Suhlaing[a], **Noulkamol Arpornpong**[b], **David A. Sabatini**[c], **Pomthong Malakul Na Ayuthaya**[a], **Ampira Charoensaeng*,**[a]

[a] The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand.
[b] International Postgraduate Program in Environmental Management, Graduate School, Chulalongkorn University, Bangkok 10330, Thailand.
[b] Center of Excellence on Hazardous Substance Management (HSM), Bangkok 10330, Thailand.
c School of Civil Engineering and Environmental Science, The University of Oklahoma, USA.

Keywords: Microemulsion biofuel, Life cycle assessment, GHG emissions, Environmental impacts

This study focuses on evaluation of Greenhouse Gas (GHG) emissions and environmental impacts of microemulsion (ME) biofuels from different formulations based on life cycle assessment (LCA) approach. The functional unit is set to be one ton of ME biofuel. LCA system boundary was separated into four stages: cultivation, oil extraction, refining and microemulsion. The ME biofuels with different formulations had been set for four different Scenarios by varying the type and ratio of raw materials used. In addition, other potential environmental impact assessments of ME biofuel including GHG emission, acidification, eutrophication, ozone layer depletion, abiotic depletion, photochemical oxidation, land use, human toxicity, fresh water aquatic, marine aquatic and terrestrial ecotoxicity were also be evaluated by using commercial software, Simapro version 7.1 with Eco-indicator 99 (H) and CML 2 baseline 2000 methods. The GHG emissions from different scenarios described that scenario IV contributes to the lowest GHG emissions (1,017 $kgCO_2$) and lowest environmental impacts among four scenarios as the result of using refined bleached deodorized palm oil (RBDPO) as a bio-based fraction in the ME formulation. When RBDPO was used to formulate ME biofuel, the total GHG emission was significantly reduced comparing to base case (1,426 $kgCO_2$). When the emissions of each impact category from four scenarios were compared based on the normalized results, ME biofuel production contributes significantly to some impact categories including global warming, abiotic depletion, land use and marine aquatic ecotoxicity.
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Process and System Engineering	PS-O-1

Sustainable Treatment for Co2 From The Coal-Fired Power Plant Through Methanol Production

Tuan B.H. Nguyen,[a] **Rafiqul Gani,**[b] **Uthaiporn Suriyapraphadilok*,**[a]

[a] The Petroleum and Petrochemical College, Chulalongkorn University,Bangkok, Thailand
[b] CAPEC, Department of Chemical and Biochemical Engineering, Technical University of Denmark, Kongens Lyngby, Denmark

Keywords: CO2 mitigation, Methanol synthesis, Aspen Plus, CO2 hydrogenation

The 6th Research Symposium on Petrochemical and
Materials Technology and The 21st PPC Symposium
on Petroleum, Petrochemicals, and Polymers
April 21, 2015, Auditorium and Meeting Room 1-4,
Chaloem Rajakumari 60, Chulalongkorn University
Bangkok, Thailand

RE-P-12 Formation of Vegetable Oil Based Microemulsion Biofuel with Butanol in Palm oil/Diesel Blends

Waritta Apichatyothin [a], David A. Sabitini [b], Ampira Charoensaeng [a*]
[a] The Petroleum and Petrochemical College, Chulalongkorn University
[b] Civil Engineering and Environmental Science Department, University of Oklahoma

Keywords: Microemulsion biofuel, Viscosity reducer, Pseudo ternary phase diagram

Vegetable oil is an option for production of renewable fuels to replace the diesel oils. Because vegetable oils have higher viscosity than diesel oils, the usability of neat vegetable oils can leads to engine stability problems such as poor atomization of the fuel. Vegetable oil viscosity can be reduced by blending with diesel fuel in thermodynamically stable mixtures using microemulsion formulation techniques. This work focuses on the formation of microemulsion fuels consisting of diesel fuel and palm (olein) blends as the oil phase with ethanol and butanol as the viscosity reducers. Methyl oleate and palm oil methyl ester (POME) were used as a surfactant and 1-octanol was used as a cosurfactant at 1:8 surfactant:cosurfactant molar ratio. This work studied the effects of surfactant structure, ethanol/butanol blending ratios and diesel/palm oil blending ratios on kinematic viscosity, microemulsion droplet size and fuel properties for microemulsion fuel formation and compared all of the fuel properties to regular biodiesel and diesel. The result showed that the phase behaviors for different surfactant systems had similar trend. The microemulsion biofuel containing butanol in the mixtures showed a remarkable result on phase behavior, but increasing in butanol to ethanol ratios have become the major challenge for the viscosity and other fuel properties of microemulsion biofuel.
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RE-P-13 Solid Acid Catalyst for Biodiesel Production via Esterification from Oleic Acid

