PROPERTIES IMPROVEMENT OF MICROEMULSION FUEL FROM ETHANOL-JATROPHA OIL-DIESEL BY SURFACTANT SELECTION

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การปรับปรุงคุณสมบัติเชื้อเพลิงไมโครอีมัลชั่นจากการคัดเลือกสารลดแรงตึงผิวที่มีเอทานอล น้ำมันสบู่ดำและดีเซลเป็นองค์ประกอบ

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Thesis Title	PROPERTIES IMPROVEMENT OF MICROEMULSION FUEL FROM ETHANOL-JATROPHA OIL-DIESEL BY SURFACTANT SELECTION
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เอกชัย แสนคำก้อน : การปรับปรุงคุณสมบัติเชื้อเพลิงไมโครอีมัลชั่นจากการคัดเลือกสารลดแรงตึงผิวที่มีเอทานอลน้ำมันสบู่ดำและดีเซลเป็นองค์ประกอบ. (PROPERTIES IMPROVEMENT OF MICROEMULSION FUEL FROM ETHANOL-JATROPHA OIL-DIESEL BY SURFACTANT SELECTION) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร. จันทรา ทองคำเภา, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ดร.นุวงศ์ ชลคุป, 94 หน้า.

ในปัจจุบันไบโอดีเซลจากน้ำมันสบู่ดำได้รับความสนใจในด้านการเป็นเชื้อเพลิงหมุนเวียนที่มีความมั่นคงด้านด้านพลังงานและคุณภาพสิ่งแวดล้อม กระบวนการทรานเอสเตอร์เป็นวิธีการที่นิยมใช้ลดความหนืดของน้ำมันพืชเพื่อผลิตไบโอดีเซล แต่กระบวนการนี้ก่อให้เกิดน้ำเสียปริมาณมาก และกลีเซอรอลคุณภาพต่ำซึ่งเป็นผลผลิตข้างเคียง ดังนั้น วิธีอิมัลชั่นจึงเป็นทางเลือกหนึ่งในการผลิตน้ำมันเชื้อเพลิงซึ่งลดปัญหาด้านของเสียที่จะเกิดขึ้น ในการวิจัยครั้งนี้ศึกษาการผลิตเชื้อเพลิงอิมัลชั่นผสมระหว่างน้ำมันสบู่ดำ เอทานอลร่วมกับสารลดแรงตึงผิวชนิดต่าง ๆ และดีเซล พบว่าสามารถผสมสารเชื้อเพลิงเป็นสารละลายเนื้อเดียวภายใต้สภาวะที่เหมาะสมทั้งกรณีสารลดแรงตึงผิวเดี่ยวและสารลดแรงตึงผิวผสม และได้มีการคัดเลือกสูตรผสมที่ได้เป็นสารละลายเนื้อเดียวนั้นสองสูตรมาทำการทดสอบคุณสมบัติของเชื้อเพลิง สูตรผสมแรก MF(E5) ประกอบด้วยน้ำมันสบู่ดำ 20% ดีเซล 75% และสารลดแรงตึงผิวเดี่ยวหรือผสมในเอทานอล 5% และสูตรผสมที่สอง MF(E10) ประกอบด้วยน้ำมันสบู่ดำ 20% ดีเซล 70% และสารลดแรงตึงผิวเดี่ยวหรือผสมในเอทานอล 10% โดยอัตราผสมของสารลดแรงตึงผิวชนิดต่าง ๆ ในเอทานอล คือ 1 ใน 3 ผลการทดสอบคุณสมบัติเชื้อเพลิงพบว่า ค่าความหนืดและปริมาณน้ำซึ่งเป็นคุณสมบัติที่สำคัญนั้นเป็นไปตามมาตรฐาน แต่ค่าความเป็นกรดและจุดวาบไฟไม่เป็นไปตามเกณฑ์มาตรฐานไบโอดีเซลของ ASTM และ EN ส่วนการวัดประสิทธิภาพของน้ำมันในการทดสอบกับเครื่องยนต์ดีเซลและวัดค่ามลพิษจากท่อไอเสียจากการใช้น้ำมันเชื้อเพลิงอิมัลชั่นนั้น พบว่าเชื้อเพลิงสูตรผสมที่มีสารลดแรงตึงผิวเดี่ยวชนิด LS1 ในเอทานอล 5% ให้พลังงาน อัตราการสิ้นเปลืองเชื้อเพลิงจำเพาะเบรก และอุณหภูมิไอเสียใกล้เคียงกับดีเซล สำหรับมลพิษจากท่อไอเสียนั้น น้ำมันเชื้อเพลิงอิมัลชั่นทุกตัวปลดปล่อยเขม่าควันต่ำกว่าดีเซล ในขณะที่ปลดปล่อยคาร์บอนมอนอกไซด์และคาร์บอนไดออกไซด์ใกล้เคียงดีเซล ดังนั้น น้ำมันเชื้อเพลิงอิมัลชั่นสูตร MF(E5) จึงมีศักยภาพสูงในการใช้เป็นเชื้อเพลิงชีวภาพกับเครื่องยนต์ดีเซลโดยไม่ต้องดัดแปลงเครื่องยนต์

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AKECHAI SANKUMGON: PROPERTIES IMPROVEMENT OF MICROEMULSION FUEL FROM ETHANOL-JATROPHA OIL-DIESEL BY SURFACTANT SELECTION. ADVISOR: ASST. PROF. CHANTRA TONGCUNPOU, Ph.D., CO-ADVISOR: NUWONG CHOLLACOOP, Ph.D., 94 pp.

At present, jatropha oil biodiesel is one of interesting renewable fuel for assuring an energy security and environmental quality. Transesterification is the most common method to reduce the viscosity of vegetable oils. However, one of the problems of transesterification process are low quality of glycerol by-product and large volume of wastewater. Therefore, microemulsion fuels from microemulsification have been introduced as an alternative method to produce proper fuel and avoid problems of waste disposal. In this study, microemulsion fuels (MFs) are produced from jatropha oil, ethanol with surfactants and diesel. The results from pseudo-ternary phase diagram show the single phase of jatropha oil, ethanol and diesel at the optimum condition with both single and mix surfactant systems. Subsequently two MFs ratio were selected based on clear phase behavior to study properties. The first ratio is comprised of 20% jatropha oil, 75% diesel and 5% single or mix surfactant in ethanol solution and the second is 20% jatropha oil, 70% diesel and 10% single or mix surfactant in ethanol solution. The ethanol with single or mix surfactant ratio was set at 3:1. For the properties of the selected MFs, kinematic viscosity and water content, which are the most importance in fuel properties, were found to meet the standard value for biodiesel while acid number and flash point did not meet biodiesel standard (ASTM and EN). In addition, MFs were examined for the engine performance and exhuasted emission. It was found that MF(E5)-S1 has power, BSFC (brake specific fuel consumption), and exhaust gas temperature similar to those of diesel. For emission, MFs showed lower smoke than those of diesel while CO and CO_2 emissions were similar to those of diesel. Thus, the microemulsion fuel of MF(E5) by microemulsification method show great potential to use as biofuel in diesel engines without modification.

Field of Study : Environmental Management Student's Signature ....
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ABBREVIATIONS

AFR = Ratio of air and fuel
AOT = Aerosol OT
D = Diesel
EO = Ethylene oxide
E/S = Ethanol/surfactant
g = Gram
g/L = Gram per liter
HLB = Hydrophile-lipophile balance
JCO = *Jatropha curcas* L. crude oil
kg/m^3 = Kilogram per cubic meter
mg/g = Milligram per gram
MF = Microemulsion fuel
mL = Milliliter
o/w = Oil in water
o/w/o = Oil in water in oil
ppm = Part per million
w/o = Water in oil
%wt = Percent by weight
%vol = Percent by volume

CHAPTER I

INTRODUCTION

1.1Introduction

The depletion of petroleum energy and the increasing of the greenhouse gases (GHSs) emission are major concerns as energy and environment aspect. Consequently, the biofuel is an interested alternative fuel that has been proposed for assuring for energy security as well as to reduce GHG emission. Among various types of biofuel such as vegetable oil, ethanol, and biodiesel are renewable fuel, non-toxic nature and less greenhouse gases emissions (Ramadhas et al,, 2004; Atadashi et al., 2010; Attaphong et al., 2011; Pidol et al., 2012). Biofuel from vegetable oils has a strong potential due to its availability in large volume. The main sources for biofuel production are rapeseed oil, soybean oil, palm oil, coconut oil, and others.

At the present, there are many claims of biofuel for the transport sector. By converting edible oil into biodiesel, food resources are actually being converted into automotive fuel. The large-scale production of biodiesel from edible oils that may bring global imbalance to the food supply and demand market, deforestation, and destruction of ecosystem (Gui et al., 2008). As a result of the term of sustainability of biofuel production as an alternative to fossil fuel sources were challenged. Likewise, feasibility of biofuels has led more and more study on the sustainability profile (Attaphong et al., 2011; Pidol et al., 2012; Yilmaz 2012; Fang et al., 2013; Lei et al., 2012). Accordingly, second and third generation biofuels are considered sources of feedstock from non-edible crop. Jatropha oil is also one of non-edible oil source; thus, it has been considered as a feedstock.

Even though vegetable oils can be directly used in diesel engine, a high viscosity property of crude oil may cause some problems on the diesel engine. In order to solve these problems, the vegetable oil modification is selected such as blending, pyrolysis, microemulsification, especially transesterification (Monreiro et al., 2008; Demirbas, 2009; Atadashi et al., 2010; Singh and Singh, 2010, Ong et al., 2011; Yasuf et al., 2011). Since biodiesel from transesterification is also renewable, non-toxic, biodegradable. Furthermore, it can be produced from vegetable oil and animal fats by reducing the viscosity of oil appropriates to diesel engine. While ethanol-diesel blends (E-diesel) or biodiesel-diesel blends (B-diesel) can be used in diesel engines without modification (Hansen et al., 2005; Li et al., 2004). In addition, biodiesel emits lower exhausted gas than petroleum fuel. For example, neat biodiesel and biodiesel blends reduce particulate matter (PM), hydrocarbon (HC) and carbon monoxide (CO) emissions and slightly increase oxides of nitrogen (NO_x) emissions compared with petroleum-based diesel fuel used in an unmodified diesel engine (Demirbas et al., 2009; Ong et al., 2011).

However, biodiesel has several drawbacks. For instance, high cloud point and pour point temperatures of biodiesel can reduce thermal stability and limit the cold weather operability of both pure biodiesel and its blends (Atadashi et al., 2010; Karavalakis and Stournas, 2010). In addition, biodiesel has shorter long shelf life due to fuel degradability. Since biodiesel is very sensitive to water, temperature, microbial activity and oxygen, unpleasant changes of biodiesel properties can occur rapidly within a few months (Singh and Singh, 2010, Yasuf et al., 2011). Another serious problem of biodiesel is its transesterification process that also yields glycerol, alcohol, catalyst, tri-, di- and monoglycerides, as well as free fatty acids as by-product or waste. Moreover, in several process of biodiesel production, large volume of wastewater is generated. Since glycerol is expensive to purify or convert to a value-added product, thus these by-products and other contaminants of biodiesel can lead to problems of disposal and environment concern (Monreiro et al., 2008).

Consequently, microemulsion fuels (MFs) from microemulsion method have been proposed and evaluated as an alternative method to produce proper fuel and avoid problems of disposal. Since this method is a simple technique with low energy consumption and acquired 100% yields product without waste production or by products (Attaphong et al., 2011; Lei et al., 2012). Furthermore, the microemulsification approach assists to overcome the immiscibility of two immiscible liquids like water and oil. Zhao et al. (2006) and Lei et al. (2012) reported that microemulsion fuel tends to reduce exhausted emission such as smoke, nitrogen oxides (NO_x), and carbon monoxide (CO) as well as to improve the combustion efficiency. In this present study on alternative fuel, Jatropha curcas oil (JCO) is selected and used as a vegetable oil due to jatropha seeds contains high content of oil. In addition, as a non-edible oil, JCO would be a good choice that is able to solve food and fuel competition. Meanwhile, surfactants were proposed to be used as emulsifiers in order to stabilize the miscibility of ethanol and diesel or vegetable oils.

The study focuses on the behavior of microemulsion fuels which comprise the addition of three nonionic surfactants with oxy-ethylene units (difference of EO group number) for single nonionic surfactant and for mix anionic surfactant to form microemulsion biofuel. Moreover, the investigation of the properties and specifications of blends of ethanol-surfactant, JCO and diesel were determined to ensure that microemulsion fuel (MF) was suitable to be used with diesel engine. Its properties were compared with biodiesel standard. The parameter determined to specify the MF's properties included stability, acid value, cloud point, density, flash point, high heating value, kinematic viscosity, oxidation stability, and water content. Additionally, the efficiency of the fuel on diesel engine's performance and emission was also tested compared with commercial diesel.

1.2 Objectives

This research aims to produce microemulsion fuel by microemusifying 3 components of JCO, ethanol with surfactants, and diesel. The objectives are as follows:

1. To develop phase diagrams and determine the phase behavior of microemulsion three-component fuel system for the surfactant with various EO group number blended with ethanol, JCO and diesel.
2. To examine temperature stability of microemulsion fuels at various EO group number for single nonionic surfactant comparing with mix anionic surfactant and without surfactant system.
3. To identify the optimum proportion of microemulsion, within the single phase region (clear microemulsion region).
4. To investigate the properties, and performances of selected microemulsion fuels by comparing with biodiesel standard.

1.3 Hypotheses

1. The microemulsion system can induce Jatropha curcas oil (JCO) raise up to appropriate fuel characteristic.
2. The microemulsion fuel of mix anionic surfactant at the optimum proportion provides good MF's properties more than single nonionic surfactant.
3. The microemulsion fuel produced from JCO by microemulsion technique can be used as fuel in twocylinder diesel engine.

1.4 Scopes of the study

This research focus on three parts; in the first part was to study the phase behavior of microemulsion systems containing of JCO, diesel and ethanol with single nonionic surfactant, mix anionic surfactant and without surfactant. The second part aimed to identify kinematic viscosity and temperature stability of microemulsion fuel with or without surfactant. The third part proposed to determine microemulsion fuel properties and evaluated performances to compare with commercial diesel fuel and biodiesel standard. The overall experimental included:

Part 1: Phase behavior study

The pseudo-ternary phase diagram was developed to describe phase behavior of microemulsions of the four components; surfactant-ethanol, JCO and diesel. In this experiment, three differences of EO group number of single nonionic surfactants, which are varied Hydrophile-Lipophile Balance (HLB), were used and compare with the systems without surfactant. The ethanol/surfactant ratio (E/S ratios) is 3:1 for single nonionic surfactant. The proportion of JCO, surfactant with ethanol, and diesel that presented the clear microemulsion area was selected for further experiments.

Part 2: Temperature stability and kinematic viscosity test

The temperature stability of microemulsion fuels were determined to evaluate in single nonionic surfactant, mix anionic surfactant and no surfactant system was able to maintain the stability of microemulsion fuel in the range of temperature between 20-40°C. While the microemulsion fuels that interested were evaluated kinematic viscosity in which system has kinematic value around 3.5-5.0 cSt. Then, the co-surfactant for the mixed surfactant system was added to investigate stability of the system compared with single surfactant systems at different temperatures. The ratio of surfactant to co-surfactant (S/Cs ratios) was 10:1 or 0.1 %wt for mixed surfactant systems. Finally, the proper microemulsion fuel was determined for its fuel properties, performance, and exhaust gas emissions.

Part 3: Microemulsion fuel properties, performance, and emission test

The interested proportions of the microemulsion fuel from Part 2 were investigated properties following to American Standard Test Method and European standard for biodiesel. The examined parameters consist of acid number, cloud point, flash point, oxidation stability, kinematic viscosity, and water content. Then the performances of the selected microemulsion fuels on diesel engine were tested. Their performances test were conducted using a two-cylinder engine at the King Mongkut's University of Technology North Bangkok. Along with the engine test run, the exhaust gas emissions (i.e., carbon monoxide, CO; carbon dioxide, CO_2; hydrocarbon, HC; and oxygen, O2) were examined. In addition, a comparison of microemulsion fuel and diesel fuel was performed.

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Biofuel

Biofuel is a type of fuel which energy derives from biological carbon fixation. Moreover, biofuels include fuels which derive from biomass conversion such as solid biomass, liquid fuels and various biogases. Accordingly, biofuels offer an attractive solution reducing the petroleum fuel in the transport sector and addressing energy security concerns. General concern for pollution and environmental impact of energy consumption based on fossil sources has led to more research on the sustainable energy sources, traditional and alternative ones.

Biofuels currently are divided into four groups designed in the term of generations. As the term ―generation” indicates, biofuels are classified according to their progressive introduction on the market for 20-30 years ago. The final goal of the generation fuels will integrate higher energy yields, lower requirements for fertilizer and land, and the absence of competition with food with low production costs. Thus, all of the integration is a truly sustainable energy source for transportation fuels.

2.1.1 First generation biofuels

First generation biofuels are based on feedstocks that uses as food such as sugarcane or corn for ethanol production and edible vegetable oils and animal fat for biodiesel production. In spite of rising of food prices and doubts on greenhouse gases emission saving improvement, First generation biofuels are debated on their sustainability.

2.1.2 Second generation biofuels

Due to the main concerns in first generation biofuels, advanced technical processed have been developed to obtain biofuels from non-edible feedstocks for producing vegetable oil, ethanol or biodiesel. Nevertheless, feedstock costs remain high and GHG emission saving still need to be determines by properly analysis of possible emission from land use change.

2.1.3 Third generation biofuels

Third generation biofuels, as same as second generation biofuels, are made from non-edible feedstocks, with the advantage that the resulting fuel represents an equivalent replacement produce from sustainable sources such as fast-growing algae or bacteria for gasoline, diesel, and aviation fuel. These alternative biofuels are anyway in developing and several technological and economic challenges still need to be faced to bring them on the market.

2.1.4 Fourth generation biofuels

Fourth generation biofuels are those which result in negative carbon impact in the atmosphere. These fuels will be obtained from genetically engineered crops that release a lesser amount of carbon dioxide during combustion that absorbed from the atmosphere for their growth (Kalita, 2008).

2.2 Ethanol

Ethanol, which is a light alcohol, is a renewable fuel source that is produced by a fermentation and distillation process. The common source of ethanol is many kinds of agricultural products such as sugar cane, saw grass, molasses, cassava root, corn and other natural products that will be conductive to the fermentation or distillation process. Ethanol is one of biofuel that has a strong potential due to its availability in large volume, especially with the second generation process that will be available in the near future. Because of this reason, the present are receiving wide attention as alternative fuels for gasoline engine.

As shown in Figure 2.1 is structure of ethanol and Table 2.1 is its properties. There are some negative factors and undesirable effects on engine relative to conventional fuels. However, there are some researchers still considered ethanol as components for diesel fuel. In spite of their ethanol properties are improper operation of a diesel engine such as lower cetane. Nevertheless, due to the addition of ethanol to diesel affects certain combustion and key properties such as viscosity, energy content, flashpoint and flammability that would contribute to reduction in emissions (F.Schafer (b). The main advantaged and disadvantages of ethanol as a light alcohol with compared to conventional gasoline and diesel fuels are briefed in Table 2.2 Ethanol solubility in diesel fuel is very poor which affect mainly by two factors, temperature and water content of the blend. While the one possibility that can be solute with diesel is the using surfactant as emulsifier.

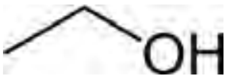


Figure 2.1 Structure of ethanol

Table 2.1 Properties of ethanol

Properties	**Unit**	**Ethanol**
Chemical formula	-	C_2H_5OH
Molecule weight	[g/mol]	46.07
Cetane Number	-	8
Density@25°C	[g/cm^3]	0.789
Heat content	[MJ/kg]	26.8
Flash point	[°C]	13
Pour point	[°C]	-117.3
Boiling point	[°C]	78.4
Autoignition temperature	[°C]	423
Freezing point	[°C]	-114
Viscosity@20°C	[mm^2/s]	1.19

Sources: Alternative Fuel Data Center; Li et al., 2005

Table 2.2 Advantages and disadvantages of alcohol motor fuels compared to gasoline and diesel

Property/ Performance Parameter	**Compared to gasoline and diesel fuel**	**Advantage**
1. Octane	Higher	A higher engine compression ratio in spark ignition (SI) engines can be used resulting in higher thermal efficiency
2. Latent heat of vaporization	Higher	Lower intake temperatures may be used to increase charge density and higher volumetric efficiency
3. Adiabatic flame temp.	Lower	Potentially lower NO_x emissions and lower heat losses
4. Flame luminosity	Lower	Lower heat losses from combustion
5. PM emissions	Lower	Due to clean burning characteristics PM emissions are even lower than the gasoline engines
6. Toxic emission	-	Lower benzene and 1,3 butadiene emissions
7. Nature of sources	Renewable	Source more widespread around the world, hence better energy security. Lower net CO_2 emissions.
Property/ Performance Parameter	**Compared to gasoline and diesel fuel**	**Disadvantage**
1. Volumetric energy content	Much lower	Higher volumetric fuel consumption hence lager fuel storage space and weight
2. Cetane number	Much lower	Cannot be directly used in compression ignition (CI) engines. Need a source of ignition increasing complexity of engine/fuel system.
3.Vapour pressure	Lower	Poor cold starting and warm up performance, higher in burned fuel emissions during starting/warm up phase
4. CO and NO_x emissions	Similar	No definite trend is observed. So, no advantage over petroleum fuels have been noted
5. Aldehyde emissions	Higher	Formaldehyde and acetaldehyde emissions are higher
6. Material corrosion/ adverse effects	Higher	Methanol and to a lesser degree ethanol is more corrosive to metals, elastomers and plastic components. Needs selection of suitable materials for the fuel system.
7. Engine wear	Higher	Washes away lubricant film during cold starting, resulting in higher cylinder and piston ring wear
8. Flame Luminosity	Almost invisible	Neat alcohols present fire safety hazards. Addition of gasoline or other material required to increase flame luminosity.

Source : Pundir, 2007

2.3 Vegetable oil

Vegetable oil, which is the one type of biofuels, are mostly composed of lipids that consist of 90-98% triglycerides and small amount of mono and diglycerides, with other minor components include antioxidants, colorants, flavors and emulsifiers. Triglycerides are one glycerol and esters of three fatty acids as shown in Figure 2.2 Moreover, it generally contains fatty acids, free fatty acids, phospholipids, phosphatides, carotenes, tocopherols, surfur compound and trace of water. The fatty acids, which are commonly found in vegetable oils, are stearic, palmitic, oleic, linoleic and lonolenic as shown in Table 2.3 However, vegetable oils from different sources have different fatty acid compositions. The fatty acids vary in their carbon chain length and in the number of unsaturated bonds that they contain (Singh and Singh, 2010).

