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Microemulsion fuels from vegetable oil based renewable resource using mixed nonionic surfactant and cosurfactant systems

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***Abstract*— Vegetable oils are of interest as a bio-based feedstock in the production of environmentally friendly alternative fuel. Microemulsification is an emerging technology to formulate mixtures of thermodynamically stable, isotropic liquid fuels, containing two or more immiscible phases stabilized by surfactant. In this study, three components including oil (vegetable oil/diesel blends), ethanol, and surfactant were conducted to formulate bio-based microemulsion fuels. The mixture of oils contain vegetable oil (palm oil or used palm oil or soybean oil) blended with regular diesel or biodiesel at a ratio of 50:50% (v/v), representing the non-polar phase. Ethanol facilitates the viscosity reducer, which is used as the polar phase. Mixed nonionic alcohol ethoxylate surfactant (C_{12-14}-$(EO)_1$-OH) and cosurfactants (octanol and ethylene glycol butyl ether) at a 1:8 molar ratio were selected to formulate reverse micelle microemulsion. The effects of vegetable oil types and cosurfactant structures onto the single phase reverse micelle microemulsion formation were investigated and compared. The results from ternary phase diagram indicated that the vegetable/biodiesel blend requires a lower surfactant concentration to formulate single phase microemulsion. The separate phase of microemulsion fuels containing octanol was significantly lower than those of systems with ethylene glycol butyl ether. The results of this work indicated potential uses of vegetable oils for biofuel production by microemulsion, which could serve as a potential technology for green mobility movement.**

***Keywords*— Biofuel, Microemulsion fuel, Vegetable oil, Nonionic surfactant, Ternary phase diagram**

I. Introduction

Due to increasing energy demands and social awareness to reduce our dependence on petroleum fuel consumption, bio-based fuel has received increasing attention over the past few decades [2]. Energy scarcity and environmental awareness perception have been a persuasive driving force to replace existing non-renewable energy such as fossil fuels. Vegetable oils as an alternative fuel, have been realistically used and the technology commercialized for many years because they have similar energy contents compared with regular diesel fuels. Besides that, they are renewable and clean energy, which are the basic criteria of being as sustainable resources. However, certain characteristics of vegetable oils that adversely affect engine performance are high viscosity, low volatile and high freezing point at low temperatures. In fact, the high viscosity can lead to engine problems e.g., coking of injector nozzles, detaching of piston rings and lubricating oil contamination [5]. There are four potential solutions to reduce the viscosity of vegetable oils including; dilution (or blending) of vegetable oil with diesel fuel, pyrolysis, transesterification and microemulsions [3].

A microemulsion biofuel derived from neat vegetable oils have been raising interest because it is produced by a simple mixing of polar and non-polar or two immiscible liquid fuels (i.e., ethanol/diesel blend) without thermochemical conversion. Microemulsions are theoretically defined as amphiphile stabilized transparent, iso-tropic and thermodynamically stable dispersions of otherwise immiscible aqueous liquid phase and oil phase. This liquid-liquid colloidal system contains the polar phase or ethanol droplets dispersing in the oil phase stabilized by surfactant. This is known as – Winsor type II – water in oil (w/o) microemulsion or reverse micelle formation. The average aggregate sizes of the equilibrium reverse micelles generally in micro-scale ranging from 10 – 100 nm [4]. The advantages of the microemulsification method overwhelms other technologies. These advantages include there being no need for toxic chemical catalyst, low production costs due to energy consumption, simple and easy implementation and the no engine modification requirement. Although, a slight loss in heating value of microemulsion fuels has been observed in previous literatures, microemulsion fuels incorporated with ethanol demonstrated lower combustion temperatures, resulting in a drastic reduction in the emissions of thermal nitrogen oxides (NO_x), carbon monoxide (CO) as well as black smoke and particulate matter [1].

However, two-phase separation of microemulsion fuels can occur when two miscible liquid fuels are mixed with either an insufficient amount of surfactant concentration or an inappropriate surfactant formulation. The phase separation is a crucial indicator to design the suitable system for formulating microemulsion fuel, due to each component i.e., surfactant, polar and non-polar phase liquid fuels, which have

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a straightforward affect on fuel properties. Throughout the experimental setup, the separate phase can be optically observed using a ternary phase diagram, thus the optimum condition containing a homogeneous solution will be selected from the plot.