Suppasate Dechakhumwat, Apanee Luengnaruemitchai [*]
The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand

Keywords: biodiesel, solid acid catalyst, p-toluenesulfonic acid, esterification, oleic acid

Esterification of oleic acid with methanol using treated solid residue as a catalyst was studied for biodiesel production. The solid acid catalyst was prepared by sulfonation of p-toluenesulfonic acid on corncob waste obtained from butanol production. Its activity was compared with the corncob activated by concentrated sulfuric acid (H_2SO_4). The result from gas chromatrography showed that the catalyst activated by TsOH can catalyze the reaction faster than that activated by H_2SO_4, at reaction temperature of 60°C for 2 h. The characterization results from an acid-base titration method and surface area analysis indicated that TsOH treated catalyst have lower acid sites than H_2SO_4; however, it exhibited higher specific surface area and pore specific volume.
* **apanee.l@chula.ac.th**

Surfactant, Separation and Environment (SE)

SE-P-1 Development of Filter Modified by Polyelectrolyte Multilayers as Adsorbent Filter for Herbicides

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[b] Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand.
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Keywords : Herbicides/Membrane filter/Polyelectrolyte/Layer-by-Layer

Currently, herbicides such as paraquat, glyphosate and atrazine residues contaminate our environment including the natural water resources and soils. Many studies conducted on the development of a method to remove the chemical residues from the natural water. A membrane filter is one process used to remove herbicides from water. In this study, polyelectrolyte multilayer films (PEMs) consisted of poly(diallyl

SE-P-22 Reverse Micelle Microemulsion Biofuel using Palm Oil/Diesel Ethanol with Renewable Nonionic Surfactant System

Sachart Manaphati [a], *Pomthong Malakul* [a], *David A. Sabatini* [b], *Ampira Charoensaeng* * [a]

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[b] School of Civil Engineering and Environmental Science, The University of Oklahoma, USA

Keywords: Reverse microemulsion, Biofuel, Palm oil, Phase behavior, Kinematic viscosity

Vegetable oils which is clean and non-toxic nature derived from agricultural feedstock, have been used for producing biofuels for many years. Due to their high viscosity, the direct use of vegetable oil in diesel engines can lead to engine durability problems. Reverse micelle microemulsion as an alternative biofuel production has been intensively studied for formulating biofuel with desirable viscosity. This work aims to formulate microemulsion biofuels of palm oil/diesel blend with ethanol using nonionic surfactants derived from renewable based feedstock (methyl oleate, Span 80 and palm oil methyl ester (PME)) mixed with cosurfactant (1-octanol) as a surfactant/cosurfactant system. The pseudo-ternary phase diagrams of the mixed liquid fuels were conducted and the appropriate microemulsion fuel formulation were selected and evaluated. The results showed that structure of the three different nonionic surfactant has no significant effect on phase behaviors of the microemulsion biofuels. While the results from kinematic viscosity measurements of the microemulsion systems showed that methyl oleate and PME system presented an improvement and had significantly lower viscosity than that of Span 80 system.
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SE-P-23 Solid-polymer Mixed Matrix Membranes for Gas Separation: Polyimide and Inorganic Solid Materials

Kyu Kyu Myint [a], *Thirasak Rirksomboon* * [a], *Santi Kulprathipanja* [b], *Chunqing Liu* [b]
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[b] UOP, A Honeywell Company, Illinois, USA

Keywords: Mixed matrix membranes, CO_2/CH_4 separation, Inorganic fillers, Matrimid 5218

