CONTINUOUS SYNTHESIS OF BIODIESEL AND GLYCEROL ETHER USING HOMOGENEOUS AND HETEROGENEOUS CATALYSTS

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การสังเคราะห์ไบโอดีเซลและกลีเซอรอลอีเทอร์แบบต่อเนื่องด้วยตัวเร่งปฏิกิริยาเอกพันธุ์และวิวิธพันธุ์

น.ส.ณัฐฐา รัตนปัญญา

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
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By	Miss Natta Rattanapanya
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Thesis Advisor	Associate Professor Surachai Pornpakakul, Ph.D.

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ณัฐฐา รัตนปัญญา : การสังเคราะห์ไบโอดีเซลและกลีเซอรอลอีเทอร์แบบต่อเนื่องด้วยตัวเร่งปฏิกิริยาเอกพันธุ์และวิวิธพันธุ์. (CONTINUOUS SYNTHESIS OF BIODIESEL AND GLYCEROL ETHER USING HOMOGENEOUS AND HETEROGENEOUS CATALYSTS) อ.ที่ปรึกษาหลัก : รศ. ดร.สุรชัย พรภคกุล

งานวิจัยนี้พบว่าการใช้ตัวเร่งปฏิกิริยาผสมระหว่างกรดพาราโทลูอีนซัลโฟนิกและกรดซัลฟิวริกเป็นตัวเร่งปฏิกิริยาสามารถเร่งปฏิกิริยาได้ดีในกระบวนการทรานส์เอสเทอริฟิเคชันของน้ำมันปาล์มกับเมทานอลและกระบวนการอีเทอร์ริฟิเคชันของไบโอดีเซลกับไอโซบิวทิลีน ในการเตรียมไบโอดีเซลตัวเร่งปฏิกิริยาผสมเร่งปฏิกิริยาได้ดีกว่าการใช้กรดพาราโทลูอีนซัลโฟนิกและกรดซัลฟิวริกเดี่ยวๆและสามารถสังเคราะห์ไบโอดีเซลสูงถึง 99.8% กระบวนการอีเทอร์ริฟิเคชันระหว่างไบโอดีเซลกับไอโซบิวทิลีนโดยใช้อัตราส่วนของไอโซบิวทิลีนต่อกลีเซอรอลที่ 6: 1 ใช้อุณหภูมิ 70 องศาเซลเซียส ใช้เวลา 5 ชั่วโมง ทำให้มีความจำเพาะที่สูงในการเกิดผลิตภัณฑ์เป็นไดและไตรเทอร์เชียรีบิวทิลกลีเซอรอลอีเทอร์ (81.4 %) นอกจากนี้ตัวเร่งปฏิกิริยาผสมยังนำกลับมาใช้ใหม่ในการเร่งปฏิกิริยาต่อเนื่องสำหรับทรานส์เอสเทอริฟิเคชันกับอีเทอร์ริฟิเคชันใช้ได้ถึง 6 รอบ การใช้ตัวทำละลายดีพยูเทคติคที่ได้จากการผสมระหว่างกรดพาราโทลูอีนซัลโฟนิกและคอรีนคลอไรด์ (ChCl-TsOH) อัตราส่วน 3:1 เป็นตัวเร่งปฏิกิริยาสามารถทำให้เกิดเป็นไบโอดีเซลสูงถึง 99.8% เมื่อใช้ตัวเร่งปฏิกิริยา 10% อัตราส่วนเมทานอลต่อน้ำมันปาล์ม 10:1 ทำปฏิกิริยาที่ 110 องศาเซลเซียส เวลา 4 ชั่วโมง การใช้ตัวเร่ง ChCl-TsOH ดังกล่าวในปฏิกริยาอีเทอร์ริฟิเคชันแบบต่อเนื่องพบว่า กระบวนการอิเทอริฟิเคชันได้เป็นไดและไตรเทอร์เชียรีบิวทิลกลีเซอรอลอีเทอร์ 89.9% อุณหภูมิ 100 องศาเซลเซียส อัตราส่วนไอโซบิวทีลีนต่อกลีเซอรอล 6:1 ใช้เวลา 5 ชั่วโมง นอกจากนี้ ChCl-TsOH ยังสามารถนำกลับมาใช้ใหม่ได้ถึง 4 รอบ การเปรียบเทียบคุณสมบัติทางเชื้อเพลิงระหว่างผลิตภัณฑ์ไบโอดีเซลและไบโอดีเซลผสมสารเติมแต่งจากกระบวนการอิเทอริฟิเคชันพบว่าจะช่วยเพิ่มประสิทธิภาพไบโอดีเซลมีจุดไหลเท ค่าความเป็นกรดและค่าปริมาณพันธะคู่ของไบโอดีเซลได้เมื่อไบโอดีเซลมีเทอร์เทียรี่-กลีเซอรอลอีเทอร์ที่เตรียมขึ้นในปริมาณ 10% ผสมอยู่ในไบโอดีเซล

