

Effect of nonionic surfactant structure on fuel properties of microemulsion-based biofuel from palm oil

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Abstract— Microemulsion is the promising techniques that can be used to reduce vegetable oil viscosity. In this study, microemulsion-based biofuel consisting of vegetable oil/diesel blends, ethanol and surfactant/cosurfactant mixture were formulated. The goal of this work focuses on the effects of a numbers of ethylene oxide group, EOn (n =1, 5, and 9) in nonionic alcohol ethoxylate surfactant and the effect of cosurfactant structures, straight chain (1-octanol) and branch chain alcohols (2-ethyl-1-hexanol) to reverse micelle microemulsion fuel formation. In addition, biodiesel and bioethanol were used to replace diesel and ethanol, receptively with the aim to formulated microemulsion fuels with absolute bio-based product. The kinematic viscosity which was selected as a key parameter was determined at 40 °C (ASTM D445). The microemulsion aggregate size was investigated as a parameter affecting by numbers of EO groups in nonionic surfactant. The results show that, no observed trend in kinematic viscosity was found when number of EO groups in nonionic surfactants increases. The kinematic viscosity of palm oil-diesel/biodiesel blends with 2-ethyl-1-hexanol was less than that of palm oil-diesel/ biodiesel blends with 1-octanol system. In additional, the kinematic viscosities of all systems containing regular diesel were higher than that of biodiesel. For the microemulsion droplet size, the size of surfactant aggregates increases with an increase in the number of EO groups. In addition, the droplet size of microemulsion fuel systems with octanol as cosurfactant were smaller than the systems with 2-ethyl-1-hexanol cosurfactant.

Keywords— Biofuel, Microemulsion, Reverse micelles, Palm oil, Cosurfactant, Surfactant, Viscosity

I. Introduction

Currently, the growth of energy demand increases dramatically when compared to previous years. Thailand, likewise, has been confronted with energy scarcity over the last decade. A number of alternative fuel policies have been

promoted to encounter a petroleum oil shortage in near future. Vegetable oils have been intensively considered for use as biofuel because they contain fuel properties comparable with those of diesel. Even more, they consist of non-hazardous substances which result in low toxic emission after combustion [7]. High viscosity and low volatilities are typical characteristics of natural vegetable oils. Long-term uses of neat viscous vegetable oils inevitably causes engine- durability problems, including coking of injector nozzles, sticking of piston rings, and lubricating oil contamination [7]. The viscosity of vegetable oil can be reduced by four technologies: (1) fuel blending, (2) pyrolysis, (3) vegetable oil transesterification or biodiesel and (4) vegetable oil-based microemulsification [4].

Microemulsions are isotropic, thermodynamically stable of two immiscible liquid phase (i.e. ethanol and diesel) in which they are well-homogenized into a single phase by appropriate surfactant system. For microemulsion-based fuels, Winsor Type II, the polar ethanol phase is solubilized in reverse micelles, which occurs in the non-polar phase. Therefore, surfactant plays an important role in single phase reverse micelle formation.

Petroleum based ethanol has been used as the polar phase in place of water to formulate microemulsion fuel with diesel. However, Ethanol can be produced from both the petrochemical process using ethylene as a raw material (ethanol) and the biochemical fermentation process, so called (bioethanol), using both agricultural feedstock and wastes of agricultural materials such as cassava, corn, sugar cane, molasses. The uses of ethanol or bioethanol blend with diesel have been investigated to formulate bio-fuel. Moreover, microemulsion biofuel is used in vegetable oil as the non-polar phase by surfactant or amphiphilic molecules. The advantages of the microemulsification over other methods are the lower production costs, simple and easy implementation, no engine modification requirement, and no chemical reactions [3].