The goal of this study is to investigate the phase behaviors of reverse micelle microemulsion containing vegetable oil/diesel or biodiesel blends with ethanol stabilized by the nonionic alcohol ethoxylate surfactant/cosurfactant system. The mixtures of microemulsion fuels consisting of the mixture of three components including vegetable oil/ diesel blend, surfactant (ethoxylate alcohol)/cosurfactant solution, and ethanol are evaluated through the ternary phase diagram. The effect of vegetable oil (palm oil, used palm oil, soybean oil)/diesel or biodiesel blends, and cosurfactants (octanol or ethylene glycol butyl ether) are investigated with the aim to formulate the microemulsion biofuels that will be used as an alternative fuel.

II. Materials and Method

A. Materials

A nonionic alcohol ethoxylate surfactant, $C_{12\text{-}14}$-$(EO)_1$-OH (Dehydol LS1 as trade name) with 99% purity was used as received from the Thai Ethoxylate Company, Ltd. (Bangkok, Thailand). Cosurfactants used in this research were 1-octanol with 99% purity, purchased from the Acros Organics chemical company and ethylene glycol butyl ether (EGBE) with 99.5% purity, purchased from the Carlo Erba Reagents. Ethanol with ≥ 95% purity (ACS reagent grade) was used as a polar liquid phase. The properties of the surfactant and the cosurfactants are summarized in Figure 1 and Table I. Pure palm oil, used palm oil and soybean oil were purchased from an available local market. Commercial-grade petroleum diesel was purchased from the Shell Thailand. A neat biodiesel was used as received, obtained from the Verasuwan Co., Ltd. (Samutsakhon, Thailand). All chemicals in this study were used as received.

B. Microemulsion fuels preparation Method

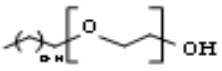
Microemulsion fuel was prepared by the mixed nonionic surfactant and cosurfactant system at a volumetric basis of the fixed mole ratio of 1:8. The non-polar phase from vegetable oil/diesel or vegetable oil/biodiesel blend were prepared at a volumetric ratio of 50:50% (v/v). Ethanol at the designed amount. The mixture of each component, surfactant/ cosurfactant, vegetable oil/diesel or biodiesel blend and ethanol were transferred into 15 ml vial with the total solution of 10 ml, then the solution was hand-shaken gently to formulate reverse micelle microemulsion fuel. Subsequently, the phase behavior of each system was determined by visual inspection with polarized light [7].

C. Ternary phase diagram Method

A ternary phase diagram was plotted indicating a phase behavior of a two miscibility separate phase and homogeneous single phase microemulsions. The ternary diagram is a triangle consisting of three vertices of three major components including surfactant solution, oil mixture, and ethanol [6]. The two vertices at the bottom of the triangle are the oil mixture (at the left side) in this study - vegetable oil/diesel or biodiesel blend (50:50% v/v) and ethanol (at the right side). The upper vertex represents the surfactant solution (in this study - the mixture of surfactant/cosurfactant was at a constant mole ratio of 1:8). The total volume of the surfactant solution, oil mixture, and ethanol was calculated to 100 percent. The composition at each point in the ternary phase diagram demonstrates the volume percentage of the three components (A,B,C) as follows equation (1):

$$x\%A + y\%B + z\%C = 100\%. \quad (1)$$

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.



nonionic alcohol ethoxylate surfactant

1-octanol

Ethylene glycol butyl ether

Figure 1. Structure of surfactant and cosurfactants in this study

TABLE I. PROPERTIES OF THE SURFACTANT AND COSURFACTANTS

Material	Type	Formula	MW	Density (g/ml)
Alcohol ethoxylate	Nonionic surfactant	$C_{12\text{-}14}$-$(EO)_1$-OH	217.15	0.837
1-octanol	Co-surfactant	$C_8H_{17}OH$	130.20	0.833
EGBE	Co-surfactant	$C_6H_{14}O_2$	118.17	0.902