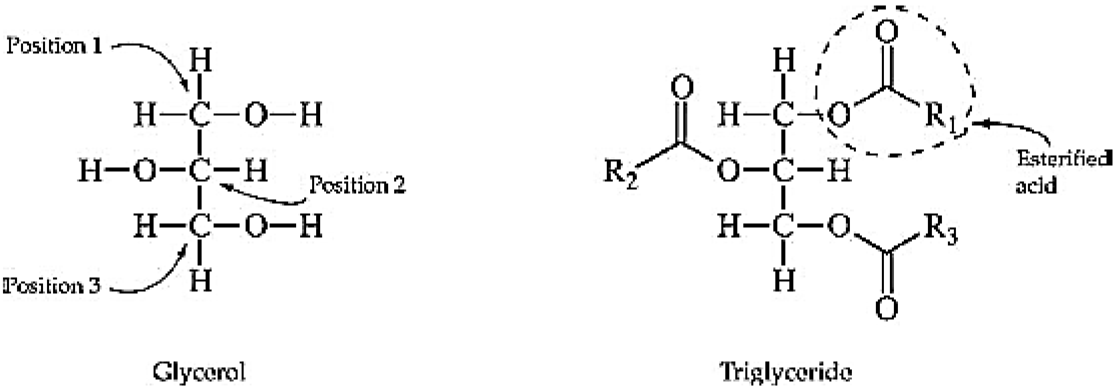


Figure 2.2 Structure of a glycerol and triglyceride (the three positions can carry different fatty acids, as illustrated by R1 (top), R2 (middle), and R3 (bootom)) (Stauffer, 2005).

The more common vegetable oils (e.g. peanut, linseed, rape, and sun flower) can be used as direct injection. In fact, vegetable oils have quite reasonable ignition qualities because of their characterization (e.g. cetane numbers over 30) although they have slightly lower calorific value and cetane number than diesel. Nevertheless, vegetable oil and diesel differs greatly in other properties; especially, their kinematic viscosity is greater than for diesel oil about 10-15 times depending on different the types of vegetable oil and age. That can cause problems in fuel handing, pumping, atomization and fuel jet penetration but there are still overcome problem in many methods such as blending, pyrolysis, transesterification, and microemulsification (Ramadhas, 2004). The advantages and disadvantages of directed using vegetable oils as fuels are summarized as follows.

Table 2.3 Chemical structure of fatty acids for common vegetable oils

Fatty acid	**Formula**	**Systemic name**	**Structure (xx:y)**[a]
Luaric	$C_{12}H_{24}O_2$	Dodecaoic	12:0
Myristic	$C_{14}H_{28}O_2$	Tetradecanoic	14:0
Palmitic	$C_{16}H_{32}O_2$	Hexadecanoic	16:0
Palmitoleic	$C_{16}H_{30}O_2$	cis-9-Hexadecanoic	16:1
Stearic	$C_{18}H_{36}O_2$	Octadecanoic	18:0
Oleic	$C_{18}H_{34}O_2$	cis-9-Octadecanoic	18:1
Linoleic	$C_{18}H_{32}O_2$	cis-9,cis-12-Octadecanoic	18:2
Linolenic	$C_{18}H_{30}O_2$	cis-6,cis-9,cis-12-Octadecanoic	18:3
Arachidic	$C_{20}H_{40}O_2$	Eicosanoic	20:0
Gadoleic	$C_{20}H_{38}O_2$	11-eicoswnoic	20:0
Behenic	$C_{22}H_{42}O_2$	Docosanoic	22:0
Erucle	$C_{22}H_{48}O_2$	Cis-13-Docosenoic	22:1
Lignoceric	$C_{24}H_{48}O_2$	Tetracosanoic	24:0

Note: [a] xx = total number of carbon atomes and y = number of double bonds.

Source: (Ong et al., 2011)

Advantages of vegetable oil

- It is produced domestically which helps to reduce costly petroleum import
- It is renewable fuel, biodegradable and non-toxic
- It has 80% heating value and reasonable cetane number compared to that of diesel
- It contains low aromatic
- It contains low sulphur that causes sulphur oxide.
- It can use within the engine with no required modification.

Disadvantage of vegetable oil

- The high viscosity of vegetable oil leads to pumping and atomization problems in injection system (filter plugging and cold starting).
- The poor volatility makes vegetable oil difficult to vaporize and ignite (thermal cracking)
- High carbon residue causes heavy smoke emission and carbon deposition on the injection nozzle tip and in the combustion chamber.

2.4 *Jatropha curcas* L.

Jatropha curcas L. is a small tree and large shrub (up to 5 to 7 m in height). It belongs to the Euphorbiaceae family with a soft wood. *J. curcas* plant, which is illustrates in Figure 2.3 is the native in tropical American but widely distributed in tropical and subtropical region throughout Africa, India and South East Asia. It was reported that the plant can grow almost anywhere, even on gravely, sandy and saline soils. Due to its characteristic, jatropha can be easily cultivated without intensive care and very minimal efforts are required to sustain its growth, it has a healthy life cycle of 30-50 years, which eliminates the need for yearly re-plantation but yet can still sustain reasonably high yield even with minimum irrigation. *J. curcas* oil (JCO) is non-edible oil that will not compete with food crops. Thus, it has interested as a feedstock; in addition, a by-product being rich in nitrogen, the seed cake is an excellent source of plant nutrients (Jingura et al., 2011; Ong et al., 2011).

As shown in Table 2.4, JCO is a branched triglycerides type of the fatty acid composition of a linoleic (C18:2) or oleic acid (C18:1) type which are unsaturated fatty acid. Because of more than 75% unsaturated fatty acid, which is reflected in the pour and cloud point of the oil. The composition and characteristics of JCO is given in Table 2.5. Due to characteristics of JCO, it is considered as a substitute for fossil fuels. The values from both Table 2.4 and Table 2.5 indicate the oil quality, which is dependent on the interaction of environment and genetic such as the seed size, seed weight and oil content.

The utilization of JCO has various uses. As a rule, JCO can be directly used in single diesel engine (C.I. engine) as it has high heat content. However, JCO has a higher kinematic viscosity than petroleum diesel fuel which leads to poor atomization of the fuel. Owing to the high viscosity, long term use of JCO would cause deposit formation (Pramanik, 2003). Thus, blending with fossil diesel, pyrolysis, microemulsification, and transesterification method can be solving that problem (Ramadhas, 2004).

Figure 2.3 *Jatropha curcas* L. plant and *Jatropha curcas* L. seed

Table 2.4 Fatty acid composition of crude JCO

Fatty acid	Formula	Systemic name	Structure	%wt
Myristic	$C_{14}H_{28}O_2$	Tetradecanoic	14:0	0.1
Palmitic	$C_{16}H_{32}O_2$	Hexadecanoic	16:0	13.38-19.5
Palmitoleic	$C_{16}H_{30}O_2$	cis-9-Hexadecanoic	16:1	0.88-0.9
Stearic	$C_{18}H_{36}O_2$	Octadecanoic	18:0	2.3-7.4
Oleic	$C_{18}H_{34}O_2$	cis-9-Octadecanoic	18:1	34.3-49.0
Linoleic	$C_{18}H_{32}O_2$	cis-9,cis-12-Octadecanoic	18:2	29.7-43.2
Linolenic	$C_{18}H_{30}O_2$	cis-6,cis-9,cis-12-Octadecanoic	18:3	0.2
Arachidic	$C_{20}H_{40}O_2$	Eicosanoic	20:0	0.2-0.3
Behenic	$C_{22}H_{44}O_2$	Docosanoic	22:0	0.2

Source: Berchmans and Hirata, 2008; Gubitz, et al., 1999

Table 2.5 JCO composition and characteristics

Parameters	Unit	Range	Mean ± S.D.
Specific gravity	[g/cm^3]	0.860 - 0.933	0.914 ± 0.018
Calorific value	[MJ/kg]	37.83 - 42.05	39.63 ± 1.52
Pour point	[°C]	-3	
Cloud point	[°C]	2	
Flash point	[°C]	210 - 240	235 ± 11
Cetane value	-	38.0 - 51.0	46.3 ± 6.2
Saponification number	[mg/g]	102.9 - 209.0	182.8 ± 34.3
Viscosity at 30 °C	[cSt]	37.00 - 54.80	46.82 ± 7.24
Free fatty acid	[%]	0.18 - 3.40	2.18 ± 1.46
Unsaponifiable	[%]	0.79 - 3.80	2.03 ± 1.57
Iodine number	[mg of I^2/g]	92 - 112	101 ± 7
Acid number	[mg of KOH/g]	0.92 - 6.16	3.71 ± 2.17
Monoglycerides	[%]	nd - 1.7	
Diglyceride	[%]	2.50 - 2.70	
Triglyceride	[%]	88.20 - 97.30	
Carbon residue	[%]	0.07 - 0.64	0.38 ± 0.29
Sulphur content	[%]	0 - 0.13	

S.D = standard deviation; nd = no data

Source: Achten et al., 2008

2.5 Biodiesel

Biodiesel (fatty acid methyl ester), which is derived from triglycerides by transesterification, was investigated as diesel fuel or alternative fuels well before the energy crises of the 1970s and early 1980s. Biodiesel is typically produced by a reaction of vegetable oils or animal fats with an alcohol such as methanol and ethanol in the presence of a catalyst to yield mono-alkyl esters. Biodiesel has combustion characteristics similar to diesel such as shorter ignition delay, higher ignition temperature and pressure as well as peak heat release compare to diesel. Especially, it is practically free of sulphur and has a high cetane number normally in the range 46-60 depending on the feedstock. Biodiesel has been receiving increasing attention due to its less polluting nature, and it is a renewable energy resource as against the conventional diesel.

Therefore, biodiesel is an environmentally friendly fuel that can be used as pure or blended at any level with diesel fuel in any diesel engine without modification. Biodiesel fuels have generally been found to be nontoxic and are biodegradable, which may promote their use in applications where biodegradability is desired. The advantages and disadvantages of using biodiesel are summarized in Table 2.6.

The fuel quality parameter, which is used to define the quality of biodiesel, can be divided in two standards. First standard is European specifications or EN 14214 have been issued in 2003, and the second standard is ASTM D6751 that it specifications describes for the composition and purity of fatty esters as same as the standard of biodiesel in Thailand that shown in Table 2.7.

Table 2.6 Advantages and disadvantages of using biodiesel as fuels

Advantages	1. Provides a domestic, renewable energy supply. 2. Biodiesel is carbon neutral because the balance between the amount of CO_2 emissions and amount of CO_2 absorbed by the plants producing vegetable oil is equal. 3. Biodiesel can be used directly in compression ignition engines with no substantial modification of the engine 4. Blending of biodiesel with diesel fuel increased engine efficiency 5. The higher flash point of biodiesel makes its storage safer. 6. Biodiesel is non-toxic. 7. Biodiesel degrades four times faster than diesel. 8. CO, CO_2 and UBHC, PAH, soot and aromatics emissions are reduced in biodiesel and its blends than in fossil diesel because biodiesel is oxygen in structure and it burns clearly all the fuel. 9. It is biodegradable.
Disadvantages	1. More expensive due to less production of vegetable oil. 2. Blends of biodiesel above 20% can cause engine maintenance problems and even sometimes damage the engine in the long term.

Source : Atabani, et al., 2012

Table 2.7 Biodiesel standard of Thailand in 2009

No.	Properties	Test Method	Limits		Unit
			min	max	
1	Methyl ester	EN 14103	96.5		[%wt]
2	Density at 15°C	ASTM D1298	860	900	[kg/m^3]
3	Kinematic viscosity at 40°C	ASTM D445	3.5	5.0	[cSt]
4	Flash point	ASTM D93	120		[°C]
5	Sulphur	ASTM D2622		0.001	[%wt]
6	Carbon residue	ASTM D4530		0.30	[%wt]
7	Cetane number	ASTM D613	51		-
8	Sulfated ash	ASTM D874		0.02	[%wt]
9	Water	EN ISO 12937		0.05	[%wt]
10	Total contaminate	EN 12662		0.0024	[%wt]
11	Copper strip corrosion	ASTM D130		No.1	-
12	Oxidation stability at 110°C	EN 14112	10		[hrs]
13	Acid value	ASTM D664		0.50	[mg KOH/g]
14	Iodine value	EN 14111		120	[g I^2/100g]
15	Linolenic acid methyl ester	EN 14103		12	[%wt]
16	Methanol	EN 14110		0.20	[%wt]
17	Monoglyceride	EN 14105		0.80	[%wt]
18	Diglyceride	EN 14105		0.20	[%wt]
19	Triglyceride	EN 14105		0.20	-
20	Free glycerol	EN 14105		0.02	-
21	Total glycerol	EN 14105		0.25	-
22	Group I metal (Na+K)	EN 14108		5.0	[mg/kg]
23	Group II matals (Ca+Mg)	pr EN 14538		5.0	[mg/kg]
24	Phosphorus	ASTM D4951		0.0010	[%wt]
25	Additive	-	-		-

Source: Department of Energy Business, 2011

2.6 Transesterification

Transesterification of glyceride with methanol to methyl esters is a technically reaction that has been used vastly in soap and detergent manufacturing industry for many years. Meanwhile for fuel productions, amongst the four techniques which are blending, pyrolysis, microemulsification and transesterification. Transesterification has been the most widely used to reduce the viscosity of triglycerides similar to petroleum diesel. In addition, this method also called alcoholysis because the reversible reaction of a fat or oil (triglycerides) with an alcohol to form biodiesel (fatty acid alkyl esters) and glycerol (Figure 2.4). Methanol and Ethanol are utilized most frequently. Recently ethanol is a preferred alcohol in transesterification reaction compared to methanol since it is derived from agricultural product and it is renewable and biodegradation. However, methanol is preferred because of its low cost, and it has shortest chain alcohol.

Even though transesterification produce biodiesel which has one alternative fuel for diesel engine and good for emissions (Monteiro et al., 2008; Demirbas, 2009; Atadashi et al., 2010; Singh et al., 2010; Ong et al,2011; Yusuf et al., 2011), another serious problem is its processes that also yields glycerol, excessed alcohol, catatalyst, tri-, d-, and nonoglycerides, as well as free fatty acids as by product or waste. Meanwhile in several process of biodiesel production, large volume of wastewater is generated. Thus, these and contaminants of biodiesel can lead to problems of disposal and environmental concern (Monteiro et al., 2008).

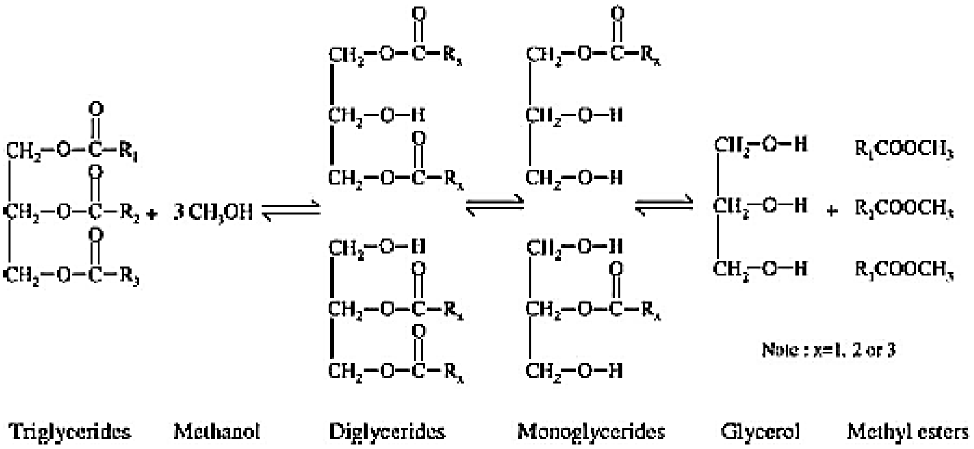


Figure 2.4 Reaction in the transesterification of a triglyceride (Balat and Balat, 2010)

2.7 Microemulsification

Microemulsion is one type of emulsions: however, the term of microemulsion and emulsion seem to indicate that such systems are very similar but just diverge in the size of the dispersed component. Back to the 1959s, Schulman and Hoar introduced the term of “microemulsion” for transparent solution in a sample consisted of four component included water, hydrocarbon, surfactant and co-surfactant. The sample were originated a clear single phase solution. However, the definition of microemulsion provided by Danielson and Lindman in 1981, which were differenced from emulsion, was isotropic and thermodynamically stable liquid solution. In the other word, microemulsion is defined as “a system of water, oil and ampliphile which is a single optically isotropic and thermodynamically stable liquid solution”.

Since microemulsification was tended to form smaller size of dispersed component than emulsion, microemulsification is attractive as alternative method for biofuel formations. Due to the solution from microemulsification can be prepared by simple mixing the component without recourse to high energy and expensive equipment; in contrast with transesterification and pyrolysis. Many research have been published the work of microemulsion-based fuel or microemulsion fuel, and described that is very advantageous to reduce the cost and much simpler to obtain optimized instrument parameters for analysis (Jesus et al., 2008; Do et al., 2011). The solution as water or alcohol content in microemulsion fuel can be increased due to the solubilization enhancement by surfactant and this fuel can reduce emission gases especially oxides of nitrogen (NO_x) and particulate (PM) (Lif and Holmberg, 2006; Ghannam and Selim, 2009; Lif et al., 2010). However, microemulsion-based fuel has some disadvantages such that microemulsion-based fuel presented a slight loss in heating value.

In the present, there are many research regard to water-in-diesel microemulsion but not much has been published on alcohol-diesel microemulsion. And there are also a few papers that deal with the combustion characteristics and the emissions from microemulsion fuel of ethanol-triglycerides-diesel.

Characteristic of microemulsion

As Table 2.8 shown the characteristic of microemulsion, it exhibits many unique properties such as being transparent and product ultralow interfacial tension and ultrahigh solubilization. By these properties reach microemulsion to various applications including cosmetic, cleaning technologies, drug delivery systems, soil remediation, and biofuel production.

Table 2.8 Some characteristic of microemulsion

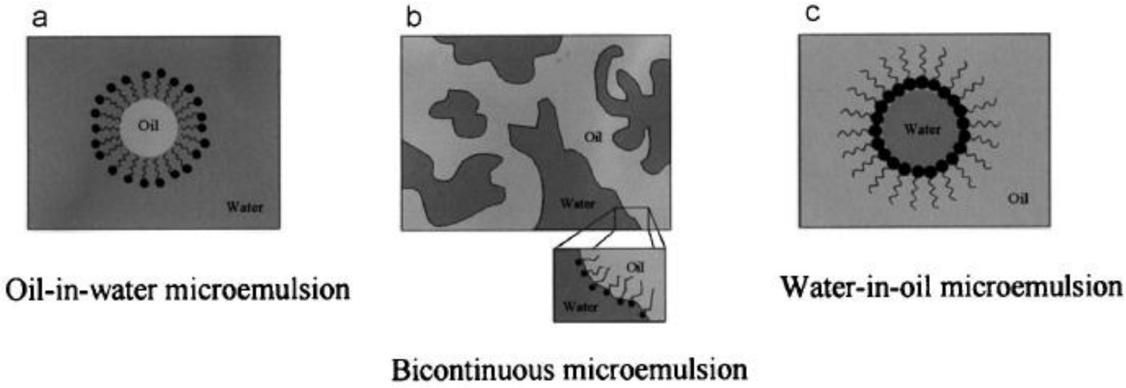
Parameter	**Microemulsion**
Formulation	Spontaneous
Stable	Thermodynamically
Droplet size (µm)	0.01 - 0.10
Appearance	Transparent
Surface are (m2 g-1)	High (200)
Interfacial tension	Ultra low
System type	W/O, O/W and bicontinuous
Surfactant concentration	Variable
Co-surfactant type	Short chain alcohol

Source: Burguera and Burguera, 2012

While the mixture between water-oil and surfactant/co-surfactant have different characteristic phase that is demonstrated by Winsor types. The mixed systems can essentially fall into four types.

- Dispersion of oil in water (O/W) in contact with essential oil called *Winsor type I*.
- Dispersion of water in oil (W/O) in contact with essential oil called *Winsor type II*.
- Both O/W and W/O dispersions are simultaneously present in the same domain in mixed state in separate contacts with both oil and water called *Winsor type III*.
- A homogeneous single phase of dispersion either O/W or W/O not in contact with any other phase called *Winsor type IV*.

Figure 2.5 shown schematic presentation of the three Winsor types of microemulsion which are mostly to be formed depending on composition. In order to formed the phase behavior of ternary or quaternary microemulsion form in combinations depend on amount of factors; namely, the type of surfactant, non-polar (oils), polar medium (water, glycerol, alcohol), the present of additive (electrolyte), the temperature, the pressure, etc. (Moulik and Paul, 1998)



Oil-in-water microemulsion

Bicontinuous microemulsion

Water-in-oil microemulsion

Figure 2.5 Schematic representation of the three most commonly encountered microemulsion structures: (a) oil-in-water; O/W, (b) bicontinuous, O/W/O and (c) water-in-oil; W/O microemulsion (Lawrence and Rees, 2000)

Moreover, the tendency toward the characteristic phase microemulsion is still dependent on the properties of the oil and the surfactant, the ration of water-oil. Thus, HLB was appointed and correlated in order to conveniently classify on experimental scale as reveled in Table 2.9. HLB or hydrophilic-lipophilic balance (HLB) generally runs from 1 to 20. In common, surfactants that have an HLB in the range of 4-6 are formed W/O microemulsion or Winsor type II. Surfactants which have an HLB in the range of about 8-16 are formed O/W microemulsion or Winsor type I. However the role of the co-surfactant can increase the interfacial fluid by penetrating into void space of the surrounded surfactant molecule.

Table 2.9 Surfactant solubility related to HLB and CPP values

Microstructure type	Surfactancy	HLB	CPP
W/O	More soluble in oil (lipophilic)	4-6	>1
O/W	More soluble in water (hydrophilic)	8-16	<1
Microemulsion	Equal affinity for oil and water	13-18	1

HLB: Hydrophilic lipophilic balance
CPP: Critical packing parameter

Source: Burguera and Burguera, 2012

2.8 Surfactant

Surfactant is abbreviation from the term SURFace ACTive AgeNT. In general, surfactants are organic compound and conventional surfactant molecules comprise of a polar head group region (hydrophilic groups) and a non-polar tail region (hydrophobic groups) as shown in Figure 2.6. Surfactants have the capability to reduce the surface tension of water by adsorbing at the liquid-gas and reduce interfacial tension between water and oil by adsorbing at the liquid-liquid. As an example, when they are incorporated into immiscible mixtures as water and oil, the surfactant molecule can be locate at the water/oil interface which is thermodynamically very favorable.