The goal of this study is to formulate microemulsion-based biofuel containing vegetable oil/diesel blend with ethanol. The effects of surfactants with different numbers of ethylene oxide groups, EOn (n =1, 5 and 9) and cosurfactants with different structures, straight chain (1-octanol) and branch chain alcohols (2-ethyl-1-hexanol) were evaluated on the reverse micelle microemulsion formation. The effects of surfactant and cosurfactant were discussed based on results from the kinematic viscosity and microemulsion aggregate size.

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II. Materials and Method

A. Materials

A series of nonionic alcohol ethoxylate surfactant (99% purity) with different numbers of ethylene oxide group, EOn ($n = 1, 5$ and 9) were obtained from Thai Ethoxylate Company, Ltd. (Bangkok, Thailand). The hydrophilic-Lipophilic Balance (HLB) values of these surfactants reported from the manufacture are 3.6, 10.3 and 13.4, respectively. Straight chain alcohol (1-octanol, 99% purity) and branch chain alcohol (2-ethyl-1-hexanol, 99% purity) were used as a cosurfactant. The palm oil used in this work is food grade product and it was purchased from Morakot Industries PCL. Petroleum diesel (commercial grade) was purchased from Shell Company of Thailand, Ltd. Biodiesel (B100) (commercial grade) produced from palm oil based transesterification, was donated from the Verasuwan Co., Ltd. Bioethanol and ethanol (industrial grade) with 95.5% purity were used as polar liquid phase. All chemicals used in this study were used as received. Properties of the surfactants and cosurfactants are shown in Table II.

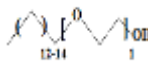
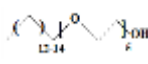
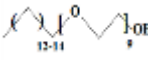


B. Microemulsion preparation Method

Microemulsion fuels were prepared by the simple mixing of three components including; surfactant mixture, nonpolar or oil phase and polar phase or ethanol. The mixture solution of the surfactant and cosurfactant were prepared at fixed molar ratio of 1:8 by a volumetric basis. The mixture of oils was prepared by 50:50 percent of vegetable oil – diesel or biodiesel blend. The amount of ethanol or bioethanol was fixed at 2 ml and then was added into the prepared solution. Finally, the mixture of surfactant/cosurfactant, palm oil/diesel blend and ethanol was completely homogenized using a vertex mixer, and the sample were kept in a temperature controlled bath at 40 °C for allowing the system to reach equilibrium.

TABLE I. THE PROPERTIES OF COMPONENT OF THE MICROEMULSION FUEL

Properties	Diesel	Biodiesel	Palm oil	Ethanol	Bioethanol
Kinematic viscosity @ 40 °C (mm ² /s)	2.95	4.69	40.88	1.17	1.04
Density @ 25 °C (g/ml)	0.84	0.89	0.92	0.82	0.80

TABLE II. PROPERTIES OF NONIONIC SURFACTANTS AND COSURFATANTS

Material	Structure	MW (g/mole)	Density (g/ml)	HLB
Nonionic surfactants				
C ₁₂₋₁₄ -(EO) ₁ OH (EO1)		217.15	0.837	3.6
C ₁₂₋₁₄ -(EO) ₅ OH (EO5)		393.23	0.924	10.3
C ₁₂₋₁₄ -(EO) ₉ OH (EO9)		569.31	0.966	13.4
Cosurfactant				
1-Octanol (Oct)		130.2	0.812	-
2-ethyl-1-hexanol (2-ethyl)		130.2	0.833	-

C. Viscosity measurement Method

The kinematic viscosity of microemulsion biofuels was measured using a Canon –Fenske viscometer (ASTM D 445). The 6.7 ml of the microemulsion fuel samples was transferred into a viscometer chamber and measured at the constant temperature of 40 °C. The kinematic viscosity was then calculated following Equation (1).

$$\mu = Kt \quad (1)$$

where, μ is the kinematic viscosity (mm²/s), K is the viscosity constant and t is the time required for the liquid sample to flow through the capillary tube.