TABLE II. POLARIZABILITY OF THE MATERIAL

Material	Polarizability (x 10^{-24} cm^3)
Ethanol	5.1±0.5
1-octanol	16.1±0.5
EGBE	13.1±0.5

TABLE III. FATTY ACID COMPOSITION OF PALM OIL AND SOYBEAN OIL [8]

Fatty acid composition (%)		Palm oil	Soybean oil
Myristic (Tetradecanoic)	C14	0.5 - 2.0	0.5
Palmitic (Hexadecanoic)	C16	32.0 - 45.0	7.0 – 11.0
Stearic (n-Octadecanoic)	C18	2.0 – 7.0	2.0 – 6.0
Oleic	C18:1	38.0 – 52.0	22.0 – 34.0
Linolenic	C18:2	5.0 – 11.0	43.0 – 56.0
Linolenic	C18:3	-	5.0 – 11.0

III. Results

A. Ternary phase diagram

In this study, the homogenized, stable microemulsion fuels were examined through visual observation from a ternary phase diagram, the components of the formulated microemulsion fuels were divided into three-phases; the surfactant, ethanol and oil phases. The surfactant system is a mixture of nonionic alcohol ethoxylate surfactant (C_{12-14}-$(EO)_1$-OH) and cosurfactant (octanol or ethylene glycol butyl ether) at a molar ratio 1:8. Ethanol represented the polar phase of the microemulsion fuel. The mixture of vegetable oil (palm oil/used palm oil/soybean oil) and diesel or biodiesel at a volumetric ratio 50:50% (v/v) is the non-polar or oil phase. The microemulsion fuels were formulated through reverse micelle formation in which the polar ethanol droplets disperses within the non-polar oil phase, stabilized by the surfactant system.

In the phase diagram, the single phase or isotropic solution (1Φ) was indicated by the region above the curve, whereas the lower region below the curve of the plot appeared as the turbid or separate phase (2Φ). The homogeneous sample was observed for one month, to ensure there was no distinct change in phase separation. The results from ternary phase diagram of the microemulsion fuels are shown in Figure 2 - 4.

B. Effects of oil types

A cosurfactant mainly facilitates a surfactant micelle to integrate and stabilize the interfacial layer between polar phase and non-polar phases. The cosurfactant molecules tend to penetrate into the palisade layer between head and tail of surfactants molecule. In this case, it promotes the solubility enhancement by helping the surfactant aggregates reduce the interfacial tension between the ethanol and oil phase.

Figure 2 shows the phase behaviors of microemulsion system using octanol as a cosurfactant and the mixture of diesel oil blended with different types of vegetable oil including palm oil, used palm oil and soybean oil as polar oil phase. It was found that there were no significant changes in the anti-isotropic regions for the three types of vegetable oil. From Table III, it can be seen that the largest fatty acid contribution in palm oil are palmitic-C16 (32.0 – 45.0%) and oleic-C18:1 (38.0 – 52.0%), while soybean oil are oleic-C18:1 (22.0 – 34.0%) and linolenic-C18:2 (43.0 – 56.0%). The slight difference in the number of carbon atoms in the fatty acid may result in an insignificant distinction between the separation phase of the system formulating with palm oil and soybean oil. This suggests that phase behavior is not influenced by type of fatty acids in vegetable oil. In comparison, the diesel fuel was substituted by pure biodiesel derived from transesterification process to form microemulsion fuels, in order to formulate naturally absolute bio-based product. The systems formulated by vegetable oil/biodiesel blend are also presented in Figure 4. Similar results found in vegetable oil/diesel blend system, there was a slight effect of the fatty acids on the phase separation of the vegetable oil/biodiesel blend.

However, vegetable oil and biodiesel blends integrated homogeneous phase as shown in the ternary plot (Figure 2) greater than those of vegetable oil and diesel blends. In addition, the systems with vegetable oil/biodiesel blends consumed surfactant per cosurfactant at a ratio of 4-6 percent, which was less than those of the surfactant used for the vegetable oil/diesel blend, which was 10-16 percent. This may be due to the fact that regular diesel contains more complex hydrocarbon molecules and various additives. Thus, the vegetable oil/diesel system requires more surfactant molecules to stabilize diesel, resulting a larger area of phase separation region.