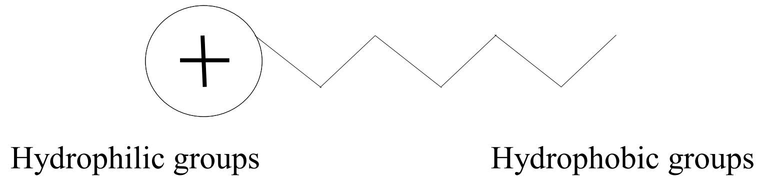


Figure 2.6 Illustration of a conventional surfactant molecule

Surfactants are generally classified according to their structure into four primary groups; namely Anionic, Nonionic, Cationic, and Zwitterionic (Salager, 2002). And there are classifies as Winsor also (mentioned in topic 2.7)

- *Anionic Surfactants* are dissociated in water in a surfactant anion, and a cation which is in general an alkaline metal (Na+, K+) or a quaternary ammonium. This type is the most commonly used; e.g., alkylbenzene sulfonates (detergents), soaps (fatty acid), lauryl sulfate (foaming agent), dialkyl sulfosuccinate (wetting agent), lignosulfonates (dispersants) etc.
- *Nonionic Surfactants* do not ionize in aqueous solution, because their hydrophilic group is of a non-dissociable type, such as alcohol, phenol, ether, ester, or amide. As the lipophilic group in often of the alkyl or alkylbenzene type, the former coming from fatty acids of natural origin, the polyether chain (polyEO, and polyPO)
- *Cationic Surfactants* are dissociated in water in to a surfactant cation and an anion, most often of the halogen type. A very large proportion of this class corresponds to nitrogen compounds such as fatty amine salts and quaternary ammoniums, with one or several long chain of the alkyl type, often coming from natural fatty acids.
- *Zwitterionic Surfactants* are a single surfactant molecule exhibit both anionic and cationic dissociations

When a variety of surfactant molecules assemble into aggregates in water, with the non-polar tail region in the interior and the polar head group at the exterior surface in a spherical form, is call micelle. Micelle formation or micellization is a mechanism to adsorption at the interfaces for removing hydrophobic groups from contact with the water, by which reduce the free energy of the system. Meanwhile, surfactant molecules from micelle have above a particular concentration which is called as critical micellar concentration (CMC). As Figure 2.7 gives an indicated of a few of the wide variety of possible self-association structures that surfactants and micelle can form in the presence of water, oil or combination of three.

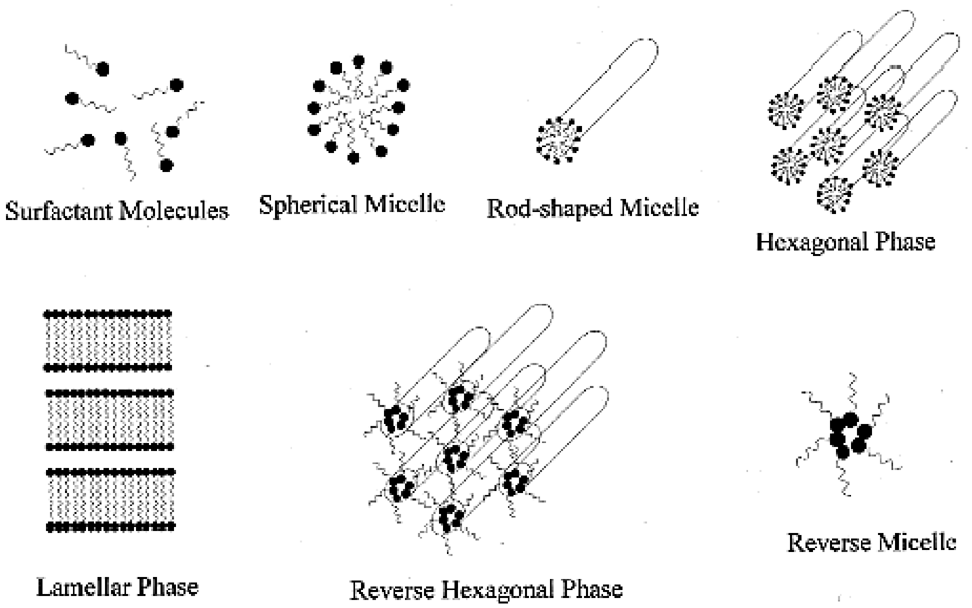


Figure 2.7 Schematic representation of the most commonly encountered self-association structures in water, oil or a combination thereof (Lawrence and Rees, 2000)

2.9 Properties of fuel

The various types of liquid fuels namely diesel, ethanol, vegetable oil, and biodiesel, are available for firing in combustion equipment. However, each types of fuel are individual characterization. The characterization relate to properties for selection of right fuel that depends on various factors such as availability, storage handing, pollution and cost. Therefore, the knowledge of the fuel properties tends to select the right purpose and efficient use of the fuel; in addition, the characteristics of fuel are generally used for assessing the quality of fuels and emissions.

Normally, diesel fuel is characterized for boil within the temperature range of 150 to 390 ºC. t While the key properties of diesel fuel that effect engine performance and emissions are ignition qualities, distillation (volatility) characteristic, density, viscosity, hydrocarbon composition, sulphur content, and stability and injection system cleanliness. In addition, other significant properties comprise cold flow characteristics at low ambient temperatures, water and sediment content, carbon residue etc (Pundir, 2007).

2.9.1 Acid number

The acid number or neutralization number expresses the amount of free fatty acids in fuel. Normally, its number must be kept as low as possible because these acids might corrode metal component in the injection systems of the engine (Stauffer 2005).

2.9.2 Cloud Point

The cloud point is the temperature at which wax first becomes visible when a fuel is cooled. Due to wax at low temperature can cause clogging of fuel filter and an interruption in fuel supply lines. It is recommended by engine manufacturers that the cloud point should be below the temperature of use and not more than 60°C above the pour point. While the cloud point of vegetable oil is generally higher than that of diesel fuel (Ali and Hanna, 1994).

2.9.3 Density

The specific gravity and density of diesel fuel are generally interrelated to volatility, cetane number, viscosity and heat of combustion etc. Moreover, the fuel density affects engine power as the fuel mass injected/stroke varies with fuel density. For example from the record, an increase in fuel density from 828 to 855 kg/m3 was indicated to result by around 5 percent increase in engine power (Pundir, 2007).

2.9.4 Flash point

The flash point is the temperature at which a combustible liquid throw off just enough vapor to produce a vapor/air mixture that will ignite when a flame is applied under standardized condition. The importance of the flash point is primarily related to safe handle and storage. While it not significant for engine performance and do not influence auto-ignition temperature or other combustion characteristic. For example, flash point of vegetable oils is higher than diesel fuel and ethanol respectively.

2.9.5 Kinematic viscosity

Viscosity of fuel is a very important property by the viscosity of a fluid is a measure of its internal resistance to flow. While the viscosity of fuel in diesel engine affects injection characteristics, fuel atomization, drop size distribution, spray cone angle and penetration. Such vegetable oils have high viscosity that causes reduce fuel flow rates to the injection system resulting in an inadequate fueling of the engine; in addition, cause of deposition and forming a film on the injector. While and alcohol is characterized as low viscosity that result in an increasing in leakage of fuel past the pumping elements (Ramadhas et al., 2004).

2.9.6 Heating value

Heating value (HV) or calorific value (CV) is an important property for fuel characterization. It defines fuel energy content and efficiency which are experimentally obtained by using an oxygen bomb calorimeter method (ASTM D240). In general, heating value of fuel is specific in unit Megajoule as energy of fuel per kilogram as mass (MJ/kg) (Fassinou et al., 2010).

2.9.8 Oxidation stability

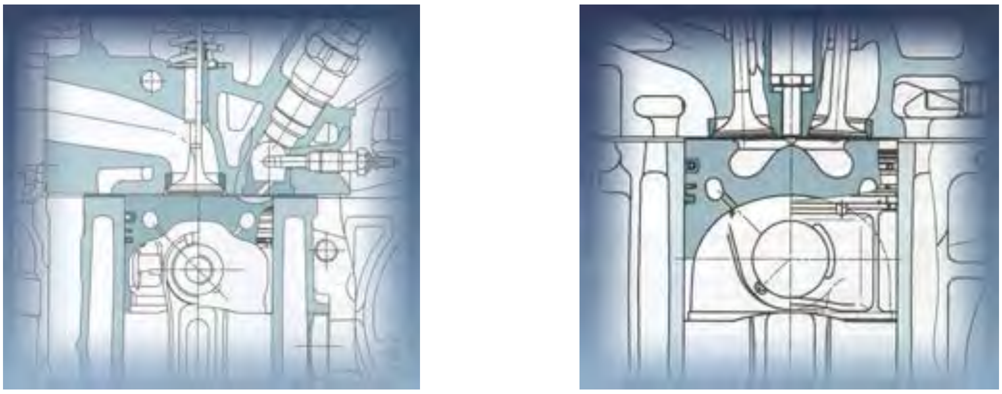
Oxidation stability is chemical reaction between fuel and oxygen. The rate of oxidation is accelerated by light, heat, temperature, water. Normally, oxidation rate increases with time along with increase in fuel's viscosity and acid number (Jain and Sharma, 2010). Thus, oxidation stability is one property to represent fuel storage characteristics.

2.9.9 Water content

Water content is the quantity of water contained in fuel. Normally, water is present in the fuel in small amounts. Its amount should be kept as low as possible because it probably extinguishing or reduce the heat of combustion. In addition it can cause erosion and corrosion in the injection systems (Atabani et al., 2012).

2.10 Diesel engine

The diesel engine is the engine of option for heavy-duty applications in industrial, construction, agriculture, and transport. In a diesel engine also known as a compression-ignites engine because of operating principles of its. The operating principles of diesel engines require both air and fuel enter the cylinder through the intake system. By this air is compressed to a high temperature and pressure then atomized fuel is sprayed into the air at high velocity. After that the well fuel-air mixture and undergoes a series of spontaneous chemical that result in a self-ignition or auto ignition. Generally, a diesel engine is divided into two basic types which are indirect injections (IDI) and direct injection (DI) as illustrated cross section of the diesel combustion chamber in figure 2.8. The difference between IDI and DI diesel engine is combustion chamber. IDI diesel engine utilize a pre-combustion chamber for mixing the fuel with air be before to enter the combustion chamber, whereas DI diesel engine inject fuel directly into the combustion chamber to ignition occurs. However, direct injection diesels are favored due to their efficiency, performance potential, and cleaner exhaust emission (Haddad and Watson, 1984).



(a) (b)

Figure 2.8 Diesel engine: (a) Indirect injection engine (b) Direct injection

2.11 Emission

Under ideal of complete combustion, all of the carbon in the fuel will burn to carbon dioxide (CO_2) with oxygen, and all of the hydrogen will burn to water vapor. Nevertheless, in fact of a diesel fuel does not have only carbon and hydrogen but it also consists of sulfur and nitrogen as same as air does not consist of only oxygen. According to diesel engine are significant part of smoke opacity, total particulate matter <10 μm (PM-10), total oxides of nitrogen (NO_x), carbon monoxide (CO), methane (CH_4), sulfur dioxide (SO_x) and total hydrocarbon (THC) because of efficiency of diesel engine and diesel fuel. Moreover, the structure and the properties of the fuel can be anticipated to the emission in the combustion process such as energy content, viscosity, water content. Therefore, the properties of diesel fuel are considered desirable by diesel or biodiesel standard.

2.11.1 Carbon monoxide (CO)

Carbon monoxide emissions result during combustion of fuel rich mixtures due to deficiency of oxygen. In the other word, it is formed due to deficiency of oxygen during combustion. It is an odorless gas but is highly toxic gas of about the same density as that of air.

2.11.2 Carbon dioxide (CO_2)

Carbon dioxide emissions result during complete combustion. In the present CO_2 are still an unregulated emission species. However, it is generally referred to as a greenhouse gas and considered responsible for global warming. There were collectively work and commitment at reducing CO_2 emissions.

2.11.3 Nitrogen oxides (NO_x)

Oxides of nitrogen NO and NO_2 are formed during combustion at high temperatures from the internal combustion engines. Nitric oxide (NO) is the major component of NO_x emissions. It is formed during combustion in the three ways. The First is *thermal NO* by oxidation of nitrogen in atmospheric at high temperature. The second is *fuel NO* by oxidation of fuel-bound nitrogen at low temperatures. And the third way is prompt NO by mechanism at the flame front. Nitrogen dioxide (NO_2) is a reddish brown gas. It has an irritating odor and low solubility.

2.11.4 Total hydrocarbon (THC)

Total hydrocarbon or unburned hydrocarbon emissions result from incomplete combustion of hydrocarbon fuels. It arises as part of the fuel inducted in to the engine escapes combustion. While there are five main sources of hydrocarbon in diesel engines are (1) over mixing of fuel and air beyond lean flammability limits (2) under mixing to fuel-air ratios too rich for complete combustion (3) impingement of fuel sprays on wall i.e., spray over penetration (4) bulk quenching of combustion reactions due to mixing with cooler air or expansion (5) poorly atomized fuel from the nozzle sac volume and nozzle holes after the end of injection (Pundir, 2007).

2.11.5 Particulates matter (PM)

Particulates are fine solid or liquid particles suspended in air. By solid particles emitted by vehicles are largely made of carbonaceous matter (soot). While the major source of particulate emission in diesel engines is heterogeneous mode of combustion where fine soot particles are generated. In the many country, emissions on a diesel engine are regulated; for example, in the United States has mandate for smoke opacity, particulate matter, carbon monoxide, total oxides of nitrogen, and total hydrocarbon according to test procedures defined by the Environmental Protection Agency (EPA). Likewise, in Thailand's emission are regulated by Pollution Control Department following USEPA standards. Since emissions of pollutants effect on human health, environment, and contribute for increasing greenhouse gases (GHGs). Table 2.10 presents the Global Warming Potentials (GWP) of greenhouse. Table 2.11 shows the effects of the emissions from fuel combustion on human health and environment.

Table 2.10 Listing of GWP values as per report IPCC WG1 AR4

Common Name	**Chemical Formula**	**Global Warming Potential for Given Time Horizon**			
		SAR			
		100-yr	**20yr**	**100yr**	**500yr**
Carbon dioxide	CO_2	1	1	1	1
Methane	CH_4	21	72	25	7.6
Nitrous Oxide	N_2O	310	289	298	153

Source: Intergovernmental panel on climate change

Table 2.11 The effects of emissions on human health and environment

Emission	Health Impact	Environmental Impact
CO	• Fatigue • Headache • Dizziness • Nausea • Vomiting • Disorientation • Loss of consciousness	• Contributes to Global warming • Component of smog
CO_2	• Asphyxiation • Frostbite (from dry ice; solid carbon) • Kidney damage or coma	• Greenhouse effect • Global warming
NO_x	• Cause respiratory problems: asthma, emphysema & bronchitis • Aggravates existing heart disease • Damage to lung tissue • Premature death	• Contributes to acid rain • Combines with particles to reduce visibility • Is a greenhouse gas
HC	• Acute respiratory symptoms • Headache • Dizziness • Vomiting • Reduce cardiovascular function • Arrhythmia • Brain damage • Coma • Premature Death	• Precursor to ground-level ozone • Major component of smog

Source: Prapatigul et al., 2008

2.12 Literature reviews

During the 1980's to 2000's, many studies involved the use of unmodified vegetable oils as a replacement for diesel. Gubitz et al. (1999) studied the performance of vegetable oils that could be used as fuel substitutes with direct and indirect injection diesel engine. Fuel conversion efficiency, specific consumption, and exhaust 24 gas emissions were compared. They found that among of vegetable oils from sunflower seeds, soybeans, rapeseeds, and jatropha seed. Jatropha oil could run a long term durability test by a modified direct injection diesel engine for 1,000 hr. test run without any wear in the engine. Furthermore, it showed the lowest exhaust gas emissions.

In 2002, Jones and Peterson claimed that many research can be used raw vegetable oils in short term performance tests. However, they tested in long term tests resulted in engine damage or maintenance problems. Thus, some author reported use raw vegetable oils as diesel fuel extenders in blends less than 20 percent, and degumming was a way to improve use of low level blends.

Previous studies early 20th century for microemulsion fuels, some researcher have reported that microemulsion induced considerable promise for providing low viscosity fuel blends containing substantial quantities of vegetable oil by microemulsification with short-chain alcohols, such as methanol or ethanol. As Ziejewski et al. (1984) prepared a nonionic sunflower oil-aqueous ethanol microemulsion by mixing 53.3% (v/v) of alkali refined and winterized sunflower oil with 13.3% (v/v)) of 190-proof ethanol and 33.4% (v/v) of 1-butanol. Lower viscosities and better spray pattern were observed with an increase of 1- butanol. Likewise, Schweb et al. (1984) found that 1-butanol was incorporated into the system (soybean oil/water: ethanol ratio of 19-1/trialkylamine surfactant) as a co-surfactant for the purpose of lowering both the viscosity and the solidification. Moreover, Schweb et al. (1985) proposed the system were prepared from vegetable oil, a C_1-C_3 alcohol, water, and 1-butanol as the nonionic surfactant. These fuels were characterized by and acceptable viscosity and compare favorably to No.2 diesel fuel. In the other hand, fuels formulated as microemulsions have low cetane numbers and low heating values as compared to No.2 diesel fuel.

As previous studies later on 20th century for microemulsion fuels, many researchers reported that w/o microemulsion tended to improve combustion efficiency and reduced air pollution. For instance, Lin and Wang (2004) produced two-phase emulsions (W/O) and three-phase emulsions (O/W/O) to feed a diesel engine. They investigated the engine performance and emissions of these systems with various water contents and compared them to regular diesel oil. It was observed that greater water content generated lower calorific values. They observed that emulsions had lower exhaust gas temperature, CO_2, CO, NO_x, and O_2 emissions and smoke opacity. The three-phase emulsions produced higher exhaust gas temperatures and lower CO and NO_x emissions as compared with two-phase emulsions with the same water proportion.

In 2006, Fernandes et al. submitted a request for a patent concerning the development of diesel-based microemulsion systems composed of anionic surfactant (1 to 5 %wt), water (1 to 9 %wt) and diesel fuel (at least 86 %wt). These w/o microemulsion fuels presented good thermal stability and their physical-chemical properties were in accord with the regulatory criteria for diesel oil in Brazil. They concluded that the new microemulsion systems can be used in diesel engines with good performance and low gaseous emissions.

The work of Qi et al. (2010) studied a single cylinder direct injection diesel engine was tested using neat biodiesel and the microemulsions as fuels under variable operating conditions. Studied microemulsion system was divided into ME1 and ME2 which contained 80:20:4:0.5 and 80:20:4:1.0 of Biodiesel (ml): Ethanol (ml): Span 80 (g): Water (ml), respectively. The results indicated that, compared with biodiesel, the peak cylinder pressure of the microemulsions is almost identical, and the peak pressure raised rate and peak heat release rate was higher at medium and high engine loads. At low engine loads, those of the microemulsions were lower. The start of combustion was later for the microemulsions than for biodiesel. Moreover the microemulsions, there was slightly higher brake specific fuel consumption (BSFC), while lower brake specific energy consumption (BSEC). Drastic reduction in smoke was observed with the microemulsions at high engine loads, and nitrogen oxide (NO_x) emissions are found slightly lower under all rang of engine load. But carbon monoxide (CO) and hydrocarbon (HC) emissions are slightly higher for the microemulsions than that for biodiesel at low and medium engine loads.

Moreover, Neto et al. (2011) studied diesel-based microemulsions and a surfactant/diesel blend, using ethoxylated (5 EO) nonylphenol as surfactant, were prepared and tested in a diesel engine to evaluate its performance and emissions. The following properties were evaluated density, viscosity, cloud point and corrosiveness. Experimental results showed that density and viscosity were greater than those obtained for neat diesel. Cloud point and corrosiveness were not affected by water and surfactant. Specific fuel consumption of the microemulsion systems was greater than that of diesel, but the small droplets of water improved diesel combustion. Compared with diesel, an increase in carbon monoxide (CO) and nitrogen oxide (NO_x) emissions and a decrease in black smoke emissions were obtained.

Including a recent study of diesel-based microemulsions investigated water diesel emulsion on engine performance and emissions. Alahmer (2013) tested in a four-stroke, four-cylinder, water cooled and direct-injection engine. The experiment examined engine torque (T), the break mean effective pressure (BMEP) and thermal efficiency for engine performances, and measured carbon dioxide (CO_2), nitrogen monoxide (NO) and nitrogen oxide (NO_x) and oxygen dioxide (O_2) for emissions. The results showed that the using of 2% by volume of Polysorbate 20 as surfactant improved the engine performance and reduce emissions. However, only 5% water emulsion was suggested to produce efficacy on performance.

In a part investigation on vegetable oil-based microemulsions; Dantas *et al.* (2001) developed diesel-based microemulsions using blends of diesel with vegetable oils (soy, palm and castor oils). Pseudo-ternary phase diagrams were constructed to evaluate the main factors that influenced the obtaining of microemulsion systems, such as: co-surfactant/surfactant ratio and nature of surfactant, co-surfactant and oil phase. The best microemulsions were obtained with blends of diesel and soybean oil, indicating the possibility of using these blends as alternative fuels.

Including the many recent works investigated on vegetable oil-based microemulsion, for instance, the work of Ploysrimongkol and Tongcumpou (2009) studied directly palm oil mixed with ethanol and diethanoamine (a nonionic surfactant). They demonstrated that microemulsion fuel made from the optimal composition (palm oil: C/S ratio at 0.5: water of 95: 4: 95: 0.05 % (w/w)), and its 5 and 20% (v/v) blends with diesel obtained meets the standard properties for biodiesel and diesel. The systems contained an anionic extended surfactant with an increasing degree of triglyceride oils unsaturation (more double bond), surfactant interaction with the triglycerides become weaker, hence requiring higher optimum salinity for higher interfacial tension values.

Phan et al., (2010) found the use of an extended surfactant ($C_{14,15}$–8PO–SO_4Na) at concentrations as low as 125 ppm in the microemulsion-based detergency of canola oil. They found that the maximum detergency (95%) was achieved in the type II microemulsion region at low temperature. However, the sulfur content in the sulfate head group causes environmental concerns in a fuel.

The work of Do et al. (2011) studied three vegetable oils that are canola, palm, and algae to blend with diesel fuel (50 %vol) with appropriate surfactant and co-surfactant systems at 24 %vol of ethanol. They found microemulsification could produce biofuels with desirable viscosity, cloud point, and pour point that satisfy the ASTM standard, and microemulsion fuels emitted NO_x lower than diesel even with the blends containing no nitrate additive. Likewise, fuel properties could be adjusted via formulation variable. While the formulated microemulsion fuels had lower heating value that diesel fuel, their CO emissions were potential higher to those of diesel fuel.

Attaphong et al. (2012) investigated carboxylate-based extended surfactants (anionic surfactant) were able to form reverse micelle microemulsion without salt addition, thereby eliminating the phase separation and precipitation, and this formulation could prevent sulfur oxide (SO_x) emissions because there was no sulfur content in the head group of the surfactant. In addition, fuel properties such as viscosity and temperature dependence were favorable at the optimum system of surfactant/cosurfactant ratio of 1-16 with canola oil/diesel ratio of 50-50 and approximately 24% volume of ethanol. Salt-free formulation, beside, cetane enhancers and anti-freezing agents could also be used as additives.

CHAPTER III

METHODOLOGY

This experiment divided into four parts; in the first part was to study the phase behavior of the microemulsion systems containing crude JCO with single nonionic surfactant at different the number of EO group by pseudo-ternary phase diagrams. Meanwhile, nonionic surfactant's selection to the study was chosen based on the Hydrophile-Lipophile Balance (HLB) approach. The second part aimed to identify temperature stability of microemulsion fuels at five temperatures in order to define MF's stability, and then the suitable ratio based on being transparent single phase and proper viscosity would be selected for further analysis. The third part proposed to determine microemulsion fuel properties compared to biodiesel standard, and the fourth part evaluated performances with emission to compare with commercial diesel fuel. The tests in the third and fourth parts were performed on compress-ignition by using a two-cylinder, indirect injection (IDI) diesel engine.

