A Study of Glycerol and Ester Phase Separation on Ethyl Ester Production from Refined and Crude Palm Oils

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ชื่อวิทยานิพนธ์ ศึกษาการแยกชั้นของกลีเซอรอลและเอสเตอร์ในกระบวนการผลิตเอทิลเอสเตอร์จากน้ำมันปาล์มบริสุทธิ์และน้ำมันปาล์มดิบ
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บทคัดย่อ

วิทยานิพนธ์นี้มีเป้าหมายเพื่อศึกษากระบวนการผลิตน้ำมันไบโอดีเซลจากน้ำมันปาล์มดิบและเอทานอล ซึ่งเคยมีปัญหาการแยกระหว่างชั้นของกลีเซอรอลและชั้นของเอสเตอร์โดยมุ่งเน้นนำไปประยุกต์ใช้ในระดับชุมชนจนถึงอุตสาหกรรมขนาดย่อม การทดลองดำเนินการโดยใช้หลักการผลิตเมทิลเอสเตอร์ซึ่งเป็นที่ทราบกันดีเป็นพื้นฐานเพื่อการเปรียบเทียบ คือใช้สัดส่วนเชิงโมลระหว่างน้ำมัน: แอลกอฮอล์ เท่ากับ 1:6.0, ใช้ 1.0% NaOH เป็นตัวเร่งปฏิกิริยา, ทำปฏิกิริยาทรานส์เอสเตอริฟิเคชัน ที่อุณหภูมิ 70^{o}C เป็นเวลา 45 นาที น้ำมันปาล์มที่นำมาใช้เป็นสารตั้งต้นมี 2 ชนิด คือ น้ำมันปาล์มบริสุทธิ์และน้ำมันปาล์มดิบ ทั้งนี้เพื่อเพื่อศึกษาปัจจัยจากแหล่งที่มาของวัตถุดิบ ประสิทธิภาพของกระบวนการผลิตประเมินจากปริมาณผลผลิตเมื่อคิดเป็นร้อยละ และคุณสมบัติทางเคมีบางประการคือ ปริมาณกลีเซอไรด์รวมและปริมาณน้ำที่ตกค้าง

ผลการทดลองแสดงให้เห็นว่าน้ำมันปาล์มดิบที่ผ่านการลดปริมาณกรดไขมันอิสระให้เหลือที่ระดับ 1.2% สามารถนำมาใช้เป็นวัตถุดิบในการผลิตน้ำมันไบโอดีเซลในรูปของเมทิลเอสเตอร์ได้โดยให้ผลผลิตประมาณ 93% ซึ่งต่ำกว่าการใช้น้ำมันปาล์มบริสุทธิ์ที่ให้ผลผลิตประมาณ 96% แต่คุณภาพของผลผลิตที่ได้จากน้ำมันทั้ง 2 ชนิด ไม่มีความแตกต่างกันอย่างมีนัยสำคัญ ($p < 0.05$) อย่างไรก็ตามเมื่อนำกระบวนการดังกล่าวมาใช้ผลิตเอทิลเอสเตอร์พบว่ามีปัญหาการแยกระหว่างชั้นของกลีเซอรอลและชั้นของเอสเตอร์ ผลการศึกษาเบื้องต้น พบว่าปัจจัยสำคัญที่มีผลต่อประสิทธิภาพของกระบวนการผลิตเอทิลเอสเตอร์ คือ ปริมาณกรดไขมันอิสระในน้ำมันปาล์มดิบควรจะต่ำกว่า 0.8% อัตราส่วนระหว่าง น้ำมัน:แอลกอฮอล์ ควรเป็น 1:6

ด้วยหลักการทำลายสมดุลของแรงยึดเหนี่ยวระหว่างโมเลกุลในของผสม พบว่าหลักการดังกล่าวสามารถเพิ่มประสิทธิภาพการแยกชั้นของกลีเซอรอลและชั้นของเอสเตอร์ วิธีที่เหมาะสมที่สุดคือพ่นไอน้ำลงไปในของผสมหลังจากทำปฏิกิริยาทรานส์เอสเตอริฟิเคชันสมบูรณ์ นอกจากนั้นการเติมสารละลายอิ่มตัวของยูเรียลงไปประมาณ 25% ของเอสเตอร์ จะช่วยเร่งให้เกิดการแยกชั้นของน้ำและชั้นของเอสเตอร์ในขั้นตอนของการทำให้บริสุทธิ์เร็วขึ้น การผลิตน้ำมันไบโอดีเซลในรูปเอทิลเอสเตอร์ด้วยวิธีนี้ให้ผลผลิตประมาณ 83% โดยมีปริมาณกลีเซอร์ไรด์เหลืออยู่ประมาณ 4% ซึ่งใกล้เคียงกับน้ำมันไบโอดีเซลที่ผลิตออกมาจำหน่ายในตลาด

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ABSTRACT

The objective of this thesis is to study the production processes of biodiesel from crude palm oil (CPO) and ethanol which separation between the glycerol and the ester phases was used to be the common processing problem. Experiments were designed in order to apply with community and small scale economic producer.

To each studied process, its efficiency was determined from percent yield as well as some chemical properties in comparison with the well known procedure for methyl ester preparation. The reference procedure was carried out using a molar ratio of oil:alcohol 1:6.0, 1.0% NaOH was a catalyst and tranesterification reaction was performed at 70^{o}C for 45 minutes. Refined palm oil (RPO) and crude palm oil were used as a reactant to compare the effect of oil sources.

Results revealed that the pre-esterified CPO that composed of 1.2% free fatty acid could be used as a reactant for methyl ester preparation with 93% yield, which was slightly lower than that 96% of the ester from RPO. It was found that the content of total glyceride in the methyl ester from both oil sources showed no significantly different ($p < 0.05$). However, when these procedures were applied with the ethyl ester preparation, the phase separation problem occurred with both of the oils. Results from preliminary study suggested that this problem was principally contributed by the free fatty acid content in reactant which should be less than 0.8%.

Also, it was found that the phase separation problem could be solved on the basis of disturbing interactions among various constituents in the reaction mixture. Result showed that the most effective one could be performed by reduction of an excess ethanol by blowing a steam of boiling water into the reaction mixture. Furthermore, at the first and second washing step, addition of saturated urea solution into the ester phase about 25% by volume accelerated the separation between aqueous phase and ester phase. With respect to initial weight of CPO, 83% of ethyl ester was obtained, and about 4% of the total glyceride was detected which comparable to the level in a commercial biodiesel.

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LIST OF ABBREVIATIONS

ASTM = American Society for Testing and Materials

B20 = 20 % biodiesel + 80 % diesel fuel

B100 = 100 % biodiesel

CO = carbon monoxide

CO_2 = carbon dioxide

CaO = calcium oxide

CPO = crude palm oil

CPK = crude palm kernel oil

K = Kelvin

^{O}C = degree Celsius

DEDE = Department of Alternative Energy Development and Efficiency

EECPO = ethyl ester from crude palm oil

EERPO = ethyl ester from refine palm oil

FAME = fatty acid methyl esters

FFA = free fatty acid

g = gram

GLC = gas liquid chromatography

GHG = greenhouse gas

h = hour

ha = hectare

HSD = high speed diesel

HC = hydrocarbon

LIST OF ABBREVIATIONS (continue)

LOD = limit of detection
LOQ = limit of quantitative detection
LPG = liquefied petroleum gas
MERPO = methyl ester from refined palm oil
MECPO = methyl ester from crude palm oil
M = Molar
MPa = megapascals
mg = milligram
ml = milliliter
NO_x = nitrogen oxide
KOH = potassium hydroxide
ppm = part per million
PM = particulate matter
% vol = percent volume/volume
% wt = percent weight/weight
pH = power of hydrogen
PAH = polycyclic aromatic hydrocarbons
H_2SO_4 = sulfuric acid
SO_2 = sulfur dioxide
RBD = refined, bleached and deodorized
NaOH = sodium hydroxide
TCD = thermal conductivity detector

LIST OF ABBREVIATIONS (continue)

UV = ultraviolet

V/V = volume/volume

W/V = weight/volume

Chapter 1

Introduction

1.1 Introduction

Most industrial sectors have being suffered from continuously increasing of fossil oil price in the world market, and this unavoidably has being effected to the living cost of overall human being. Accordingly, alternative energy source is needed to be developed. Among several forms of energy, the biodiesel is received the most attractive due to its pose several advantages such as renewability, sustainability, reducing the pollutant, and it can be directly used without modifying the engine (Ma and Hanna, 1999). According to the American Society for Testing and Materials (ASTM), biodiesel defined as monoalkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat, for use in diesel engines (Vicente et al., 2004). So far, most of the commercially available biodiesel is produced by transesterification involving the chemical conversion of vegetable oils with short-chain alcohols, in the presence of a catalyst, into their corresponding fatty acid esters. (Department of Energy Business, Ministry of Energy, on specifications and qualities of biodiesel in Thailand, 2010). However, a high cost of production appears to be the main drawback of the alternative energy.

The production cost of biodiesel may be varied from place to place which primarily depends on available raw materials, especially the source of oil (Hass et al., 2006) and type of alcohol. In the first glance, the used-frying oil was reused as feedstock to reduce the cost of production. However, it seems that its supplying quantity is inadequate for using in commercial scale. In addition, it exhibits difficulty to process due to the compositions therein are not consistence which is difficult to control the product quality. Therefore, the crude palm oil (CPO) which is locally available raw material in Thailand was considered.

In conventional process, methanol is the common alcohol used in transesterification reaction because of its availability, cheap and convenient in processing. However, it should be noted that the reactant is not only extremely toxic, but it is also an imported product which is leading to the imbalance of international trade. Therefore, ethanol that could be produced from several agricultural products in this country was considered as an alternative reactant. So far, several attempts have been made to produce biodiesel from ethanol, but most of them have confronted with a similar processing problem especially at the step of phase separation between ethyl ester phase and glycerol phase.

Korus et al. (1992) studied the transesterification reaction using rape oil with different alcohols, namely, methanol and ethanol. The authors reported that the phase separation efficiency of ethyl ester and glycerol was much lower than that of methyl ester. They pointed out that the molar ratio between ethyl alcohol and oil may be the principal effect.

Zhou and Boocock (2006) studied on distribution of alcohol, glycerol and catalyst in the ester phase following transesterification of soybean oil with methanol and ethanol. They reported that as the chain length of alcohol was increased from methanol to ethanol the more content of alcohol and glycerol was found in the ester phase. They suggested that this presumably due to the less-polar ethanol was the more partition in the ester phase. Consequently, its polarity increased, and that enhance partition of glycerol into the ester phase.

Černoch et al. (2010) studied the partition of ethyl ester, glyceride and glycerol in an ester phase and glycerol phase following transesterification reaction of rapeseed oil with ethanol and methanol. The authors reported that the higher contents of ethyl ester, soap and monoglyceride were found in the glycerol phase than that of the methyl ester. Finally, they suggested that this is a principal factor contributed to the yield decreasing due to the ethyl ester was lost during washing process.

It seems that the phase separation problem during the processes of biodiesel production from crude palm oil and ethanol contribute by both reactant properties as well as reaction conditions. Accordingly, this study was carried out step by step to investigate the principal factors leading to the problem such as free fatty acid (FFA) content, water content in the feed stock, molar ratio between oil and alcohol as well as reaction time. The efficiency of processing was determined from percent yield, time spent at each step. In addition, some properties of the produced biodiesel were also investigated.

1.2 Review of literature

1.2.1 Scope of review

This review intends to provide essential background of biodiesel including production processes and characteristics. Since most published data has confined with the biodiesel in form of methyl ester, basic information will be provided in comparison with rarely information of ethyl ester. The following aspects will be covered: diesel engine and its fuel, development of biodiesel, common feedstock, production process, properties and characterization, advantage and disadvantage, drawback, Thailand's economics aspect, summary and conclusion.

1.2.2. Performance of diesel engine and fuel requirements

Refining processes of fossil fuels or petroleum carry out on the basis of fractional distillation, and yield a range of products, such as liquefied petroleum gas (LPG), gasoline, kerosene, aviation fuel, diesel oil, fuel oil and asphalt. In comparison, due to its low price and combustion of the diesel fuel gives relatively higher energy than those other forms, heavy duty engines to use in industrial plants, agricultural and transportation have been designed to use diesel as a fuel base.

Principally, diesel engine work by pumping and injecting the hydrocarbon fuel through orifice into a heated cylinder. After evaporation, the fuel vapor is mixed with an air to an optimum stoichiometric ratio therein, and is compressed to a high temperature and pressure until ignition spontaneously occurs. Once the primary chemical reaction is taken placed, then, the free radical will be generated for further autoignition.

The heating value following combustion of diesel depends on the refinery process and the source of the petroleum feedstock. In the other word, the value is dominated by composition of the fuel such as averaged molecular weight of the hydrocarbon and percentage of aromatic content.

Accordingly, the quality of diesel depend on several properties such as specific gravity, energy content, melting temperature, viscosity, flash point, cloud point, pour point and the contents of sulfur, ash and water.

1.2.3 Development of biodiesel

As there is a rapid growth of world population coupled with industrial and technological developments, the demand for energy is also continuously increased. So far, the principal energy source has been confined to fossil oil which is predicted to deplete in the near future. Also, the higher consumption rate of the oil would also exert the adverse effects on the environment and public health. In addition, its price has continuously increased during the last decade. Accordingly, several alternative energy sources such as nuclear energy, solar energy, wind energy, geothermal energy as well as biofuel that obtained from renewable biological sources seem to have had an attention to developed.

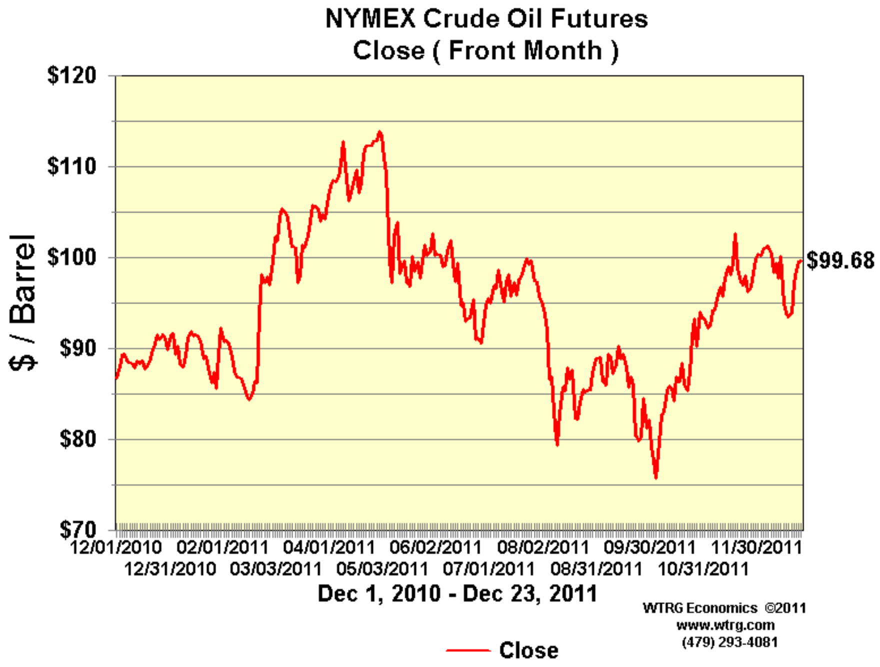

Figure 1.1 crude oil prices (Image:http://www.wtrg.com)

Since vegetable oils compose mainly of triglycerides which its hydrocarbon combustion provide a similar heating value to that of diesel fuel, there had been focus to use as an alternative fuel for diesel engines. However, their use in direct injection diesel engines is restricted by some critical physical properties, predominantly due to their high viscosity (about 10–20 times higher than that of diesel fuel) and low volatility. These disadvantages results in poor fuel atomization, incomplete combustion, carbon deposition on the injector and fuel build up in the lubricant oils. Hence, several attempts have been studied to solve these technical problems such as dilution with a suitable solvent, emulsification, pyrolysis and transesterification. Finally, chemical treatment of the vegetable oils by transesterification reaction to obtain biodiesel appears to be the most promising. These processes involve the chemical conversion of vegetable oils with short-chain alcohols, in the presence of a catalyst, into their corresponding fatty acid esters.

According to the American Society for Testing and Materials (ASTM), biodiesel is defined as monoalkyl esters of long chain fatty acids derived from a renewable triglyceride feedstock, such as vegetable oil or animal fat, for use in diesel engines. Because these esters have molar mass only one third of those of their triglycerides, they are less viscous, and perform well in diesel engines. Biodiesel exhibits comparable chemical and physical properties to the diesel, therefore, it can be substituted for petroleum fuel in all proportions without engine modifications. Moreover, biodiesel is biodegradable, cleaner burning and safer; it also has environmentally friendly attributes: being renewable and thereby mitigating greenhouse effect.

Transesterification consists of a number of consecutive, reversible and alkali-catalytic reactions. The triglyceride which is principal constituent in the oil feedstock, is converted stepwise to diglyceride, monoglyceride and finally glycerol is produced as a by-product. The methanol is used commercially because of its low price. Thus, the resulting esters or biodiesel are in the form of fatty acid methyl esters (FAME).

So far, biodiesel is not widely used because the cost of biodiesel is relatively higher than petroleum-based diesel by approximately one and a half of petroleum-based diesel. It is revealed that approximately 70–95% of the total biodiesel production cost is dominated by raw material; that is, vegetable oil or animal fats (Shey, 1993). Therefore, the low cost of production process is needed to develop.

1.2.4 Biodiesel quality

The quality and performance of biodiesel depend on compositions of feedstock as well as processing procedures. A good property of the fuel could be summarized as follow:

Firstly, following combustion, it provides a high heating value per unit volume. The higher density fuels, the greater energy per liter obtain. Secondly, the fuel should not limit the operability of the engine at low temperature. The higher contents of wax and long chain fatty acids contribute to the problem. Thirdly, the fuel should not contribute to corrosion of engines. These mostly relate to water, ash and sulfur contents. Fourthly, the fuel must not contain sediment that could plug orifice. Fifthly, the fuel should not cause excessive pollution. This usually contributes by the contents of sulfur, aromatic compounds.

Although triglycerides are the major composition in both vegetable and animal oils, the different oils usually comprising of different fatty acid constituents which govern their properties. On the other words, the variations in property of fatty acid are largely depends on chain length or molecular weight, number and double bond isomer. These factors reflect energy content, melting point (mp), cloud point, pour point, density, shelf-life, etc. Fatty acid profiles and properties of some vegetable oils are shown in table 1.1.