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KEYWORD: Biodiesel Glycerol Etherification p-toluenesulfonic acid tert-butyl glycerol ether, Deep Eutectic Solvent

Natta Rattanapanya : CONTINUOUS SYNTHESIS OF BIODIESEL AND GLYCEROL ETHER USING HOMOGENEOUS AND HETEROGENEOUS CATALYSTS. Advisor: Assoc. Prof. Surachai Pornpakakul, Ph.D.

In our study, a mixture of *p*-toluenesulfonic acid and sulfuric acid (TsOH-H_2SO_4) as a catalyst showed a good performance in transesterification of palm oil (PO) with methanol and etherification of biodiesel with isobutylene. For biodiesel production, the catalyst noticeably accelerated the reaction faster than TsOH and H_2SO_4 alone and also gave up to 99.8% of the conversion. Etherification of biodiesel with isobutylene in the etherification process using isobutylene/glycerol molar ratio 6:1 at 70°C, in the period of 5 h reaction time, gave high selectivity to produce DTBG and TTBG (81.4%). Furthermore, the catalyst can be reused for 6 cycles of continuous synthesis (transesterification and etherification). When using deep eutectic solvents (DESs) as catalyst, the highest conversion of biodiesel (99.8%) were obtained from the condition of 10%wt ChCl-TsOH (3:1 ratio), 10:1 methanol/PO ratio at 110°C and reaction time 4 h. In the etherification process for the next step of the etherification synthesis using ChCl-TsOH as catalyst, isobutylene/glycerol molar ratio 6:1, reaction temperature 100°C, and 5 h reaction time, it gave high selectivity to produce DTBG and TTBG (89.9%). Furthermore, the ChCl-TsOH catalyst could be reused for 4 cycles. In comparison of fuel properties between biodiesel and biodiesel blending with 10% the prepared *tert*-butyl glycerol ethers blend would enhance the biodiesel efficiency as follows; acid value, pour point and iodine value.

Field of Study: Petrochemistry Student's Signature ....
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DESs	Deep Eutectic solvent
DTBG	di-*tert*-butyl glycerol ether
FAME	fatty acid methyl ester
FFA	Free fatty acid
h	hour
mg	milligram
min	minute
MTBG	mono-*tert*-butyl glycerol ether
PO	palm oil
ppm	parts per million
TsOH	*p*-toluenesulfonic acid
TTBG	tri-*tert*-butyl glycerol ether
Wt	weight
°C	degree celcius

CHAPTER I
INTRODUCTION

Most of the large trucks, buses, and tractors around the world have engines that require diesel fuel. Biomass-based diesel fuels are biofuels made from biomass or biomass-derived materials which include biodiesel and renewable diesel. From the record, the forecast of energy and fuel demand towards a sustainable road transport sector (2016–2035) represented around 27.8% of the total world energy demand [1].

Biodiesel, the methyl esters of fatty acids, is produced by transesterification of triglycerides with methanol. In the transesterification process, glycerol is obtained as a by-product equivalent to approximately 10 wt% of the obtained biodiesel. The amount of glycerol is expected to grow at an annual rate of demand for biodiesel. Glycerol can also be applied to various uses including textiles (24%), food and beverages (21%), cosmetics and toiletries (18%), drugs (18%), tobacco (6%), and paper and printing (5%), and others [2]. However, recovery and purification of the crude glycerol contributes to high production costs and energy consumption. Therefore, direct use of crude glycerol needs to be investigated, and a great deal of research is focused on the conversion of glycerol into value-added products, for example, fuel additive, acrolein, glycerol carbonate, glycerol acetal, etc [3].