C. Effects of cosurfactants

The effect of cosurfactants structure, octanol and ethylene glycol butyl ether (EGBE) on the phase behaviors of microemulsion fuels is illustrated in Figure 3. It can be observed from the miscibility curves that the systems formed by palm oil/diesel blend with octanol as a cosurfactant has better solubilization than those of the system with EGBE because the system with octanol required lower minimum surfactant concentration to formulate a single phase invert microemulsion. The homogenous solution with octanol as the cosurfactant can be achieved at ranges of 72-80 percent of oil fraction, while a slightly lower amount of oil phase range of 70-78 percent was obtained by EGBE. The differences in the phase separation regions may have been expressed through the solubilization behaviors of cosurfactant. The octanol molecule has higher polarizability ($16.1\pm0.5\ 10^{-24}cm^3$) – see from Table II. Thus, it tends to aggregate near the surfactant tails, which facilitate the solubilization of the non-polar phase or oil phase, resulting in a lower amount of surface use. On the other hand, EGBE has slightly lower polarizability properties ($13.1\pm0.5\ 10^{-24}cm^3$) comparing with octanol. Therefore, it prefers to penetrate close to the polar ethanol interface of the surfactant head, which assists the solubilization of the polar ethanol droplet, which leads to an increase in the separation boundary of the ternary plots. For the effect of oil types on the microemulsion fuel formulated by EGBE, not surprisingly the same trend with the octanol system was obtained for both diesel and biodiesel systems and the systems with different types of vegetable oils.

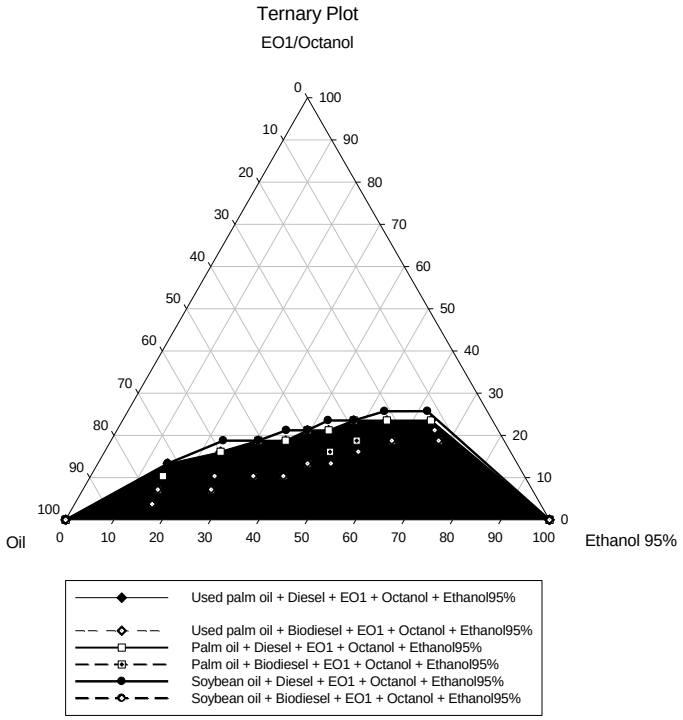


Figure 2. Ternary phase diagram depicting equilibrium for the comparision of EO1/octanol (1:8 molar ratio), vegetable oil/diesel and vegetable oil/biodiesel (50:50% v/v) at 25°C