Table 1.1 Fatty acid profiles and properties of some vegetable oils (Slightly modified from Leung et al., 2009)

Oil	Main chemical composition (Fatty acid composition % wt.)	Density (g/L)	Flash point (°C)	Kinematic viscosity (cSt, at 40 °C)	Acid value (mg KOH/g)	Heating value (MJ/kg)
Soybean	C 16:0, C 18:1, C 18:2	0.91	254	32.9	0.2	39.6
Rapeseed	C 16:0, C 18:0, C 18:1, C 18:2	0.91	246	35.1	2.92	39.7
Sunflower	C 16:0, C 18:0, C 18:1, C 18:2	0.92	274	32.6	-	39.6
Palm	C 16:0, C 18:0, C 18:1, C 18:2	0.92	267	39.6	0.1	39.7
Physic nut	C 16:0, C 16:1, C 18:0, C 18:1, C 18:2	0.92	225	29.4	28	38.5

Apart from fatty acid compositions, other constituent of oil also dominate quality of feedstock to produce biodiesel. These including the contents of ash, sulfur, nitrogen, water. In addition, the present of long chain hydrocarbon, wax, even in a small amount, it could plug fuel filter, orifice and prevent engine operation.

1.2.5 Feedstock for biodiesel production

To reduce production costs and make biodiesel competitive with petroleum diesel, low-cost feedstock, such as non-edible oils, waste frying oils and animal fats, could be used as raw materials (Gerpen, 2005). However, it seems that its supplying is inadequate quantity to use in commercial scale. In addition, it exhibits difficulty to process due to the compositions therein are not consistence which is difficult to control the product quality.

Although almost vegetable oils can be used as feedstock for biodiesel production, its availability which depends largely on climatic geography is principal factor. Recently, more than 80% of the world biodiesel has produced from rapeseed and sunflower oils which are commonly planted in Europe. Soybean is the most common planted in the United States while palm is commonly planted in the Southeast Asia such as Malaysia, Thailand and Indonesia. In addition, several alternative feedstock were evaluated to produce biodiesel such as rubber seed oil

(Ramadhas et al., 2005), salmon oil (El-Mashad et al., 2007), coffee oil (Oliviera et al., 2008), etc.

Apart from supplying quantity, properties of feedstock which reflect the diesel quality are also needed to consider. Numerous studies were also indicated that oil palm was shown a promising to be a suitable feedstock for supply demand of energy consumption (Lee et al., 2007, Winayanuwattikun et al., 2008, Jayed, et al., 2009, Papong et al., 2010).

Feedstock in Thailand

Several oil-yielding plants are cultivated in Thailand such as palm, physic nut, coconut, soybean, peanut, castor, and sesame, etc. In 2004, Department of Alternative Energy Development and Efficiency (DEDE), Ministry of Energy was investigated a production of oil-yielding plants and reported that there are various type of, Among these, oil palm has the highest annual yield, followed by coconut. Table 1.2 summarizes the productivity of major oil-yielding plants in Thailand. In addition, apart from the plants mentioned, there are other sources of oil can be used for biodiesel production, such as the physic nut, animal oil, and used vegetable oil.

To summarize, regarding to meet the strategic plan for biodiesel production of Thailand, physic nut, used vegetable oil and oil palm were found to be most suitable feedstock. Besides that oil from algae was attended recently.

Table 1.2 Major oil-yielding plants in Thailand (slightly modified from Winayanuwattikun et al., 2008)

Commom name	Average productivity yield (kg·ha^{-1})	Average oil yield (kg·ha^{-1})
Oil palm	27,788	10,504
Physic nut	4940	2163
Coconut	3680	404
Peanut	1680	811
Castor bean	1408	878
Soybean	1260	210

Physic nut

Jatropha currcas is a plant in Euphorbiaceae family, commonly known as physic nut. The physic nut oil is inedible oil because of poisonous, toxic substances known as curcine or curcasin, and then the dry seeds cannot be used as animal feed. Due to its advantage, fast-growing bush and grows well even in dry conditions, moreover, consisting of oil 50% by weight of the seed, physic nut oil was found to be the major feedstock of the biodiesel program (Winayanuwattikun et al., 2008). Currently, cultivation and utilization of the plant is no longer found in Thailand, then, the projections for plantation and development were started since 2008 to supplement of utilized edible oil for production of biodiesel. Unfortunately, low productivity and complicated harvest is seemed to be disadvantages that reduce the potential of use as feedstock for large-scale process because it could affected to cost of biodiesel production.

Used vegetable oil

Used vegetable oil is another feedstock that has potential for biodiesel production. The advantage of these, being available locally, renewable and cheap can make a good consideration to be feedstock. In addition, used vegetable oil is usually disposed of inappropriately or reused in frying food, then using it as feedstock would beneficially to environment and health (Tashtoush et al., 2003). However, the low consistency due to obtaining from food processing and insufficient for demand of biodiesel production could be the cause of less attention in large-scale production of biodiesel.

Oil palm

Palm oil is a product from oil palm, an economic plant in Thailand that obtains from the mesocarp of fruit and the production of oil palm is highest among Thailand's oil-yielding plants. From this reason, palm oil seem to be a more suitable and attractive candidate as the source of biodiesel production. From chemical compositions and properties, both crude palm oil and crude palm kernel oil could use as a feedstock for biodiesel production (Jitputti et al., 2006, Alamu et al., 2008). Many sources of oil palm products could achieved to produce biodiesel, namely used frying oil, RBD (refined, bleached and deodorized) palm oil, degummed and deacidified palm oil, palm stearin and superhard palm stearin (Tongurai et al., 2001). To minimize the cost of production, crude palm oil, the cheapest oil palm products, would favorable in process.

Microalgae oil

However, recent studies were indicated that the production of biodiesel from edible oil and inedible oil cannot realistically satisfy even a small fraction of the existing demand for fuel consumption (Chisti, 2007). In addition, the increasing of biodiesel production to supply the demand could also lead to compete with edible oil and result in higher price of edible oil. Consequently, to solve these, several studied was attempted to find an alternative feedstock. Oil from microalgae was found to be an attractive candidate with its advantage such as, high efficiency of oil yielding, providing a reliable and continuous supply of oil, can be grown in variable area, etc.

(Schenk et al., 2008, Hossain et al., 2008, Li et al., 2008, Griffiths and Harrison, 2009 and Gouveia and Oliveira, 2009).

In conclusion, at a present, palm oil could be a most attractive feedstock for biodiesel production commercially. With the beneficial of environment, Southeast Asia region including Thailand would be a prominent exporter of biodiesel. However, in term of economic, crude palm oil would favorable to use in production by needing a complicated process.

1.2.6 Biodiesel production process

The economic production of biodiesel is a chemical processing such as basic catalytic, acid catalytic, etc. Conventional biodiesel production was a transesterification batch process using short chain alcohol as reactant in the presence of basic catalyst. This has the economic attractions of low temperatures and pressures in the reaction, high efficiency of oil conversion. Production procedure consisted of oil preparation, solvent preparation, reaction step, glycerol separation, washing step and finishing step (Tongurai et al., 2001). Regarding to the type of catalyst, these was categorized as followed;

Basic-catalytic transesterification

Transesterification in the presence of basic is a common process to produce biodiesel commercially. At the end of reaction, desirable ester and glycerol as by-product were appeared. Due to low cost of production, methanol and sodium hydroxide as catalyst are usually employed in this process.

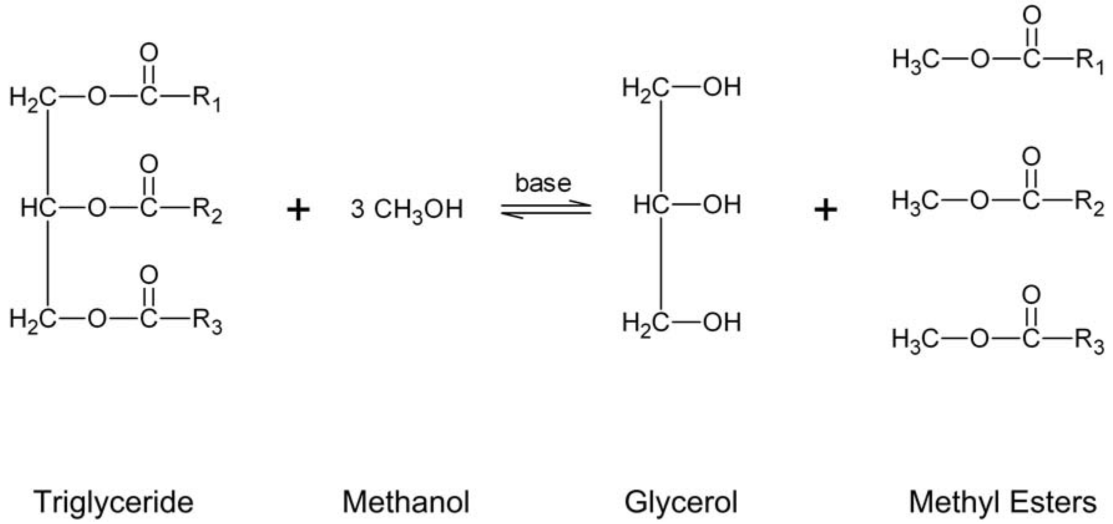

Figure 1.2 Base-catalyzed transesterification reactions (Image:http://ww2.mackblackwell.org/web/research/ALL_RESEARCH_PROJECTS/2000s/2092/images/MBCTcompletionreport2092final_img_4.jpg)

In a transesterification reaction, the yield of biodiesel is affected by these factors, amount of alcohol, catalysts, reaction temperature, reaction time, free fatty acid content and water content. An excess alcohol was used to shift the reaction equilibrium to the right side and produce more esters as the proposed product. From literature reviews, several studies were also indicated the optimum condition for biodiesel production that using the molar ratio of oil to alcohol as 1 to 6 at least, which equal to 20 % by weight of oil, basic catalyst was 0.5-1.0 % wt. of oil and using temperature as 60-80^{O}C (Ma and Hanna, 1999; Tongurai et al., 2001; Eevera et al., 2009; Keera et al., 2010).

However, to minimize the cost production, the poor quality feedstocks that contain high free fatty acid contents or water content were usually employed for processing. When the feedstock have had high free fatty acid content or water content, the alkali catalyst will strongly react with the free fatty acid content to form soap. The water can hydrolyze the triglycerides into diglycerides and form more free fatty acids. Both of reactions are undesirable and reduce yield of biodiesel. To reduce the soap formation, many researches were carried out the process by using acid esterification.

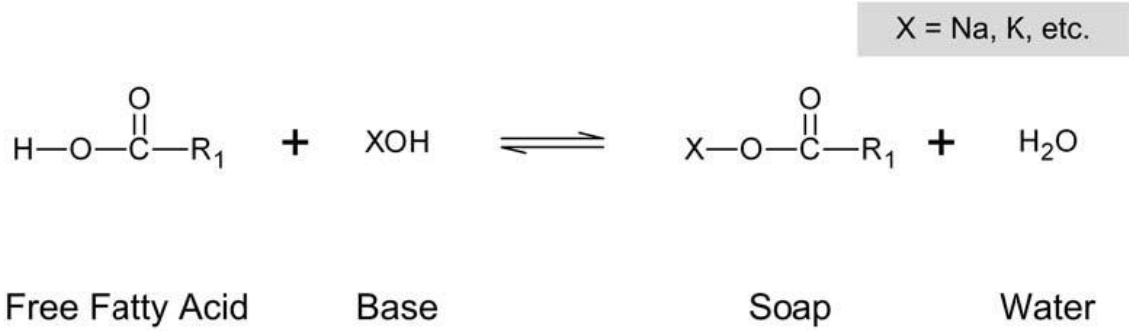

Figure 1.3 Saponification reaction

(Image:http://ww2.mackblackwell.org/web/research/ALL_RESEARCH_PROJECTS/2000s/2092/images/MBCTcompletionreport2092final_img_5.jpg)

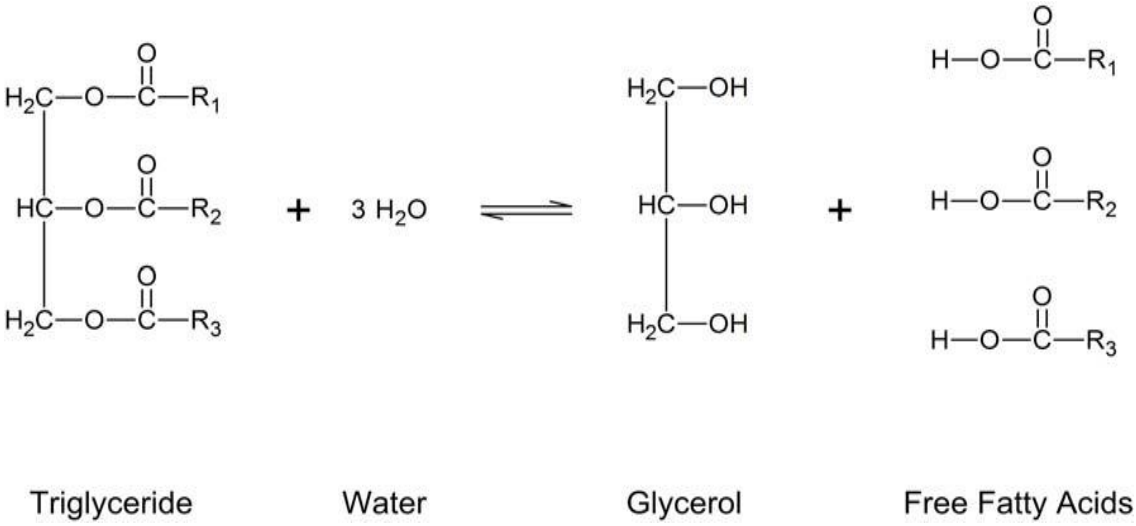

Figure 1.4 Hydrolysis reaction of triglycerides

(Image:http://ww2.mackblackwell.org/web/research/ALL_RESEARCH_PROJECTS/2000s/2092/images/MBCTcompletionreport2092final_img_7.jpg)

Acid catalytic esterification

Acid esterification is a reaction that uses alcohol in the presence of acid for conversion oil into ester. This process was favorable when using poor quality feedstock such as high free fatty acid content and/or high water content. As same as basic transesterifiction reaction, the factors that affecting the yield of acid catalyzed were amount of alcohol, amount of catalyst and reaction temperature (Crabbe et al., 2001). Several studies were investigated this reaction, for example as below.

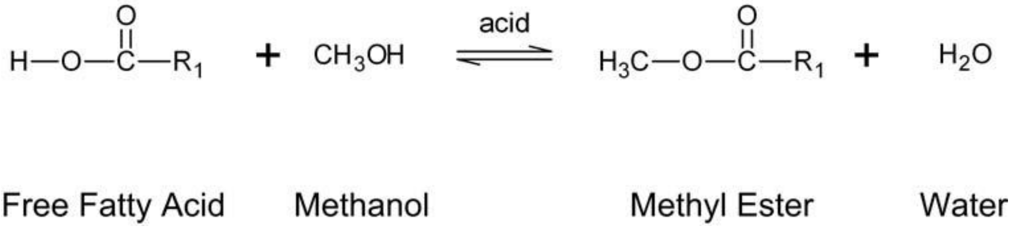

Figure 1.5 Esterification reaction
(Image:http://ww2.mackblackwell.org/web/research/ALL_RESEARCH_PROJECTS/2000s/2092/images/MBCTcompletionreport2092final_img_6.jpg)

Crabbe et al. (2001) were optimized esterification process to produce biodiesel from crude palm oil and reported that the optimum condition for ester conversion was using molar ratio of methanol to oil as 40 to 1 with 5% by volume of sulfuric acid reacted at 95^{O}C for 9 hours, yielded 92% by weight.

Aranda et al. (2008) demonstrated the acid-catalyzed homogeneous esterification reaction to produce biodiesel in a batch reactor. In this study, the type of homogeneous acid catalyst was investigated, namely, sulfuric acid, phosphoric acid, trichloroacetic acid and methanesulfonic acid. The results indicated that methanesulfonic and sulfuric acid were the best catalyst as they shown greater yields for biodiesel production.

In 2010, Khan et al. were optimized acid esterification of a high free fatty acid crude palm oil and crude rubber seed oil blend for biodiesel production. The results indicated that the optimum conditions for acid esterification which 95% reduction of free fatty acid content in the feedstock were using molar ratio of methanol to oil as 15 to 1 with sulfuric acid 0.5% by weight reacted at 65^{O}C for 3 hours.

From previous studies, sulfuric acid (H_2SO_4) usually used as economic catalyst to perform esterification reaction. Unfortunately, these results indicated that this process was shown less economic attraction by high energy consumption because it required large amount of alcohol and long reaction time. However, the main conclusion to be drawn from these mention is that the process of esterification with alcohol in the presence of acid is not only an alternative reaction to produce biodiesel but also can be used as a pretreatment for basic transesterifiction reaction to convert the free fatty acid into esters that result in avoid saponification, especially when free fatty acid content is higher than 1% by weight.

Two-step process

From above mention, in case of high free fatty acid contents contained feedstock such as crude vegetable oil, using 2-step process was developed to enhance the efficiency of biodiesel production. The first step is acid-esterification to reduce free fatty acid content lower than 2% wt., then, esterified product was carried out a basic-transesterification to ester conversion. Numerous studies were evaluated this process, for example as below;

Ramadhas et al. (2005) studied the 2-step process to produce biodiesel from crude rubber seed oil that contain about 17% wt. of free fatty acid contents. The authors reported that the first esterification step has been carried out with 6 to 1 molar ratio of methanol to oil in the presence 0.5% wt. sulfuric acid and reacted at 50^{O}C for 30 minutes at atmospheric pressure, then, followed the second transesterification step with 9 to 1 molar ratio of methanol to oil in the presence 0.5% wt. sodium hydroxide and reacted at 50^{O}C for 30 minutes. The important properties of these were acceptable with comparative diesel fuel.

Chongkhong et al. (2007) studied the 2-step process for biodiesel production from palm fatty acid distillate that consists of 93% by weight of free fatty acid. The results indicated that the optimum condition for the continuous esterification process was molar ratio of methanol to oil at 8 to 1 with 1.8% wt. of sulfuric acid at 70^{O}C under its own pressure with a retention time of 60 minutes. At the end of esterification process, the free fatty acid content was sharply reduced to less than 2% wt. After that, the esterified products was purified by neutralization with 3 M sodium hydroxide in water solution at a reaction temperature of 80^{O}C for 15 minutes and followed by transesterification process with 0.396 M sodium hydroxide in methanol solution at a reaction temperature of 65^{O}C for 15 minutes. The final ester product was met the biodiesel quality standard.