. One possible application of glycerol is etherification of glycerol into mono-, di- and tri-*tert*-butyl glycerol. These ethers, mainly di- and tri- *tert*-butyl glycerol ethers, can be used as an additive in diesel fuel, biodiesel and gasoline. The mixture of ethers and esters is added to the diesel fuel and such prepared reformulated diesel fuel (diesel with oxygenates) has lowered the cloud point and reduced emission of particulate matters [3]. The glycerol ethers are preferably produced via etherification of glycerol and isobutylene. Filiminov *et al.* [4] studied etherification of glycerol with isobutylene using *p*-toluenesulfonic acid (TsOH), Amberlyst 15, 1-(4-sulfobutyl)-3-hexylimidazolium trifluomethanesulfonate (IL6) and silicotungstic acid $H_4SiW_{12}O_40$ (HSiW) as catalysts. The optimal condition for etherification process using TsOH (7.5 wt% based on glycerol), 4:1 molar ratio of isobutylene and glycerol, at the condition of 60°C and 5 h reaction time resulted in 99% conversion and 70% of di and tri-glycerol ether. Klepacova *et al.* [3] studied etherification of glycerol with isobutylene using Amberlyst type (15 and 35), *p*-toluenesulfonic acid (TsOH) and by two large-pore zeolite H-Y and H-Beta. The highest glycerol conversion 88.7% was achieved over zeolite H-Y after 8h. In the presence of *p*-toluenesulfonic acid (TsOH), the etherification (in dioxane) ran faster in comparison with heterogeneous catalyst in a period of 4 h. The glycerol conversion up to 90% was achieved and provided better results in DTBG formation. Likewise, di- and tri-ethers can also act as cold flow improvers for biodiesel.

In biodiesel production, H_2SO_4 and TsOH were also used as a catalyst for the transesterification. Guan *et al.* [5] studied the transesterification of corn oil with methanol using *p*-toluenesulfonic acid (TsOH), benzenesulfonic acid, H_2SO_4 as catalysts and dimethyl ether (DME) as the co-solvent. The result showed the highest catalytic activity and the yield of FAME reached 97.1% when the reaction in the presence of DME was carried out by using 4wt% of TsOH based on the oil weight with methanol/oil 10:1 at 80 °C for 2 h. In the case of using H_2SO_4 as catalyst, the yield of FAME reached 60.3% in the same condition of TsOH. Freedman *et al.* [6] reported that the transesterification of soybean with methanol using 1 wt% sulfuric acid (H_2SO_4), methanol/oil 30:1, at 65°C for 69 h gave over 99% yield of fatty acid methyl ester (FAME).

As a new type of catalyst, acidic ionic liquid has been also applied in glycerol production [3]. Ionic liquids (ILs) has become a new eco-benign approach toward modern chemistry, having found applications in a wide range of areas, including catalysis, synthesis, analysis, and gas absorption, etc., especially those functionalized with Lewis and/or Brønsted acid sites. The ionic liquid, with the properties of flexibility, non-volatility, non-corrosivity, and immiscibility with many organic solvents, can afford higher yields and selectivities with potential application in replacing conventionally homogeneous/heterogeneous acid catalysts [6]. However, high cost is the limitations of ILs [7]. As a new and green type of ILs, deep eutectic solvents (DESs), have emerged recently. DESs are simple mixture of quaternary ammonium salt (usually choline chloride (ChCl)) and a hydrogen bond donor (HBD). In comparison with conventional ILs, DESs can be easy to synthesize through mixing quaternary ammonium salt and HBD with gentle heating (70-90°C). And most of DESs are liquid at room temperature, with unique properties such as high purity and environmental friendliness. Based on their unique properties, DESs have been widely used as solvent in many fields, such as extraction, separation, catalysis and so on. For example, DESs have been used in organic transformations as eco-friendly solvent/catalyst systems.

According to the literatures, TsOH, H_2SO_4, and DESs were individually used as the catalyst in transesterification of triglycerides and the etherification of glycerol. However, it is difficult to separate this catalyst from the reaction mixture and it also produces corrosion and environmental problems. In this work, similar catalytic ability to homogeneous acid catalysts in transesterification process and glycerol ether production were studied. Herein this report will show the performance of TsOH-H_2SO_4 mixed catalyst and DESs in the transesterification of PO and the etherification of glycerol. Reusability of the TsOH-H_2SO_4 mixed catalyst and DESs were studied.