The fabrication and separation performances of solid-polymer mixed matrix membranes (MMMs) using three different inorganic fillers (4A zeolite, gamma-alumina and activated carbon) as the dispersed phases in Matrimid polymer matrix were investigated. The solution-casting method was used to fabricate 15 wt% and 25 wt% inorganic filler-Matrimid MMMs. Single gas permeation measurements of CO_2, CH_4 and H_2 were carried out using a dense film permeation unit by a time-lag method at 50 °C and an upstream pressure of 100 psig. Both permeability and selectivity of the pairs of gases (CO_2/CH_4 and H_2/CH_4) increased with a certain loading amount of activated carbon in Matrimid polymer compared to Matrimid dense membrane and other MMMs. These results could be considered the activated carbon has higher adsorption selectivity for CO_2 (polar gas) than for CH_4 (non-polar gas) and the mechanism of preferential surface diffusion of CO_2 (more adsorbable gas) over CH_4 (less adsorbable gas). On the other hand, molecular sieving characteristics played a dominant role in transport mechanism for the smallest gas, H_2.
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SE-P-21 Electrochemical Biosensors to Detect Microbes in Petrochemical Processes

Chayut Yaempho [a], *Dong Shik Kim* [b]*, *Pomthong Malakul* [a,c]
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[b] Department of Chemical and Environmental Engineering, University of Toledo, Ohio, USA
[c] Center of Excellence on Petrochemical and Materials Technology, Bangkok, Thailand

Keywords: Electrochemical Biosensor, Self-Assembled Monolayer, Cyclic Voltammetry, Electrochemical Impedance Spectroscopy

The presence of microorganisms in petrochemical processes and systems can be harmful to the process efficiency and production yield. For example, biofouling in pipelines and storage tanks may jeopardize a process. Bacterial or fungal growth in petrochemical materials may cause unwanted degradation of the materials and final products. An electrochemical biosensor that can detect the presence of bacteria even at a very low concentration is necessary in order to maintain the system free of microbial impacts. In this study, an electrochemical biosensor was investigated

Saturday Poster Session I: 10:45 - 12:15
Room: 606

7336
Conversion of Black Wattle to Bio-Oil and Chemicals on the Continuous Pyrolytic Reactor
Witchakorn Charusiri, Srinakhannwirot University, Thailand

12510
Modelling and Analysis of Real Underwater Acoustic Signals Produced by Marine Energy Devices
Oshoke Ikpekha, Dublin City University, Ireland
Stephen Daniels, Dublin City University, Ireland

13345
Praseodymium-Doped Ce0.5Co0.5O2 Catalyst for Use on the Bioethanol Steam Reforming Reaction to Produce Hydrogen
Josh Y.Z. Chiou, National Defense University, Taiwan
Ya-Ping Chen, National Defense University, Taiwan
Chen-Lung Chuang, National Defense University, Taiwan
Pei-Di Jeng, National Defense University, Taiwan
Chen-Bin Wang, National Defense University, Taiwan

13790
Comparison Analysis Between Rice and Cassava for Bioethanol Production in Japan Considering Land Use Efficiency
Marisabel Cuberos Balda, Tohoku University, Japan
Takaaki Furubayashi, Tohoku University, Japan
Toshihiko Nakata, Tohoku University, Japan

13838
Effect of Ce and Ca Dopants Over La1-X-Ycexcaynio3 Catalysts on the Steam Reforming of Ethanol to Produce Hydrogen
Chen-Lung Chuang, National Defense University, Taiwan
Pei-Di Jeng, National Defense University, Taiwan
Ruei-Ci Wu, TransWorld University, Taiwan
Jong Hwa, TransWorld University, Taiwan
Chen-Bin Wang, National Defense University, Taiwan

13914
Effect of Cosufactant Structure on Renewable Microemulsion Fuels Properties Using Palm Oil/Diesel Blend with Ethanol
Sachart Manaphati, Chulalongkorn University, Thailand
Pomthong Malakul, Chulalongkorn University, Thailand
David A. Sabatini, The University of Oklahoma, USA
Ampira Charoensaeng, Chulalongkorn University, Thailand

13916
Aqueous Micellar-based Extraction as Alternative Solvent for Residual Oil Extraction of Spent Bleaching Earth
Ratiprach Aiamthongkham, Chulalongkorn University, Thailand
David A. Sabatini, The University of Oklahoma, USA
Ampira Charoensaeng, Chulalongkorn University, Thailand