In conclusion, 2-step process was achieved to produce biodiesel from high free fatty acid contents feedstock. These process would beneficial by reducing the overall cost production of biodiesel, as it used low cost, unrefined non edible oils.

Other biodiesel production processes

Since biodiesel which is derived from triglycerides by chemical process with alcohol, transesterification, has attracted considerable attention during the past decade as a economic processing. To improve the efficiency of process for supply the demand of energy consumption, several studies were attempted to develop the processes for biodiesel production such as heterogeneous catalytic transesterification, enzymatic transesterification, and supercritical alcohol process.

Heterogeneous catalytic transesterification

However, both basic and acid catalysts that commonly used commercially to produce biodiesel were homogeneous catalyst. However, the alkali homogeneous catalysts are highly hygroscopic and absorb water from air during storage. They also form water when dissolved in the alcohol reactant and affect the yield of esters, and then properly handle was needed on both catalysts.

From above mentions, to avoid the disadvantage by using homogeneous catalyst, heterogeneous catalysts such as calcium oxide (CaO), zirconium oxide (ZrO_2), zinc oxide (ZnO), sulphated stannous oxide (SO_4^{2-}/SnO_2), etc. were investigated by numerous studies and successful to produce biodiesel (Schuchardt et al., 1998, Jitputti et al., 2006, Marchetti and Errazu, 2008, Boey et al., 2009).

However, some heterogeneous catalysts are solid and it could be rapidly separated from the product by filtration, which reduces the washing requirement. In addition, these catalysts can stimulatingly catalyze the transesterification and esterification reaction that can avoid the pre-esterification step, thus these catalysts are particularly useful for high free fatty acid content feedstocks. Unfortunately, using a solid catalyst, the reaction is shown a slower rate because the reaction mixture constitutes a three-phase system (Leung et al., 2009).

Enzymatic transesterification

Enzymatic transesterification using lipase as heterogeneous catalyst was investigated by numerous studies (Lara Pizarro and Park, 2003, Moreira et al., 2007 and Yagiz et al., 2007). It has become more attractive for biodiesel production, since the glycerol produced as a by-product can easily be recovered and the purification of esters is simple to accomplish.

The main drawbacks to the commercialization of this process are the high cost production of lipase and needing much longer incubation times to achieve more than 90% ester conversion. To reduce the cost, the use of whole cell biocatalysts immobilized within support particles is significantly advantageous since immobilization can be achieved spontaneously during batch cultivation, and in addition, no purification is necessary. The lipase production cost can be further lowered using genetic engineering technology, such as by developing lipases with high levels of expression or stability towards alcohol. Hence, whole cell biocatalysts appear to have great potential for industrial application (Fukuda et al., 2001).

Supercritical alcohol process

The other process to produce biodiesel is supercritical alcohol process. This process is improved the efficiency biodiesel production process in term of shorter reaction time and lesser purification steps, but, high temperature and pressure were needed. This process was allowed alcohol and triglycerides to forming a single phase, and the reaction is completed in a very short time. However, in the catalytic supercritical alcohol transesterification method, the yield of conversion rises to 60-90% for the first 1 minute (Demirbas, 2008).

Hawash and coworker (2009) were studied a non-catalytic supercritical methanol transesterification process for biodiesel production by using physic nut oil as feedstock. The results revealed that within 4 minutes, 100% yield of esters can be obtained by using these condition, temperature of 593 K (320^{O}C) and under a pressure of 8.4 megapascals (MPa) and the molar ratio of methanol to oil was 43 to 1.

Supercritical alcohol method has a high potential for biodiesel production due to two major advantages, the reaction time can be very short and the separation of the products as well as the by-products can be achieved efficiently under these condition.

In conclusion, the common process to produce biodiesel is a basic-transesterification. Due to the quality of feedstocks, acid-esterification was favorable to employ for reduction free fatty acid content before transesterification, which known as 2-step process. However, to improve the efficiency of process, several processes were developed such as heterogeneous catalytic transesterification, enzymatic transesterification, and supercritical alcohol process. By the way, regarding to economic attraction, the basic catalytic transesterification seem to be a suitable process for commercial biodiesel production at a present.

Table 1.3 Comparison of transesterification process (slightly modified from Leung et al., 2009 and Demirbas 2006)

Type	Catalyst	Advantage	Disadvantage
Alkali *Homogeneous*	NaOH, KOH	High catalytic activity, Low cost, Favorable kinetics, Modest operation condition	Low FFA requirement, Anhydrous conditions, Saponification, Emulsion formation, More wastewater from purification, Disposable
Alkali *Heterogeneous*	CaO, $CaZrO_3$, KOH/Al_2O_3, etc.	Noncorrosive, Environmentally benign, Recyclable, Fewer disposal problem, Easily separation, Higher selectivity, Longer catalyst lifetimes	Low FFA requirement, Anhydrous conditions, More wastewater from purification, High molar ratio of alcohol to oil requirement, High reaction temperature and pressure, Diffusion limitations, High cost
Acid *Homogeneous*	Concentrated sulfuric acid (H_2SO_4)	Catalyze esterification and transesterification simultaneously, Avoid soap formation	Equipment corrosion, More waste from neutralization, Difficult to recycle, Higher reaction temperature, Long reaction times, Weak catalytic activity
Acid *Heterogeneous*	ZrO_2, ZnO, sulphated zirconia, etc.	Catalyze esterification and transesterification simultaneously, Recyclable, Eco-friendly	Low acid site concentrations, Low microporosity, Diffusion limitations, High cost
Enzymes	Lipase	Avoid soap formation, Nonpolluting, Easier purification	Expensive, Denaturation
Supercritical alcohol	Can achieved with using catalytic or non-catalytic	Fast reaction times, Easily separation, Easier purification	High reaction temperature and pressure, High cost

1.2.7 Ethyl ester production process

A transesterification process to produce biodiesel is a reaction between triglyceride and alcohol in the presence of catalyst. Alcohol used in common process is methanol because of its advantage, such as, cheap, easy to provide and simplified process. Consequence, methanolysis reaction is a favorable process to studied (Jin et al., 2007, Predojević, 2008, Feralla et al., 2010). However, methanol is highly toxic, can be absorbed through the skin and is fully miscible with water. In contrast, ethanolysis process which using ethanol that safer than methanol has rarely been studied because of appearing of some problem.

Phase separation between biodiesel and glycerol was appeared to be a serious problem in large-scale production of ethanolysis process. In 1992, Korus and coworkers was studied the transesterification process required to manufacture the ethyl ester of rapeseed oil and found the problem of separation that the two phases cannot occurred when using ethanol as a substitute for methanol. However, the authors suggested that the type of catalyst and excess alcohol was a major factor affected to separation of the ethanol ester phase and recommended that sodium methoxide ($NaOCH_3$) or potassium hydroxide (KOH) was favorable to use as catalyst for ethyl ester production. In addition, the presence of water in the reaction mixture was reduced the ester conversion. These studied was resulted in hypothesis that soap formation and water are major factor to decreasing the efficiency of phase separation.

To investigate the problem, phase distributions in the transesterification of ethyl ester from soybean oil was studied by Zhou and Boocock (2006), and reported that when using ethanol, more alcohol and glycerol were found in the final ester phase of a transeterification. The ester is non-polar and therefore the less-polar ethanol was more soluble in the glycerol phase than was the methyl ester. Consequently, the upper phase actually became more polarity in the case of ethanolysis, and as a result, more glycerol moved into it. So, the authors suggested that the removal of the ethanol would result in a better separation from glycerol.

These results was also agreed with Černoch et al. (2010) who's researched on distribution of ethyl esters, glycerides and glycerol between ester and glycerol phase by using rapeseed oil as raw material, were reported that soaps and monoglycerides formed by the transesterification reaction increase the amount of ethyl esters in the glycerol phase. This causes a decrease in the yield of the ester phase so elimination of soaps and monoglycerides forming can reduce the losses of ethyl esters and thereby increase biodiesel yield. In addition, the authors also suggested that the increasing of molar ratio of oil to ethanol has a positive effect unambiguously by decreasing the concentrations of glycerides and soaps in the reaction mixture and increasing the ethyl ester concentration in the mixture and the yield of biodiesel (Černoch et al., 2010).

Although, the investigation about phase separation was revealed by previous study, consequently, to improve the efficiency of ethyl ester production, numerous studies were investigated to enhancing the phase separation by remove the interference which is excess alcohol with rotary evaporator (Domingos et al., 2008, Bouaid et al., 2009).

Since 1996, Peterson and coworker were optimized a batch type ethyl ester process from rapeseed oil. The results indicated that separation does not occurred when using ethanol contain water content higher than 1%. The addition of a small amount of alcoholic KOH or water was recommended to enhance the separation of the glycerol from ester.

In 2002, Al-Widyan and Al-Shyoukh were demonstrated in the transesterification of waste palm oil with ethanol and suggested that as transesterifying of used vegetable oils is limited to acidic catalysts, sulfuric acid (H_2SO_4) was recommended using as a catalyst, to avoid the soap formation. The problem about phase separation of ethyl ester was not reported by the authors with this method. This studied was supported the hypothesis that soap formation during process was affected to the occurrence of phase separation.

To avoid the soap formation from using high free fatty acid content oil as raw materials, Marchetti et al. (2007) were evaluated the esterification reaction into biodiesel by using basic resins as catalyst and reported that this methods were success to produce ethyl ester from frying oil, the ester conversion yielded around 80%.

In the same year, Encinar et al. were studied on ethanolysis of used frying oil and successfully improved the phase separation by adding 25 % wt. of glycerol, the optimum conditions to produce ethyl ester was obtained by using molar ratio of oil to ethanol as 1: 12, potassium hydroxide as catalyst (1 % wt.), and reacted at $78^{O}C$.

However, yield of this condition was 72.5 % wt., only. To improve the yield, the authors recommended that the two-stage transesteification was better than the one-stage process, and the yields of ethyl ester were improved 30% in relation with the one-stage transesterification, 94.5 % wt.

From literature reviews, it is hypothesized that the major factor that reduces the separation of ethyl ester was water (by-product from the esterification step), the FFA content and presence of excess alcohol. The presence of both water and FFA leads to soap formation whereas ethanol seems to play a role as a stabilizing agent between the ester and the glycerol phase. Then, development of a procedure for improving the efficiency of separation was successful achieved. Unfortunately, most of these would not satisfy for large-scale production that needs low cost.

In conclusion, biodiesel from ethanol was attended by numerous studied because not only it has had comparable properties to methyl ester for substitute diesel fuel but it is also harmless raw material for production process. In addition, both of raw materials, vegetable oil and ethanol could derive from agricultural product. That would leaded a biodiesel from ethanol be a renewable energy.

1.2.8 Utilization of biodiesel

Since higher carbon built up and lubricating oil contamination resulting in engine failure appear to be a potentially serious problem with the use of unmodified vegetable oil, then processed vegetable oils, either chemically modified or blended with diesel fuel which known as biodiesel were investigated to solve these. To evaluate the potential of using biodiesel, either methyl esters or ethyl esters, on diesel engine, some properties and characterization were investigated.

The use of biodiesel in neat or blended form has no effect on the energy based engine fuel economy. The lubricity of these fuels is better than diesel fuel, and this property is also better when blending at level above 20% by volume (B20). Emissions of particulate matter (PM) can be reduced dramatically through use of biodiesel in engines that are not high lube emitters. Emissions of nitrogen oxide (NO_x) increase significantly for both neat and blended fuels (Graboski and McCormick, 1998).

In case of utilization of ethyl ester as fuel, since 1995, Peterson and coworker was studied the using of ethyl ester from rapeseed oil to perform non-modified diesel engine for 14,000 km. and concluded that the emissions of hydro carbon (HC), carbon monoxide (CO) and nitrogen oxide (NO_x) was significantly reduced, on the other hand, the emissions of carbon dioxide (CO_2) and particulate matter (PM) was increased with comparative diesel fuel. However the vehicle performance was extremely good and no problems were noted during his test. The results indicated that the using of ethyl ester was not encounter a problem to run on diesel engine.

Tashtoush et al. (2003) studied a combustion performance and emissions of ethyl ester in a water-cooled furnace to investigate the feasibility of utilizing this renewable and low cost fuel raw material as a diesel fuel replacement in small-scale applications such as in residential heating boilers. Results clearly indicated that ethyl ester is a potential candidate as fuel for furnaces and boiler combustors. In addition to being available locally, renewable and cheap, biodiesel can make a good substitute for diesel fuel in those applications.

In 2005, May et al. were studied some fuel properties of palm oil alkyl esters such as methyl ester and ethyl ester by using transesterification process and reported that these alkyl esters shown higher viscosity compared to that of diesel fuel. In addition, compared to diesel fuel, these alkyl esters exhibit acceptable gross heat of combustion and the low sulfur content in alkyl esters emits much lower sulfur dioxide (SO_2). These esters are much safer than diesel fuel in terms of safety for storage and transportation as they possess high flash points. From these results, it indicated that both alkyl esters exhibit comparable fuel properties with methyl ester and diesel fuel, however, methyl ester would be the preferred choice in term of the cost, since, methanol is less expensive than ethanol.

Table 1.4 Some fuel characteristics of alkyl ester from palm oil products (slightly modified from May et al., 2005)

Characteristics	Unit	Crude palm oil (CPO)		Crude palm stearin (CPS)		Diesel fuel
		Methyl ester	Ethyl ester	Methyl ester	Ethyl ester	
Density @ 40^{O}C (ASTM D 4052)	Kg/L	0.855	0.857	0.857	0.858	0.823
Sulfur content (IP 242)	% wt.	< 0.04	< 0.04	< 0.04	< 0.04	0.20
Viscosity @ 40^{O}C (ASTM D 445)	x 10^{-6} m^2/s	4.4	4.7	4.5	4.8	4.0
Pour point (ASTM D 97)	^{O}C	15	12	18	15	15
Cloud point (ASTM D 2500)	^{O}C	16	16	19	16	18
Gross heat of combustion (ASTM D 2382)	MJ/kg	39.7	39.7	39.9	39.9	45.8
Flash point (ASTM D 93)	^{O}C	178	-	165	-	80

In 2007, Utlu and Kocak were demonstrated the methyl ester on a diesel engine with turbocharged four cylinders and direct injection and studied the effect of using these on engine performance and exhaust emissions. Results indicated that engine performances are nearly the same as compared with No. 2 diesel fuel. In addition, amount of emission such as carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NO_x) and smoke darkness of biodiesel are less than diesel fuel.

Swanson et al. (2007) were investigated the exhaust of biodiesel fuels and reported that which relative to petroleum diesel, biodiesel emissions have been shown to contain less particulate matter (PM), carbon monoxide (CO), and polycyclic aromatic hydrocarbons (PAH). Furthermore, sulfur containing compounds appear to be undetectable. However, the combustion of biodiesel in a diesel engine typically does increase the release in nitrogen oxides (NO_x).

Shahid and Jamal (2008) studied on some characterization when using biodiesel as vehicular fuel and reported that there was a slightly decrease in brake power and slightly increase in fuel consumption. However, the lubricant properties of biodiesel are better than diesel fuel, which can help to increase the engine life. Moreover, biodiesel fuel is environment friendly, produces much less NO_x and HC and absolutely no SO_x and no increase in CO_2 at global level.

Lapuerta et al. (2008) studied the effect of both methyl ester and ethyl ester from waste cooking oil on diesel performance and emissions and reported that using biodiesel as fuels, compared to diesel fuel, were resulted in a slight increase in fuel consumption, in very slight differences in NO_x emissions, despite the encouraging potential to reduce hydrocarbon emissions, smoke opacity and particulate matter emissions. This potential was even higher in the case of methyl esters.

In 2009, Basha et al. were studied on some characterization of biodiesel and reported that the combustion characteristics of biodiesel are similar as diesel and blended fuels were found shorter ignition delay, higher ignition delay, higher ignition temperature, higher ignition pressure and peak heat release. The engine power output was found to be equivalent to that of diesel fuel. The emission of nitrogen oxides from the engine found to be higher on the all fuel blends as compared to diesel.

In conclusion, none of argument on several studies indicated that biodiesel can be used on diesel engine to replace diesel fuel. Analyses of the environmental impact of using biodiesel as fuel indicated that using biodiesel effectively reduces the emission of pollutants, except for nitrogen oxides (NO_x).

1.2.9 Some properties and characterization

In 2006, Tyson and McCormick reviewed the using of biodiesel and biodiesel blends. The authors described some properties and characterization of these that biodiesel is an fuel comprised of mono-alkyl esters of long chain fatty acids that derived from vegetable oil or animal fats, which designated as B100.

In addition, The American Society for Testing and Materials International (ASTM) was noted a specification for biodiesel (B100) as ASTM D6751-03. This specification is characterized the quality of biodiesel to be used as a blend stock at

20% (B20) and lower blend levels. Regarding to diesel engine operation, ASTM D6751 is based on the physical and chemical properties needed for safe and satisfactory to operate diesel engine. The biodiesel fuel must meet the properties specified in Table 1.5 below.

Table 1.5 Requirements for Biodiesel (B100) Blend Stock as Listed in ASTM D6751-03 (Tyson and McCormick, 2006)

Property	ASTM Method	Limits	Units
Flash Point	D93	130.0 min.	°C
Water and Sediment	D2709	0.050 max.	% vol.
Kinematic Viscosity, 40°C	D445	1.9 - 6.0	mm^2/s
Sulfated Ash	D874	0.020 max.	% mass
Sulfur*	D5453	0.0015 max. (S15) 0.05 max. (S500)	% mass
Copper Strip Corrosion	D130	No. 3 max.	
Cetane Number	D613	47 min.	
Cloud Point	D2500	Report to Customer	°C
Carbon Residue**	D4530	0.050 max.	% mass
Acid Number	D664	0.80 max.	mg KOH/g
Free Glycerin	D6584	0.020 max.	% mass
Total Glycerin	D6584	0.240 max.	% mass
Phosphorus Content	D4951	0.001 max.	% max.
Distillation Temperature, 90% Recovered (T90)***	D1160	360 max.	°C

* Sulfur content of on-road diesel fuel to be lowered to 15 ppm in 2006

** Carbon residue shall be run on the 100% sample

*** Atmospheric equivalent temperature

Some of the test methods listed in Table 1.5 perform more than one role to ensure that the fuel performs as intended in compressed ignition (CI) engines and as tests to ensure that the manufacturer produced a high-quality B100. The intent of each quality requirement in Table 2 is described below:

Flash point

A minimum flash point for diesel fuel is required for fire safety. Flash point of biodiesel is typically much higher than diesel fuel to ensure that the manufacturer has removed excess methanol used in the manufacturing process. Residual methanol in the fuel is a safety issue because even very small amounts reduce the flash point. Residual methanol, which can be found in biodiesel with low, out-of-specification flash point, can also affect fuel pumps, seals and elastomers, and can result in poor combustion properties.