Objective of the research

1. To synthesize biodiesel and glycerol ether in continuously using homogeneous, heterogeneous and ionic liquid containing acid group catalysts

2. To evaluate of reusability of homogeneous, heterogeneous and ionic liquid containing acid group catalysts

3. To determine of % yield of *tert*-butyl glycerol ethers and properties of biodiesel with the glycerol including iodine number, pour point and acid value

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Palm oils

Palm oil is a form of edible vegetable oil obtained from the fruit of the oil palm tree. It is the second-most widely produced edible oil. Palm oil is a potential raw material for biodiesel production. The palm oil is a monocotyledon belonging to the genus *Elaeis*. It is a perennial tree crop and the highest oil producing plant. The fleshy monocarp produces palm oil, which is used mainly for its edible properties and the kernel produces palm kernel oil, which has wide application in the oleochemical industry. The genus *Elaeis*, comprise two species, namely *E. guineensis* and *E. oleifera.* Current, most of the world's production of palm oil comes from South-East Asia, in particular Malaysia, Indonesia and Thailand.

In Thailand, palm tree is mainly growing in the southern part. The major area for palm plantation is in five provinces including Krabi, Surat Thani, Chumphon, Trang and Satun.

The palm oil fruit is a drupe, which forms in a tight bunch. The pericarp comprises four layers: the exocarp (skin), mesocarp (outer pulp containing palm oil); endocarp (a hard shell enclosing) and the Kernel as shown in Figure 2.1 [8]

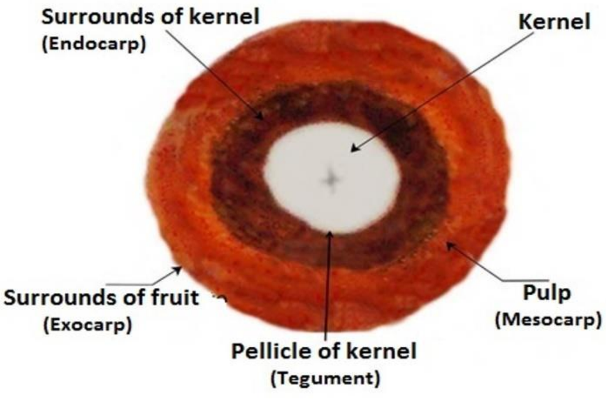


Figure 2.1 Composition of palm oil fruit [8]

2.1.1 Chemical composition of palm oils

The palm oil and palm kernel oil are composed of fatty acids, esterified with glycerol like any ordinary fat. Both are high in saturated fatty acids, about 50%. The oil palm gives its name to the 16 carbon saturated fatty acid palmitic acid found in palm oil; monounsaturated oleic acid is also a constituent of palm oil while palm kernel oil contains mainly lauric acid.

Table 2.1 The approximate concentration of fatty acids in palm kernel oil [8]

The fatty acid content	**Percentage**
Saturated	Total : 82%
Lauric C12:0	48.2%
Myristic C14:0	16.2%
Palmitic C16:0	8.4%
Capric C10:0	3.4%
Caprylic C8:0	3.3%
Stearic C18:0	2.5%
Mononsaturated	
Oleic C18:1	15.3%
Polyunsaturated	
Linoleic C18:2	2.3%

2.2 Biodiesel

Biodiesel fuel, an alternative energy, has been more focused to develop because it could be replacing the diesel fuel, which is a relatively clean-burning, renewable biological source such as vegetable oils and animal fats. Biodiesel produces significantly less harmful emission than diesel when burned in a combustion engine.

2.2.1 Advantages of biodiesel

Biodiesel can be considered as a new technology, taking into account all the year consumers have to settle for traditional diesel. Using biodiesel has many advantages [9].

- Biodiesel reduces unburned hydrocarbons, carbon monoxide and particulate matter in exhaust fumes.
- Biodiesel exhaust is not offensive and does not cause eye irritation.
- Biodiesel is a much better lubricant than diesel and extends engine life.
- Biodiesel has a higher the cetane number; the more efficient the fuel; the engine starts more easily, runs better and burns cleaner.
- Biodiesel can be used directly or as a mixture with hydrocarbon-based diesel fuels.
- Biodiesel is nontoxic, safe to handle and biodegradable.

2.2.2 Biodiesel production

There are four primary ways to make biodiesel, direct use and blending, thermal cracking, esterification and transesterification. The most commonly used method is the transesterification of vegetable oils and animal fats with small alcohols. The description of each production way is provided below [10].