13918
A Comparative Study on the Phase Equilibrium Characteristics of Hydrates for Natural Gas Hydrate (NGH) Transportation and Storage
Young-Hun Kim, Jeju National University, South Korea
Sung-Seek Park, Jeju National University, South Korea
Woo-Joong Kim, Jeju National University, South Korea
Nam-Jin Kim, Jeju National University, South Korea

13929
A Comparative Study on the Characteristics of Thermoacoustic Waves for Applying Solar Energy
Sung Seek Park, Jeju National University, South Korea
Yoo Joong Kim, Jeju National University, South Korea
Young Hun Kim, Jeju National University, South Korea
Yong Hwan Kim, Jeju National University, South Korea
Nam Jin Kim, Jeju National University, South Korea

Effect of Cosufactant Structure on Renewable Microemulsion Fuels Properties using Palm oil/Diesel Blend with Ethanol

Abstract

Due to main problems of the drain of petroleum feedstocks and greenhouse gas emissions, green technologies of biofuels have been developed continuously. Biofuel is one of renewable energy which is derived from agriculture products such as oils from plants and animals. Because of high kinematic viscosity of vegetable oils, their direct use causes diesel engines' problems. Reverse micelle microemulsion is the easy biofuel production method and reduces viscosity of vegetable oil in biofuels. The microemulsion biofuel is a thermodynamically stable and isotropic mixture between vegetable oil/diesel with ethanol as a viscosity reducer and stabilized by surfactant and cosurfactnat. The goals of this work are to study effect of cosurfactant structures on phase behavior of microemulsion biofuel using pseudo-ternary phase diagram and to compare their kinematic viscosity, cloud point and microemulsion droplet size. In this research, microemulsion systems consist of palm oil/diesel blend at a ratio of 1:1 (v/v) with ethanol and added palm oil methyl ester (PME), as a surfactant to stabilize microemulsion biofuel with a cosurfactant at a molar ratio of 1:8. 1-octanol and 2-ethyl-1-hexanol were selected as a cosurfactant. The results of phase behavior study were observed that 2-ethyl-1-hexanol's system needed to amount surfactant to formulate single phase microemulsion slightly lower than that of 1-octanol's system. However, for kinematic viscosity, cloud point and droplet size study, there were no significantly difference that contains linear or branch structure of cosurfactants.

Session

Energy : Renewable Energy and Environment Solutions

Authors

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- Pomthong Malakul, The Petroleum and Petrochemical College, Chulalongkorn University, Thailand
- David A. Sabatini, The University of Oklahoma, USA
- Ampira Charoensaeng, The Petroleum and Petrochemical College, Chulalongkorn University, Thailand

Conference

The Fifth Asian Conference on Sustainability, Energy and the Environment 2015 (ACSEE2015)

Art Center of Kobe, Kobe, Kansai Region, Japan
Thursday, June 11, 2015 - Sunday, June 14, 2015 (All Day)

Abstract Submission Deadline: February 15, 2015
Registration Deadline for Presenters: May 15, 2015

http://iafor.org/conferences/acsee2015/

Effect of Cosufactant Structure on Renewable Microemulsion Fuels Properties Using Palm Oil/Diesel Blend with Ethanol

Sachart Manaphati [a], Pomthong Malakul [a], David A. Sabatini [b], Ampira Charoensaeng [a]

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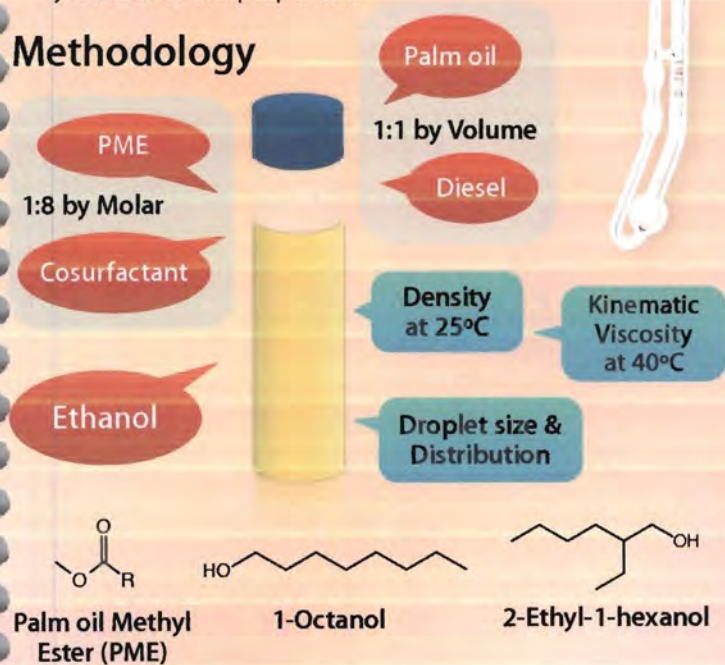
Introduction