D. Dynamic light scattering (DSL) measurements Method

Droplet size measurement of microemulsion biofuels is a technique to measure Dynamic light scattering (DLS) that is measured using a Nano Zetasizer 3600 (Malvern). Dynamic light scattering (DLS) was used to measure particle size in the range of 0.6 nm - 6 μ m. The measurements were performed at 25 °C at a fixed angle of 173°. The light source was a Helium-Neon laser ($\lambda = 633$ nm, $V = 4$ mW).

III. Results

A. Viscosity measurement

The kinematic viscosities were measured at 40 °C for all microemulsion fuels system. Figure 1 shows the kinematic viscosity of microemulsion fuel systems formulated by petroleum based ethanol. In comparison between the two different types of oil phases (palm oil/diesel and palm oil /biodiesel blends) contained in the microemulsion fuels. It can be seen that the viscosities of all microemulsion systems formed by diesel oil are lower than those of the system with biodiesel, this due to basic property of oil component in

microemulsion fuel in which neat biodiesel has higher viscosity compare with diesel fuel. As, it can be seen in Table I, both of density and kinematic of neat diesel (0.84 g/ml and 2.95 mm²/s) are lower than those of neat biodiesel (0.89 g/ml and 4.96mm²/s)

For the effect of numbers of EO group in alcohol ethoxylate surfactants, the observed trends were found in the systems formed by palm oil/ diesel blend and with octanol and 2-ethyl-1-hexanol as a cosurfactant. The numbers of EO group increased with slightly increasing the viscosity of the system form by straight chain octanol, whereas the viscosities of microemulsion fuel using the 2-ethyl-1-hexanol were declined with increasing the number of EO group in the surfactants. However, no observed trend on the kinematic viscosity with the number of ethylene oxide group in the surfactants was found with the system formed by biodiesel.

Due to the second generation of biofuel production scheme, a bioethanol has been intensively investigated on biofuel production in order to replace the uses of ethanol derived from petroleum products. However, the ethanol specification used in fuel production normally prefer with more 99.5 percent purity or anhydrous ethanol. The fact that bioethanol produced by bio-fermentation of various agricultural feedstocks, is typically commercialized at 95 percent purity; however, it is assumed that another 5 percent is water content obtained from biochemical conversion. In this study, the viscosity of microemulsion fuels formulated with ethanol manufactured from petroleum derivatives so called petro-ethanol and ethanol derived from bio-based feedstocks so called bioethanol were compared.

Figure 1 and Figure 2 represent the results of kinematic viscosity on microemulsion fuel with petro-ethanol and bioethanol, respectively. In comparison, it is interesting to note that at the same degree of purity in ethanols (95%), all microemulsion fuels formed with bioethanol, performed lower in viscosity than those of petro-ethanol systems.

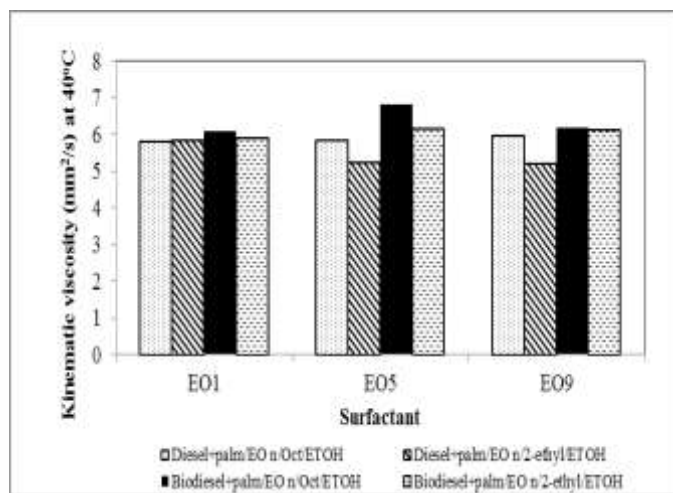


Figure 1. The kinematic viscosity measurement of microemulsion fuels with petro-ethanol system at temperature 40 °C