Water and sediment

Water and sediment refers to the presence of free water droplets and sediment particles. The allowable level for B100 is set at the same level allowed for conventional diesel fuel. Poor drying techniques during manufacturing or contact with excessive water during transport or storage can cause B100 to be out of specification for water content. Excess water can lead to corrosion and provides an environment for microorganisms. Fuel oxidation can also raise sediment levels, so this test can be used in conjunction with acid number and viscosity to determine if fuels have oxidized too much during storage.

Viscosity

A minimum viscosity is required for some engines because of the potential for power loss caused by injection pump and injector leakage. This is not an issue for B100 and the minimum is set at the same level as for petroleum diesel. The maximum viscosity is limited by the design of engine fuel injection systems. Higher viscosity fuels can cause poor fuel combustion that leads to deposit formation as well as higher in-cylinder penetration of the fuel spray which can result in elevated engine oil dilution with fuel. The maximum allowable viscosity in ASTM D975 for No. 2 diesel is 4.1 mm^2/s, at 40°C although most engines are designed to operate on fuels of higher viscosity than 4.1 mm^2/s. ASTM D6751 allows for slightly higher viscosity than D975 primarily because that is where the normal viscosity of B100 lies.

Sulfated ash

The sulfated ash test measures the amount of residual alkali catalyst present in the biodiesel as well as any other ash forming compounds that could contribute to injector deposits or fuel system fouling.

Sulfur

Sulfur is limited to reduce sulfate and sulfuric acid pollutant emissions and to protect exhaust catalyst systems when they are deployed on diesel engines in the future. Biodiesel generally contains less than 15 ppm sulfur.

Copper strip corrosion

The copper strip corrosion test is used to indicate potential difficulties with copper and bronze fuel system components. The requirements for B100 and conventional diesel fuel are identical, and biodiesel meeting other D6751 specifications always passes this test. While copper and bronze may not corrode in the presence of biodiesel fuel, prolonged contact with these catalysts can cause fuel degradation and sediment formation.

Cetane number

An adequate cetane number is required for good engine performance. Conventional diesel fuel must have a cetane number of at least 40. Higher cetane numbers help ensure good cold start properties and minimize the formation of white smoke.

Cloud point

Cloud point is important for ensuring good performance in cold temperatures. B100 cloud point is typically higher than the cloud point of conventional diesel fuel. Low temperature properties and strategies for ensuring good low-temperature performance of biodiesel blends are discussed in more detail in the following chapters.

Carbon residue

Carbon residue gives a measure of the carbon-depositing tendency of a fuel and is an approximation of the tendency for carbon deposits to form in an engine. For conventional diesel fuel the carbon residue is measured on the 10% distillation residue. Because B100 boils entirely in the high end of the diesel fuel range and at approximately the same temperature it is difficult to leave only a 10% residual when distilling biodiesel. So biodiesel carbon residue specifies that the entire biodiesel sample be used rather than the 10% distilled residue.

Acid number

Acid number for biodiesel is primarily an indicator of free fatty acids (natural degradation products of fats and oils) and can be elevated if a fuel is not properly manufactured or has undergone oxidative degradation. Acid numbers higher than 0.80 have been associated with fuel system deposit and reduced life of fuel pumps and filters.

Free and total glycerin

Free and total glycerin numbers measure the amount of unconverted or partially converted fats and by-product glycerin present in the fuel. Incomplete conversion of the fats and oils into biodiesel can lead to high total glycerin. Incomplete removal of glycerin can lead to high free glycerin and total glycerin. If these numbers are too high, storage tank, fuel system, and engine fouling can occur. Fuels that exceed these limits are highly likely to cause filter plugging and other problems.

Phosphorus

Phosphorus content is limited to 10 ppm maximum in biodiesel because phosphorus can damage catalytic converters and phosphorus above 10 ppm can be present in some vegetable oils. Biodiesel produced in the United States generally has low phosphorus levels, on the order of 1 ppm.

T90 distillation

The T90 distillation specification was incorporated to ensure that fuels have not been contaminated with high boiling materials such as used motor oil. B100 exhibits a boiling point rather than a distillation curve. The fatty acids from which biodiesel are produced are mainly straight chain hydrocarbons with 16 to 18 carbons that have close boiling temperatures. The atmospheric boiling point of biodiesel generally ranges from 330°C to 357°C.

Currently, there are ASTM specifications for B100 (D6751) and for diesel fuel (D975), but there is not a separate approved specification for biodiesel blends. Current practice to insure the quality of biodiesel blends is to use diesel fuel (No. 1 or No. 2) meeting D975 and biodiesel meeting D6751 prior to blending. However, B5 and lower blends generally meet the properties listed in ASTM D975, which defines the properties of conventional diesel fuel.

The advantage of biodiesel

From above mentioned, it summarized the advantages of biodiesel as; environmentally friendly fuel, safer for transportation and other uses, preventing engines failure, can be directly used in diesel engine and high efficiency of combustion.

Environmentally friendly fuel

Biodiesel is environmentally friendly because it is renewable, non-toxic fuel, easily biodegradable, and typically produces about 60% less net-lifecycle carbon dioxide emissions, as it is itself produced from atmospheric carbon dioxide via photosynthesis in plants. In comparison with diesel fuels, air pollution due to engine combustion of biodiesel fuels drops. The National Biodiesel Board and the US Environmental Protection Agency (USEPA) reported their analytical and experimental work on various biodiesel blends on diesel engines that the B100 and B20 formulas significantly cut combustion exhausts. The Department of Naval Dockyards, Royal Thai Navy, reported a 60% cut in black smoke through using biodiesel on a 145-horsepower diesel engine. Since it is derived from plants, biodiesel use reduces greenhouse gas emission. And, using biodiesel derived from used cooking oil automatically cuts down on the reuse of cooking oil and prevents used cooking oil, which contains carcinogenic dioxin materials, from being used in animal feed preparation (DEDE, 2004).

Safer for transportation and other uses

In addition, biodiesel has a higher flash point than diesel oil, making it safer for transportation and other uses. Biodiesel are classified as nonflammable as their flash or ignition points are above the minimum level of 130^{O}C (Kemp, 2006).

Preventing engines failure

In term of engine performance, Biodiesel is good lubricant and also can prevent engines failure, which help to reduce fuel system and engine wear. A 1-2% blend of biodiesel with diesel raises the lubricity index. The research and Technology Institute under PTT Plc found that blending the biodiesel obtained from used cooking oil and coconut oil, at 0.5% concentration, would increased two times of the lubricity index (DEDE, 2004).

Can be directly used in diesel engine

Otherwise, biodiesel can be directly used in diesel engine because biodiesel, which known as methyl ester or ethyl ester has comparable properties with diesel oil. Considering the impact on engines of using biodiesel, by international standards, biodiesel is more or less equivalent to diesel oil in all properties, so biodiesel has no negative impact on engines. However, some older engines may need rubber seal changes (DEDE, 2004).

High efficiency of combustion

The cetane value is a rating of the relative ignition quality of diesel and biodiesel fuels, with higher ratings offering improved ignition performance. As the cetane value increases, fuel ignition will be smoother and more complete, improving combustion and reducing emissions from unburned fuel. Because of this the combustion efficiency of biodiesel is higher than that of diesel fuel. Additionally, more efficient combustion, as biodiesel contains roughly 10% by volume of oxygen, which enables air and fuel to be evenly distributed and raises the volumetric ratio of air to fuel (DEDE, 2004).

The disadvantage of biodiesel

On the other hand, the disadvantages of these were shown as below; Oxidation and bacteriological stability, Nitrogen oxide emissions, Cold flow issues, Lower energy content.

Oxidation and bacteriological stability

Less stability of biodiesel seems to be a problem for long-term storage. When exposed to air or high temperatures, biodiesel are easily oxidized and resulting in polymerization which lead to plugged filter within the fuel injection system. To prevent storage degradation, anti-oxidant additives would be added. In addition, water content could destabilized biodiesel as well as encourages the growth of microorganism (Kemp, 2006).

Nitrogen oxide emissions

Numerous studies have confirmed that overall emissions from the combustion of biodiesel are low but show slightly elevated levels of nitrogen oxides (NO_x). This increase is regarded as a problem related to higher combustion cylinder temperatures and is not inherently a fuel-related issue. Manufacturers believe that improvements in engine sensor and management technology as well as NO_x catalytic reduction are just around the corner (Kemp, 2006).

Cold flow issues

A major problem of biodiesel is poor low temperature properties indicated by relatively high cloud and pour points. The cloud point is usually higher than the pour point and is the temperature at which a liquid fatty material becomes cloudy due to the formation of crystals and solidification of saturates. This eventually leads to the clogging of fuel lines (Kemp, 2006).

Lower energy content

In case of lower energy content, the energy content of a fuel was indicated by the heating values. The heating value is an important property to define not only the energy content but also thereby efficiency of fuels. The heating value of biodiesel is slightly lower than that of diesel fuel. The oxygen content of biodiesel improves the combustion process and decreases its oxidation potential and resulting in lower energy content. By the way, engines running on biodiesel are 3% less powerful than if it were to run on regular diesel oil, equivalent to a 3% increase in fuel consumption (Sivaramakrishnan et al., 2011).

1.2.10 Current situations of biodiesel in Thailand

The potential use of biodiesel to replace diesel fuel in engines has long attracted interest in Thailand (DEDE, 2004). Regarding raw material supply and production cost, palm oil found to be an admirable suitable raw material for biodiesel in Thailand (Pleanjai et al., 2004). In addition, palm diesel (methyl ester from palm oil) exhibits fuel properties comparable to those of petroleum diesel and can be used directly in unmodified diesel engines. The production and usage of palm diesel has great environmental impact with its closed carbon cycle. A fuel switch from fossil fuel to palm diesel will contribute greatly to the reduction of greenhouse gas (GHG) emissions that lead to global warming (May et al., 2005).

Since 2002, Vanichseni and coworkers studied a potential biodiesel production from palm oil for Thailand. The results indicated that if 20% of diesel production from the amount of imported crude oil in 2000, was compensated by this biodiesel production, it would reduce imported crude as estimated value as Bt 13,436 million. To avoid conflict with feedstock for food production, plantation areas of at least 4.4 million rais in 12.9 million rais (1 rai = 0.16 ha) of suitably available lands will be required. Oil palm is quantitatively the highest commercially potential production among the existing Thailand’s major oil crops. Transesterification can provide chemical transformation of crude palm oil (CPO) and crude palm kernel oil (CPK) to biodiesel. The product of this process has been acceptable as diesel substitute. Environmental impacts from biodiesel utilization show positive results compared to diesel fuel No. 2 (or high speed diesel; HSD).

Nevertheless, within this initial stage, another market for biodiesel would be a fuel additive because of more restrictive regulation on sulfur content in diesel fuel. Biodiesel’s high lubricity and CN properties are comparable with today’s diesel fuel additive, which their prices are normally substantially higher than petroleum diesel itself.

However, the government plans to have an installed biodiesel production capacity of 8.5 million liters per day by 2012, so that B10 (10% biodiesel in diesel fuel) can meet the total national diesel demand. Use of 8.5 million liters per day of biodiesel will reduce the import bill by 27 billion Baht per year (Winayanuwattikun et al., 2008).

In 2010, Department of Alternative Energy Development and Efficiency (DEDE) reported that the energy consumption had increased at the rate of 5.3% from 2009. Almost energy consumption was commercial energy (80.9%) which comprises petroleum products, natural gas, coal and electricity and the other was renewable energy (19.1%), including fuel wood, charcoal, paddy husk, and bagasse. The total value of final energy consumption was 1,639,515 million Baht.

Petroleum products still showed the greatest proportion or 56.5% of the final commercial energy consumption. Petroleum products consumption totaled 32,096 kilo ton of oil equivalent (ktoe), an increase of 1.4% from the previous. Petroleum products were mainly consumed in transport sector (71.6%), followed by agricultural sector, manufacturing sector, residential sector, commercial sector, construction sector and mining sector, shared 10.8%, 8.1%, 5.2%, 3.7% and 0.6%, respectively. The main proportion of petroleum products consumption was diesel (including palm diesel and HSD B5) shared 49.6%, followed by gasoline (including gasohol), LPG, jet fuel, fuel oil and kerosene, shared 17.2%, 14.1%, 12.0%, 7.1% and 0.04%, respectively (DEDE, 2010).

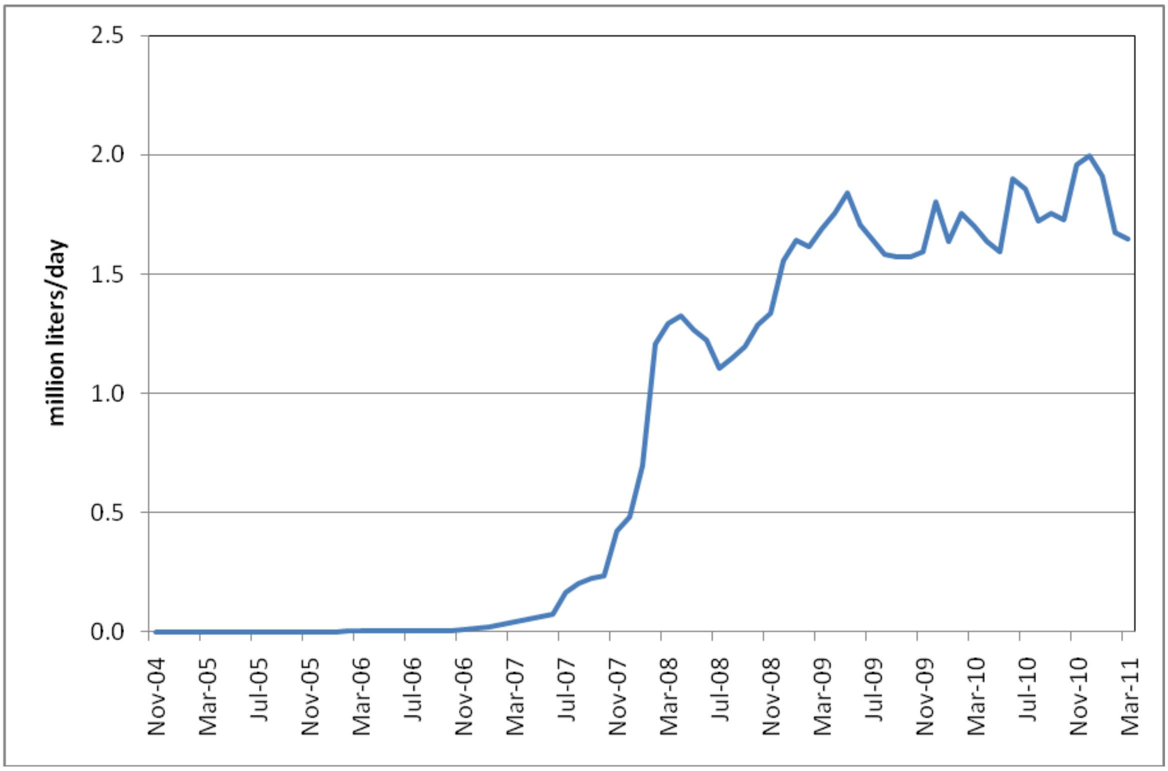

Figure 1.6 Biodiesel (B100) consumption in Thailand (dede.go.th)

From above mention, the Royal Thai Government (RTG), through the Ministry of Energy was attempted to strengthening the energy supply security by promote using the biodiesel. Since 2006, to promote more abstractly using of biodiesel, NEPC (the National Energy Policy Council) had its resolution to agree with establishing the price structure of B5 biodiesel by setting the retailed price of B5 high speed diesel (HSD) lower than of regular diesel at 0.50 Baht per liter (Baht/l).

Unfortunately, due to problems of the B100 biodiesel production and qualities such as unreliability in production process, limitations of nozzles and underground fuel tanks, no confidence and no acceptance in the B5 HSD quality of the automaker groups and car users were results in biodiesel consumption did not increase much as it should be. Therefore, to promote using biodiesel commercially, on April 2007 NEPC gave its resolution to agree with a HSD shall be blended with biodiesel at not over 2 percent (B2) with a compulsory blending of 2 percent biodiesel to HSD from April 2008 onwards.

However, since the biodiesel plants have B100 production capacity at a required quality sufficient to blend with all B2 HSD, therefore to promote increasing use of biodiesel the NEPC gave its resolution on December 2007 to encourage the enforcement, of blending regular HSD with B100 biodiesel of 2 percent by volume, at sooner from February 2008 onwards.

Subsequently, the NEPC had its resolution on April 2010 to agree with the requirement on blending of 3 percent biodiesel into regular HSD (B3) from June 2010 and to adjust a differential retail pricing of B3 HSD and B5 HSD to reduce 0.30 Baht/l (from 1.20 Baht/l to 0.90 Baht/l) through reducing the B2 HSD levy of the Oil Fund by 0.20 Baht/l and reducing the compensated rate of B5 HSD by 0.30 Baht/l whereas fixing the B5 HSD retail price (Biodiesel Fuel Group, Bureau of Biofuel Development, 2011).