3.1 Chemicals and materials

3.1.1 Nonionic surfactant

Fatty alcohol (C12-C14) ethylene oxide (Dehydol) of approximate 99.9% active strength (see Figure 3.1), supported by Thai Ethoxylate Company Limited, was used as the surfactant in this research. The physical and chemical properties are shown in Table 3.1.

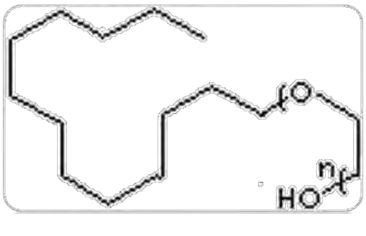


Figure 3.1 Empirical structure of Dehydol surfactant

Table 3.1 Physical and chemical properties of fatty alcohol ethylene (LS)

Properties	**Unit**	**Fatty alcohol ethylene oxide**		
		Dehydol LS1	**Dehydol LS3**	**Dehydol LS7**
CAS NO.	-	98439-50-9	68439-50-9	68739-50-9
Active substance	%m/m	99.95	99.95	99.91
Appearance at 25 °C	-	liquid	liquid	liquid
Cloud point	°C	-	52.4	56.3
Color at 40 °C	APHA	2	2	2
Density @ 70 °C	g/cm^3	0.827	0.891	0.949
EO mole	mole	0.9	2.89	6.97
Emulsifier	-	w/o	o/w	o/w
Molecular Weight	g/mol	238.81	326.91	503.12
HLB	-	3.6	7.9	12.1
pH at 25 °C	-	6.3	6.1	6.2
Hydroxyl value	Mg KOH/g	239	175	115
Water content	%m/m	0.05	0.05	0.09

3.1.2 Anionic surfactant

Sodium bis (2-ethlhexyl) sulfosuccinate (AOT) of more than 96% anionic active, purchased from Sigma-Aldrich, was used as mixed surfactant with Dehydol in this investigation for phase stability of different temperature. The physical and chemical properties are listed in Table 3.2.

3.1.3 Crude *Jatropha curcus* oil

Crude *Jatropha curcas* oil (JCO) was purchased from Kampengsan, Kasetsart University was used in this study. The characteristics of JCO are shown in Chapter 2, Table 2.5.

3.1.4 Commercial diesel fuel

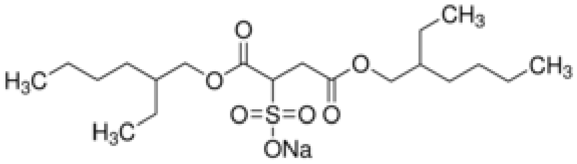
The commercial diesel fuel (D) or petroleum diesel was blended as one compound of microemulsion fuel (MF) in the study, which was purchased from PTT

Public Company Limited. Standard of commercial diesel in Thailand is shown in Table 3.3.

3.1.5 Ethanol

Absolute ethanol alcohol (E) at 99.9% concentration, which was purchased from RCI Labscan Limited, was used as a compound of microemulsion fuel in this research. The properties of ethanol are shown in Table 2.1.

Table 3.2 Physical and chemical properties of sodium bis (2-ethlhexyl) sulfosuccinate (AOT)

Properties	**Unit**	**Sodium Bis (2-ethlhexyl) Sulfosuccinate**
		AOT
CAS NO.	-	577-11-7
Formula	-	$C_{20}H_{37}NaO_7S$
Chemical Structure	-	
Active substance	%	≥ 95.5
Appearance at 25 °C	-	sticky solid or white flakes
Emulsifier	-	o/w
Melting point	°C	173-179
Molecular Weight	g/mol	44.56
HLB	-	13.5
pH	-	6
Water content	%	≥ 4.5

Source: http://www.sigmaaldrich.com/catalog/product/aldrich/d201170?lang=en&region=TH

3.2 Instruments

3.2.1 A Tirando Automatic Potentiometric Titratior was used for analyzing acid value.

3.2.2 A LECO AC-350 Automatic Calorimeter was used for analyzing the heating value.

3.2.3 An ISL CPP 5Gs Cloud & Pour Point Tester was used for analyzing the cloud point and pour point.

3.2.4 An Anton Paar DMA-4500 Digital Density Meter was used for analyzing the density.

3.2.5 An APM-7 Pensky-Martens Closed Cup Tester, as shown in was used for analyzing the flash point.

3.2.6 A D445-E20L Kinematic Viscometer was used for analyzing kinematic viscosity at 40 oC.

3.2.7 A Rancimat was used for investigating oxidation stability.

3.2.8 A Karl Ficher tritratior was used for analyzing the water content.

All instrument pictures are shown in Appendix A.

Table 3.3 Commercial diesel standard in Thailand, 2013

No.	**Properties**	**Test Method**	**Limits**		**Unit**
			min	**max**	
1	Methyl ester of fatty acid	EN 14078	4.5	5	[%vol]
2	Specific gravity at 15.0°C	ASTM D1298	810	870	-
3	Kinematic viscosity at 40°C	ASTM D445	1.8	4.1	[cSt]
4	Flash point	ASTM D93	52		[°C]
5	Sulphur	ASTM D2622		0.005	[%wt]
6	Carbon residue	ASTM D189		0.05	[%wt]
7	Cetane number	ASTM D613	50		-
8	Ash	ASTM D482		0.01	[%wt]
9	Water and sediment	ASTM D2709		0.05	[%wt]
10	Pour point	ASTM D97		10	[°C]
11	Copper strip corrosion	ASTM D130		No.1	-
12	Oxidation stability	ASTM D2274		25	[g/m^3]
13	Distillation	ASTM D86		357	[°C]
14	PAH	ASTM D2425		11	[%wt]
15	Color (hue)	ASTM D2392	Yellow		-
16	Color (intensity)	ASTM D1500		4.0	-
17	Lubricity, Wear Scar	CFC F-06096		460	[μm]
18	Additive	-	-		-

Source: Department of Energy Business, B.E. 2556

3.3 Experimental section

3.3.1 Jatropha oil preparation

Prior to this experiment, gum and scraps shell of JCO were removed by centrifugal separation at 2750 × g for 10 minute then the supernatant or oil was separated from settle sediment for further study. The oil was carefully kept at 25 degree Celsius without exposed to light during this experiment.

3.3.2 Microemulsion fuel preparation

Microemulsion fuel was prepared on a volumetric basis for single nonionic surfactant system (LS), Jatropha curcas oil (JCO), ethanol (E), com diesel (D), while for mix anionic surfactant system (AOT) was prepared by weight basis.

Ethanol and surfactant were mixed by ratio at 3:1 and was considered as one component (so called E/S) to blend with diesel and JCO to achieve totally 10 mL for phase behavior study in 15 mL glass vial with well cap.

The microemulsion, which is consisted of JCO: ethanol/surfactant: diesel mixtures (JCO: E/S: D), was mixed by vortex then kept at room temperature to allow the systems reach equilibrium. Accordingly, phase behavior on transparent, clear, and homogeneous was then observed. Phase behavior had also conducted at various temperatures in order to evaluate the temperature stability of microemulsion fuel.

3.3.3 Study of phase behavior by pseudo-ternary phase diagram

In order to investigate phase behavior and miscibility of the microemulsion fuel, a ternary phase diagram was modified to be pseudo-ternary phase diagram. The principles of ternary phase diagram representing three-component system were applied. The pseudo-ternary phase diagram was an equilateral triangle which consisted of three vertices of three components. Two vertices at the bottom of triangle represented JCO and diesel (D) at the left side and the right side, respectively, while the upper vertex represented the ethanol/surfactant mixtures (E/S). The composition at each point in a pseudo-ternary phase diagram illustrated the volume percent of the three components (A, B, C) as shown in Figure 3.2.

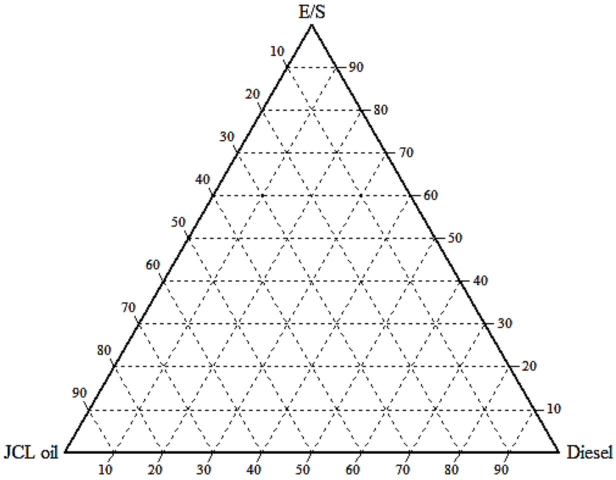


Figure 3.2 A pseudo-ternary phase diagram

3.3.4 Temperature stability test

All of the MFs from the single surfactant systems obtained, from the previous study were kept in incubator for two days at 20, 25, 30, and 40 ºC to observe their stability on transparent phase which examined by visual inspection. The wide range of temperature stability would be one of criteria in addition to kinematic viscosity for selection of the single surfactant system in the further study. The selected proportion of the single surfactant systems were repeat prepared as mixed surfactant systems by adding anionic surfactant. The concentrations of anionic surfactant to nonionic surfactant at 0.1 %wt was conducted on this part of experiment. Then the selected formulation of the MFs with mixed surfactant would be evaluated for physical stability as the same procedure as MFs with single surfactant. It was expected that the MF with mixed surfactant would have wider range of temperature stability than those of single surfactant.

3.3.5 Properties of microemulsion fuel test

The MFs which had the physical stability in the wide range of temperature would be examined for the kinematic viscosity. The MFs that meet the kinematic viscosity of biodiesel standard (range of 3-5 cSt.) were chosen for the evaluation their properties for other parameters by following the standard testing method as shown in Table 3.4 and then compared with the biodiesel standard (Table 2.3 in Chapter 2).

Those parameters were examined at the Biofuel Testing Laboratory of the National Metal and Materials Technology Center (MTEC).

Table 3.4 The parameters and testing methods of the microemulsion fuels

Properties	Instruments	Methods
Acid value (mgKOH/g)	Tirando Automatic Potentiometric Titrator	ASTM D664[a]
Cloud point (°C)	ISL CPP 5Gs Cloud & Pour Point Tester	ASTM D2500[a]
Density (kg/m^3)	Anton Paar DMA-4500 Digital Density Meter	ASTM D4052[a]
Flash point (°C)	APM-7 Pensky-Martens Closed Cup Tester	ASTM D93[a]
High heating value	AC-350 Automatic Calorimeter	ASTM D240
Kinematic viscosity (cSt)	D445-E20L Kinematic Viscometer	ASTM D445[a]
Oxidation stability	Rancimat	EN 14112[b]
Water content (ppm)	Karl Fischer Coulometer	ASTM D6304[a]

[a]: American Standard Testing Method
[b]. European Standard Testing Method

3.3.6 Performances tests of microemulsion fuel

The experimental testing for the selected MFs' performance and emission was carried out at King Mongkut's University of Technology North Bangkok laboratories. The four selected MF for testing in this part were:

- MF-E5 (20:75:5 of JCO:D:E/S)
- MF-E5 (20:75:5 of JCO:D:E)
- MF-E10 (20:70:10 of JCO:D:E/S)
- Diesel (PTT Public Company Limited)

The engine used is a diesel engine, and tests were performed using a four-stroke, two-cylinders, water cooled and indirect injection diesel engine shown in Appendix B, Figure B-1 and the engine specifications are listed in Table 3.5. The schematic of the experimental set up is shown in Figure 3.3 and the performance parameters are shown in Table 3.6 In addition, all of the figure's real experimental set up are shown in Appendix B.

In order to measure the engine power, the engine was coupled to hydraulic dynamometer which was loaded by water. The engine speed was measured by an electromagnetic speed sensor. Meanwhile, the fuel consumption rate of the engine was determined with an electronic weighing scale that was readability 0.1 g and an electronic chronometer having a sensitivity of 0.1 s.

All tests were performed under steady state condition by running the engine with diesel fuel prior to obtain the characteristic of the engine. Then the same procedure was maintained for each MFs fuel. In order to carry out engine performance tests, all tests were performed at two-load conditions consist of low load (25% of accelerator) and medium load (50% of accelerator) and the engine speed were studied in range of 900 – 1300 rpm for low load and 900 – 2100 rpm for medium load.

Table 3.5 The specification of the diesel engine in the experiment

Make	**Engine**
Cylinder number	2
Type	Four stroke, indirect injection, water cooled
Displacement	570 cc
Charge of the air	Naturally aspirated

Table 3.6 The performance parameters and procedures for fuel

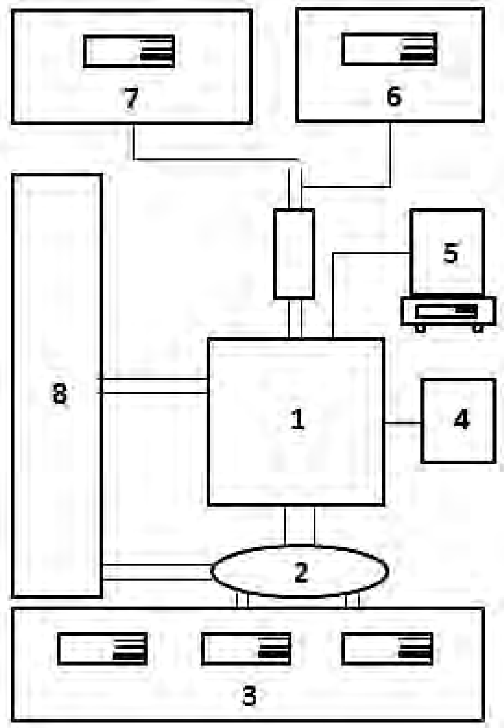
Performance Parameters	**Procedure**
Power	Testing the performance of the engine, i.e, the power of the electrical generator
Brake specific fuel consumption	Measuring the consumed fuel during operation
Exhaust gas temperature	Measuring the temperature at the exhaust nozzle
Exhaust gas	Using an exhaust gas analyzer

3.3.7 Emission measurements of microemulsion fuel

The exhaust emission such as CO, CO_2, and smoke were measured as shown in Table 3.7 by using HORIBA gas analyzer and Diesel Smoke meter shown in Appendix B (Figure B-6 and B-7, respectively). The emissions analyzer had been conducted at 25% low load and 50% middle load conditions and speed as same as performance tests by gas analyzer probe on the pipe of gas exhaust.

Table 3.7 Types of emission gas examination.

Exhaust Gas	Units
Carbon monoxide (CO)	%vol
Carbon dioxide (CO_2)	%vol
Black smoke	%



1. Two-cylinder diesel engine (Figure B-1)	5. Balance for fuel consumption (Figure B-5)
2. Hydraulic dynamometer (Figure B-2)	6. Emission detector (Figure B-6)
3. Dynamometer’s controller (Figure B-3)	7. Smoke meter (Figure B-7)
4. Accelerator’s controller (Figure B-4)	8. Cooling tower

Figure 3.3 Schematic outline of the experimental setup

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Phase behavior of microemulsion fuel

The microemulsion fuel, which is homogenous mixture, was obtained in pseudo-ternary phase diagram as shown in Figure 4.1. The left side and right side of triangle represent *Jatropha curcas* oil (JCO) and diesel (D), respectively, while the upper vertex represent the mixture of ethanol and surfactant (E/S). The phase behavior of JCO, ethanol/LS and diesel is illustrated in this session which will be discussed into 3 main parts.

The first part presents the effects of EO group from three different single nonionic surfactants (LS1, LS3, and LS7) which possess different of Hydrophili-Lipophile Balance (HLB) number. The optimum system obtained from the first part would be further use for the experiment in the second part. The second part focuses on the effect of anionic surfactant addition into the system to become mixed surfactant system. Then the third part, it describes the effect of temperature change on their phase behavior for both single and mixed surfactant systems which is considered as temperature stability of a fuel.

4.1.1 Effects of EO group on microemulsion fuel

The surfactant with different EO group; LS1, LS3 and LS7 were mixed with ethanol at ratio of 3:1 (E/S) and mixed with JCO and diesel were compared for their phase behavior by pseudo-ternary phase diagrams. In the other word, these pseudo-ternary phase diagrams were prepared from various proportions of the three components; JCO, diesel and E/S in order to identify the effect of different number of EO group or HLB of the surfactant (see Figure 4.1). Figure 4.1 shows obviously the role of surfactant on enhancement of miscibility of the two oil; JCO and diesel with ethanol since single phase area of the system without are much smaller than those of the system with surfactant. Likewise, Xu et al. (2001) have found that decaglycerol mono-oleate (MO750) as a nonionic surfactant could stabilize vegetable oil-ethanol, and summarized that the stability of emulsions depended on the ethanol content and concentration of MO750. Once focusing on HLB or EO group of the surfactant in the system, it found that LS1 and LS3 are lipophilic surfactant having low both EO group and HLB, show capability to facilitate JCO, diesel and alcohol to present in a single phase assuming to be water in oil (W/O) microemulsion. From this reason both LS1 and LS3 are able to generate a single phase from wider range of proportion compared to the system with LS7. However, in this work the preference proportions was the systems that contained at 20% and E/S component at 5% and 10%,20%:5%:75% and 20%:10%:70% for JCO, E/S and diesel-were found to be a single phase for all surfactants (LS1, LS3 and LS7). Thus, MFs at these ratios for all surfactant were selected to determine the effects of behavior on different temperature.

4.1.2 Effects of mixed surfactant on temperature stability

Nonionic surfactant is generally sensitive to temperature. At a certain temperature for a nonionic surfactant known as cloud point, phase separation or cloud phase may be occurred. In many cases, anionic surfactant is mixed with nonionic surfactant in order to get more temperature insensitive product (Rosen, 2004). Therefore this experiment was conducted to evaluate the MFs from the systems obtained from phase behavior of single nonionic surfactant and from the systems of mixed surfactant. Figure 4.2 shows the phase behavior of the systems with single nonionic surfactants at the temperature range 20 ºC to 40 ºC compared with the system without surfactant. The results show that temperature in this range slightly affected to the single phase area either the system without surfactant or with surfactant. In addition, once anionic surfactant (AOT) was added in the selected system, the single phase of the MFs still maintained as expected (Table 4.1). So, it can be concluded that our system either single or mixed surfactant are relatively stable within the temperature range from 20 to 40 ºC. Subsequently, some of the MFs with meet the criteria which are critical parameter on fuel such as kinematic viscosity and water content are considered to further property test. Thus, the 14 proportions of MFs including the ones without surfactant, with single nonionic surfactant and mixed surfactant were selected as described in Table 4.1.

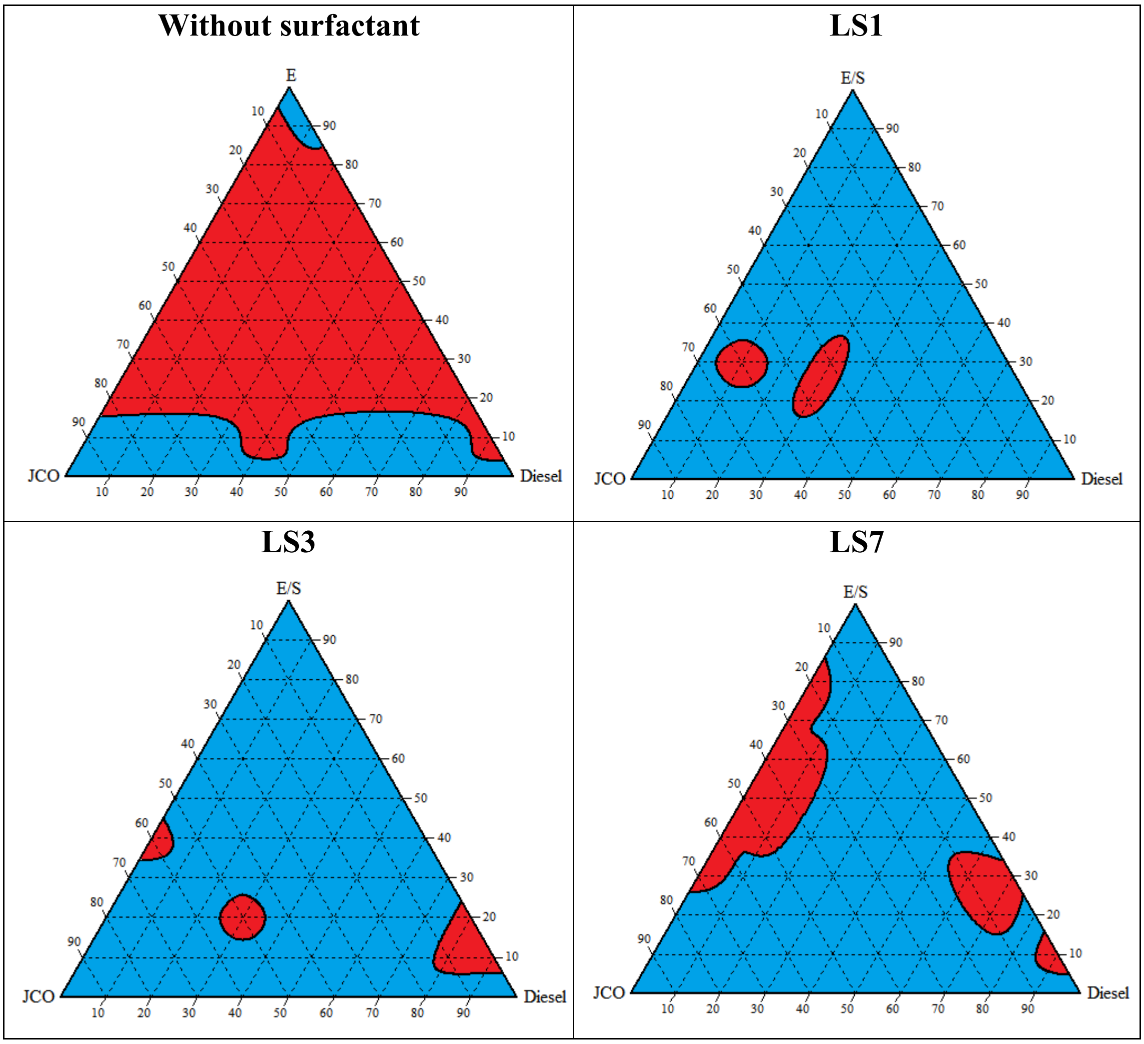


Figure 4.1 The comparison of phase behavior on JCO-Diesel-E/S by differing EO number of nonionic surfactant at room temperature; red color represents the area of phase separation, blue color represents the area of single phase

