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Ethanol-in-palm oil/diesel microemulsion-based biofuel: Phase behavior, viscosity, and droplet size

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HIGHLIGHTS

- Surfactants and cosurfactants were studied for formulating optimized biofuel.
- Surfactant had greater effect on viscosity than cosurfactant.
- Viscosity of biofuel tends to be greater with smaller size of droplets.
- Methyl oleate surfactant can reduce viscosity and produce uniform droplet size.
- Biofuel was formulated without byproducts and less energy consumption.

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ABSTRACT

Increased environmental awareness and depletion of resources are driving industry to develop viable fuels from renewable resources. Vegetable oils are one alternative being considered for the production of renewable fuels. Surfactant reverse micelle microemulsions can be used as an alternative method for reducing high viscosities of vegetable oil without chemical wastes generated from the transesterification reaction. The objective of this research is to study the effects of surfactant saturation, unsaturation, and ethylene oxide groups on the phase behavior, kinematic viscosity, and microemulsion-droplet size with the goal of formulating optimized surfactant based biofuel. Four nonionic surfactants, stearyl alcohol (saturated), oleyl alcohol (unsaturated), methyl oleate (unsaturated with ester group), and Brij-010 (EO groups), were investigated in this research. It was found that the presence of methyl oleate unsaturated surfactant can greatly reduce the bulk viscosity and produce uniformly size of microemulsion droplets while use the least amount of surfactant for solubilizing ethanol-in-oil in the system. Thus, these results show that reverse micelle microemulsion can produce biofuels with desirable viscosity and fuel properties as compared to diesel.

1. Introduction

Concerns over the energy crises and environmental restrictions have increased the development and use of non-petroleum-based renewable fuels. Vegetable oils are one alternative being considered for the production of renewable and domestically produced fuels. It has been shown that their use can result in substantial reductions of CO, unburned hydrocarbon, and particulate matter emissions [1]. However, vegetable oils have very high viscosities, low volatilities, and often freeze at low temperatures. Thus, the long-term use of neat vegetable oils causes engine durability problems such as coking of injector nozzles and sticking of piston rings [2].

One approach to improving the utilization of vegetable oil-based fuels is mixing it with conventional diesel fuel. However, these blends fall short of meeting goals of energy self-sufficiency. Cracking and refining are effective in upgrading vegetable oils, but add considerably to the expenses and negate direct utilization. Transesterification with alcohol to produce fatty acid methyl ester (FAME) also known as biodiesel yields a fuel with lower viscosity

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and acceptable performance properties. However, biodiesel has a higher cloud point (CP) and pour point (PP) in cold weather than No. 2 diesel, which is a limitation and lower the feasibility of direct use. The combustion of biodiesel in some cases slightly increases nitrogen oxides (NO_x) in exhaust emissions [3–5]. In terms of the environmental aspect, water washing process is typically used for biodiesel purification after the transesterification reaction therefore 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 [6–8].

The concept of blending vegetable oil and/or diesel with ethanol (E-diesel) has been receiving interest as a means for reducing emissions as a fuel substitute. E-diesel contains higher oxygen concentrations, providing the potential for complete combustion and particulate emission reductions [9]. However, a major drawback of ethanol–diesel blends is that ethanol is slightly miscible in conventional diesel fuel and separate phases can easily occur. Phase separation begins to occur either when the mixture is doped with water due to high humidity in the fuel delivery tank, for instance, or when the temperature drops below 10 °C [10]. Prevention of this sort of phase separation can be accomplished by adding an emulsifier or a surfactant to stabilize the miscibility of the ethanol and diesel.

Microemulsions are homogenous, transparent, thermodynamically stable colloidal dispersions of otherwise immiscible water and oil, stabilized by the interfacial film of amphiphile, usually in combination between surfactant with co-surfactant [11–15]. Microemulsion-based biofuel is a Winsor Type II (water-in-oil or W/O) microemulsion, in which the polar ethanol phase is solubilized in reverse micelles occurring in the non-polar phase. Therefore, in the production of ethanol-in-oil microemuslion-based biofuel, ethanol is used in place of water as the polar phase that disperses in the vegetable oil and/or diesel blend, as the non-polar phase is stabilized by reverse micelles under appropriate conditions [13,14,16,17]. The use of reverse micelle microemulsions has been receiving increased attention for biofuel production since this technique can reduce the high viscosity of vegetable oil without large amount of wastewater [17]. Furthermore, by increasing the burning efficiency, the presence of water or ethanol in diesel fuels brings about considerable reductions in the emissions of nitrogen oxides (NO_x) and particulate matters (PM) through exhaust gas efficiency [3,4,18].