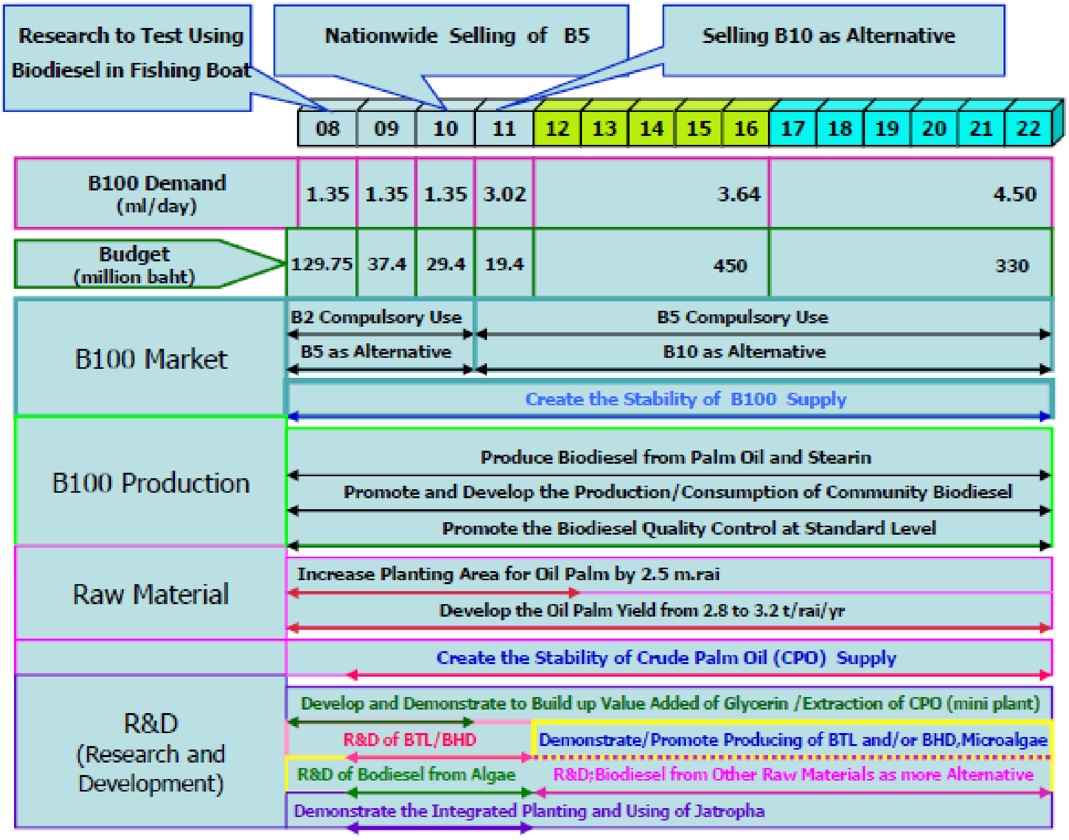

Figure 1.7 Biodiesel development plan: 2008-2022 (dede.go.th)

In addition, the Cabinet resolution on January 2009 agreeing with the **Fifteen Year Renewable Energy Development Plan (REDP)** (2008-2022) for a target of substitute using diesel by biodiesel and requirement on blending HSD with biodiesel at not less than 5 percent (B5) by 2011. This plan was aimed to improve biodiesel productivity to 5.97 million liter per day (currently 1.62 million liter per day) by research and development the marketing, production and alternative raw materials such as algae oil, physic nut including biodiesel from ethanol (fatty acid ethyl ester; FAEE).

In conclusion, the use of biodiesel, one of renewable energy in Thailand was encouraged utilizing through government plan (REDP). These is one of strategic national plan to support Clean Development Mechanism (CDM) Projects for reducing GHGs release and will also add benefits of replacing Thailand's need to spend foreign exchange on the import of fossil fuels as well as strengthening the energy supply security (DEDE, 2010).

1.2.11 The hurdle of using biodiesel

From literature reviews, low temperature property and high cost production appeared to be the main drawback of using biodiesel widely.

A major problem of biodiesel is poor low temperature flow properties indicated by relatively high cloud and pour points. From characteristics, biodiesel shown that they can be conveniently used as fuel in warm climatic areas, on the other hand, it might however lead to filter plugging in very cold climates (Abayeh et al., 2007). The modification of biodiesel chemical structure through the use of alternate alcohols such as butanol was investigated and shown improving of cold weather performance (Chotwichien et al., 2009). Unfortunately, these alcohols have a higher cost and this process is of limited value in the current. However, blending with diesel fuel seems to be an effective method to solve these.

Another problem of biodiesel is high cost production. The problem of cost production in the conventional process is comprised with raw materials, production process and purification process. The raw material, especially feedstock was mainly affected in cost production process (Hass et al., 2006). Then, alternative feedstock was investigated to solve these as describe on feedstock for biodiesel production.

On processing, Papong et al. (2010) studied life cycle energy efficiency and potentials of biodiesel production from palm oil in Thailand to analyze the energy performance and potential of the palm oil methyl ester production in Thailand. The results shown that transesterification would be a major energy consumption of process, 57% of the total energy usage. The impact on energy consumption comes from the production of methanol used for biodiesel production, which could possibly be reduced by installing a methanol recovery unit. In addition, the agricultural stage is the second highest contributor to the energy consumption, 31%, which results from the production of chemical fertilizers used in the cultivation stage. However, with the B5 use projection and potential palm oil output, it could be substituted for 1133.75 million liters of diesel fuel.

Besides that, one of the most serious obstacles for using is the complicated and costly purification processes in its production including separation of glycerine. Only hot water washing has enough to purified biodiesel (Karaosmanoğlu et al., 1996) but it has some disadvantages; water supply and cost, emulsions, wastewater treatment and drying of final product. Then, several studies were attempted to improve these purification step for results in reduce cost production such as using ionic liquids as a solvent for extracting glycerine from biodiesel (Hayyan et al., 2010), using ion exchange process (Berrios and Skelton, 2008), using silica gel and phosphoric acid treatments (Predojevic, 2008). By the way, most of these were suitable for a large-scale production. In addition, the liberation of glycerol in the end of reaction generates a potentially saleable co-product.

To reduce cost of wastewater treatment in process, biodiesel production in the presence of potassium hydroxide (KOH) as catalyst could have a potential to further utilize wastewater as liquid fertilizer after neutralized with phosphoric acid and added urea as a nitrogen source (Alamu et al., 2007).

In conclusion, biodiesel could have some hurdle that opposed utilization. From above mention, biodiesel production from ethanol in the presence of KOH as catalyst could be a suitable process to reduce cost of biodiesel production with an efficiency process.

1.2.12 Summary of review

Biodiesel is a mono-alkyl ester that made from oil from plant or animal. With the problem uncertainty of global energy price, of especially the fluctuation of crude oil price, biodiesel was attended as an alternative diesel fuel.

At a present, palm oil could be a most attractive feedstock for biodiesel production commercially. To avoid conflict on food production, microalgae oil was attracted recently. However, in term of economic, crude palm oil would favorable to use in process.

Regarding to economic attraction, the basic catalytic transesterification seem to be a suitable process for commercial biodiesel production at a present. The poor quality feedstock was needed a 2-step process, acid-esterification for reduction free fatty acid content before transesterification. Several processes were developed to improve the efficiency of production. Unfortunately, most of these were suitable for industrial scale.

Recently, biodiesel from ethanol was attended by numerous studied in recently because not only it has had comparable properties to methyl ester for substitute diesel fuel but it is also safer raw material for production process. In addition, both of raw materials, vegetable oil and ethanol could derive from agricultural product which is a renewable source.

Several studies indicated that biodiesel can be used on diesel engine to replace diesel fuel. Analyses of the environmental impact of using biodiesel as fuel indicated that using biodiesel effectively reduces the emission of pollutants with comparative diesel fuel, except for nitrogen oxides (NO_x).

From above mentioned, it summarized the advantages of biodiesel as; environmentally friendly fuel, safer for transportation and other uses, preventing engines failure, can be directly used in diesel engine and high efficiency of combustion. On the other hand, the disadvantages of these were shown as; oxidation and bacteriological stability, nitrogen oxide emissions, cold flow issues and lower energy content.

In Thailand, the use of biodiesel was encouraged to utilize since 2000. The strategic national plan was attempted to support the reduction of GHGs release and will also reduce the import of fossil fuels which resulting in strengthening the energy supply security.

To summarize, biodiesel production from ethanol in the presence of KOH as catalyst could be a suitable process to meet strategic national plan, Renewable Energy Development Plan (2008-2022). Thus, the low cost and high efficiency method that suitable for either large scale or small scale production (community biodiesel) was needed to investigate.

1.3 Objectives

This study aims to reduce the cost of biodiesel production sustainably by using crude palm oil and ethanol as substitutes for the typical raw materials used: vegetable oil, particularly RBD palm oil and methanol, and to improve the efficiency of separation of the ethyl ester from the glycerol phase .

Chapter 2

Materials and Methods

2.1 Materials:

Chemicals: all chemicals used were analytical grade or otherwise indicated.

Chemical name	Manufacturer
iso-Butyl alcohol	Hopkin & Williams, England
Chloroform ($CHCl_3$)	E. Merck, Germany
Chromotropic acid	Sigma, U.S.A.
Diesel fuel, Commercial grade	Shell, Netherlands
Ethanol (C_2H_5OH)	E. Merck, Germany
Glycerol	E. Merck, Germany
n-Hexane	Ajax Finechem, Australia
Methanol (CH_3OH)	E. Merck, Germany
Phenolphthalein	Fluka, Switzerland
Phosphoric acid (H_3PO_4)	J.T. Baker, U.S.A.
Polyethylene glycol; PEG 6000	BDH, England
Potassium hydroxide (KOH)	Ajax Finechem, Australia
Sodium chloride (NaCl)	Fluka, Switzerland
Sodium hydroxide (NaOH)	J.T. Baker, U.S.A.
Sodium metabisulphite ($Na_2S_2O_5$)	Ajax Finechem, Australia
Sodium periodate ($NaIO_4$)	Carlo Erba, U.S.A.

Chemicals: (continue)

Chemical name	Manufacturer
Sulfuric acid (H_2SO_4)	E. Merck, Germany
Thiourea (NH_2CSNH_2)	BDH, England
Tristearin	Sigma, U.S.A.
Toluene	Labscan, Ireland
Urea (NH_2CONH_2)	Ajax Finechem, Australia

Equipments:

Equipment	Manufacturer
Analytical balance, PL802-S	Mettler, Switzerland
Analytical balance, AE240	Mettler, Switzerland
Gas liquid chromatography, HP6890	Agilent, U.S.A.
High vacuum pump, E2M8	Edwards, England
Hot air oven, FD115/FD240	WTB-Binder, Germany
Hot plate & Magnetic stirrer, MS300HS	Mi Sung Scientific, Korea
pH meter, Accumet model 5	Fisher Scientific, U.S.A.
Reflux unit	Exelo, England
Rotary evaporator, Rotavapor-R	Buchi, Switzerland
UV-visible spectrophotometer, UV-160	Shimadzu, Japan
Vortex Genie 2, G560E	Scientific Industries, U.S.A.
Waterbath, GP-500	NESLAB, U.S.A.

2.2 Methods

2.2.1 Feedstock and free fatty acid (FFA) content analysis

The palm oil feedstock in this study was refined palm oil (RPO) and crude palm oil (CPO). The former was commercially vegetable oil grade while the latter was kindly donated from Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops, Faculty of Engineering, Prince of Songkla University.

Because the free fatty acid (FFA) in feedstock effect processing procedure of biodiesel, the content in the oil was analyzed and was standardized prior to used. This was carried out by titration method according to the method recommended by Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops. In erlenmeyer flask, 1.0 g of the oil was dissolved with 50 ml ethanol that has been neutralized using phenolphthalein as an indicator, the solution was titrated with 0.1 N NaOH until the end point was reached. Then, the FFA content was calculated using the following formula:

$$FFA(\%wt.) = \frac{NaOH(ml) \times 0.1N \times 25.6}{oil(g)}$$

2.2.2 Standardization of free fatty acid content in feedstock

Since preliminary study showed that RPO samples usually comprise of less than 1% (w/w) FFA, they were directly used as reactant in transesterification reaction. However, the contents in CPO samples were found within a range of 6-8%, therefore, esterification process was applied prior to use as the reactant for preparation of both methyl ester and ethyl ester. This was performed in order to make a level comparable with those found in RPO, and to minimize a soap formation during the transesterification reaction. The process was carried out on the basis of the procedure recommended by Chongkhong et al. (2007). In brief, 100 g of CPO and 1 % wt H_2SO_4 were dissolved with alcohol (molar ratio of oil:alcohol, 1: 8.0) in 250-mL boiling flask, and were equipped with reflux condenser, heated at $70^{O}C$ for 60 minutes. The reaction mixture was transferred into separatory funnel to allow separation between the oil phase and aqueous phase. The oil phase was neutralized with 10 % wt. alcoholic KOH, and it was washed with distilled water, then, it was kept for further use as reactant transesterification reaction.

2.2.2 Evaluation of biodiesel quality

The quality of biodiesel, in these experiments was determined from the contents of glyceride and water which were calculated on percent weight basis. The contents were quantitatively analyzed as following procedures:

2.2.2.1 Analysis of total glyceride in biodiesel

The lower triglyceride levels remaining in biodiesel reflect the completeness of transesterification reaction. Also, because it exhibits the higher boiling point and higher viscosity, this is the one parameter used to determine the biodiesel quality. Hence, its content in the biodiesel product from each experimental condition was determined by colorimetric technique according to the method recommended by Ausa Chandumpai (in patent process). Although the result from this technique covers all natural forms of glyceride, i.e. including monoglyceride, diglyceride, and triglyceride, it has known that more than 95% of most vegetable oils are triglyceride, whereas the others are trace constituents (Bhosle and Subramanian, 2005). This was selected because it is simple procedure, reliable and low cost.

In brief, calibration curve was performed by taking aliquot of 0.1ml standard solution of tristearin in chloroform at 5 concentrations ranging from 150 - 900 µg/ml. These were transferred into the screw capped-test tube, the solvent was evaporated in water bath at $70^{O}C$. The triglyceride was saponified at $70^{O}C$ for 20 minutes with 0.5 ml of 0.1% alcoholic KOH. To each tube, 0.5 ml of 0.2 N H_2SO_4 was added, and was incubated at $100^{O}C$ for 10 minutes. After standing to room temperature, 0.1 ml of 0.5 % wt $NaIO_4$ and 0.1 ml of 5 % wt $Na_2S_2O_5$ were added and further left for 10 minutes. Then, 3.0 ml of chromotropic acid solution was added, and was incubated at $100^{O}C$ for 30 minutes. The color was stabilized using 0.3 ml of 7%

thiourea, then, an absorbance at 570 nm was read against reagent blank within 2 hours. Similar was performed with the biodiesel samples which have been diluted to the optimum range of concentration, the triglyceride content was determined by comparison with the calibration curve.

2.2.2.2 Determination of water content in biodiesel

In this experiment, water content in biodiesel was analyzed on Agilent Technologies Series 6890 gas liquid chromatography (GLC) equipped with thermal conductivity detector (TCD). As summarized in Table 1, 0.1 l of the sample was injected with automatic injector at 240^{o}C onto HP-INNOWax column (30 m x 0.53 mm I.D., 1.0 µm film thickness) with helium as the carrier gas. The column was operated isothermally using oven temperature and detector temperature at 100^{o}C and 240^{o}C, respectively. The chromatographic operation system was controlled by the Agilent Technologies Chemstation software (Rev. A.06.01), and this was also used for data acquisition as well as the analysis of the chromatogram.

Table 2.1 Some parameter of GLC-TCD

column	: HP-INNOWAX
Detector	: TCD
Carrier gas	: helium
Flow rate	: 1.0 ml/min
Inlet temperature	: 240^{O}C
Oven temperature	: 100^{O}C
Detector temperature	: 240^{O}C
Split ratio	: 20.0 : 1
Injection volume	: 1 µl

As solubility of biodiesel and the lowest impurity was concerned, *i*-butanol (GLC grade) was used as a solvent. In addition, due to toluene has a boiling point close to water (110°C), it was selected as internal standard (IS). Five standard water solutions were calculated and prepared by dissolving in *i*-butanol to a range of 0.16% - 1.24% by weight (equivalence to 0.13% - 1.00 % by volume) of water. Prior to inject onto a column, each standard solution was mixed with appropriate known weight of IS. Following acquisition of data, area ratios of the 5 different water concentrations and IS were calculated. Calibration curve was established by plotting a correlation between the area ratio against the weight ratios of water and IS. Triplication was performed for each sample. Preliminary study revealed that although *i*-butanol is GLC grade, a trace amount of water was still detected. Therefore, this factor was evaluated and used as a correction factor for calculation of the water content in sample.

To validated method, the limit of detection (LOD) and limit of quantitation (LOQ) was evaluated from the slope (S) of the calibration curve and the standard deviation (SD) of response by using equation as 3.3(SD)/S and 10(SD)/S, respectively.

2.2.3 Preparation of methyl ester from refined palm oil (MERPO)

As transesterification of RPO with methanol at a molar ratio of oil:alcohol 1:6.0 using NaOH as a catalyst is recognized as a common practice for biodiesel production, these was principally used as a reference condition. An effectiveness of procedure was determined from percent yield, duration of phase separation as well as total glyceride content in the product.

The transesterification reaction was carried out by weighing 100 g (approximately 0.12 moles) of RPO in 250 ml boiling flask. The oil was mixed with NaOH-MeOH solution which was freshly prepared by dissolving 0.5 g NaOH in 28.6 ml methanol. The mixture was refluxed at 70°C for 30 minutes, then, transferred into separating funnel to allow separation between glycerol phase and methyl ester phase. This could be accomplished within 10 minutes. Following a lower, glycerol phase, was drained off, purification of methyl ester (MERPO) was performed by mixing the upper phase with warm distilled water until the washing solution became neutral. The methyl ester was dried by heating at $105^{O}C$ for 60 minutes, then, percent yield was determined by weighing.

Analysis of total glyceride in MERPO as above described procedure, however, revealed that the content was higher than that of the commercial biodiesel (PSUME). It appeared that extending the reaction time from 30 minutes to 45 minutes reduced glyceride content to a similar level of the PSUME biodiesel.

Preliminary study also revealed that transesterification process using an equivalent amount of 1.5% KOH gave a similar result to that of using 1.0% wt. of NaOH. As KOH residue in glycerol phase could be reused as fertilizer following neutralizing with H_3PO_4, it was used as catalyze throughout these experiments. Hence, the reference condition for MERPO preparation was conducted by using 1.0% wt. of NaOH and refluxed at $70^{O}C$ for 45 minutes, whereas 1.5% wt of KOH was used in the other studied conditions.

Since results showed that methyl phase and glycerol phase separation could be achieved within 5 minutes, this procedure was adopted as a reference for further studies. The molar ratio of oil:methanol for preparation of MERPO were also examined at 5 difference ratios, i.e. 1:3.0, 1:4.5, 1:6.0, 1:7.5 and 1:9.0. These results were also used as the reference conditions to evaluate the effects of molar ratios in other experiments.

2.2.4 Preparation of methyl ester from crude palm oil (MECPO)

For preparation of methyl ester from crude palm oil (MECPO), the reference conditions as above described for the MERPO preparation were applied. In these experiments, the pre-esterified products containing approximately 1.2 % FFA was used as a reactant. Effects of the other molar ratios of oil:methanol, i.e. 1:3.0, 1:4.5, 1:6.0, 1:7.5 and 1:9.0 were also investigated.