Table 4.1 The composition of the interested MFs with meet viscosity standard

Systems	Composition (vol%)			Type of surfactant
	JCO	99.9%Ethanol	C-Diesel	
MF(E5)-N	20	5	75	-
MF(E10)-N	20	10	70	-
MF(E5)-S1	20	5	75	LS1
MF(E5)-S3	20	5	75	LS3
MF(E5)-S7	20	5	75	LS7
MF(E10)-S1	20	10	70	LS1
MF(E10)-S3	20	10	70	LS3
MF(E10)-S7	20	10	70	LS7
MF(E5)-M1	20	5	75	LS1+AOT
MF(E5)-M3	20	5	75	LS3+AOT
MF(E5)-M3	20	5	75	LS7+AOT
MF(E10)-M1	20	10	70	LS1+AOT
MF(E10)-M3	20	10	70	LS3+AOT
MF(E10)-M7	20	10	70	LS7+AOT

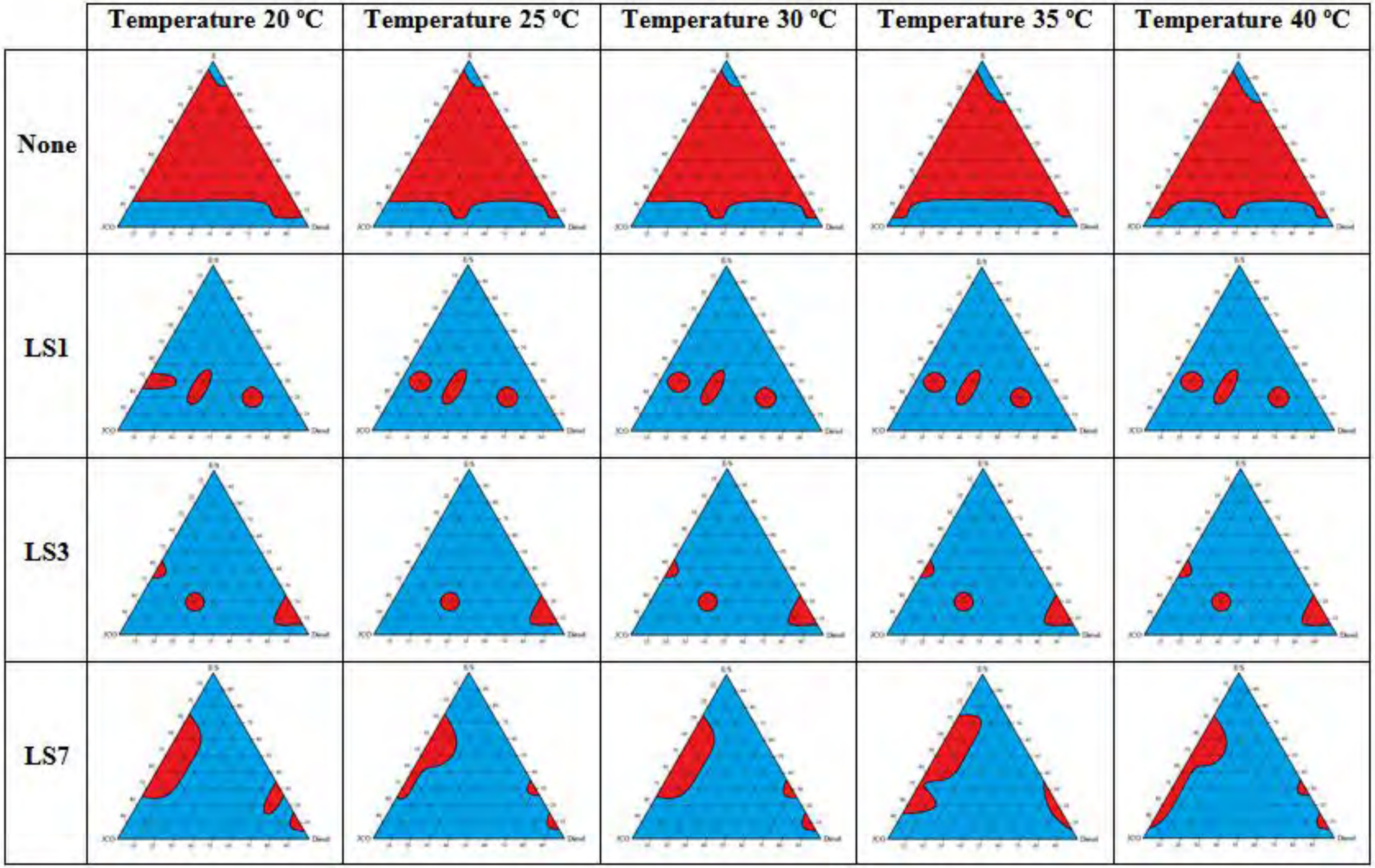


Figure 4.2 Phase behavior of the microemulsion fuels with single surfactant system at different temperature.

4.2 Properties of the microemulsion fuel

In this part of the study, the properties of selected MFs (14 systems) were analyzed consisting of optical, acid value, cloud point, density, flash point, kinematic viscosity, oxidation stability, and water content. In addition, crude JCO, 99.9% ethanol and commercial diesel were evaluated for their properties as original components of the microemulsion fuels as shown in Table 4.2. The results of the 14 selected MFs in Table 4.3 and Table 4.4 for 5% and 10% E/S component, respectively. The characteristics of the microemulsion fuels were compared with biodiesel standard.

Table 4.2 Properties of original components of microemulsion fuels

Parameter	**Unit**	**Original compounds of a microemulsion fuel**		
		Crude JCO	**99.9% Ethanol**	**Diesel**
Optical	-	Clear	Clear	Clear
Acid value	mgKOH/g	4.73±0.02	0.06±0.00	0.07±0.01
Cloud point	°C	2.1	< -35.0	9.7
Density@ 15°C	g/mL	0.917±0.00	0.796±0.00	0.831±0.00
Heating value	MJ/kg	39.35±0.07	28.95±0.35	45.60±0.14
Flash point	°C	> 260	12	61
Kinematic vis.@ 40°C	cSt	34.62±0.31	1.05±0.01	2.96±0.01
Oxidation stability	hr	13.05±0.13	-	-
Water content	ppm	929.00±6.08	1873.75±148.00	67.25±4.03

Table 4.3 Properties of the microemulsion fuels comprise of 5 %vol ethanol

Parameter	Unit	Biodiesel std.	Microemulsion fuels						
			MF (E5)-N	**MF (E5)-S1**	**MF (E5)-S3**	**MF (E5)-S7**	**MF (E5)-M1**	**MF (E5)-M3**	**MF (E5)-M7**
Optical	-	Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear
Acid value	mgKOH/g	0.50	0.94±0.07	0.94±0.01	0.94±0.00	0.92±0.03	0.94±0.00	0.93±0.01	0.95±0.01
Cloud point	°C	-	11.0	11.2	11.1	11.2	11.0	11.4	11.2
Density @ 15°C	g/mL	0.860-0.900	0.836±0.00	0.847±0.00	0.848±0.00	0.849±0.00	0.847±0.00	0.848±0.00	0.849±0.00
Flash point	°C	120	15	17	17	17	15	15	15
High heating value	MJ/kg	-	43.35±0.07	43.40±0.00	43.40±0.00	43.35±0.07	43.30±0.14	43.35±0.07	43.25±0.07
Kinematic vis. @ 40°C	cSt	3.5-5.0	4.55±0.05	4.43±0.04	4.55±0.04	4.63±0.10	4.56±0.01	4.6124±0.02	4.6584±0.08
Oxidation stability	hr	10	23.43±0.39	14.66±0.48	13.80±0.18	14.36±0.93	20.84±1.40	19.79±0.78	18.55±0.26
Water content	ppm	500	425.43±3.18	430.55±3.89	410.15±9.55	399.60±12.02	453.70±14.00	443.15±16.90	419.05±38.11

Remark MF(E5)-N is Microemulsion fuel-ethanol 5%,

MF(E5)-S1 is Microemulsion fuel-ethanol 5% with single surfactant LS1,

MF(E5)-S3 is Microemulsion fuel-ethanol 5% with single surfactant LS3,

MF(E5)-S7 is Microemulsion fuel-ethanol 5% with single surfactant LS7,

MF(E5)-M1 is Microemulsion fuel-ethanol 5% with mixed surfactant LS1,

MF(E5)-M3 is Microemulsion fuel-ethanol 5% with mixed surfactant LS3, and

MF(E5)-M7 is Microemulsion fuel-ethanol 5% with mixed surfactant LS7

Table 4.4 Properties of the microemulsion fuels comprise of 10 %vol ethanol

Parameter	Unit	Biodiesel std.	Microemulsion fuels						
			MF (E10)-N	MF (E10)-S1	MF (E10)-S3	MF (E10)-S7	MF (E10)-M1	MF (E10)-M3	MF (E10)-M7
Optical	-	Clear	Clear	Clear	Clear	Clear	Clear	Clear	Clear
Acid value	mgKOH/g	0.50	0.94±0.00	0.96±0.01	0.95±0.00	0.95±0.01	0.96±0.01	0.95±0.01	0.97±0.00
Cloud point	°C	-	11.4	11.2	11.1	11.4	11.3	11.4	11.3
Density @ 15°C	g/mL	0.860-0.900	0.834±0.000	0.846±0.000	0.847±0.000	0.849±0.000	0.847±0.000	0.848±0.000	0.849±0.000
Flash point	°C	120	13	13	13	13	13	13	13
High heating value	MJ/kg	-	43.70±0.00	42.45±0.21	42.55±0.07	42.40±0.00	42.50+0.00	42.50±0.00	42.25±0.07
Kinematic vis.@ 40°C	cSt	3.5-5.0	4.23±0.04	4.31±0.00	4.34±0.02	4.38±0.01	4.33±0.03	4.34±0.04	4.43±0.09
Oxidation stability	hr	10	21.79±1.17	11.12±0.49	11.02±0.20	10.36±0.54	16.68±0.80	15.53±0.57	14.42±1.09
Water content	ppm	500	483.54±14.54	500.55±0.92	510.40±6.65	517.50±5.80	583.60±5.66	609.65±9.55	550.40±1.70

Remark MF(E10)-N is Microemulsion fuel-ethanol 10%,

MF(E10)-S1 is Microemulsion fuel-ethanol 10% with single surfactant LS1,

MF(E10)-S3 is Microemulsion fuel-ethanol 10% with single surfactant LS3,

MF(E10)-S7 is Microemulsion fuel-ethanol 10% with single surfactant LS7,

MF(E10)-M1 is Microemulsion fuel-ethanol 10% with mixed surfactant LS1,

MF(E10)-M3 is Microemulsion fuel-ethanol 10% with mixed surfactant LS3, and

MF(E10)-M7 is Microemulsion fuel-ethanol 10% with mixed surfactant LS7

4.2.1 Optical

This property obtained from visual observation in order to examine physical appearance of MFs product at our selected proportion. It found that for all 7 systems with 5% E/S component and another 7 systems with 10% E/S component, were clear, homogenous single phase product in all temperature range from 20 to 40 °C. So, they were satisfied with the first preference characteristics of fuel. This can be assumed that for the systems without surfactant, possible to solute with three solvents by without microemulsion phenomena. While for the systems with any surfactant can be also assumed that was possible to be occurred microemulsion.

4.2.2 Acid number

The acid number indicates the amount of free acid present in the fuel as an indicator of fuel degradation and corrosive. In this study, only main source of free fatty acid of MFs is from JCO (see Table 4.2). From 14 samples of MFs were contain equal 20% JCO, so it is not surprising that for all selected MFs showed insignificantly different value of acid number which ranged from 0.94 to 0.97 mg KOH/g (Figure 4.3 for single surfactant and Figure 4.4 for mix surfactant). This has been confirmed by the analysis of variance. This acid number is around 20% of the acid number of JCO, so it may conclude that JCO mainly contribute free acid to MFs. This can be explain by the fact that JCO possesses a triglyceride structure which can easily convert to free fatty acid by oxidation reaction (Jain and Sharrna, 2010). In addition, the different EO group in the surfactant did not affect acid number of the MFs. However, increasing free acid in oil product is very depending on age of oil and storage condition. As shown in Table 4.3 and 4.4, the maximum acid number specified by ASTM standard D6751 for biodiesel is 0.50 mg KOH/g. While MFs were acid number higher than the maximum limit of biodiesel standard around 2 times. As the results, the presence of MFs may harm injection systems and other metallic components (the Worldwide Fuel Charter Committee, 2009). Therefore, JCO preferred to stabilize fatty acid, increase oxidation stability by adding an antioxidant or keep the MFs in suitable condition may be necessary.

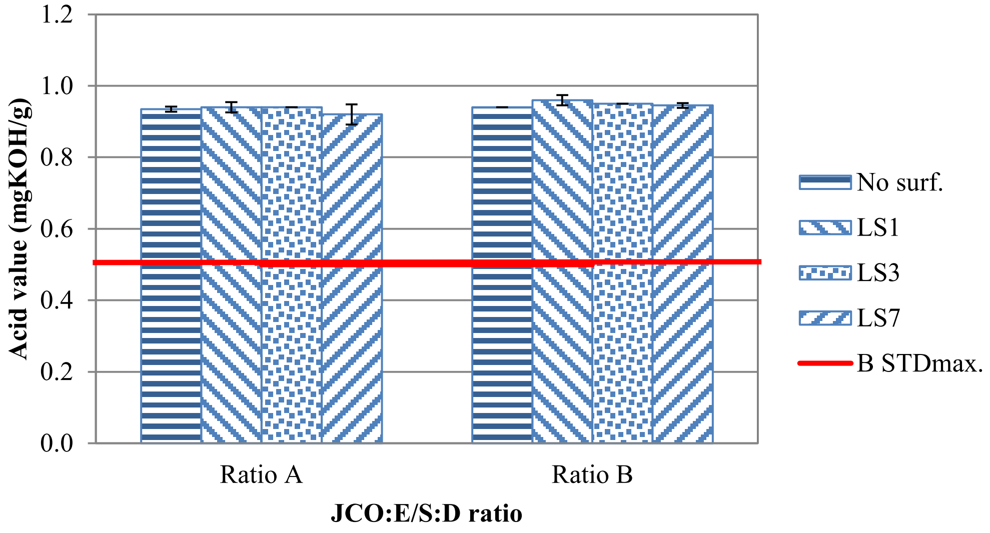


Figure 4.3 Acid number of microemulsion fuels at JCO:E/S:D ratios of (A) 20:5:75 and (B) 20:10:70 using the single surfactant systems

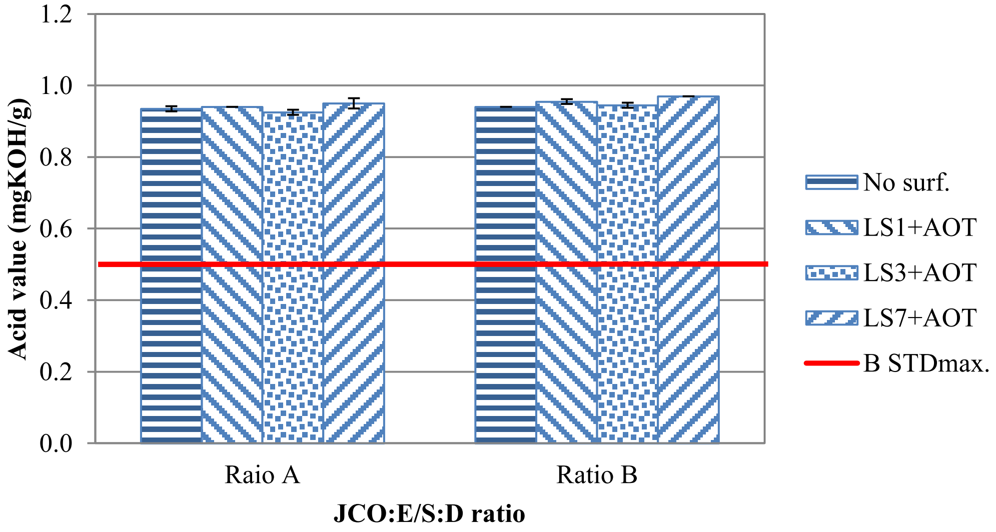


Figure 4.4 Acid number of microemulsion fuels at JCO:E/S:D ratios of (A) 20:5:75 and (B) 20:10:70 using the mix surfactant systems

4.2.3 Cloud point

The cloud point is the temperature at which the fuel becomes cloudy due to the formation of crystals. It may cause blockage of the fuel lines and filters, leading to fuel starvation, problems of starting, driving, and engine damage due to inadequate lubrication (Erhan et al., 2006). As the result, the cloud points for the MFs fuels are presented in Figure 4.5 and Figure 4.6. All the MFs were found to have the similar cloud point around 11.2 °C. While the cloud points of the three original components presented in Table 4.2 are -35.0 °C, 2.1 °C and 9.7 °C for ethanol, JCO and commercial diesel respectively. Due to the high proportion of diesel in MFs sample, all MFs have the cloud point close to that of diesel. Thus, the result showed that the present of ethanol, JCO and surfactant did not significantly affect the cloud point of the MFs which correspond to the analysis of variance, that a number EO group of surfactant and surfactant systems were not different results. Even though different nonionic surfactant may have different cloud point temperature, the small amount of surfactant (less than 3%) would not affect overall cloud point of the products. Moreover, Ajav and Akingbehin (2002) revealed their study on diesel-ethanol's properties that the cloud point of the diesel-ethanol mixture was close to that of diesel as a major phase.

The limit of cloud point by ASTM standard D2500 for biodiesel is not specified. Assuming the average lowest and highest temperatures of Thailand in 30 years (B.E. 2514-2543 from Thai Meteorological Department), the MFs' cloud point at around 11 ºC should not be a problem for its use. However, It was recommended by engine manufacturers that cloud point should be below the temperature of use and not more than 60 °C above all pour point (Atabani et al., 2012).

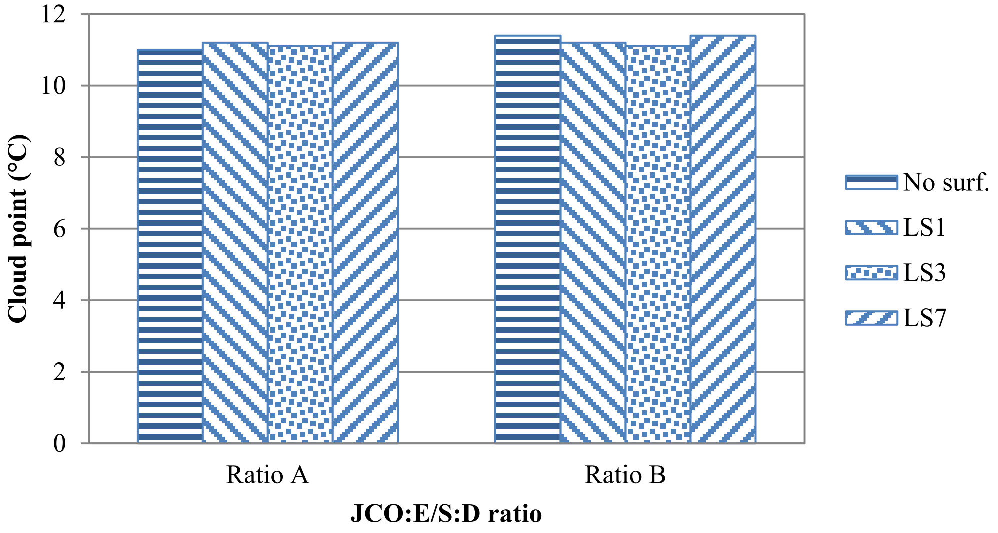


Figure 4.5 Cloud point of microemulsion fuels at JCO:E/S:D ratios of (A) 20:5:75 and (B) 20:10:70 using the single surfactant systems

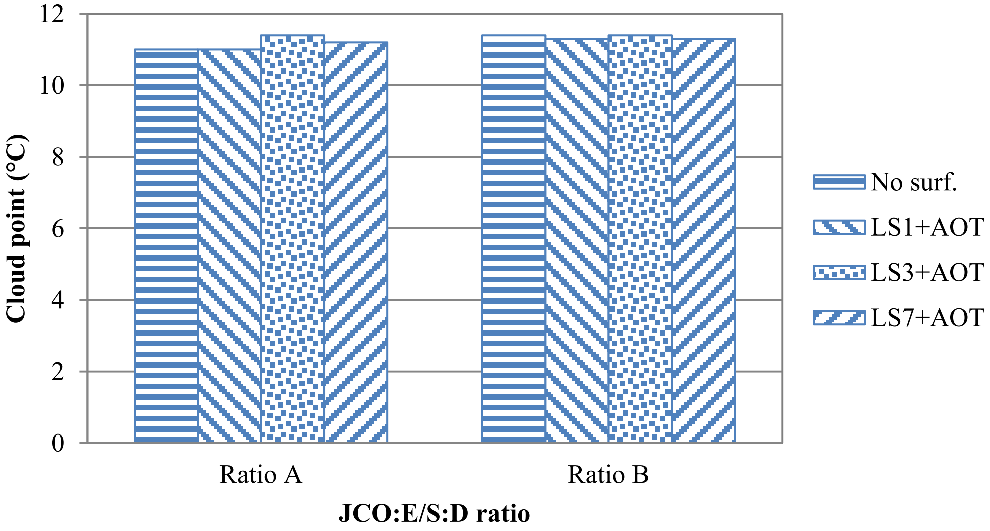


Figure 4.6 Cloud point of microemulsion fuels at JCO:E/S:D ratios of (A) 20:5:75 and (B) 20:10:70 using the mix surfactant systems

4.2.3 Density

The fuel density is defined as the ratio of mass of the fuel to the volume of the fuel at a reference temperature of 15 °C. The greater the fuel density as well as the greater the mass of fuel that can be stored. Fuel density also generally increases with increasing molecular weight of the component atoms of the fuel molecules. The relative density of the MFs at different composition and the number EO group of surfactant are shown in Figure 4.7 and Figure 4.8, while the density of the three original fuels is given in Table 4.2. The density of mixed fluid generally follows the mixing rule. As a consequent, the density of all the MFs was around 0.840 g/mL which is close to diesel's density the highest proportion component in MFs. Similar, the Ajav and Akingbehin (2002) observed that the percentage of ethanol in the diesel was increased the relative densities decreased, and Ribeiro et al. (2007) reviewed that the presence of ethanol in diesel reduced the density. However, once we compared among MFs, the one without surfactant has significantly lower than those with surfactant. This is on the fact that all surfactant LS1, LS 3 and LS7 have higher molecular weight than that of ethanol. From the analysis of variance, the differences at number EO group of surfactant and surfactant systems were slightly different.

As shown in Table 4.3 and 4.4, the proper range of density specified by ASTM standard D1298 for biodiesel minimum at 0.860 to maximum 0.900 g/mL, while MFs were density lower than the minimum limit of biodiesel standard. However, biodiesel standard generally tends to have higher density, in range of 860 to 0.900 g/mL, compare to a typical range of 800 to 869 g/mL for mineral diesel (Demirbas, 2009). Accordingly, the range of specification is merely recommended for biodiesel to calculate the quantity and assess ignition quality. Moreover, the higher mass of fuel would give higher energy available for work output per unit volume (Rao, 2011).