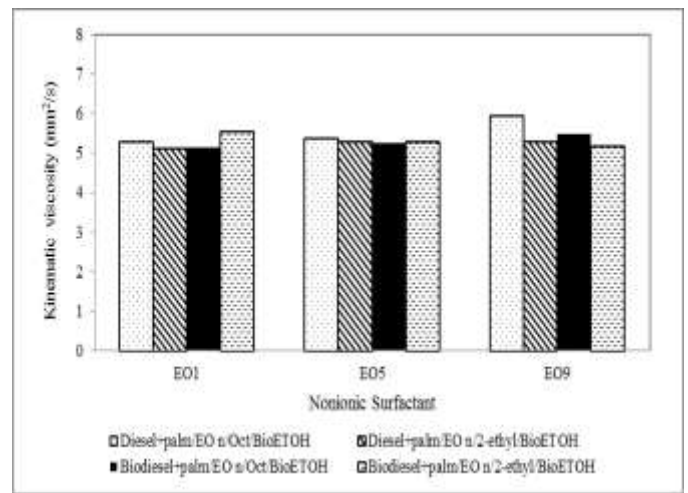


Figure 2. The kinematic viscosity measurement of microemulsion fuels with bioethanol system at temperature 40 °C

The effects of cosurfactants with different structures; straight chain (1-octanol) and branch chain alcohols (2-ethyl-1-hexanol) on the viscosity of microemulsion fuel were investigated. From Figure 1 and Figure 2, It can be seen that the microemulsion fuels formulated by 2-ethyl-1-hexanol has lower kinematic viscosity than those of the systems formulated by octanol as a cosurfactant. The kinematic viscosities of the microemulsion fuels of both palm oil/diesel blend and palm oil/biodiesel blend with petro-ethanol (ranging from 5.8-6.8 mm²/s) were slightly higher than those of the system with bioethanol (ranging from 5.2-6.1 mm²/s). This could be due to the fact that kinematic viscosity and density of bioethanol is less than ethanol as shown in Table I. Evenmore, this perhaps water molecule in bioethanol facilitates the solubilization of polar ethanol phase, resulting in a reduction in the net viscosity of microemulsion fuels.

B. Effects of the droplet size on microemulsion fuel viscosity

The size and size distribution of microemulsion droplets was measured throughout DLS technique. The reverse micellar droplets of nonionic alcohol ethoxylate surfactant containing 1 EO, 5 EO and 9 EO groups in single phase microemulsion fuels were investigated. Table III presents the sizes of reverse the micelle aggregates in each microemulsion fuel system. The remarkable trend was observed in the microemulsion fuel systems of palm oil/diesel in ethanol with branching chain octanol (2-ethyl-1-hexanol) that the numbers of EO groups increases with the size of the microemulsion droplets. This similar trend but less in a deviation also was found in the microemulsion fuel systems of palm oil/diesel in ethanol with straight chain octanol. As expected, when the ethylene oxide group in the nonionic surfactant molecule increases, the core of polar region of surfactant head also increases which could lead to an increase in the diameter size of reverse micellar aggregates. In addition, it is interesting to

compare that the size of microemulsion droplets is affected by branch chain octanol than straight chain ethanol, especially more double for the system with $C_{12-14}-(EO)_9OH/2$ -ethyl-1-hexanol (radius around 34 nm). This could be due to the fact that the branch structure partitioning near the tail of surfactant molecule, extends the larger arrangement of hydrophobic tails leading to an dramatic increment in the size of the microemulsion droplets.

Table III also compares the size of microemulsion droplet on microemulsion fuel viscosity. The result indicates that the reversible trend was observed in the system with straight chain ethanol and branch chain ethanol (2-ethyl-1-hexanol). When the size of microemulsion droplets increases, the microemulsion viscosity also increases for the system with octanol. The systems with 2-ethyl-1-hexanol, on the other hand, the droplet sizes increases with a decrease in the fuel viscosity. Based on previous literatures, the viscosity of liquid solution is affected by interactions between interfacial layers of the dispersed colloidal droplet and liquid phase. So, this could be due to the arrangement of hydrophobic parts of surfactant and cosurfactant structure affecting the interfacial region between oil phase and ethanol phase; however, this finding should be further study.