2.2.5 Preparation of ethyl ester from refined palm oil (EERPO)

In ethyl ester from refine palm oil (EERPO) preparation, preliminary study was carried out on the basis of the reference conditions for the preparation of MERPO using the molar ratio of oil:ethanol at 1:6.0. Results showed that the separation between ethyl ester and glycerol phases did not observed although the reaction mixture was stood at room temperature overnight. So, the other 9 molar ratios of oil:ethanol, i.e., 1:3.0, 1:4.5, 1:6.0, 1:6.5, 1:7.0, 1:7.5, 1:8.0, 1:8.5 and 1:9.0 were examined. Fortunately, the separation was achieved within 15 minutes at the ratios within a range of 1:7.0 to 1:9.0. Therefore, the oil:ethanol at a molar ratio of 1:7.0 was used for further studying on EECPO preparation.

2.2.6 Preparation of ethyl ester from crude palm oil (EECPO)

On preparation ethyl ester (EECPO), the pre-esterified CPO containing 1.2% of FFA was used as a reactant. Experiment began with the reference condition for the preparation of MERPO, but the molar ratio of oil:ethanol at 1:7.0 was used, and 1.5% wt of alcoholic KOH was a catalyst. Results showed that the separation between ethyl ester phase and glycerol phase did not observe although the reaction mixture was stood at room temperature overnight.

Since FFA content in RPO was about 0.8%, it was presumed in the first sight that the content in pre-esterified CPO might contribute to the problem. To prove this hypothesis, the content was reduced to 0.88 % which relatively similar to that of the RPO by extending the reaction time of esterification from 45 minutes to 60 minutes. Then, this pre-esterified oil containing a low level of FFA was used as a reactant of transesterification with the molar ratio of oil:ethanol 1:7.0. Result showed that the phase separation was improved, but duration was inconsistent that may be varied between 15 minutes to overnight. Also, a fluffy layer of soap between the phases usually occurred at the first washing step, and this leading to difficulty of separation as well as decreasing of percent yield. However, this suggested that the level of free fatty content is one of the major factor contribute to the phase separation problem.

Accordingly, several factors which may contribute to the phase separation problem had been examined. Experiments were designed on the basis of disturbing interactions among various constituents in the reaction mixture, such as adjusting pH, changing of ionic strength changing of polarity, and removal of the excess ethanol.

2.2.7 Factors effecting on separation efficiency of ethyl ester and glycerol phases

Since transesterification products of EERPO at all examined conditions exhibit a clear solution, this indicated an equilibrium interactions which provide an optimum solubility among various compositions therein. Therefore, it was proposed that disturbance of the interactions within the mixture might be the means to enhance separation between ethyl ester and glycerol phases.

From the principal concept as above described, preliminary investigation was carried out using the reaction mixture of EERPO that had been transesterified with the reference conditions for MERPO preparation. This was prepared by using a molar ratio of oil to ethanol 1:6.0, 1.5% KOH was used as a catalyst. The reaction was performed by refluxing at 70^{O}C for 45 minutes. This reaction mixture was, then, used to examine the phase separation by several studied effects such as pH, ionic strength, and polarity. Moreover, the reaction mixtures which were transesterified at the other studied molar ratios of oil to ethanol were also examined for phase separation efficiency by the similar way. To each studied effect, practical and cheap process was considered, and was performed as following:

i) Effect of pH adjustment

In 100 ml beaker, 25 ml of the reaction mixture was titrated with 10 % (v/v) of phosphoric acid in methanol to reach 4 pH levels, i.e. 9.0, 7.0, 5.0 and 3.0. Then, phase separation efficiency was investigated.

ii) Effect of ionic strength

The effects of ionic strength on phase separation were examined. This began by addition of 0.5 ml of the saturated NaCl and urea solutions into 25 ml of the reaction mixture, and was vigorously mixed with vortex for 10 seconds. If separation did not promising after standing at room temperature, the more 0.5 ml was added successively.

iii) Effect of polarity changing

Effects of polarity on the phase separation were investigated following addition of some solvents which exhibit the difference of polarity index into 5 ml of the reaction mixture. These began by successively addition of 0.5 ml n-hexane which is regarded as the lowest polarity solvent. It was vigorously mixed with vortex for 10 seconds, then, the phase separation was observed after standing at room temperature. If the separation did not appear within 10 minutes, the more 0.5 ml was added successively. A similar procedure was also applied to examine the effect of the commercial diesel fuel.

In addition, a similar procedure of examination was applied with some other polar solvents such as glycerol, polyethylene glycol 6000 as well as neutralized glycerol phase that has been a waste from previous experiments.

iv) Effect of H-bond breaking compound

Effects of H-bond breaking compound on the phase separation were investigated by successively addition of 0.5 ml of saturated urea solution into 5 ml of the reaction mixture. Following vigorously mixing with vortex for 10 seconds and standing at room temperature, then, the phase separation was observed. If the separation did not appear within 10 minutes, the more 0.5 ml was successively added until the separation was reach.

v) Effect of remaining alcohol

An excess amount of ethanol in the reaction mixture might contribute for the phase separation problem. This was examined by transferring 50 ml of the reaction mixture in 100 ml beaker, and was heated at $80^{O}C$ with stirring for 10 minutes. The phase separation efficiency was investigated after standing to cool to room temperature.

2.2.3 Data analysis

Analysis of variance (ANOVA) was performed using the statistical analysis for Windows operating system to examine effects of molar ratio of oil to alcohol on yield of production including total triglycerides and water content. Significance of polynomial effects were determined using $\alpha = 0.05$.

Chapter 3

Results and discussions

3.1 Free fatty acid (FFA) contents in crude palm oil (CPO) and refined palm oil (RPO) and standardization of the CPO feed stock

Table 3.1 showed that the contents of free fatty acid (FFA) in the samples of crude palm oil (CPO) and refined palm oil (RPO) were fallen within a range of 7.86-8.11% wt. and 0.22-0.25% wt, respectively. However, after CPO was esterified with the studied alcohol, they were reduced to a range of 1.15- 1.28% wt. Otherwise stated, therefore, the RPO was directly used as a substrate for transesterification reaction, while CPO was a pre-esterified product.

Table 3.1 Percent free fatty acid (FFA) content in the refined palm oil (RPO), crude palm oil (CPO) and pre-esterified crude palm oil (CPO). The presented data are mean ± S.D. of 3 replications.

Sample	FFA content (% wt.)
RPO	0.24 ± 0.02
CPO	7.97 ± 0.13
Pre-esterified CPO	1.24 ± 0.08

3.2 Evaluation of GLC-TCD technique for determination of water content

Figure 3.1a showed GLC chromatogram of a pure solvent (*i*-butanol). It was found that although the solvent was GLC grade, the peaks corresponding to retention time of water as well as some other impurities were also detected. This suggested that a correction factor of the water impurity in the solvent must be taken into consideration on calculation of the actual water content in sample.

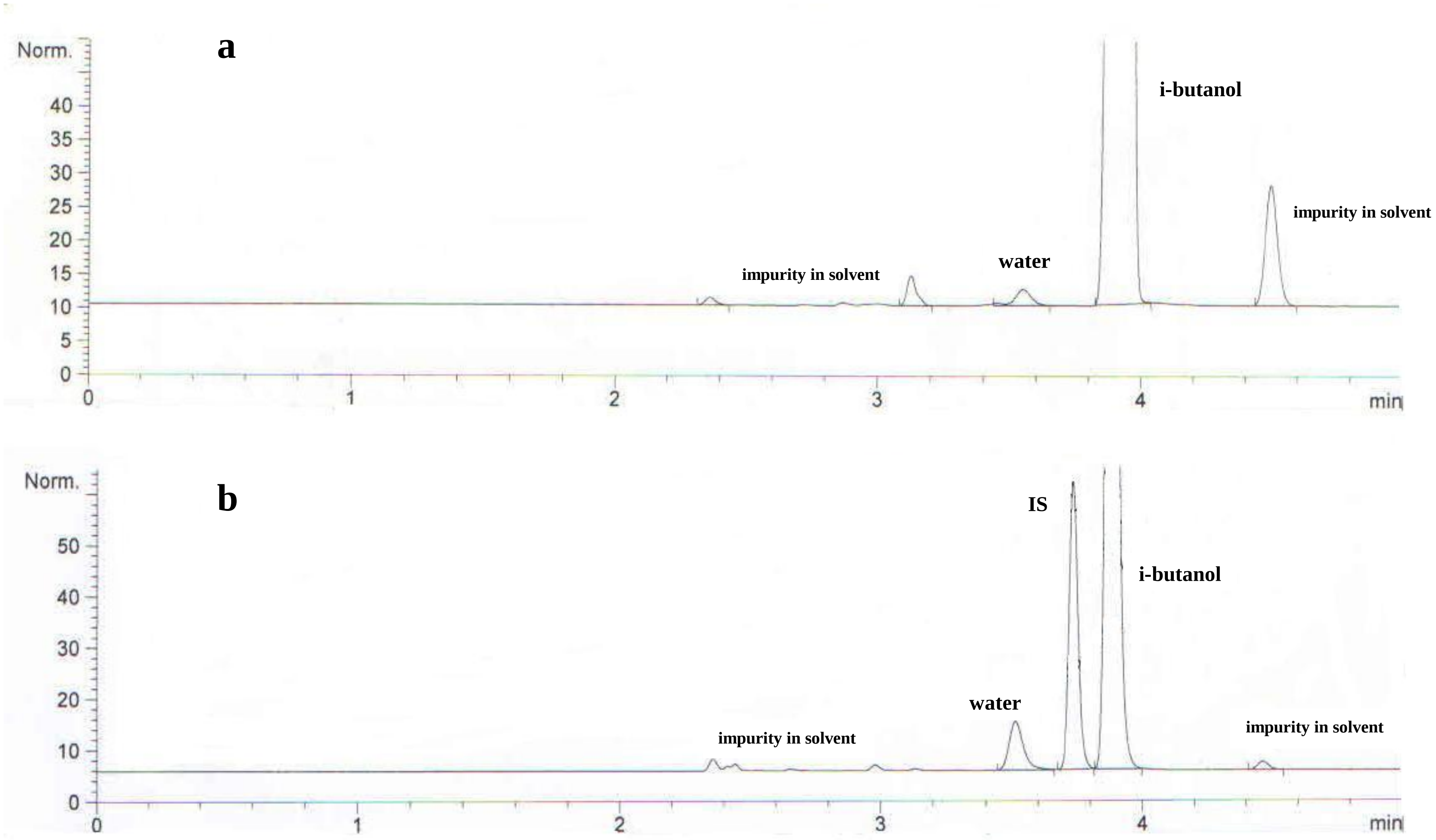

Figure 3.1 a) GLC chromatogram of a pure solvent (*i*-butanol) b) GLC chromatogram of ethyl ester from CPO (EECPO)

Figure 3.1b showed GLC chromatogram of EECPO sample that has been dissolved in *i*-butanol and mixed with toluene (IS). It was found that water and toluene that used as an internal standard was completely resolved from each another. This indicated that the toluene was an ideal compound to use as internal standard for determination of water in biodiesel by GLC method. In addition, it should be noted that the analytical time was taken about 5 minutes for each injection which was relatively effective method.

From the acquired data, the area ratios and weight ratios between water/*i*-butanol of the 5 standard water concentrations were calculated and calibration curve was plotted. Result in Figure 3.2 showed that a linear correlation was found with $R^2 = 0.999$ as the following equation.

$$y = 0.977x + 0.752$$

Table 3.2 Correlation between the area ratios and weight ratios of water/internal standard (IS). The presented data are mean ± S.D. and %RSD of 10 injections.

water (% vol.)	water (% wt.)	wt. ratio (water/IS)	area ratio (water/IS)	area ratio – C	%RSD
0.13	0.16	0.30	1.05	0.29 ± 0.03	3.24
0.25	0.31	0.57	1.32	0.57 ± 0.02	1.20
0.50	0.62	1.15	1.86	1.11 ± 0.05	2.65
0.75	0.93	1.72	2.43	1.68 ± 0.10	4.31
1.00	1.24	2.29	3.00	2.24 ± 0.04	1.48

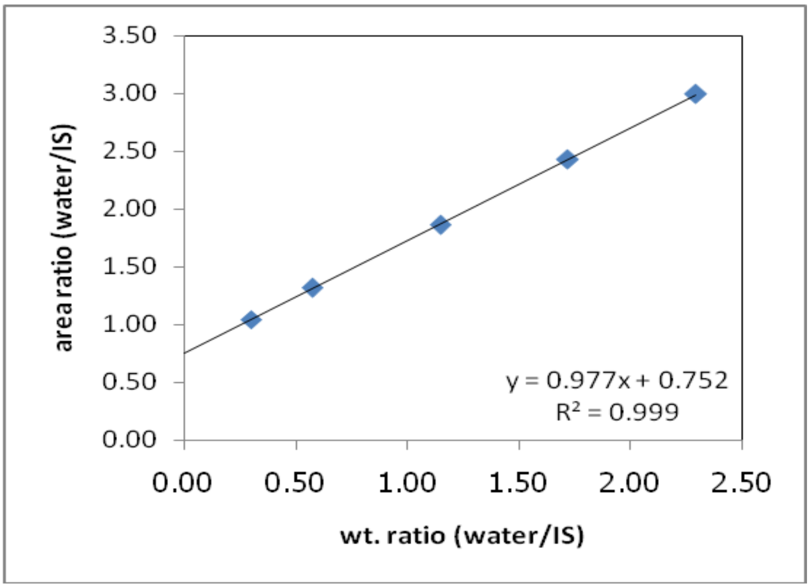

Figure 3.2 Correlation between the area ratios and weight ratios of water/internal standard (IS) without correction of water content in the solvent (*i*-butanol). The presented data are mean of 3 replications.

It was noted that the correlation was not pass through the origin. This represents the water content in the solvent. Therefore, the value of 0.752 was used as a correction factor for transformation the value of area ratio in the calibration curve and in the samples. Figure 3.3 showed a linear correlation between the area ratios which had been transformed with the correction factor and weight ratios between water/*i*-butanol.

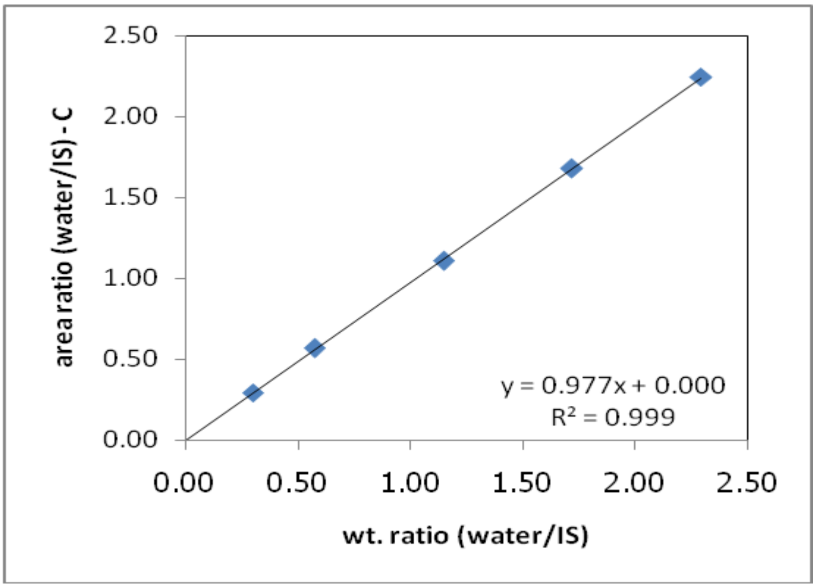

Figure 3.3 Correlation between the area ratios which had been subtracted with the correction factor and weight ratios between water/*i*-butanol. The presented data are mean of 10 injections.

Validation of method was evaluated from the limit of quantitative detection (LOQ) and the limit of detection (LOD) using the following equations (Sharbir, 2003):

Limit of quantitative detection (LOQ)

$$LOQ = \frac{10\sigma}{S}$$

Limit of detection (LOD)

$$LOD = \frac{3.3\sigma}{S}$$

σ = standard deviation at lowest concentration (n=10)

S = slope from calibration curve

As showed in Table 3.3, results indicated that GLC is relatively high sensitive method for determination the water content in sample. The lowest level that could be detected and quantitatively determined was 0.06% wt and 0.20% wt (0.05% vol and 0.16% vol), respectively. According to ASTM, the method D2709 gives LOD of 0.068 % wt (equivalence to 0.054 % vol). This indicated that the GLC method could be used as an alternate procedure for analysis the water content in biodiesel.

Table 3.3 The lowest limit of detection (LOD) and the lowest limit of quantitative detection (LOQ) of water content determine using GLC method. The presented data are mean of 3 replications.

Parameters	area ratio (water/IS)	wt. ratio (water/IS)	wt. water (g)	wt. water (mg)	water (% wt.)	water (% vol.)
LOD		0.13	0.0005	0.54	0.06	0.05
LOQ		0.38	0.0016	1.63	0.20	0.16
Correction factor (c)	0.75	0.77	0.0033	3.31	0.42	0.33

3.3 Preparation of methyl ester from refined palm oil (MERPO) and their total glyceride contents

Table 3.4 showed that the molar ratios of oil:alcohol in transesterification reaction exerted significant effects on the percent yield of methyl ester preparation. As the ratios were increased from 1:3.0 to 1:6.0, the yields were increased from 79.2% to 97.3%, but it did not significantly change since then. These agree well with the other reports (Ma and Hanna, 1999).

In addition, analysis of total glyceride content in the MERPO products revealed that the molar ratios of oil:alcohol also posed a significant effect on the content. The highest at 15.88% was detected at a ratio of 1:3.0, then, progressively lower to 1.84% and 1.21% at 1:6.0 and 1:9.0, respectively. With the same analytical procedure, however, it was found that the total glyceride content in PSUME was 2.61 %.

Therefore, the following processes were adopted to use as a reference conditions throughout these studies. These were performed by weighing 100 g of RPO in 250 ml boiling flask. The oil was mixed with NaOH-MeOH solution which was freshly prepared by dissolving 0.5 g NaOH in 28.6 ml methanol. These volumes were calculated to obtain the molar ratios of oil:alcohol 1:6.0. The mixture was refluxed at 70^{O}C for 45 minutes, then, transferred into separating funnel to allow separation between glycerol phase and methyl ester phase. This could be accomplished within 10 minutes. Following a lower, glycerol phase, was drained off, purification of methyl ester (MERPO) was performed by mixing the upper phase with warm distilled water until the washing solution became neutral. The methyl ester was dried by heating at 105^{O}C for 60 minutes, then, percent yield was determined by weighing.