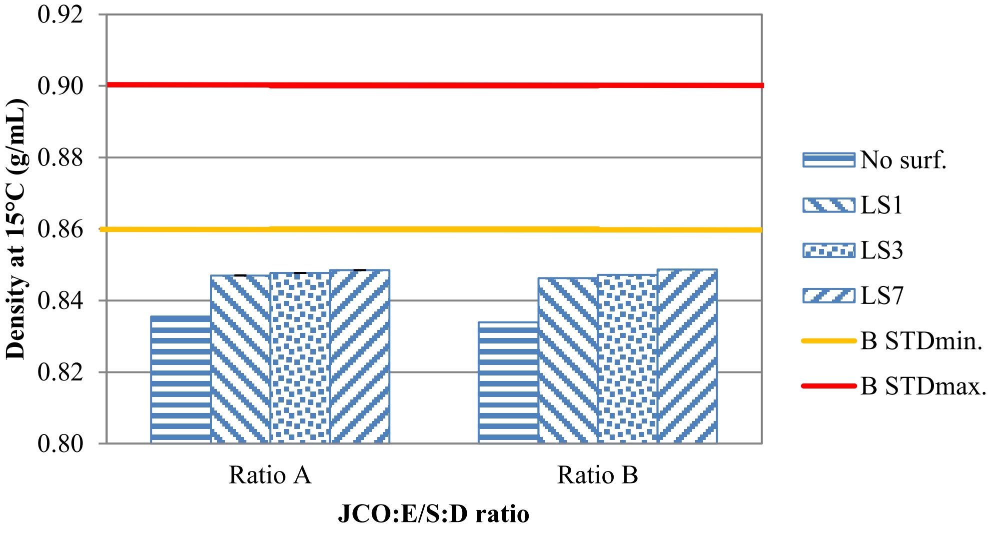


Figure 4.7 Density at 15°C of microemulsion fuels at JCO:E/S:D ratios of (A) 20:5:75 and (B) 20:10:70 using the single surfactant systems

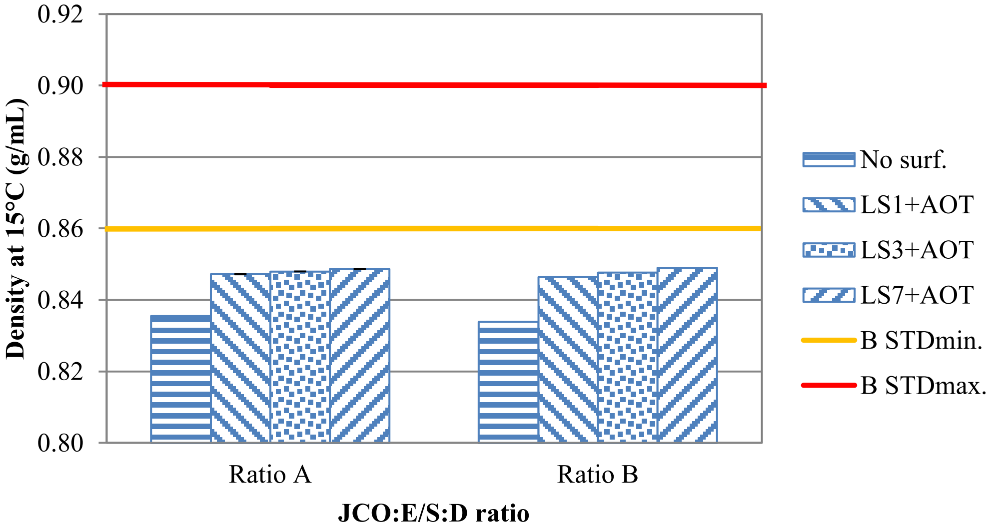


Figure 4.8 Density at 15°C of microemulsion fuels at JCO:E/S:D ratios of (A) 20:5:75 and (B) 20:10:70 using the mix surfactant systems

4.2.4 Flashpoint

Flashpoint is the lowest temperature at which the vapor pressure of the fuel is sufficient to produce a flammable mixture in the air above the fuel surface with in vessel. As shown in Figure 4.9 and Figure 4.10, MF(E5), which is the microemulsion fuels with 5% ethanol (without surfactant), was approximately 15 °C flashpoint while MF(E10), which is the microemulsion fuels with 10% ethanol, was 13 °C flashpoint. The temperatures were obtained from all MFs were below ambient room temperature (approximately 27.5 °C). All MFs had flashpoint values much lower than those of neat diesel and JCO (61 °C and upper 260 °C, respectively as presented in Table 4.2) though diesel and JCO are mainly compositions. Likewise, 5% and 10% of ethanol with all number EO group and systems of both systems single and mixed surfactants (S1, S3, S7, M1, M3, and M7) in MFs had flashpoints close to the one of pure ethanol. This result agrees with Li et al. (2005) that just 5 percent of ethanol in diesel was able to dominate the decrease of flashpoint to 20 ºC, and similar results reported by Ribeiro et al. (2007) that the presence of ethanol in diesel reduced the flashpoint. The result indicates that high proportion of JCO oil and diesel were not significantly affected to flashpoint. Ethanol is only the component to signify the flash point of the fuels.

As shown in Table 4.3 and 4.4, the maximum flashpoint specified by ASTM standard D93 for biodiesel is 100°C, while all MFs had flash point are lower than the minimum limit of biodiesel standard around 8 times. In guidelines established by the National Fire Protection Agency (NFPA) in the US for safe storage and handling of flammable liquids are classified fuels into two classes. Class I is liquids as ethanol and gasoline have flashpoints below 37.8 °C, whereas Class II is liquids as biodiesel and diesel fuel have flashpoints above 37.8 °C (Hansen et al., 2005). Therefore, the MFs were classified into Class I liquids fuel because of their flashpoint, and they are required for proper safety during handling.

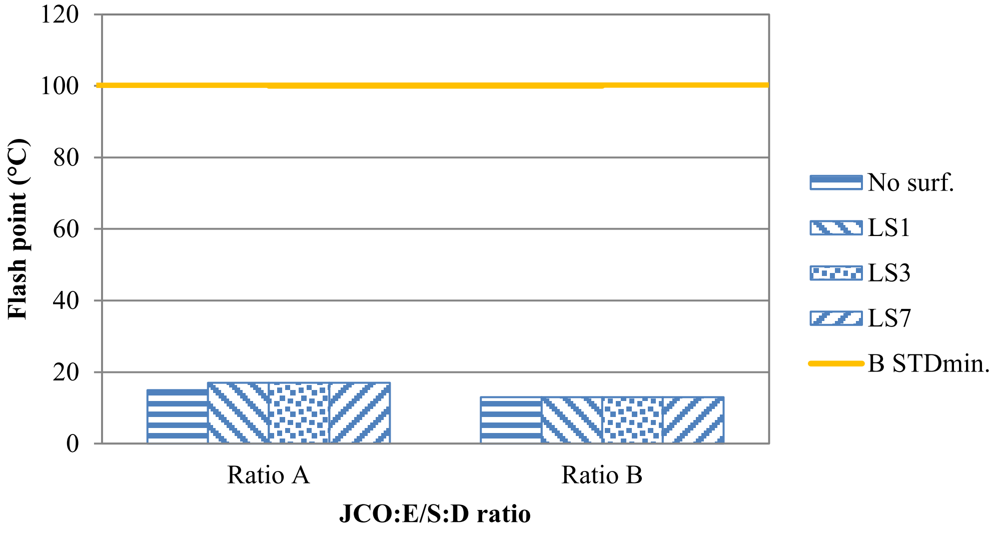


Figure 4.9 Flashpoint of microemulsion fuels at JCO:E/S:D ratios of (A) 20:5:75 and (B) 20:10:70 using the single surfactant systems

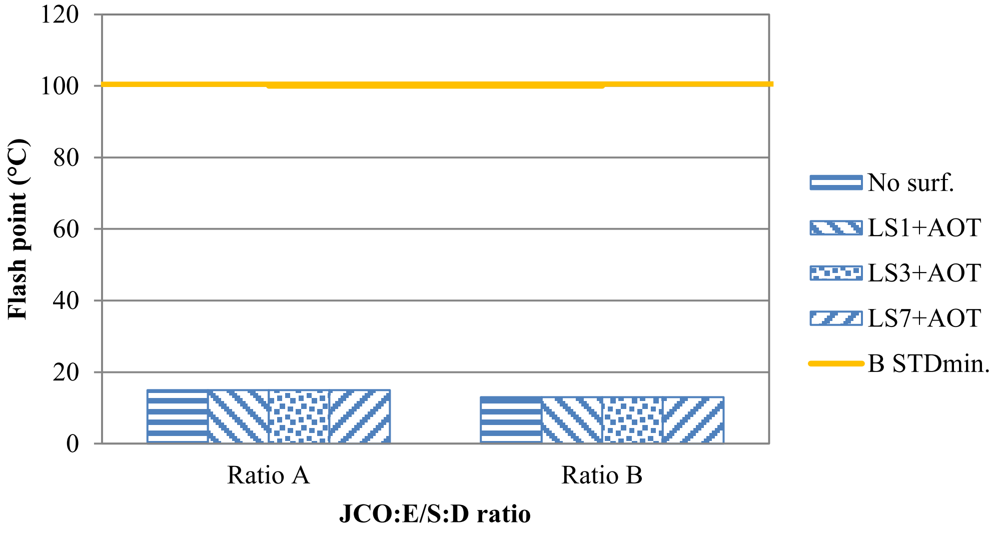


Figure 4.10 Flashpoint of microemulsion fuels at JCO:E/S:D ratios of (A) 20:5:75 and (B) 20:10:70 using the mix surfactant systems

4.2.5 High heating value

High or gross heating value is the energy content of fuel per unit mass (MJ/kg) that amount of heat produced and taken into account with the latent heat of vaporization of water in complete combustion. It is indicated the energy potential content. Results of three original fuels were showed in Table 4.2, the greatest amount of energy was diesel (45.60 MJ/kg) followed by JCO (39.35 MJ/kg), and ethanol (28.95 MJ/kg), respectively. While the study of the various ethanol percentage showed that MF(E5) exhibited the greater specific combustion heat of 43.25-43.40 MJ/kg more than 42.25-42.70 of MF (E10) as shown in Figure 4.11 and Figure 4.12. Compared with diesel, the study of Hansen et al (2005) mentioned that the energy content of ethanol-diesel blends decreased by approximately 2% for each 5% of ethanol added, while this study that of MFs decreased by approximately 7% for each 5% ethanol added. Thus, from these results can be claimed that the amounts of heat depends on percent ethanol. However, the results of this study should be considered as the mixing rule. Meanwhile from the analysis of variance, the differences at number EO group of surfactant and surfactant systems were non-significant.

The limit of heating value by ASTM standard D240 is not specified. Gross heat of combustion of commercial diesel was about 45-46 MJ/kg, while biodiesel from jatropha oil was about 42 MJ/kg (Okullo et al., 2012). However, it can be performed in diesel engine to investigate performance, combustion, and emission by without modification (Sahoo et al., 2009; Rao, 2011; Chauhan et al., 2012)

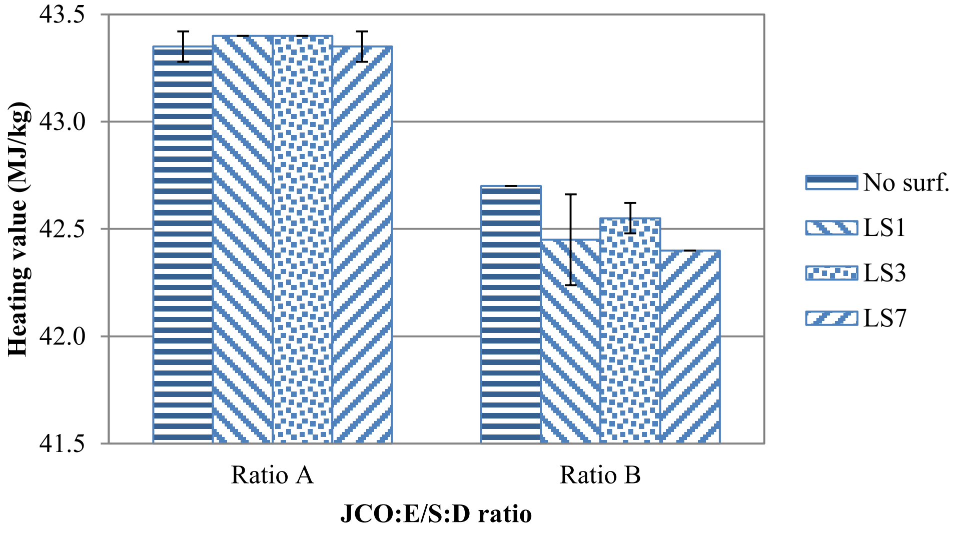


Figure 4.11 Heating value of microemulsion fuels at JCO:E/S:D ratios of (A) 20:5:75 and (B) 20:10:70 using the single surfactant systems

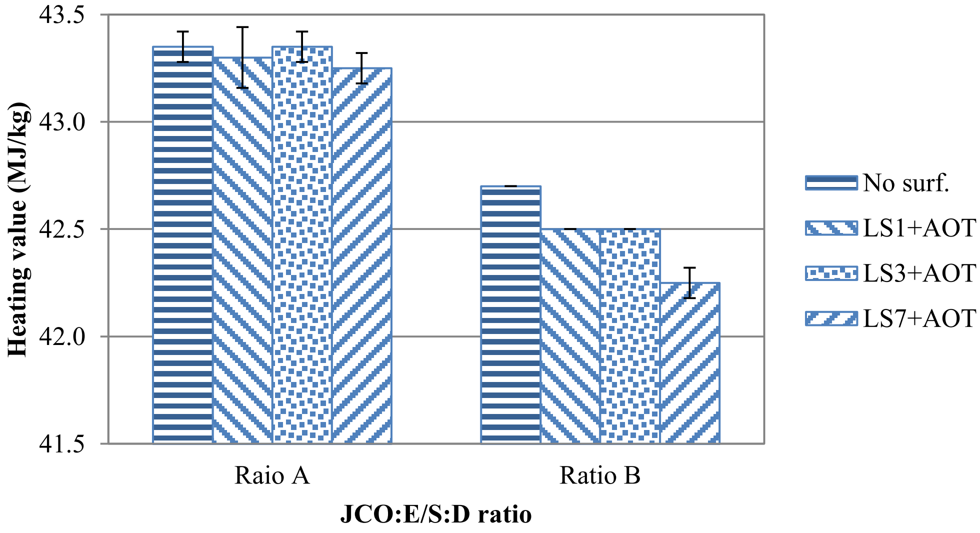


Figure 4.12 Heating value of microemulsion fuels at JCO:E/S:D ratios of (A) 20:5:75 and (B) 20:10:70 using the mix surfactant systems

4.2.5 Kinematic viscosity

Viscosity is the most important physical characteristic of any fuel as it indicates the ability of material to flow (Haddad and Watson., 1984; Ali and Hanna., 1994). It influences the degree of pre-heat required for the operation of the fuel injection equipment and spray atomization. As these parameters have a significant effect on the combustion process. The results show that the high viscosity at 40 °C of JCO, which was 34.6219 cSt, had been drastically decreased by partial substitution of diesel oil and ethanol (2.9631 and 1.0522 cSt respectively). In other word, by using JCO without the process of transesterification, to mix with diesel is required in order to make kinematic viscosity suitable as biodiesel standard to be used in the diesel engine.

The viscosity of the MFs measured at temperature 40 °C is as presented in Figure 4.13 and Figure 4.14. The results showed viscosity values, MF(E5), which is the microemulsion fuels with 5% ethanol, was approximately 4.5 cSt. As MF(E10), which is the microemulsion fuels with 10% ethanol, was approximately 4.3 cSt. From the results, the viscosity of All MFs was decreased on increasing the percentage of ethanol. The differences in the number EO group on surfactant (LS1, LS3, and LS7) were found to be slightly different on kinematic viscosity.

There was however no significant difference in the surfactant systems (single nonionic and mix anionic surfactants). Therefore, it can be noted that the viscosity of MFs is dependent on the viscosity and the ratio of JCO, ethanol, and diesel. Likewise, Li et al. (2005) found that diesel blended with 5 to 25 percent of ethanol decreased viscosity diesel-ethanol until lower than the minimum requirements for diesel fuel, and Ribeiro et al. (2007) also revealed that the presence of ethanol in diesel reduced the viscosity. For this study, two proper MF ratios at 20% JCO with 5% or 10% ethanol and with 75% or 70% diesel with any the surfactants have the viscosity close to the ASTM minimum standard.

The standard test method for kinematic viscosity, ASTM standard D445, was used to measure the viscosity of MFs as shown in Table 4.3 and 4.4. The proper range of viscosity specified for biodiesel standard in Thailand is minimum at 3.5 cSt to maximum at 5.0 cSt; likewise, the viscosity of all MFs are closed maximum specifications. Accordingly, all MFs are ensured that fuel injection system durability is not trouble relative to diesel fuel usage and that engine is able to start reliably when hot.

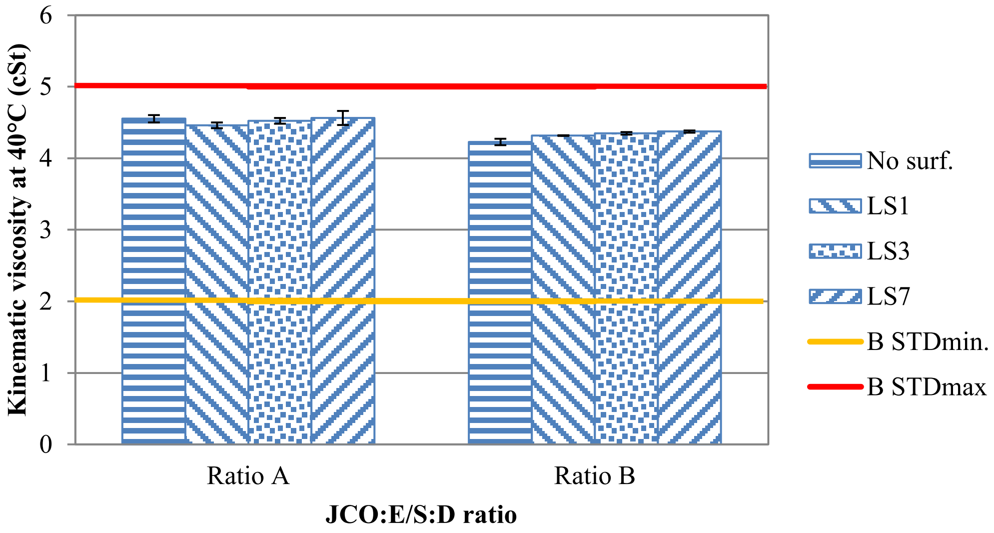


Figure 4.13 Kinematic viscosity at 40°C of microemulsion fuels at JCO:E/S:D ratios of (A) 20:5:75 and (B) 20:10:70 using the single surfactant systems

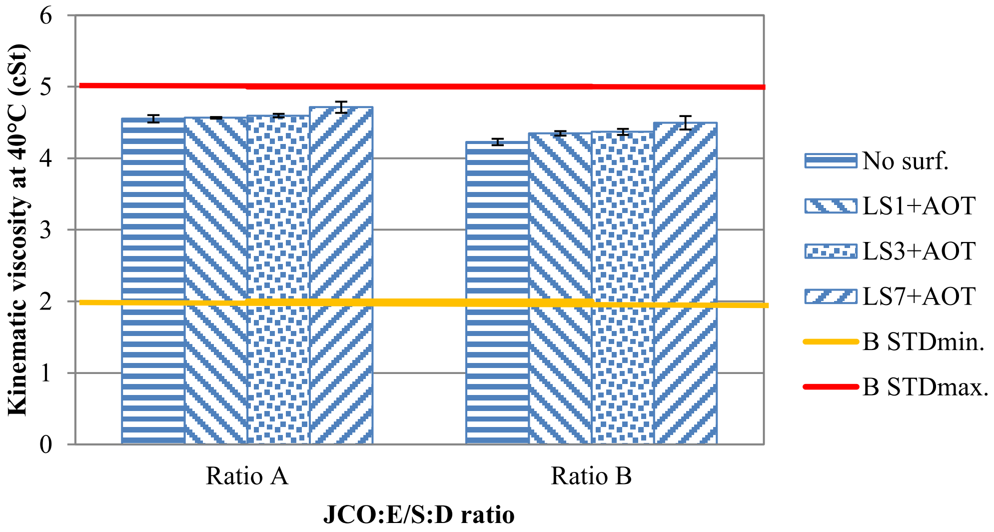


Figure 4.14 Kinematic viscosity at 40°C of microemulsion fuels at JCO:E/S:D ratios of (A) 20:5:75 and (B) 20:10:70 using the mix surfactant systems

4.2.5 Oxidation stability

Oxidation stability (OS) was evaluated by using Rancimat to report result as induction time, which evaluate the storage stability of fuel. Due to fuel instability can give rise to sediments and gum formation and fuel darkening. With this method, JCO was only one original component that can be measured since this parameter relative to fatty acid of oil. This is why OS is an important parameter for biodiesel standard. MFs in this present study were the fuels contain vegetable oil as a component, it is necessary to evaluate the OS. The oxidation stability of JCO was 13.05 hours which is higher OS than that of biodiesel standard. This agree with an explanation that unrefined vegetable oils which still contain their natural levels of antioxidants usually have improved oxidative stability (Knothe, 2007) However, it is surprising that the MFs with surfactant both single and mixed surfactants tended to lower OS of the fuels (see Figure 4.15 and Figure 4.16). As compared between system at ratio A and B which have the same proportion of JCO at 20%, the system with higher ethanol (10%) shows lower OS of the fuels. It may assume that an increase of ethanol proportion may decrease OS of the MFs.

Compared the systems with different for all cases, LS7 tended to have the lowest stability (see Figure 4.15 and Figure 4.16). The effect of EO group is obviously seen for the MFs with mixed surfactant. However, once compared the same proportion ratio between single and mixed surfactants (Figs. 4.15A & 4.16A, and Figs. 4.15B & 4.16B), the MFs with mixed surfactant show the higher OS for both cases; likewise, Prapatigul (2008) has reported that microemulsion fuel with mixed surfactants system was higher stability to resist an oxidation than single surfactant system. This may be because AOT perform as co-surfactant to enhance the stability of microemulsion (Rosen, 2004).

As shown in Table 4.3 and 4.4, the oxidation stability specified by EN standard 14112 for biodiesel is not below 10 hours, while all of MFs had induction time higher than the standard minimum values. This indicates that all of the MFs can keep for long term storage and secured engine causes operational problem such as fuel filter plugging, injector fouling (Jain and Sharma, 2010).