2.2.2.1 Direct use and blending

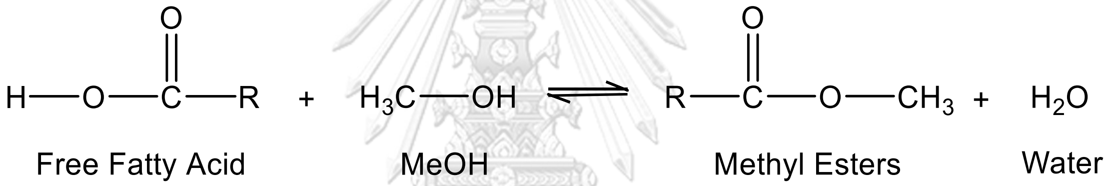
Direct use of 100% vegetable oil was not practical due to high viscosity, low cetane and low flash point at low temperature. Blending as a mixture of 20% vegetable oil and 80% diesel fuel can replace diesel fuels without any adjustment of the engine. The high viscosity, polymerization during storage and carbon deposit are obvious problems.

2.2.2.2 Thermal cracking

Thermal cracking means applying heat in the absence of air or oxygen with temperatures ranging from 450 °C – 850 °C. The pyrolysis successfully produces many smaller chain compounds. The ratios of light to heavy compounds are temperature and time dependent.

2.2.2.3 Esterification

Esters are derived from carboxylic acids. A carboxylic acid contains the -COOH group, and the hydrogen in this group is replaced by a hydrocarbon group of some kind to give ester. Esterification are catalyzed and this requires two reactants, carboxylic acids (fatty acids) and alcohols. The equation for an esterification of free fatty acid shown in Figure 2.2

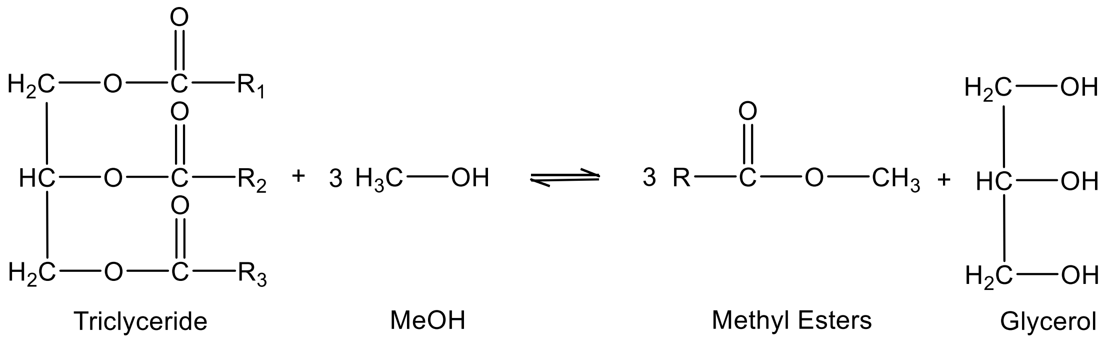


$$H{-}O{-}\overset{\overset{O}{\|}}{C}{-}R + H_3C{-}OH \rightleftharpoons R{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_3 + H_2O$$

Figure 2.2 Esterification of free fatty acid with methanol [10]

2.2.2.4 Transesterification

Transesterification is the reaction of an ester with alcohols to give another ester. The main reaction for converting oil to biodiesel is called transesterification. In transesterification process triglyceride, contained in vegetable oils, animal fats, or recycled greases, reacts with alcohol to form fatty acid alkyl esters (biodiesel) and glycerin. A catalyst is usually used to improve the reaction rate and the yield of fatty acid alkyl esters. Simple alcohols such as, methanol, ethanol and butanol can be used in transesterification. Methanol is most often used for commercial. However, ethanol is becoming popular as it is less toxic than methanol. The equation for a transesterification of triglycerides with methanol is shown in Figure 2.3 [15].