Table 3.4 The effects of oil:methanol molar ratios on percent yield and total glyceride content of methyl ester prepared from refined palm oil (RPO) and crude palm oils (CPO). The presented data are mean ± S.D of 3 replications.

Oil : MeOH	MERPO		MECPO	
(Molar ratio)	Yield (% wt.)	Total glycerides (% wt.)	Yield (% wt.)	Total glycerides (% wt.)
1: 3.0	79.19 ± 0.92	15.88 ± 1.01	89.22 ± 0.97	10.72 ± 1.53
1: 4.5	95.91 ± 0.41	3.52 ± 0.09	91.95 ± 0.43	3.09 ± 0.74
1: 6.0	97.28 ± 0.49	1.84 ± 0.24	93.43 ± 0.29	1.40 ± 0.22
1: 7.5	97.25 ± 0.64	1.42 ± 0.32	93.35 ± 0.31	1.01 ± 0.39
1: 9.0	96.38 ± 0.61	1.21 ± 0.56	93.14 ± 0.29	1.30± 0.15

3.4 Preparation of methyl ester from crude palm oil (MECPO) and their total glyceride content

For MECPO preparation, experiments began with the reference conditions, but pre-esterified CPO was used as a reactant and 1.5% of KOH was a catalyst. It appeared that separation of the upper phase and lower phase could be accomplished within 10 minutes. Table 3.4 also showed that variations of the oil: alcohol molar ratios provided a similar effect on percent yield and glyceride content in the MECPO product as those found in the reference condition. The lowest yield, 89.2%, was observed at the oil: alcohol molar ratio of 1:3.0, and increased to 93% at 1:6.0, then, maintained at this level. As transesterification is a reversible reaction, an excess amount of alcohol is required in order to shift the equilibrium to the right direction. These results agree well with the other reports (Tongurai et al., 2000; Rashid and Anwar, 2008; Keera et al., 2010).

It should be noted that percent yield of MECPO at the same molar ratio are markedly lower than those of MERPO products. This was presumably due to partially losing of the oil at esterification step. A similar result has been demonstrated by Bhosle et al. (2005) who reported that percent yield of RPO may be decreased by 20% with respect to CPO during the process of FFA reduction. However, these indicated that CPO can be used as a raw material for biodiesel production, but two processing steps are required. In addition, degumming process could be omitted from preparation scheme.

Analysis of total glyceride in MECPO showed that the contents were usually lower than MERPO which prepared under identical molar ratio of oil:alcohol. This suggested that the more completeness of the transesterification reaction was obtained when 1.5% KOH was used as a catalyst.

Surprisingly, at the molar ratio of oil:alcohol 1:3.0, the percent yield of MECPO (89.22%) was higher than MERPO (79.19%), while the reverse was observed with those of the other molar ratios. It was likely that some extents of the alcohol still remained in the pre-esterified CPO, and this contribute to the actual molar ratio in the reactant was higher than the denoted 1:3.0.

3.5 Preparation of ethyl ester from refined palm oil (EERPO) and their total glyceride content

For preparation of ethyl ester from refined palm oil (EERPO), experiment began on the basis of the optimum reference conditions using a molar ratio of oil:ethanol 1:6.0. Results showed that separation between the ester phase and glycerol phase of the reaction mixture had never been separated even the reaction mixture was stood at room temperature for more than 24h.

Studying on the effects of the molar ratio between oil:ethanol showed that the phase separation did not occur while they were varied between 1:3.0 to 1:7.0. However, when the molar ratios were increased from 1:7.0 to 1:9.0, the separation was observed within 15 minutes. This results indicated that a molar ratio of oil:ethanol was the one important factor contribute to the phase separation problem of EERPO preparation.

Table 3.5 showed the effects of different oil:ethanol molar ratios on phase separation, percent yield and glyceride content in EERPO products. It was found that at the ratio of 1:7.0 to 1:9.0, percent yield varied between 88.4%-91.2% which statistical analysis showed no significantly difference.

Table 3.5 Effects of the oil:ethanol molar ratio on phase separation, percent yield and glyceride contents in EERPO which were prepared on the basis of the reference conditions. The presented data are mean ± S.D. of 3 replications.

RPO : EtOH	Ethyl ester	
(Molar ratio)	Yield (% wt.)	Total glycerides (% wt.)
1: 3.0	No phase separation	ND
1: 4.5	No phase separation	ND
1: 6.0	No phase separation	ND
1: 6.5	No phase separation	ND
1: 7.0	88.52 ± 1.40	6.51 ± 0.29
1: 7.5	88.43 ± 0.39	6.36 ± 0.67
1: 8.0	91.19 ± 1.45	5.50 ± 0.44
1: 8.5	90.53 ± 2.03	4.00 ± 0.55
1: 9.0	89.82 ± 0.79	3.13 ± 0.80

Note: ND = not determine

Also, it was found that vigorously addition of hot water into the upper phase as well as shaking at the first and second washing step should not perform, otherwise, difficulty of separation between the ester phase and aqueous phase may be found. In addition, results revealed that while the molar ratio increased, the contents of total glyceride were reduced from 6.51% to 3.13%. As costing was concerned, the ratio at 1:7.0 was used in preliminary studying on EECPO preparation.

3.6 Preparation of ethyl ester from crude palm oil (EECPO) and their total glyceride content

On preparation of ethyl ester (EECPO) using the pre-esterified CPO containing 1.2% of FFA was use as a reactant. The reference conditions were applied with other procedures, but the molar ratio of oil: ethanol at 1:7.0 was used, and 1.5% wt of alcoholic KOH was a catalyst. Results showed that the separation between ethyl ester phase and glycerol phase did not observe although the reaction mixture was stood at room temperature overnight.

Studying on the effect of FFA contents in the reactant showed that the level of less than 0.8% was required. When the pre-esterified CPO containing FFA was used in transesterification reaction, it was found that the phase separation was improved, but duration was inconsistent that may be varied between 15 minutes to overnight. Also, a fluffy layer of soap between the phases usually occurred at the first washing step, and this leading to difficulty of separation as well as decreasing of percent yield. However, this suggested that the level of free fatty content is one of the major factor contribute to the phase separation problem. Results in this study, however, suggested that the level of free fatty content is one of major factor contribute to the phase separation problem.

3.7 Factors effecting on separation of ester phase and glycerol phase

Apart from the oil:ethanol molar ratio and FFA content, there are some important factors contribute to the phase separation problem of EECPO preparation. Studying on the basis of disturbing interactions among various constituents in the reaction mixture was summarized in Table 3.6.

Table 3.6 Factors affecting on the phase separation efficiency of the reaction mixture of EERPO prepared on the basis of the reference condition, but a molar ratio of 1:7.0 was used.

Conditions	Efficiency	Soap formation
Adjust pH of mixture	+	+ + + +
Saturated NaCl solution	+	+ + + + +
Water (Distilled water; DW)	+ + + +	+ +
Methanol	+	+ + +
Ethanol	+	+ + +
Pure glycerol	+ + +	+ +
Neutralized glycerol phase	+ + +	+ +
1% Polyethylene glycol (PEG 6000)	+ + +	+ +
n-Hexane	+ +	+ + +
Diesel fuel	+ +	+ + +
Saturated urea	+ + + + +	+
Remove excess alcohol by heating	+ + + + +	+

Note: + + + + + = High rate
+ + + = Medium rate
+ = Low rate

3.7.1 Effect of pH adjustment

Initially, pH of the reaction mixture was about 9.5. After addition of 0.1M H_3PO_4 and mixing to reduce pH by an interval of 0.5 unit to 3.0, the phase separation was poorly observed with highly soap formation between the 2 phases following standing at room temperature. Therefore, it was concluded that this effect did not promising to solve the problem.

3.7.2 Effect of ionic strength

Results showed that after slowly adding saturated NaCl solution into the reaction mixture about 10% (v/v), the phase separation was observed. However, a highly soap formation was found even though it was stood overnight at room temperature.

3.7.3 Effect of polarity changing

Several polar solvents as well as the neutralized glycerol phase, pure glycerol and 1% polyethylene glycol were added to investigate the effect of phase separation. With only exception for methanol and ethanol, it seemed that most of the examined solvents at approximately 10% (v/v) promoted the phase separation efficiency. However, degree of soap formation was varied which depend on type of solvent.

It was found that when the non polar solvents such as n-hexane and diesel fuel were added into the reaction mixture, phase separation occurred when more than 60% (v/v) was added. Furthermore, difficulty at purification step was also observed.

3.7.4 Effect of H-bond breaking compound

It was found that addition of saturated urea solution at approximately 10% (v/v) enhanced the phase separation effectively.

3.7.5 Effect of the excess ethanol removal

An excess alcohol in the reaction mixture was removed by evaporation in ventilated hot air oven at 80^{o}C and blowing a stream of boiling water. Result showed that a clear phase separation could be achieved within 10 minutes by both procedures. In comparison, however, evaporation in hot air oven usually provided the EERPO product turn to brown color, while it did not observe with another one. This suggested that an excess ethanol remaining in the reaction mixture is one of principal factor contributed to the phase separation problem of EERPO preparation.

Therefore, it could be concluded from above experiments that interactions among various constituents in the reaction mixture could be disturbed and promoted the phase separation, but they exerted with different efficiency. However, reduction of the excess ethanol with a stream of boiling water seemed to be the easiest practice and economic process.

Moreover, it appeared that the phase separation efficiency with hot water at the first washing step was still not satisfaction i.e. it may took over half an hour with highly fluffy soap formation. Finally, it was found that the separation at this step could be effectively improved by addition of about 50% (v/v) saturated urea solution into the upper phase. This might due to the H-bond between urea and the remaining glycerol was formed, and this promoted the more partition of polar components into the aqueous phase. The saturated urea solution was selected because the washing waste could be reused as fertilizer after neutralizing with phosphoric acid.

As costing was concerned, the effects of oil:ethanol molar ratio was further investigated for the preparation of EECPO. In these experiments, the pre-esterified CPO that FFA content was reduced to a level of 0.8%, was used as a reactant. Eight different oil:ethanol molar ratios ranging from 1:0.5 to 1:9.0 were studied. Table 3.7 showed that percent yield of EECPO varied from 52.9% to 78.6% at the ratio 1:0.5 to 1:2.0, whereas it was increased by 82.3% - 86.2% at the ratio of 1:3.0 to 1:9.0. However, statistical analysis showed no significant different in percent yield with later range of the molar ratios. Again, these was confirmed that the actual molar ratio of oil:ethanol in the reactant was not 1:3.0, but it was contributed by the remaining ethanol in the pre-esterified product. These results agreed with those found in EERPO production.

Table 3.7 Effects of oil:ethanol molar ratios on percent yield and total glyceride content (wt %) in ethyl ester prepared from pre-esterified CPO at a low FFA content. The presented data are mean ± S.D. of 3 replications.

CPO : EtOH	Ethyl ester	
(Molar ratio)	Yield (% wt.)	Total glycerides (% wt.)
1: 0.5	52.87 ± 9.41	21.90 ± 1.79
1: 1.0	60.27 ± 8.75	10.19 ± 1.96
1: 2.0	78.63 ± 4.99	6.32 ± 0.49
1: 3.0	86.23 ± 1.32	4.08 ± 0.09
1: 4.5	83.41 ± 0.40	3.83 ± 0.15
1: 6.0	82.29 ± 1.08	4.03 ± 0.30
1: 7.5	84.94 ± 1.02	3.39 ± 0.39
1: 9.0	84.26 ± 1.25	2.80 ± 0.39

Table 3.7 also showed that the high glyceride contents in EECPO produced from the former molar ratio, fallen within a range of 21.9% - 6.3%, then, gradually declined from 4.1% to 2.8% when the ratios were increased from 1:3.0 to 1:9.0. These suggested that the higher ethanol used, the transesterification reaction was more shifted to the right.

Again, as costing was concerned, to obtain the EECPO product comprising of glyceride content comparable with the PSUME level (4.54%), further experiments were carried out to by variation of the molar ratio, amount of catalyst and transesterfication time. Results in Table 3.8 indicated that variation in an amount of catalyst and increasing the reaction time did not improve both percent yield and total glyceride content in the products. However, the products obtained from the molar ratios of oil:ethanol at 1:6.0 comprising of the glyceride about 4.5%-4.9% which were comparable to the PSUME quality.

Table 3.8 Effects of the oil:ethanol molar ratios, amount of catalyst and transesterfication time on percent yield and total glyceride contents in EECPO. The presented data are mean ± S.D of 3 replications.

Condition			Ethyl ester	
MR	KOH (% wt.)	Reaction time (min)	Yield (% wt.)	Total glycerides (% wt.)
1: 3.0	1.5	45	79.91 ± 0.87	7.62 ± 0.35
1: 3.0	1.5	60	80.86 ± 0.77	8.15 ± 0.76
1: 3.0	3.0	45	67.81 ± 0.72	3.47 ± 0.96
1: 6.0	1.5	45	82.99 ± 0.73	4.93 ± 0.20
1: 6.0	2.0	45	69.99 ± 1.05	4.54 ± 0.20

Note:MR = Molar ratio of oil to alcohol

3.8 Determination of biodiesel quality

3.8.1 The content of total glyceride

Figure 3.4 showed the content of total glyceride in various forms of the biodiesel samples prepared in this laboratory. It was found that the contents lower than PSUME (4.54 % wt.) when the molar ratio of oil to alcohol higher than 1: 4.5. Therefore, the biodiesel that produced with the conditions as above described, were acceptable quality. Remarkably, total glyceride contents data of EERPO were exclude due to the contents lower than PSUME when the molar ratio of oil to alcohol higher than 1: 8.5.

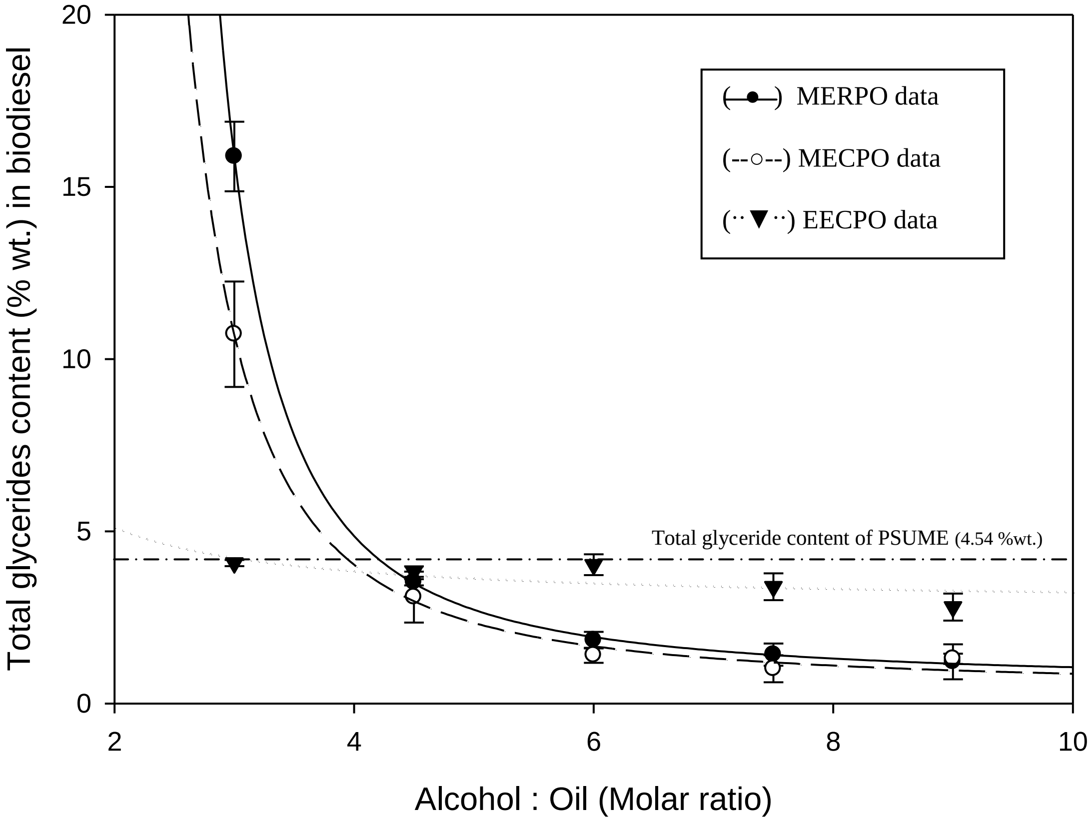

Figure 3.4 Total glyceride content in biodiesel. The presented data are mean ± S.D. of 3 replications.

3.8.2 Water content in biodiesel samples

Table 3.9 showed the water content in various forms of biodiesel samples which were analyzed by GLC-TCD method. Results showed that the mean of water contents in MERPO and MECPO was 0.18% wt (varied between 0.15% - 0.22% wt), meanwhile the contents of 0.22% - 0.14% were detected in EERPO and EECPO.

Table 3.9 Water content (% wt) in various biodiesel samples prepared in these experiments. The presented data are mean ± SD of 3 replications.

	water content (% wt.) of each molar ratio (Oil : alcohol)						
	(1:9.0)	(1:7.5)	(1:6.0)	(1:4.5)	(1:3.0)	mean	SD
MERPO	0.19 ± 0.04	0.17 ± 0.03	0.15 ± 0.04	0.16 ± 0.04	0.22 ± 0.05	0.18	0.03
MECPO	0.18 ± 0.00	0.18 ± 0.01	0.17 ± 0.06	0.18 ± 0.01	0.18 ± 0.01	0.18	0.00
EERPO	0.21 ± 0.01	0.22 ± 0.03	no phase separation	no phase separation	no phase separation	0.22	0.01
EECPO	0.15 ± 0.01	0.13 ± 0.01	0.15 ± 0.01	0.15 ± 0.01	0.13 ± 0.01	0.14	0.01
PSUME			0.15				

The water content in EECPO samples which were prepared under different conditions such as molar ratios, amount of KOH catalyst as well as time of transesterification, was also analyzed. Result in Table 3.10 showed that their water contents were fallen within a range of 0.17% - 0.23% wt which seem independent on the used preparation condition.

Regardless of the preparation conditions, the water contents in all biodiesel samples prepared in this laboratory were higher than the ASTM D6751-02 requirement which the maximum content has limited at a level of 0.06% wt (0.05% vol). This variation may due to the different of analytical procedure. In comparison with the same analytical procedure, a level of 0.15% wt was detected in the commercial biodiesel (PSUME) which was relatively similar to the biodiesel prepared in this laboratory.

Table 3.10 The water content in EECPO samples prepared under different conditions.