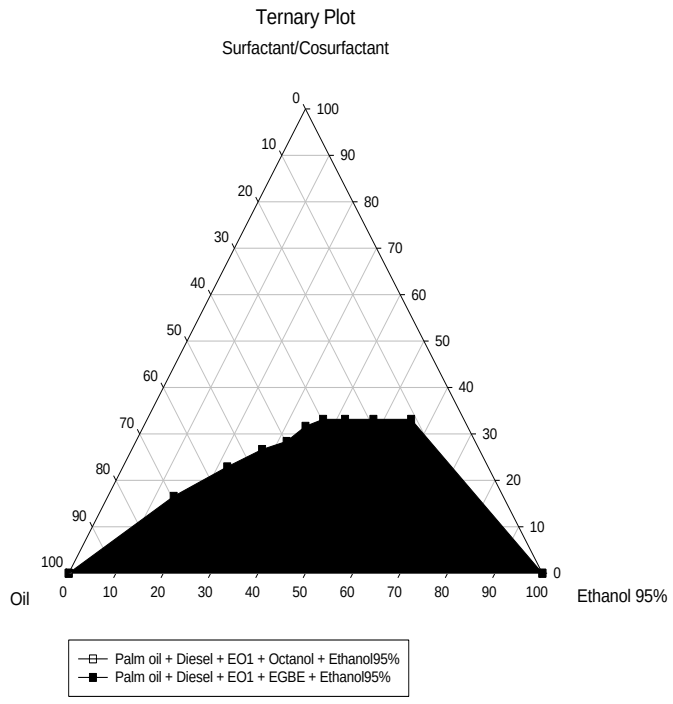


Figure 3. Ternary phase diagram depicting equilibrium for the comparision of EO1/octanol and EO1/ethylene glycol butyl ether (1:8 molar ratio), palm oil/diesel (50:50% v/v) at 25°C

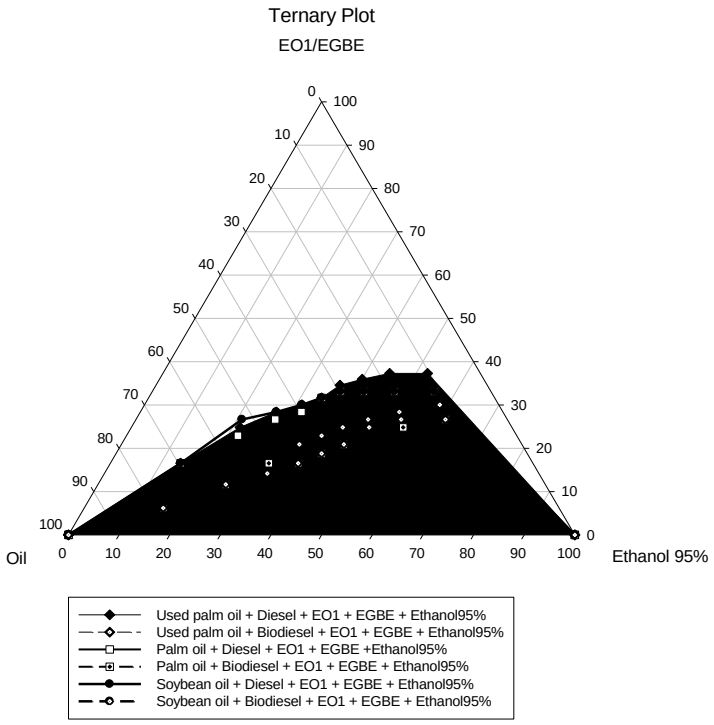


Figure 4. Ternary phase diagram depicting equilibrium for the comparision of EO1/ ethylene glycol butyl ether (1:8 molar ratio), vegetable oil/diesel and vegetable oil/biodiesel (50:50% v/v) at 25°

IV. Conclusions

This study demonstrated the effects of using cosurfactant to formulate microemulsion fuels from vegetable oil (palm oil, used palm oil, soybean oil) blends with diesel or biodiesel on phase behaviors. The phase behaviors of the system, which contained different types of vegetable oil were not significantly affected by the fatty acid composition in vegetable oils. The systems with vegetable oil/biodiesel blends provided two lower phase separate regions when compared with those of the vegetable oil/diesel blends. The suitable surfactant mixture for formulating microemulsion fuel was achieved with ethanol as a cosurfactant. The minimum surfactant required for formulating microemulsion biofuel can be enhanced by selecting an appropriate cosurfactant.

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About Author (s):

Microemulsion biofuel derived from neat vegetable oils have been raising interest because alternative fuel, clean energy, low cost and produced by a simple mixing two immiscible liquid fuels of thermodynamically stable, isotropic and amphiphile stabilized transparent.