Vegetable oils are an alternative fuel from agricultural feedstocks. Several vegetable oils have been used for substituting diesel fuel. The use of vegetable oil in diesel engine causes engine's performance problem due to high viscosity of vegetable oil. Reverse micelle microemulsion as an alternative biofuel production has been intensively studied for formulating biofuel with desirable viscosity. Microemulsion biofuel is mixed liquid fuels between diesel fuel and vegetable oil with surfactant as an emulsifier to form a single phase microemulsion. In micellar microemulsion system, ethanol is used in place of the polar phase and it can reduce viscosity of vegetable oil and diesel mixture.

Objectives

- To formulate biofuels with vegetable oil/diesel blend and ethanol using through reverse micelle microemulsion.
- To study effect of the structure of cosurfactants on phase behaviour and kinematic viscosity in the microemulsion system and their properties.

Methodology

Palm oil / Diesel — 1:1 by Volume

PME / Cosurfactant — 1:8 by Molar

Ethanol

Density at 25°C — Kinematic Viscosity at 40°C

Droplet size & Distribution

Palm oil Methyl Ester (PME)   1-Octanol   2-Ethyl-1-hexanol

References

- *Arpornpong, N., Attaphong, C., Charoensaeng, A., Sabatini, D. A., Khaodhiar, S. (2014). Fuel. 132(0), 101-106.*
- *Attaphong, C., Sabatini, D. A. (2013). Energy & Fuels. 27(11), 6773-6780.*

Results

Phase Behavior Study

For the effect of cosurfactant's structure on the phase behavior, the kinematic viscosity of 2-ethyl-1-hexanol's systems was less than those of 1-octanol's systems.
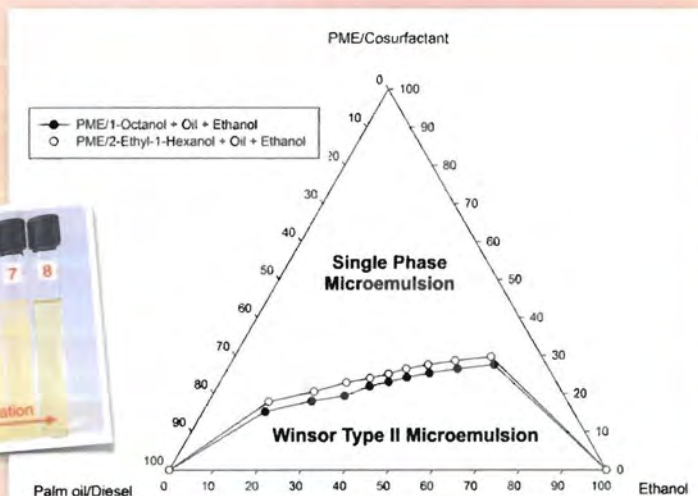
Fuel Properties Determination

Systems	Formula (% vol.) (surfactant : palm oil/ diesel : ethanol)	Properties of microemulsion biofuels			
		Kinematic Viscosity at 40°C (cSt)	Droplet size (nm)	Density (g/mL)	Heat of combustion (MJ/kg)
Methyl oleate	23 : 57 : 20	5.64	5,495	0.8545	39.0
PME	25 : 55 : 20	5.51	5,228	0.8384	38.5
Palm oil/diesel [a]	-	11.7	4.32	0.879	42.5

[a] The data obtained from Arpornpong et al., 2014

Conclusion

The cosurfactant structure showed no significant effect to the phase behavior, the remarkable result were observed on the kinematic viscosity. This study formulated microemulsion biofuels using palm oil with diesel blended and ethanol. Phase behaviour study, the different types of cosurfactant were not affected to amount of surfactant to formulate single phase microemulsion. The appropriate viscosity was obtained by PME/1-octanol system.

Acknowledgements

Download Abstract