Trial no.	1	2	3	4	5
Molar ratio (pre-esterified CPO : EtOH)	(1 : 3.0)	(1 : 3.0)	(1 : 3.0)	(1: 6.0)	(1: 6.0)
KOH (% wt.)	1.5	1.5	3.0	1.5	2.0
Reaction time (min)	45	60	45	45	45
Water content (% wt.) ± SD	0.19 ± 0.03	0.18 ± 0.02	0.23 ± 0.04	0.22 ± 0.04	0.17 ± 0.01
Average water content (% wt.) of each molar ratio	0.21			0.21	
SD	0.03			0.04	

According to the notice of the Department of Energy Business on the regulation of community indicated that water content in biodiesel should be lower than 0.2 % vol. Therefore, the procedure from these experiments could be applied for the production of biodiesel from CPO and ethanol applicable with agricultural diesel engine.

To reduce the water content to meet standard quality of biodiesel, however, there are 2 practical procedures which could be consecutively carried out. Firstly, the product is flowed though a column containing sodium sulphate pentahydrate ($Na_2SO_4.5\ H_2O$) (Buasri et al., 2009). Secondly, the product was evaporated under vacuum with vigorously stirring at 105^{o}C. With the second procedure, the longer evaporation time, the more intensity of color may be expected.

Chapter 4

Conclusion

4.1 Biodiesel from refined palm oil

In addition, most of previous studies were improved phase separation by remove excess alcohol with rotary evaporation (Bouaid et al., 2009, Joshi et al., 2009). It indicated that excess alcohol was the other factors that also affected to low efficiency phase separation. However, this process would have a poor potential to employ in both large-scale and small scale of biodiesel production because it required long time for separation and obtained low yield.

From literature reviews, numerous studies were studied the ethyl ester production from various feedstock and achieved satisfied yield. The results indicated that several fatty acids in feedstock seem to be the cause of these, ambiguously. The fatty acid profiles of feedstock were shown in table 4.1.

From results in table 4.2, easier process and yield around 90-98 % wt. was obtained when using feedstock such as soybean oil, *Brassica carinata* oil, palm kernel oil and coconut oil. In contrast, used vegetable oil which obtained from palm oil, and refined palm oil were yielded around 70-90 % wt. However, the improvement process by using lipase as catalyst and using microwave power or ultrasonic irradiation to replace heating were achieved satisfy yield, unfortunately it was affected to cost of production.

Table 4.1 Comparison of fatty acid profile from various feedstocks

Fatty acid	Notation	Fatty acid composition (% wt.)							
		CPO	PKO	UVO	SBO	BCO	RSO	PNO	CCO
Caprylic	C 8:0		3.3						
Capric	C 10:0		3.4						
Lauric	C 12:0		48.2	0.5				0.1	64.4
Myristic	C 14:0	0.9	16.2	0.9				0.2	20.5
Palmitic	C 16:0	47.6	8.4	37.1	10.8	2.9	5.7	14.8	7.7
Palmitoleic	C 16:1							0.8	0.1
Stearic	C 18:0	2.5	2.5	4.8	3.0		2.2	4.2	1.7
Oleic	C 18:1	41.0	15.3	46.2	26.5	33.9	34.5	41.0	4.6
Linoleic	C 18:2	8.0	2.3	10.5	47.3	8.2	17.8	38.6	1.0
Linolenic	C 18:3				9.0	1.1	12.5	0.3	
Arachidic	C 20:0						1.0	0.1	
Eicosenoic	C 20:1				1.4	10.9	10.0		
Erucic	C 22:1				1.1	42.0	16.4		

Note: CPO; Crude palm oil (Suppalakpanya et al., 2010)
PKO; Palm kernel oil (Alamu et al., 2008)
UVO; Used vegetable oil (Lertsathapornsuk et al., 2009)
SBO; Soybean oil (Bol and Mohammed, 2009)
BCO; *B. carinata* oil (Bouaid et al., 2009)
RSO; *R. sativus* oil (Domingos et al., 2008)
PNO; Physic nut oil (Winayanuwattikun et al., 2008)
CCO; Coconut oil (Winayanuwattikun et al., 2008)

Table 4.2 Comparison of ethyl ester from previous studies

Feedstocks	Molar ratio (EtOH:Oil)	Catalyst (%wt.)	Temp. (^{O}C)	Reaction time	Yield (%wt.)	Reference
Used frying oil	12:1	1.0% KOH	78	120 min	74	Encinar et al., 2007
Palm oil	18:1	Lipase	58	24 h	98	Moreira et al., 2007
PKO	5:1	1.0% KOH	60	120 min	96	Alamu et al., 2008
Soybean oil	6:1	1.0% NaOH	55	60 min	92	Bol and Mohammed, 2009
Soybean oil	12:1	1.0% KOH	30	60 min	96	Joshi et al., 2009
Brassica carinata oil	Excess	1.5% KOH	35	60 min	98	Bouaid et al., 2009
Coconut oil	6:1	0.75% KOH	Ultrasonic irradiation	7 min	98	Kumar et al., 2009
RPO	9:1	1.5% KOH	78	45 min	90	This studied

4.2 Biodiesel from crude palm oil

Biodiesel from crude palm oil (CPO) and ethanol could be achieved by using 2-step process. The first step is acid-esterification to reduce free fatty acid content lower than 2% wt., then, esterified CPO was carried out a basic-transesterification. An optimum conditions to prepare biodiesel from ethanol could be performed by transesterification of esterified crude palm oil with using molar ratio of oil to ethanol is 1 to 6, at 78^{O}C for 45 minutes in the presence of 1.5% wt. KOH as catalyst. The product was a light red solution and yielded about 82% wt. calculated with regard to initial weight of crude palm oil while, methyl ester from CPO was yielded around 93% wt. In comparative with commercial grade biodiesel, total triglycerides content in this ethyl ester was acceptable unfortunately water content was slightly higher than specification.

Since separation between ester phase and glycerol phase could not occur, the using of hot steam would be a beneficial method to improve the efficiency of phase separation. With this method, a separation rate could improve for about 10 times. It is important to note that this method would have a potential to employ in both large-scale and small scale of biodiesel production because of its advantage such as low cost and uncomplicated process. However, removing of excess alcohol (Domingos et al., 2008) and addition of pure glycerin (Encinar et al., 2007 and Suppalakpanya et al., 2010) were also success to enhance phase separation but they were relatively high cost production.

Regarding to minimize cost production, crude vegetable oil seems to be a favorable feedstock currently. Unfortunately, crude vegetable oil needs a 2-step process to produce biodiesel. Due to chemically control of ethanolysis process (Marjanović et al., 2010), yield of these was obtained around 80-90 % wt. depend on feedstock. In contrast, some studied was have a controversial hypothesis which the ester conversion is strongly affected by molar ratio of ethanol to oil (Sulistyo et al., 2009). However, yield of ethyl ester at optimum condition in this study was obtained around 80% wt. maximally which no matter how much of employed latter alcohol as same as results from previous studies (table 4.3), thus it indicated that this reaction was chemically control. In addition, the amount of alcohol in second step seems to depend on molar ratio of alcohol that employ in first step.

To improve yield of process, 2-stage transesterification was recommended in the production (Encinar et al., 2007and Domingos et al., 2008). In addition, using lipase as catalyst and using microwave power or ultrasonic irradiation to substitute heating for improve efficiency of process seem to achieve satisfy yield unfortunately it would suitable for large scale production.

Table 4.3 Comparison of ethyl ester production by 2-stage and 2-step process from previous studies

Feedstock	**process**	**Molar ratio (EtOH:Oil)**	**Catalyst** (% wt.)	**Temp. (^{O}C)**	**Reaction time (min)**	**FFA (%wt.)**	**Molar ratio (EtOH:Oil)**	**Catalyst** (% wt.)	**Temp. (^{O}C)**	**Reaction time (min)**	**Yield (%wt.)**	**Reference**
Used frying oil (FFA= 0.3% wt.)	2-stage	12:1	1.0% KOH	78	120	(Y=74)	5:1	0.75% KOH	78	80	95	Encinar et al., 2007
R. sativus crude oil (FFA= 0.6% wt.)	2-stage	12:1	0.4% NaOH	45	60	(Y=78)	6:1	0.03% NaOH	45	60	95	Domingos et al., 2008
Crude candlenut oil (FFA= 7.8% wt.)	2-step	10:1	0.25% H_2SO_4	70	60	1.5	8:1	1.5% KOH	Ambient condition	60	99	Sulistyo et al., 2009
CPO (FFA= 7-8% wt.)	2-step	10:1	2.0% $Fe_2(SO_4)_3$	95	60	< 2	6:1	1.0% KOH	65	60	85	Buasri et al., 2009
CPO (FFA= 7.5% wt.)	2-step	6:1	1.0% H_2SO_4	microwave power	60	1.7	4:1	1.5% KOH	microwave power	5	80	Suppalakpanya et al., 2010
CPO (FFA= 7.5% wt.)	2-step	6:1	1.0% H_2SO_4	microwave power	60	1.7	9:1	1.5% KOH	microwave power	5	85	Suppalakpanya et al., 2010
CPO (FFA= 8.0% wt.)	2-step	9:1	1.0% H_2SO_4	78	60	1.2	6:1	1.5% KOH	78	45	82	This studied

Note: FFA; free fatty acid content, EtOH; ethanol, Y; yield

4.3 Summary and suggestion

Crude palm oil (CPO) could be used as a feedstock to produce biodiesel in the form of ethyl ester. However, the following are some critical factors which need to take into consideration:

1. The content of free fatty acid (FFA) in reactant is the principal factor dominates the separation efficiency between glycerol phase and ester phase. Therefore, it should be reduced to a level of less than 0.8% w/w prior to used.
2. On transesterification reaction, the molar ratio of oil:ethanol at 1:6.0 give a high percent yield of biodiesel with the lowest total glyceride content. As a waste reusing is concerned, 1.5% KOH was an optimum catalyst concentration, while the reaction should be performed at 70^{o}C for 45 minutes.
3. Following transesterification, removal of an excess ethanol in the reaction mixture with a steam of boiling water seem to be the most effective practical procedure to improve the separation efficiency between the glycerol phase and the ester phase.
4. To increase phase separation efficiency at the washing step, it could be carried out by slowly addition of approximately 25% v/v saturated urea solution into the remaining upper phase. Vigorously mixing should be avoided at this step.
5. On the basis of the recommended procedure, more than 82% yield of biodiesel could be obtained. This was calculated with respect to the initial weight of CPO prior to acid esterification.
6. Water content in biodiesel could be determined using GLC-TCD method which LOD and LOQ at the level of 0.06%-0.2% wt could be obtained.

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APPENDICES

APPENDICES

APPENDIX A Preparation of chromotropic acid reagent

Chromotropic acid solution was prepared by dissolving 1.14 g of chromotropic acid in small amount of 33% H_2SO_4, make up volume to 500 ml with the acid. The solution was filtered through sinter glass, and was kept in amber-bottle at 0-4 ^{o}C.

APPENDIX B Calibration curve standard triglyceride.

To construct a calibration curve for analysis of total glyceride contents in sample, 5 appropriated concentrations of standard glycerides (tristearin) were carried out with chromotropic acid method (Chandumpai, in patent process) and measure the absorbance at 570 nm.

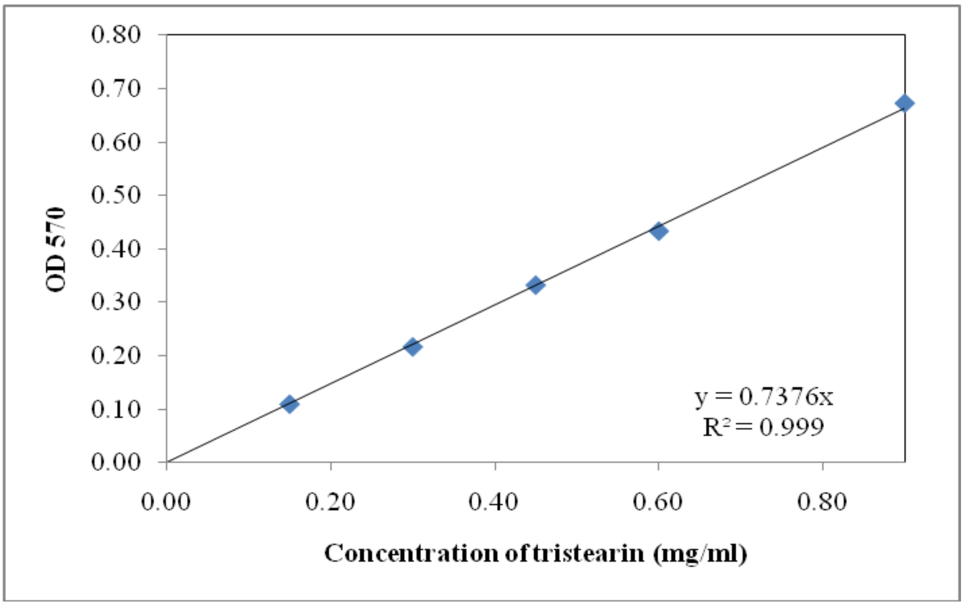

Figure A Calibration curve of standard total glyceride (tristearin)

From the acquired data, calibration curve of the 5 standard glycerides concentrations was plotted. Figure A showed that a linear correlation was found with $R^2 = 0.999$ as the following equation $y = 0.7376x$. From these results, LOD and LOQ of this method were calculated according to the method recommended by Shabir (2003) as 0.03 and 0.08 mg/ml, respectively. After that, the total glyceride contents in sample were calculated in term of percent by weight comparable with tristearin.

APPENDIX C Calculations of validated method for water content analysis

Validation method

Standard (std.) water solution (density = 0.80 g/ml)

pipet 0.99 ml = 0.795 g

Internal standard (50% vol. toluene in i-butanol)

pipet 0.01 ml = 0.0043 g

From linear equation; $y = 0.977x + 0.000$; $R^2 = 0.999$

slope = 0.977 (area ratio/wt. ratio)

standard deviation (SD) at 0.125 % vol. = 0.037 (area ratio)

From LOQ equation;

$$\text{LOQ} = \frac{10\ (0.037)\ \text{(area ratio)}}{0.977\ \text{(area ratio/wt. ratio)}} = 0.378\ \text{(wt. ratio)}$$

wt. ratio = 0.378

$$\frac{\text{wt. water}}{\text{wt. IS}} = 0.378$$

wt. water (g) = 0.378 x wt. IS (g)

wt. water (g) = 0.378 x (0.0043 g)

$$= 0.0016 \text{ g}$$

$$\text{water (\% wt.)} = \frac{0.0016 \text{ g}}{0.795 \text{ g}} \times 100$$

$$= 0.205 \text{ \% wt.}$$

- LOQ of this method is 0.205 % wt.

From LOD equation;

$$\text{LOD} = \frac{3.3\,(0.037)\text{ (area ratio)}}{0.977\text{ (area ratio/wt. ratio)}} = 0.125 \text{ (wt. ratio)}$$

$$\text{wt. ratio} = 0.125$$

$$\frac{\text{wt. water}}{\text{wt. IS}} = 0.125$$

$$\text{wt. water (g)} = 0.125 \times \text{wt. IS (g)}$$

$$\text{wt. water (g)} = 0.125 \times (0.0043 \text{ g})$$

$$= 0.0005 \text{ g}$$

$$\text{water (\% wt.)} = \frac{0.0005 \text{ g}}{0.795 \text{ g}} \times 100$$

$$= 0.068 \text{ \% wt.}$$

- LOD of this method is 0.068 % wt.

Water content analysis

From linear equation;

$$y = 0.977x + 0.000 \qquad ;\ R^2 = 0.999$$

$$\text{area ratio} = 0.977 \text{ (wt. ratio)}$$

$$\text{wt. ratio} = \frac{\text{area ratio}}{(0.977)}$$

At correction factor, 0.752 (area ratio);

$$\text{wt. ratio} = \frac{0.752}{(0.977)}$$

$$= 0.770$$

$$\text{wt. water (g)} = 0.770 \text{ x wt. IS (g)}$$

$$= 0.770 \text{ x } 0.0043 \text{ g}$$

$$= 0.0033 \text{ g}$$

$$\text{water (\% wt.)} = \frac{0.0033 \text{ g}}{0.795 \text{ g}} \text{ x } 100$$

$$= 0.42 \text{ \% wt.}$$

- At correction factor (0.752 area ratio) have water content 0.42 % wt.

APPENDIX D Specification of Biodiesel (B100) in Thailand.

Property	**ASTM Method**	**Limits**	**Units**
Methyl ester	EN14103	96.5 min.	% mass
Density, 40^oC	D1298	860 - 900	kg/m^3
Flash Point	D93	120 min.	Degrees C
Water	EN ISO 12937	0.050 max.	% mass
Viscosity, 40^oC	D445	3.5 - 5.0	cSt.
Sulfated Ash	D874	0.02 max.	% mass
Sulfur	D2622	0.0010 max.	% mass
Copper Strip Corrosion	D130	No. 1 max.	
Cetane	D613	51 min.	
Methanol	EN 14110	0.20 max.	% mass
Iodine value	EN 14111	120 max.	gm I_2/100 gm
Acid Number	D664	0.50 max.	mg KOH/gm
Free Glycerin	EN 14105	0.02 max.	% mass
Total Glycerin	EN 14105	0.25 max.	% mass
Phosphorus Content	D 4951	0.0010 max.	% mass

Source: www.dede.go.th

APPENDIX E Specification of Biodiesel (B100) for agricultural diesel engine (community biodiesel).

Property	**ASTM Method**	**Limits**	**Units**
Flash Point	D93	120 min.	Degrees C
Water & Sediment	D2709	0.2 max.	% vol.
Kinematic Viscosity, 40 C	D445	1.9 - 6.0	mm2/sec.
Sulfated Ash	D874	0.020 max.	% mass
Sulfur	D2622	0.0015 max.	% mass
Copper Strip Corrosion	D130	No. 3 max.	
Cetane	D613	47 min.	
Density, $40^{o}C$	D1298	860 - 900	kg/m^3
Acid Number	D664	0.80 max.	mg KOH/gm
Free Glycerin	D6584	0.02 max.	% mass
Total Glycerin	D6584	1.5 max.	% mass

Source: www.dede.go.th

VITAE

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List of Publication and Proceeding

Roekngam, N., Chandumpai, A. and Tongurai, C. 2011. Improvement the Phase Separation of Biodiesel Production from Crude Palm Oil and Ethanol. Proceeding of the 6th Conference on Science and Technology for Youths: 2011. Bangkok International Trade and Exhibition Centre, Bangkok, Thailand. March 18-19, 2011. pp. 114-123.