TABLE III. THE DROPLET SIZE OF MICROEMULSION FUEL ON THE KINEMATIC VISCOSITY AT TEMPERATURE 40 °C

Surfactant	Oil phase	Polar phase	Hydrodynamic diameter (d.nm)	Kinematic viscosity (mm ² /s)
EO1/ Oct	Palm+diesel	Ethanol	12	5.81
EO5/ Oct	Palm+diesel	Ethanol	13	5.85
EO9/ Oct	Palm+diesel	Ethanol	15	5.96
EO1/ 2-ethyl	Palm+diesel	Ethanol	12	5.83
EO5/ 2-ethyl	Palm+diesel	Ethanol	17	5.24
EO9/ 2-ethyl	Palm+diesel	Ethanol	34	5.19

iv. Conclusions

The results of this research was to investigate effect of using surfactant, cosurfactant and ethanol to formulate microemulsion fuels from palm oil/diesel or biodiesel blends. The kinematic viscosity and the microemulsion size were selected as significant parameters to describe the solubilization behaviors of microemulsion fuel. The results obtained of this work indicated that the kinematic viscosity and the microemulsion droplet sized depending on structures of both surfactant and cosurfactant, oil phase and polar phase. The significant difference in the kinematic viscosity for the microemulsion fuel systems with branch chain alcohol was more remarkable than using straight chain alcohol as a cosurfactant. The microemulsion systems formed by bioethanol as a polar phase, has lower kinematic viscosity than those of petro-ethanol system. The number of ethylene oxide groups in alcohol ethoxylate surfactant also is the affecting parameter to either the viscosity or size of microemulsion fuels. The correlation between kinematic viscosity and the microemulsion

aggregate size of microemulsion fuel needs to be further investigate.

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References

- [1] C. Attaphong, L. Do, and D. A. Sabatini, "Vegetable oil-based microemulsion using carboxylate-based extend surfactants and their potential as an alternative renewable biofuel," *Fuel*, vol. 94, pp.606-613, 2012
- [2] EH. Pryde, "Vegetable oils as fuel alternatives," symposium overview. *JAOCs*, vol. 61, pp. 1609-1610, 1984.
- [3] L. Do, V. Singh, L. Chen, T.C.G. Kibbey, S. R. Gollahalli, and D. A. Sabatini, "Algae, canola, or palm oils- disel microemulsion fuels: phase behaviors, viscosity, and combustion properties," *International Journal of Green Energy*, vol. 8, pp. 748-767, 2011.
- [4] M. Balat, "Modeling Vegetable Oil Viscosity," *Energy Resources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 30, no. 20, pp. 1856-1869, 2008.
- [5] MJ. Rosen, "Surfactants and interfacial phenomena," Hoboken, NJ: John Wiley & Sons, 2004.
- [6] RO. Dunn, "Cold weather properties and performance of biodiesel," In: Knothe G, Jurgen K, and Van GJ (Eds.) *The Biodiesel Handbook*, AOCS Press, Champaign, pp. 83-125, 2004.
- [7] RO. Dunn and MO. Bagby, "Solubilization of Methanol and Triglyceride: Unsaturated LongaChain Fatty Alcohol/MediumaChain Alkanol Mixed Amphiphile Systems," *J. Am. Oil Chem, Soc*, vol. 71, pp. 101-108, 1994.
- [8] T. Dasta, A.C. Siliva, and A.A.D. Neto, "New microemulsion systems using diesel and vegetable oils," *Fuel*, vol. 80, pp. 75-81, 2001.

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The microemulsion method is interested in this study. Microemulsion is the promising techniques that can be used to reduce vegetable oil viscosity, low production cost, simple, no engine modification and no chemical reactions. Therefore this method makes it ideal to be used to produce biofuel.