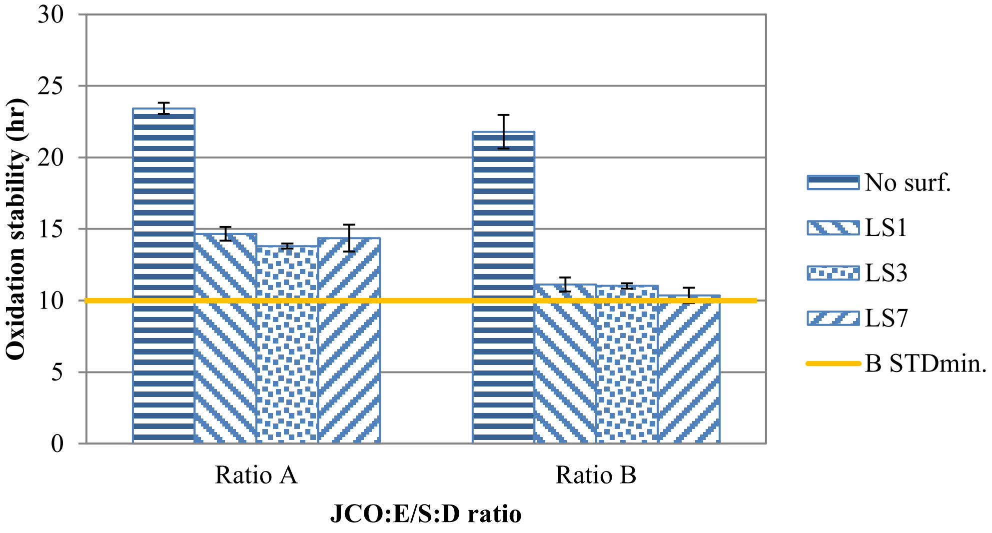


Figure 4.15 Oxidation stability of microemulsion fuels at JCO:E/S:D ratios of (A) 20:5:75 and (B) 20:10:70 using the single surfactant systems

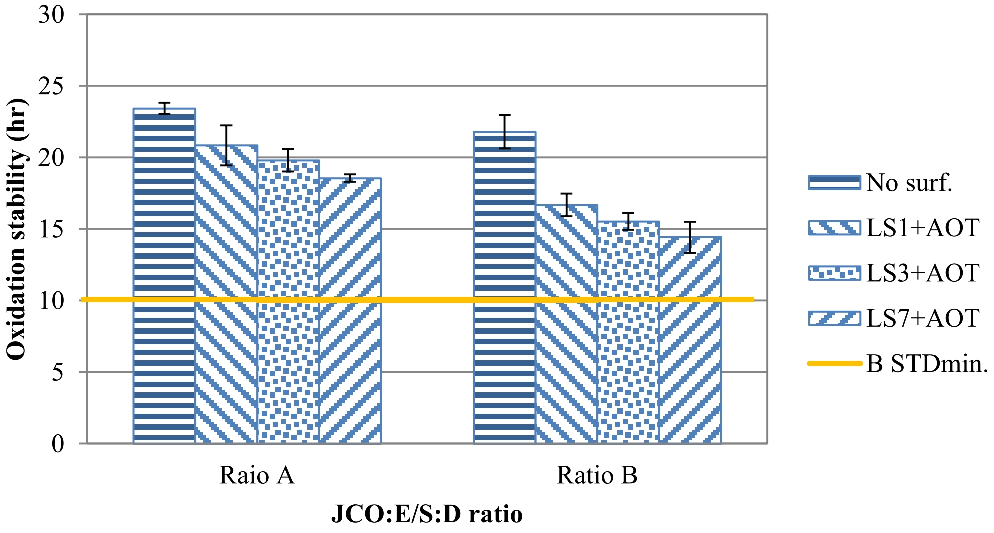


Figure 4.16 Oxidation stability of microemulsion fuels at JCO:E/S:D ratios of (A) 20:5:75 and (B) 20:10:70 using the mix surfactant systems

4.2.6 Water content

Water content is the quantity of water contained in fuel. Generally, water in fuel causes to accelerate oxidation, contribute corrosion, and enhance microbial growth (Demirbas, 2009). Comparing water content of the three original fuels the values (Table 4.2) show that 99% ethanol purity has the highest water content at 1873.75 ppm, while JCO and diesel have water content at 929.00 ppm and 67.25 ppm, respectively. As shown in Figure 4.17 and Figure 4.18, the measured water content increased as the percentage of ethanol in the MFs increased. MF(E5), which is the microemulsion fuels with 5%vol ethanol, was approximately 425 ppm. As MF(E5), which is the microemulsion fuels with 10%vol ethanol, was approximately 550 ppm.

As shown in Table 4.3 and 4.4, The EN specification uses measurement by Karl Fischer (KF) method which measures total water, and the maximum water content specified by EN standard 12937 for biodiesel is 500 ppm. The MF(E5) were water content meet the maximum limit, while The MF(E10) were slightly higher than the maximum limit of biodiesel standard. Therefore, the MFs with 5%vol ethanol are suitable; likewise, MFs with 10%vol in the single nonionic surfactant system were adequate agree with little excess water content for diesel engine. However, MFs should be kept during storage and distribution in dried condition. Moreover, if necessary water present should be removed in JCO by vacuum driers before blending. Whereas, many researchers agree with water present in fuels that have advantages to reduce in the emissions of nitrogen oxides (NO_x) and particulate matters (PMs), and reduction in fuel consumption due to better burning efficiency (Armas et al, 2005; Lif and Holmberg, 2006; Alahmer, 2013).

In conclusion, all property parameters were summarized in Table 4.5. All of selected MFs for this study were found to meet standard values for important properties as a fuel such as kinematic viscosity, water content and oxidative stability. Some properties i.e. Density and acid value which are parameters that very specific for type of fuel were found different from biodiesel. However, from overall properties, the MFs are relatively suitable for low speed diesel engine.

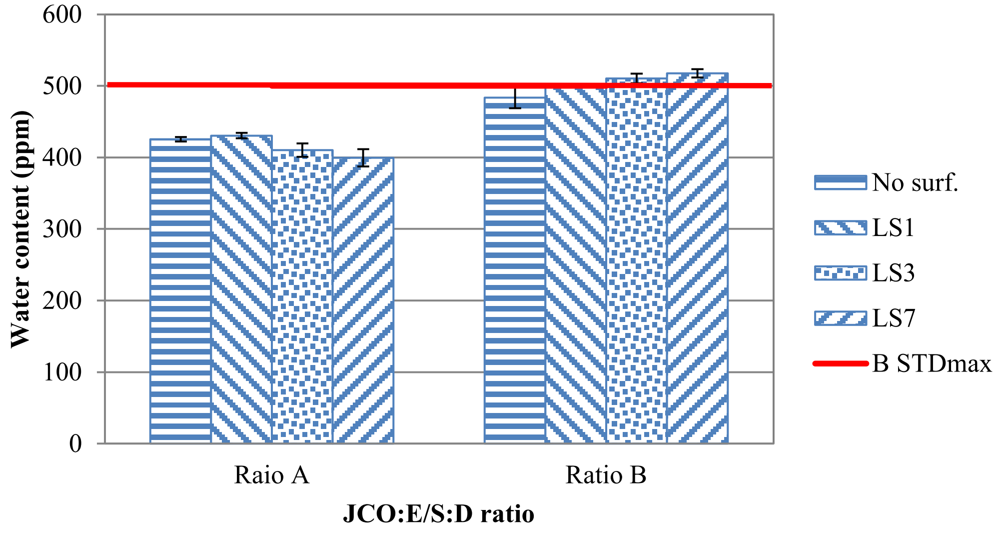


Figure 4.17 Water content of microemulsion fuels at JCO:E/S:D ratios of (A) 20:5:75 and (B) 20:10:70 using the single surfactant systems

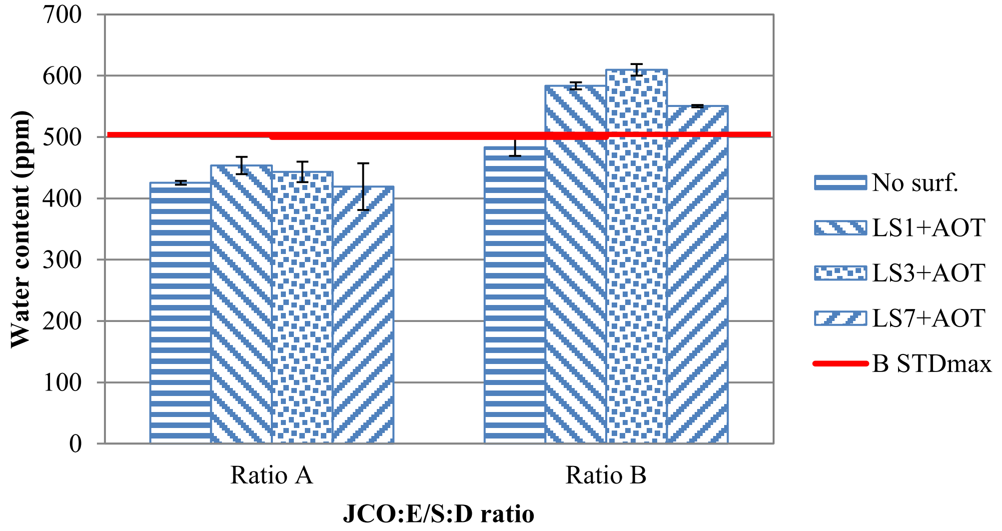


Figure 4.18 Water content of microemulsion fuels at JCO:E/S:D ratios of (A) 20:5:75 and (B) 20:10:70 using the mix surfactant systems

Table 4.5 Comparison of the properties of microemulsion fuels with biodiesel standard

	MF(E5)-N	**MF(E5)-S1**	**MF(E5)-S3**	**MF(E5)-S7**	**MF(E5)-M1**	**MF(E5)-M3**	**MF(E5)-M7**
Optical	√	√	√	√	√	√	√
Acid value	X	X	X	X	X	X	X
Cloud point	*	*	*	*	*	*	*
Density @ 15°C	X	X	X	X	X	X	X
Flash point	X	X	X	X	X	X	X
High heating value	*	*	*	*	*	*	*
Kinematic vis. @ 40°C	√	√	√	√	√	√	√
Oxidative stability	√	√	√	√	√	√	√
Water content	√	√	√	√	√	√	√

	MF(E10)-N	**MF(E10)-S1**	**MF(E10)-S3**	**MF(E10)-S7**	**MF(E10)-M1**	**MF(E10)-M3**	**MF(E10)-M7**
Optical	√	√	√	√	√	√	√
Acid value	X	X	X	X	X	X	X
Cloud point	*	*	*	*	*	*	*
Density @ 15°C	X	X	X	X	X	X	X
Flash point	X	X	X	X	X	X	X
High heating value	*	*	*	*	*	*	*
Kinematic vis. @ 40°C	√	√	√	√	√	√	√
Oxidative stability	√	√	√	√	√	√	√
Water content	√	√	X	X	X	X	X

Remark √ - meet biodiesel standard, X – do not meet biodiesel standard, * - No specify in biodiesel standard

4.3 Performance of microemulsion fuel and diesel

For this part, power, fuel consumptions and exhaust gas temperature are significant parameters used to explain the efficiency of engine with various types of fuels. The performances of MFs are compared to those of diesel. The two loads of engine, consisting of 25% (low load) and 50% (medium load), were investigated for performances at different speeds. It is noted that the full load (100%) cannot be done due to the incompatibility of present dynamometer for this experiment.

4.3.1 Power

The power of different fuels is shown in Figure 4.19 for low load and Figure 4.20 for medium load. The results show that the power of low load decrease steadily with increasing engine speed. On the contrary, the engine power of medium load increases with increasing engine speed till peak power, 1700 - 1900 rpm, and sharply drops. While the maximum power of all of the MFs is lower than those of commercial diesel, among MFs, MF(E5) and MF(E5)-LS1 have higher power than MF(E10)-LS1, especially, at low load. At the low load, the presence of 3.25% (MF(E5)-LS1) and 7.5% (MF(E10)-LS1) ethanol compared to diesel can reduce the engine power approximately 11.09 – 38.96 % and 22.91 – 50.74%, respectively. At medium load, the results of MFs show that the power slightly decreases compared to diesel at speed < 1700 rpm but shows significant drop for 1900-2100 rpm.

Thus, it can be concluded that the reduction of engine power mainly depends on the percentage of ethanol and JCO in fuels since both ethanol and JCO have lower heating value compared to diesel (see Table 4.3). The use of surfactant in the mixture shows insignificant power reduction. In brief, the optimal use of all microemulsion fuels is at medium load up to 1700 - 1900 rpm.

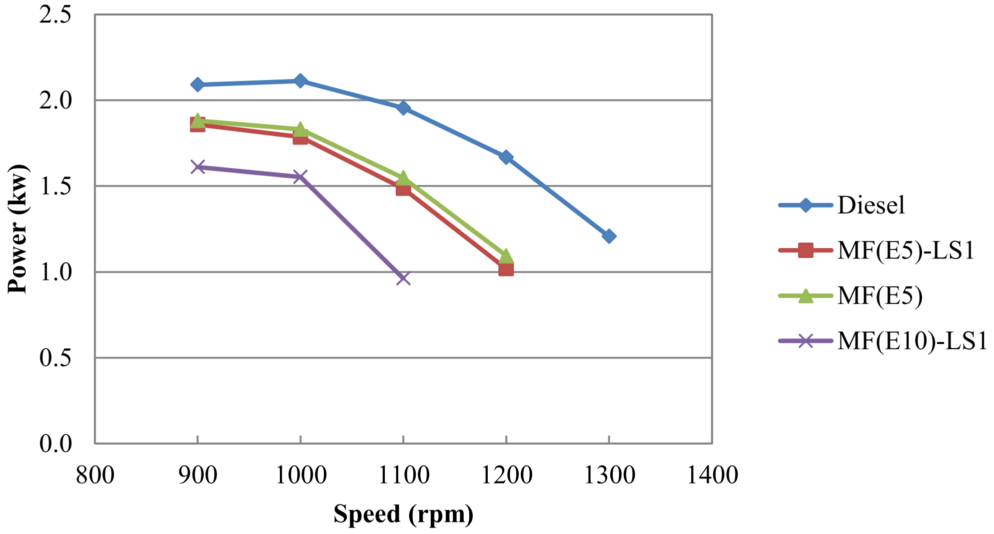


Figure 4.19 The power of the engine with various fuels at low load

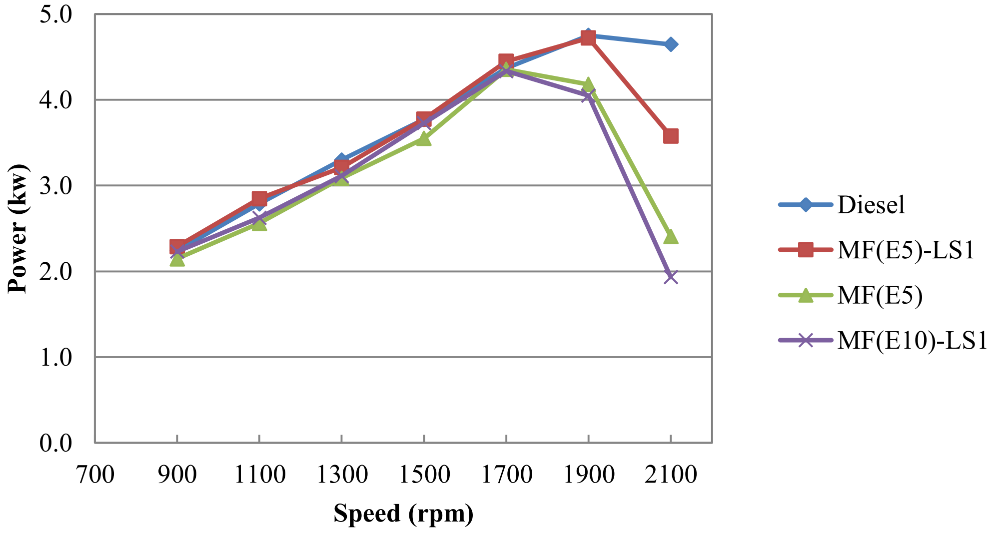


Figure 4.20 The power of the engine with various fuels at medium load

4.3.2 Brake specific fuel consumption

Brake specific fuel consumption (BSFC) is the ratio between mass flow of the fuels and its power (Mofijur et al., 2013). The brake specific fuel consumptions of different fuels at low and medium load are shown in Figure 4.21 and Figure 4.22, respectively. For the low load, the trend of BSFC is increased as the increment of engine speed. On the other hand, the BSFC of medium load is higher at low speed (900 rpm) then slightly decreases until 1900 rpm speed, and increases again at 2100 rpm speed. For the MFs, the BSFC are higher than that of diesel. Moreover, among MFs, increase of ethanol fraction in the MFs is correlated with the increase of fuel consumption (BSFC) in the following order: MF(E5)-LS1, MF(E5), and MF(E10)-LS1, respectively. Compared to diesel, BSFC of all MFs at low load increases significantly with increasing speed. For 50% load (medium load), MFs show similar fuel consumption compared to diesel, except at 2100 rpm as shown in Figure 4.22 due to increasing ethanol content in MFs. Hence, MFs containing lower than 5% ethanol shows similar fuel consumption to diesel at medium load in range of speed at 900-1900 rpm.

From lower heating values of ethanol and JCO than that of diesel, the engine needs more MFs for combustion to generate the same amount of power output in low load but similar fuel amount at medium load. Furthermore, MF(E10)-LS1 with highest ethanol fraction also shows effect of higher latent heat of vaporization from ethanol on lower temperature in-cylinder, causing the increase of BSFC (Fang et al., 2013).

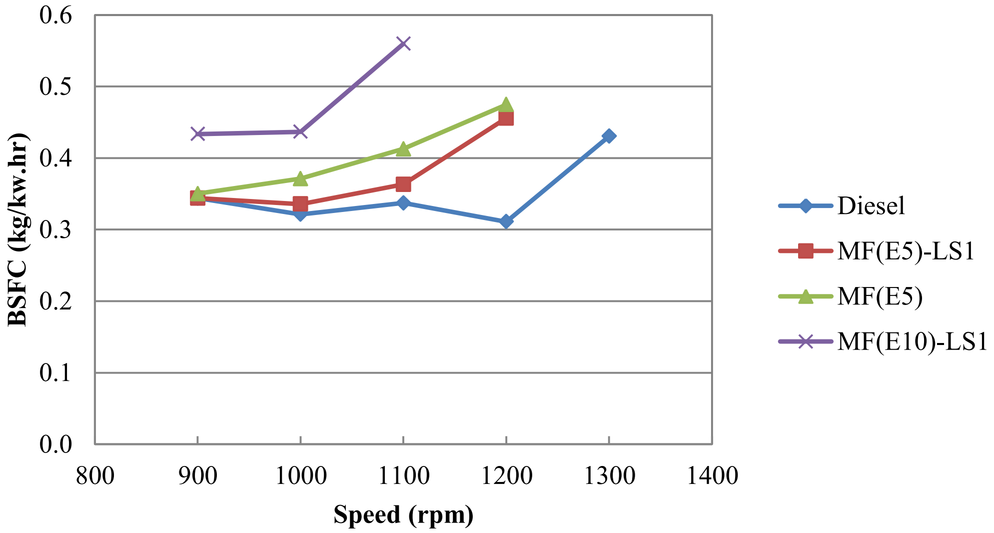


Figure 4.21 The brake specific fuel consumption of different fuels at low load

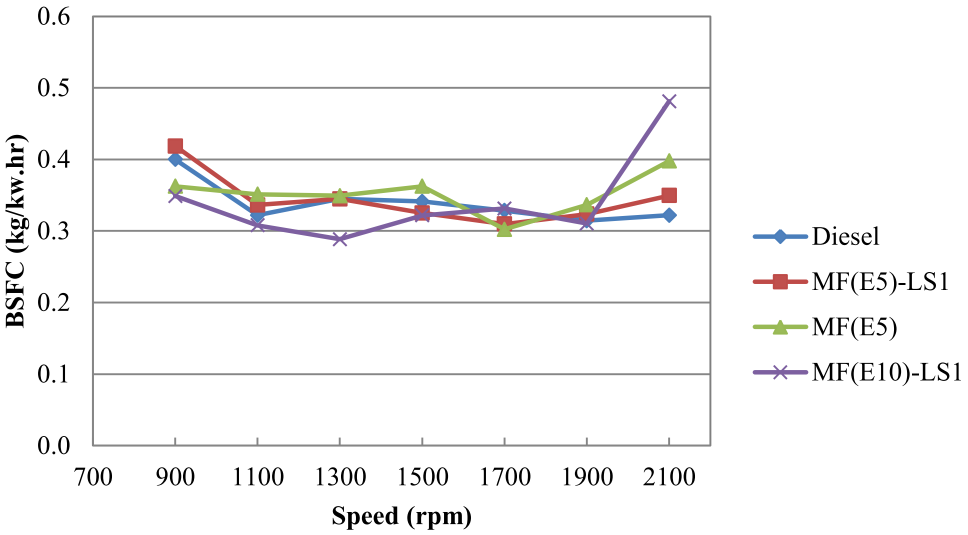


Figure 4.22 The brake specific fuel consumption of different fuels at medium load

4.3.3 Exhaust gas temperature

The variation of the gas exhausts temperature with engine speed for different fuels is presented in Figure 4.23 (low load) and in Figure 4.24 (medium load). With increasing load (low to medium), more amount of fuel is combusted leading to increases in the cylinder pressure and temperature (Rao, 2011). The temperature of exhaust gas is observed to be lower for MFs as compared to commercial diesel for two reasons. First, higher heating value of commercial diesel release more heat in the combustion chamber causing higher exhaust gas temperature. Second, ethanol fraction in the MFs can absorb heat from higher latent heat of vaporization leading to the decrease in the exhaust gas temperature (Karabektas and Hosoz, 2009). With increasing of engine speed, the exhaust temperature is expected to increase due to more power being delivered. However, as for MFs, the power is decreased for all engine speed in low load (Figure 4.19) and high engine speed in medium load (Figure 4.20) so the exhaust temperature of MFs in these conditions is decreased. Normally, NO_x will be emitted at high temperature of combustion; therefore, this kind of MF may reduce NO_x emission due to its lower exhaust gas temperature. This might also be an advantage of this fuel that was claimed by previous research (Fang et al., 2013).