Triglyceride Methanol Methyl esters Glycerol

Figure 2.3 Transesterification of triglycerides with methanol [15]

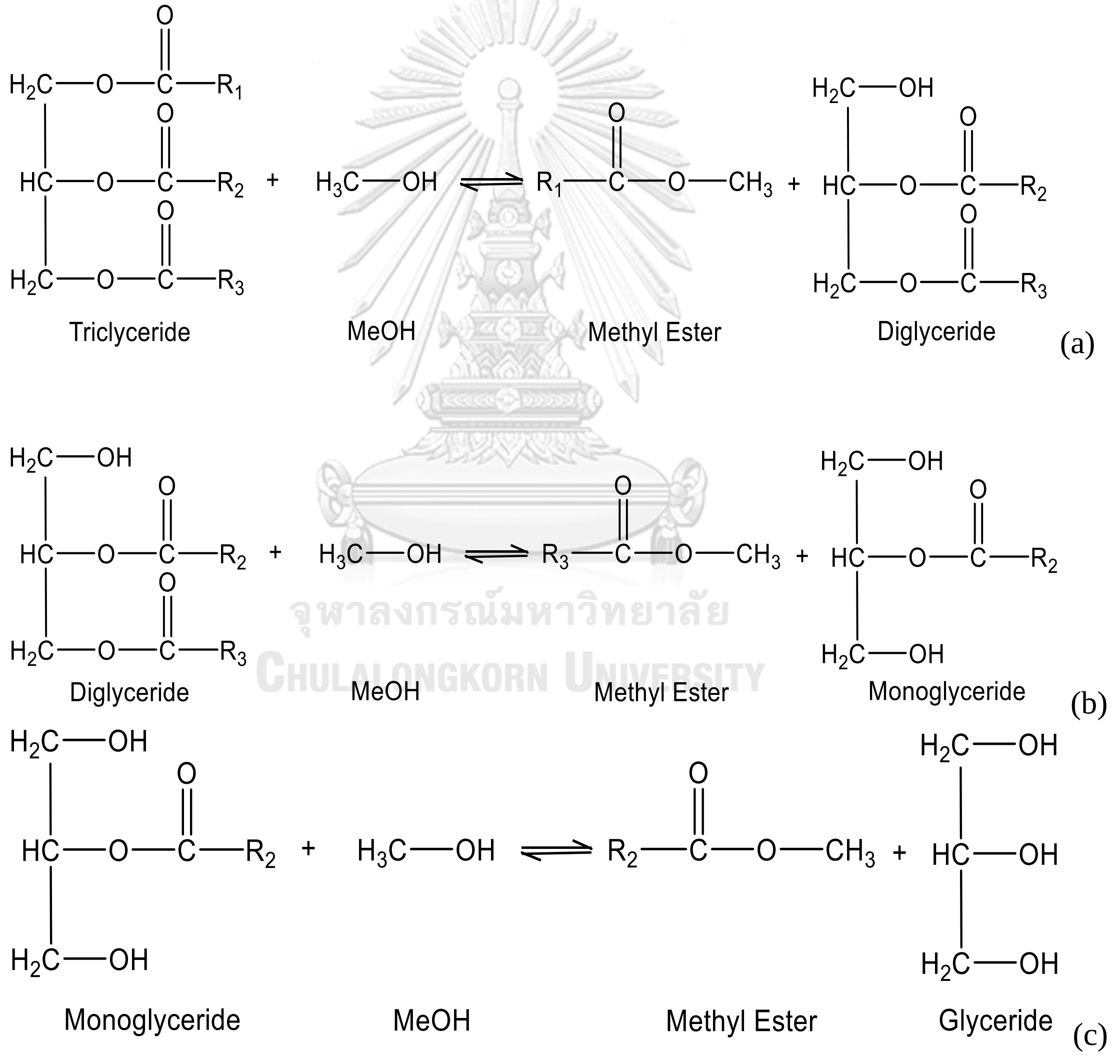


Figure 2.4 Three-consecutive transesterification for methyl esters synthesis from triglyceride [15]

Basically, the transesterification of triglyceride with methanol consists of a number of consecutive and reversible reactions as shown in Figure 2.4. The first step reaction is the conversion of the triglyceride to a diglyceride (Figure 2.4a), followed by the successive conversion of the diglyceride to a monoglyceride (Figure 2.4b), and terminal step is the conversion of the monoglyceride to glycerol (Figure 2.4c). In each step, a methyl ester is generated and thus three ester molecules are produced from one molecule of triglyceride. The conversion of the monoglyceride to methyl ester and glycerol is believed to be the rate determining step because monoglycerides are the most stable intermediates [10].

Hydrolysis is a side reaction of biodiesel process. The hydrolysis of glycerides takes place in the lipid phase in several stages via partial glycerides (diglycerides and monoglyceride). The homogenous lipid phase consists of fatty acids and glycerol shown in Figure 2.5 [3].