Generally, the mean droplet sizes (droplet diameters) of reverse micelle microemulsions are in the range of 2–200 nm [11]. Depending on their preparation method and composition, different droplet size distributions are achieved, which can significantly influence microemulsion stability and viscosity. Other parameters, including the volume fraction of the dispersed phase, viscosity of the continuous phase, nature and concentration of the emulsifying agents, and temperature, also affect the viscosity of microemulsion-based biofuel [15,19–21].

Selecting an appropriate surfactant is important for microemulsion formation with vegetable oil. The advantage of using nonionic surfactants over ionic surfactants is that salt addition is not required for formulating reverse phase micelles. Moreover, the head group of ionic surfactants (e.g., SO_4^{2-}, SO_3^-) can cause residual problems for the engine emissions. While many studies [2,22,23] have evaluated the effect of surfactant hydrophobicity and carbon chain length on their use in biofuel, the effects of the surfactants' structure has not been intensively investigated in this regard. The structure of a surfactant might affect micelle formation and micelle aggregation size, and thus impact the bulk viscosity of microemulsion-based biofuel.

Most of the studies on nonionic surfactants are based on ethoxylate fatty alcohol, which are broadly used surfactants [24–26]. Previous study [16] showed that mixed amphiphile systems consisting of a long-chain fatty alcohol and an *n*-alkanol are effective in solubilizing methanol/ethanol in triglycerides which has been refer to microemulsification in general. Methyl ester of oleic acid (methyl oleate) and alcohol of oleic acid, obtained from natural raw materials, can also act as a nonionic surfactant in the oil phase. Even though fatty acid esters in general are not considered as surfactant since they do not form micelles in water phase, they can be considered as surfactants in the oil phase since they have been reported to form reverse micelles in oil phase [4,13,14] and adsorb at oil/water interface [16,22,27,28]. Thus, while in certain systems methyl oleate can be considered as an oil phase [29], they can also act as surfactants when solubilized into an alternate oil phase [4,13,14,16].

Therefore, in this study, various structures of nonionic surfactants were utilized to formulate reverse micelle microemulsion-based biofuel. The nonionic surfactants studied all had the same C18 carbon chain length but varied in terms of their chemical structure (unsaturation/methyl ester/ethylene oxide group). The cosurfactant-chain length was varied from *n*-butanol to *n*-decanol. This study aims to provide valuable information on the use of these surfactants in microemulsion formulation in the production of alternative diesel.

This work thus formulates single phase reverse micellar microemulsions of palm oil/diesel blends to stabilize ethanol in the oil phase while reducing the viscosity of the neat palm oil for use as a biofuel. The specific objectives are as follows: (1) to determine the phase behavior and kinematic viscosity of ethanol-in-oil microemulsions containing a surfactant, a cosurfactant, ethanol, and a vegetable oil/diesel blend; (2) to investigate the effects of the chemical structure of the surfactants and the chain lengths of the cosurfactants (*n*-alkanols) on viscosity and microemulsion droplet size; and (3) to evaluate gross calorific values of microemulsion-based biofuel in comparison to those of neat diesel fuel.

2. Methodology

2.1. Materials

Polyoxyethylene (10) oleyl ether (Brij-010, 99% purity), oleyl alcohol (85% purity), stearyl alcohol (99% purity), and methyl ester of oleic acid (methyl oleate, technical grade) were purchased from Sigma Aldrich. The fatty acid composition in methyl ester of oleic acid was a mixture of C18:1 = 71%, C18:2 = 10%, C18:0 = 5%, and other configurations of C18 fatty acid ester, as confirmed by gas chromatography (6890N, Agilent) with a capillary split injector, innowax column (30 m × 0.32 mm, Agilent) and FID detector. These surfactants all have the same carbon chain length (C18) but possess different chemical structures.

ACS reagent grade ethanol, with ⩾99.5% purity, was used as the polar liquid phase. 1-butanol (99% purity), 1-octanol (99% purity), 1-decanol (99% purity), and 2-ethyl-hexanol (⩾99.6% purity) were used as the cosurfactants. All of these chemicals were purchased from Sigma Aldrich. The properties of the surfactants and cosurfactants are shown in Table 1.

Food-grade palm oil (Morakot Industries PCL, Bangkok, Thailand) and commercial-grade petroleum (low sulfur) diesel (PTT Public Company Limited, Bangkok, Thailand) were used in this study.

2.2. Methods

2.2.1. Microemulsion preparation

Microemulsions were prepared on a volumetric basis for the surfactant mixtures by mixing nonionic surfactant and cosurfactant. The surfactant and cosurfactant mixtures were prepared at a fixed mole ratio of 1:8 and were gradually added into 15 mL glass