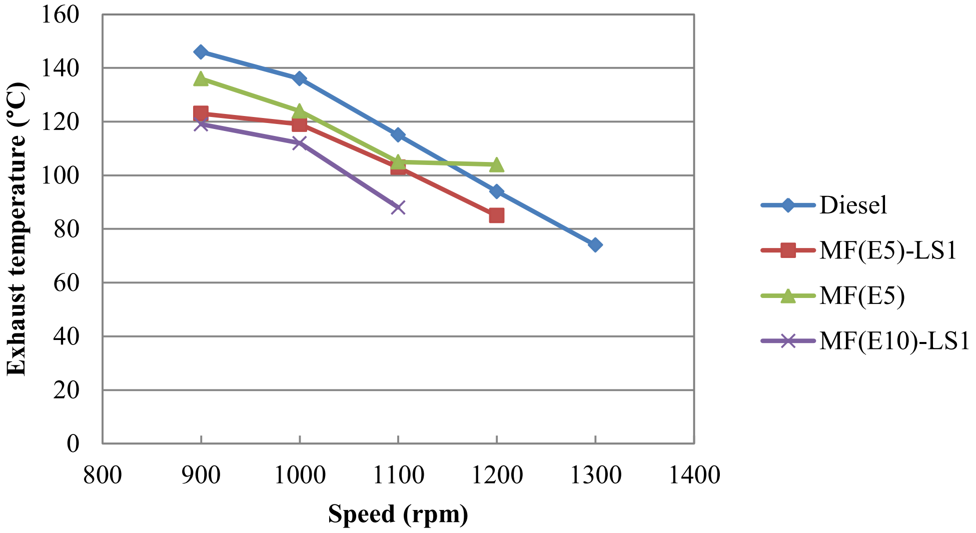


Figure 4.23 The exhaust gas temperature of different fuels at low load

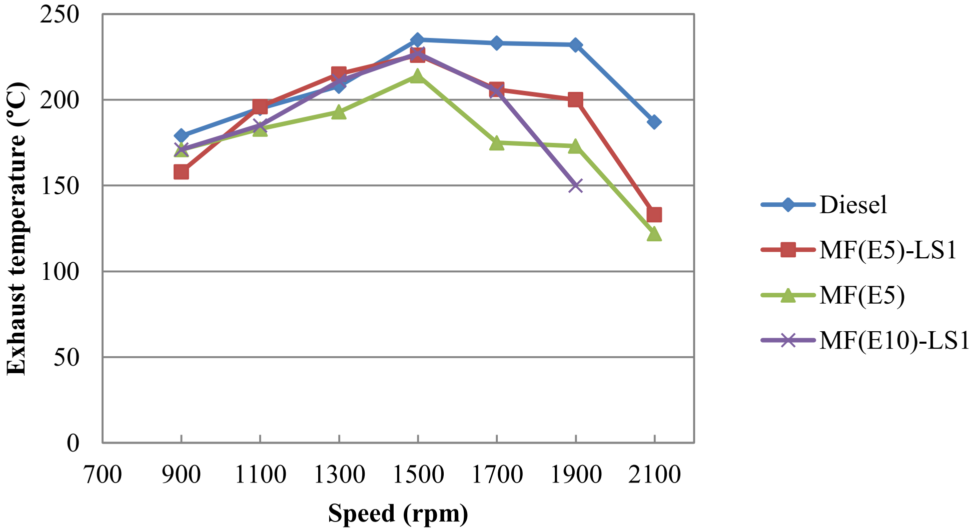


Figure 4.24 The exhaust gas temperature of different fuels at medium load

4.4 Emission of microemulsion fuels and diesel

4.4.1 Carbon dioxide emission

Carbon dioxide (CO_2) emission is resulted from any combustion process when complete combustion occurred. Figure 4.25 and Figure 4.26 show CO_2 emissions of

MFs and diesel with respect to engine load between low load and medium load, respectively. For low load, CO_2 increase with engine speed and ethanol fraction. The combustion of MFs provided lower CO_2 emission as compared to commercial diesel similar to Li et al. (2005). CO_2 emissions for medium load of MFs were similar to diesel, because MFs contains more oxygen in molecules of ethanol, surfactant, and jatropha oil, which could possibly provide enough oxygen in combustion chamber for complete combustion occurrence.

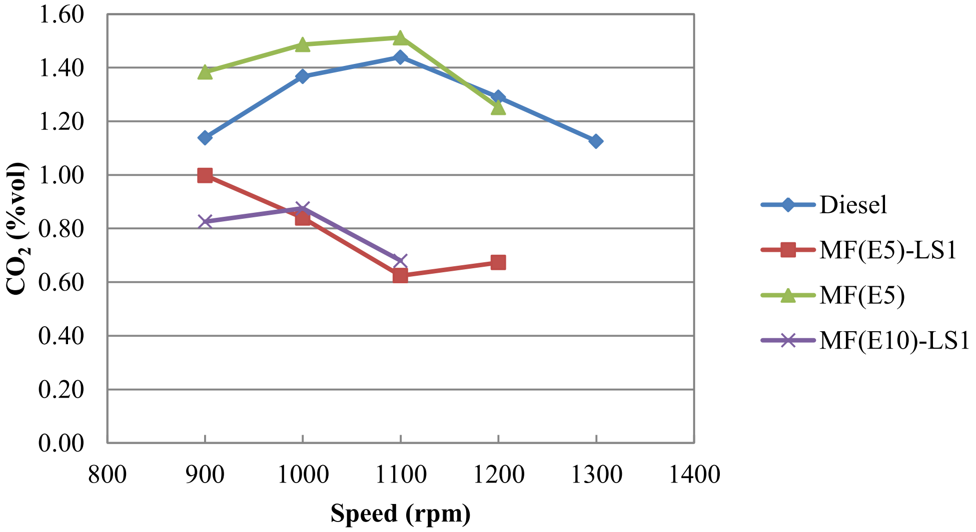


Figure 4.25 CO_2 emissions of different fuels at low load

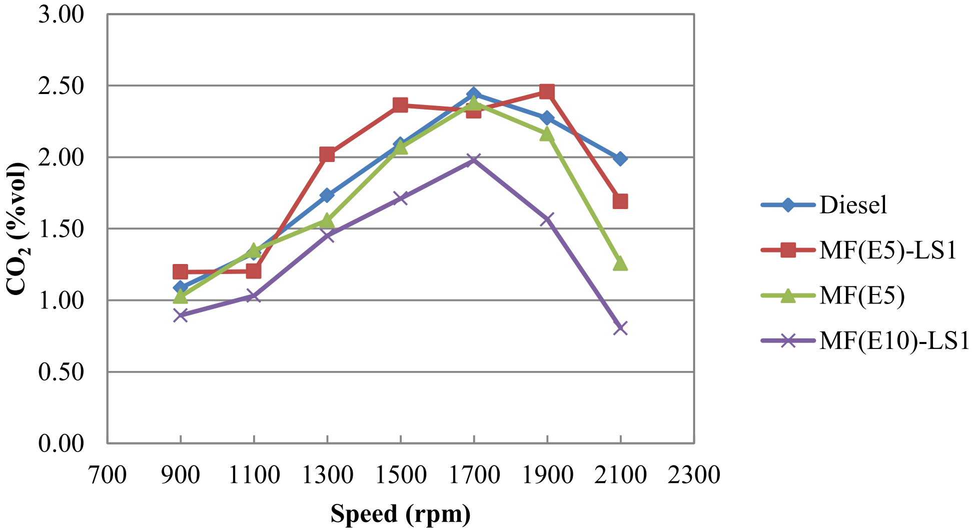


Figure 4.26 CO_2 emissions of different fuels at medium load

4.4.2 Carbon monoxide emission

Carbon monoxide (CO) emission results during combustion when fuel is deficient of surrounding oxygen. CO emissions at various speeds under low load and medium load are presented in Figure 4.27 and Figure 4.28, respectively. At low load, CO emissions decrease with increasing engine speed for most fuels, similar to medium load. When comparing MFs with diesel, CO emissions of MFs seem to fluctuate around or lower than the diesel value since oxygenated fractions of JCO and ethanol could improve complete combustion, resulting in lower CO emission

Considering the engine speed and engine load, the addition of ethanol causes the reduction of exhaust gas temperature, and restrains the oxidation of CO at low load. While increasing engine speed at medium load, gas temperature and wall of chamber temperature increase with oxygen content from ethanol, which could enhance the oxidation condition of CO. Furthermore, the effect of C/H ratio and Air-Fuel ratio could contribute to lower CO emission (Can et al., 2004).

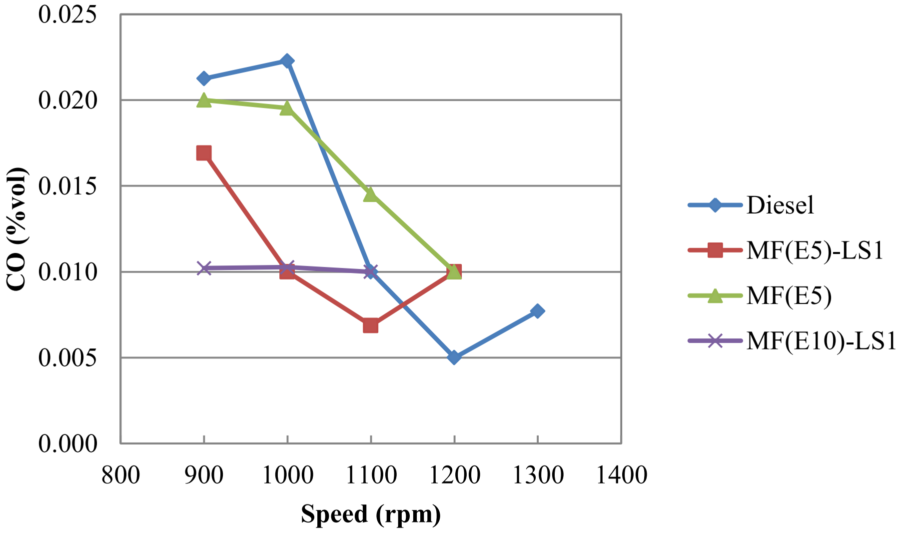


Figure 4.27 CO emissions of different fuels at low load

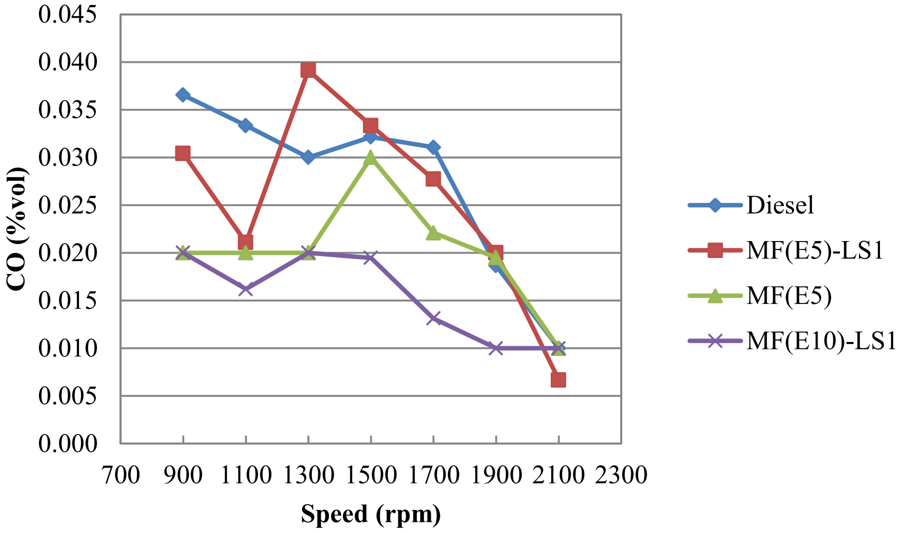


Figure 4.28 CO emissions of different fuels at medium load

4.4.3 Smoke opacity

The smoke opacity of the MFs compared with commercial diesel with various speeds at low load (Figure 4.29) and medium load (Figure 4.30). For both low load and medium load, the smoke opacity results of all of the MFs: (MF(E5)-LS1, MF(E5), and MF(E10)-LS1), are lower than those of diesel especially at low speed. Among MFs, smoke opacity of MF(E10)-LS1 is the lowest due to its viscosity that favors well atomization of the fuel. Thus, the smoke opacity of the MFs decrease with the increasing ethanol fraction since oxygen content of ethanol can provide oxygen in the fuel-rich mixture and inhibit the formation of smoke. Moreover, ethanol has lower carbon and viscosity, which can encourage the spray and combustion characteristics of the MFs for less smoke emission (Kumar et al., 2003).

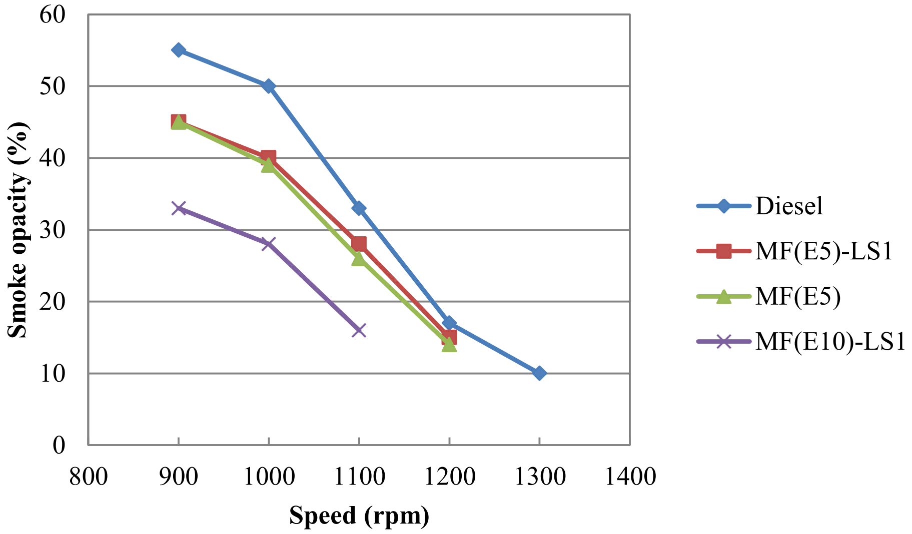


Figure 4.29 Smoke emissions of different fuels at low load

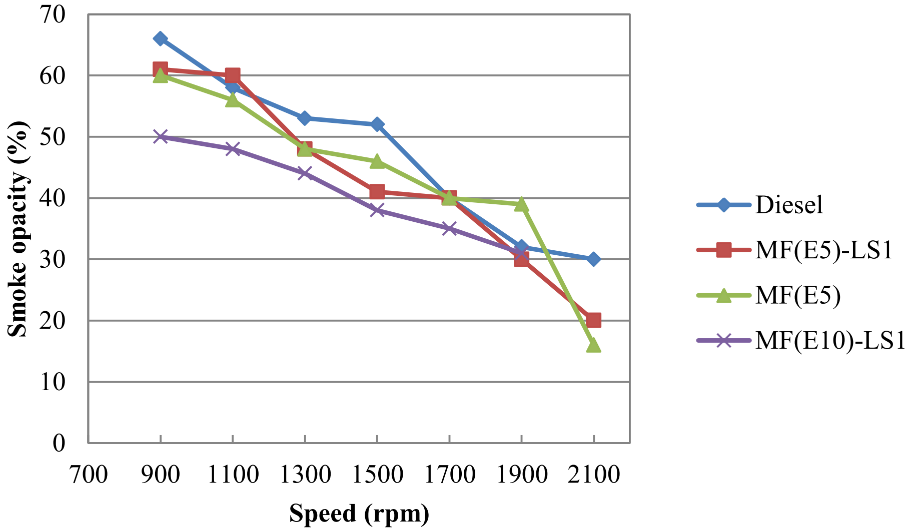


Figure 4.30 Smoke emissions of different fuels at medium load

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

There are three parts presented in this study. The first on phase behavior study of the microemulsion oil (MFs) which illustrated in pseudo-ternary phase diagram can be concluded that the microemulsion areas of the systems with low number of EO group between 1EO to 3EO group (or HLB values close to 3.6-7.9) are proposed to make microemulsion fuels (MFs) with JCO-ethanol-diesel. While temperature stability test suggested that at 20 - 40 °C, the stability of MFs with different EO group number has almost similar behavior or the other words the selected MFs were stable in this range of temperature for both systems with single and mixed surfactant.

The second part, two MFs, which were 20% jatropha oil, 75% diesel and 5% surfactant in ethanol solution (MF-E5) and 20% jatropha oil, 70% diesel and 10% surfactant in ethanol solution (MF-E10), were selected to examine the fuel properties. The four properties which are the most importance in fuels characteristic for injection and combustion namely; heating value, kinematic viscosity, oxidation stability and water content, found to meet the biodiesel standard. Therefore, in the long-term durability run is expected that MFs does not adversely affect engine wear. Nevertheless, some properties such as acid number, cloud point, density, flashpoint, exceed biodiesel standard. Thus, MFs may cause some problems to engine and storage. In fact, they can harm injection systems and other metallic components in diesel engine because of the high value of acid number. Moreover in the storage, MFs should be treated as Class I liquids because their flashpoint below 37.8 °C according to the NFPA in the USA, and should be avoided to keep at lower temperature around 11 °C. Furthermore, they tend to increase in fuel consumption compared to diesel because of their density lower than commercial diesel.

The third part on engine performances and exhaust emissions, the potential in combustion of microemulsion fuel -ethanol 5% with single surfactant LS1 or MF(E5)-

LS1, microemulsion fuel ethanol 5% without surfactant MF(E5) and microemulsion fuel -ethanol 10% with single surfactant LS1 or MF(E10)-LS1 has been evaluated on two-cylinder diesel engine. MFs with low percentage of ethanol, which are MF(E5)-LS1 and MF(E5) have power, BSFC, and exhaust gas temperature close and to those of diesel, especially at low speed engine. For the emission of the MFs, emissions of CO and CO_2 have trended results lower than those of diesel. Likewise, smoke opacity was reduced at high ethanol fraction when compared to that of diesel. Therefore, surfactant addition can improve MFs' properties such as behavior stability and oxidation stability. While ethanol fraction can improve their property such as viscosity and their emission such as smoke.

Finally, the microemulsion fuels by microemulsification method have been potential to use as biofuel in diesel engines without modification; Due to their stability were suitable for weather at tropical region as Thailand. In addition, they reduce emissions, especially smoke. Nevertheless, the microemulsion fuels had have drawback to engine. In fact, they can harm injection systems and other metallic components due to high acid, required for proper safety during handling as same as ethanol's handing because their flashpoint, and provide less power than that diesel.

5.2 Application perspective

In fact for Thailand, although microemulsion fuel is known as a one of feasible alternative fuel that easily to be produced such as MF from JCO-ethanol-diesel. The MF may have been not yet accepted because of cost especially jatropha oil prices at present which is rather expensive compared to diesel price. This is because jatropha oil has not been widely commercialized in the market. Moreover most of agriculturists still hesitate to use it due to a concern on their engine maintenance. To solve this problem, promotion of the local government agency on agriculturists to grow jatropha in some of their land and cultivate for use within their community would help to reduce its cost. In addition, the research on long run engine test in order to evaluate the effect of the MF on engine should be investigated. The campaign for using alternative energy as well as sustainable living on their own resource should also be conducted continuously.

5.3 Recommendations

Due to the restriction of research time and budget, the microemulsion fuels (MFs) from jatropha oil as non-editable oil should be more studied for convincing MFs can practically use at least in agricultural diesel engine. Thus, in the personal ideas have been providing a future plans following these:

1. The production of crude jatropha oil such as plantation areas, season, oil extraction, and storage should be considered because they involve with quality of crude jatropha oil, yield and water contamination.
2. The other characteristic of MFs should be examined such as cetane number in order to convince that the fuel can practically use in diesel engine.
3. The study on pre-procedure or new additive of MFs is interested due to eliminate the weakness of characteristic such as acid value, cloud point and flash point.
4. The stability of MFs should be investigated at extremely low and high temperatures because not only weather at tropical region as Thailand but also at other weather can use.
5. The MFs which are the best one should be tested at long-term engine durability and studied at the other types of diesel engine such as single or four cylinders, or direct injection (DI) diesel engine.
6. The MFs from this research only was laboratory scale that has not information to support a large scale. Thus, economic and ecology analysis namely Life Cycle Assessment (LCA) ought to be investigated.

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APPENDICES

Appendix A Instrument of fuel properties test figure

Figure A-1 A Tirando Automatic Potentiometric Titratior

Figure A-2 A LECO AC-350 Automatic Calorimeter

Figure A-3 An ISL CPP 5Gs Cloud & Pour Point Tester

Figure A-4 An Anton Paar DMA-4500 Digital Density Meter

Figure A-5 An APM-7 Pensky-Martens Closed Cup Tester

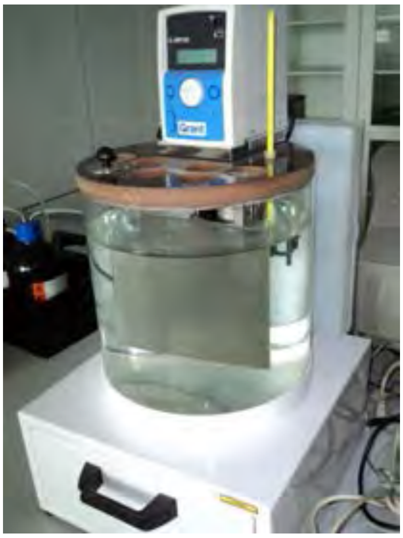

Figure A-6 A D445-E20L Kinematic Viscometer

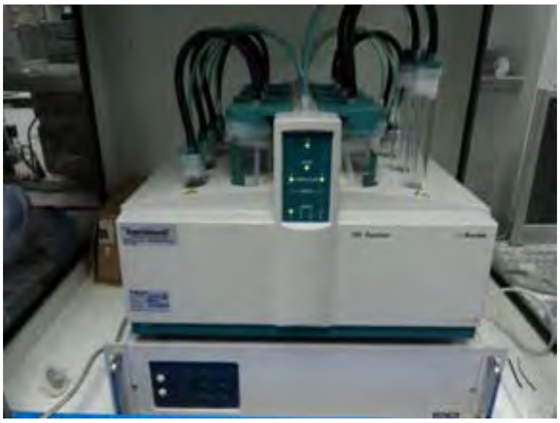

Figure A-7 A Rancimat

Figure A-8 A Karl Ficher titratior

Appendix B Experimental setup of engine test figure

Figure B-1 A two-cylinder diesel engine

Figure B-2 A hydraulic dynamometer

Figure B-3 A dynamometer’s controller

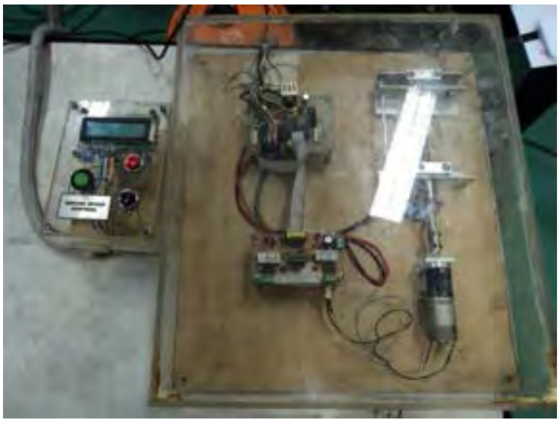

Figure B-4 An accelerator’s controller

Figure B-5 A balance for fuel consumption

Figure B-6 An emission detector

Figure B-7 A smoke meter

VITA

Mr. Akechai Sankomgon was born on September 20, 1987 in Bangkok, Thailand. He graduated Bachelor’s degree of Science (Environmental Technology) from Faculty of Applied Science, King’s Mongkut University of Technology North Bangkok, Thailand in 2005. He pursued Master’s degree studies at the International Post Graduated Programs in Environmental Management (Hazardous Waste Management), Chulalongkorn University, Thailand. His work in the title of “Properties of improvement of microemulsion fuel from jatropha oil-ethanol-diesel by surfactant selection” was presented and published as the proceeding of EHSM 2013 (Environmental and Hazardous Substance Management) on May 21 – 23, 2013 in Bangkok. He finished his Master degree of Science in Environmental Management in October, 2013.