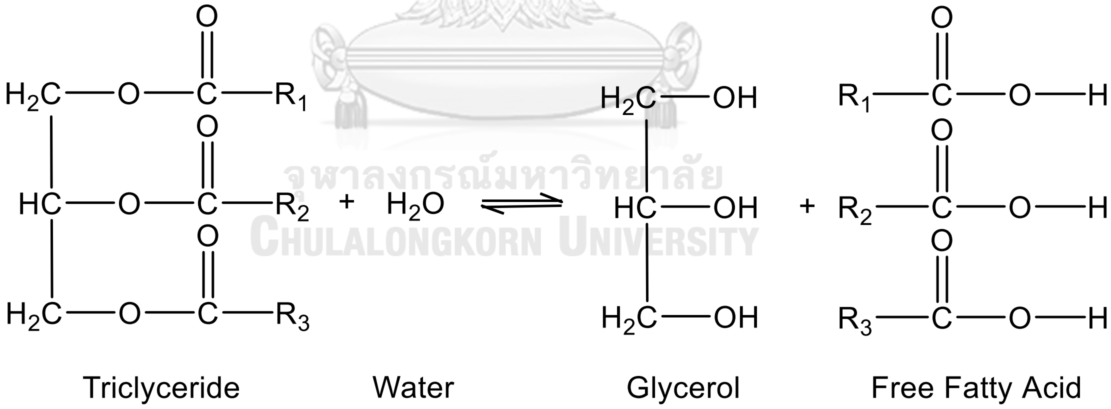


Figure 2.5 Hydrolysis of triglycerides

When free fatty acids occur in base-catalyzed transestrification, the problem is caused by undesired saponification reaction. This problem, also noted in other studies, include catalyst depletion, soap formation, and separation difficulties due to the saponification reaction (specifically base catalyst) as shown in Figure 2.6 [3].

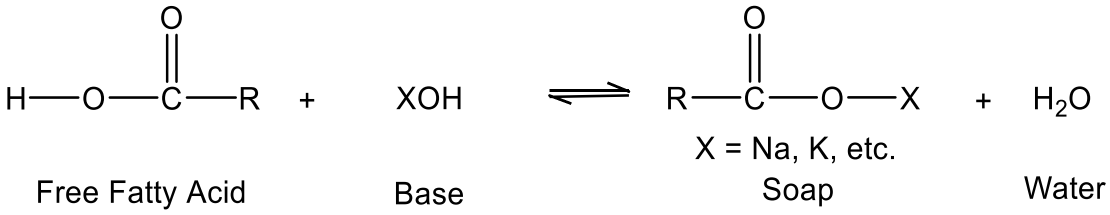


Figure 2.6 Saponification reaction [3]

2.2.3 Biodiesel properties

Triglyceride is made up of fourteen different types of fatty acids, which are transformed into fatty acid methyl esters (FAME) by transesterification. Different fractions of each type of FAME present in various feed stocks influence some properties of fuels such as cold flow properties of biodiesel production. Table 2.2 shows comparison of fuel properties between diesel and biodiesel in the ASTM standards and Table 2.3 shows characteristic and quality of biodiesel (methyl ester of fatty acids) in Thailand [11].

Table 2.2 Comparison of fuel properties between diesel and biodiesel [11]

Fuel properties	**Diesel**	**Biodiesel**
Fuel standard	ASTM D975	ASTM PS 121
Fuel composition	C10-C21 HC	C12-C22 FAME
Lower heating value, Btu/gal	131,295	117,093
Viscosity, @ 40 °C	1.3-4.1	1.9-6.0
Specific gravity kg/l @ 60 °F	0.85	0.88
Density, lb/gal @ 15 °C	7.079	7.328
Water, ppm by wt	161	0.05% max
Carbon, wt%	87	77
Hydrogen. wt%	13	12
Oxygen, by dif. wt%	0	11
Sulfur, wt%	0.05 max	0.0 – 0.0024
Boiling point (°C)	188-343	182-338
Flash point (°C)	60-80	100-170
Cloud point (°C)	-15 to 5	-3 to 12
Pour point (°C)	-35 to -15	-15 to 10
Cetane number	40-55	48-65
Stoichiometric air/fuel ratio wt./wt.	15	13.8
BOCLE Scuff, grams	3600	>7000

Table 2.3 Characteristic and quality of biodiesel (methyl ester of fatty acids) in Thailand [11]

Characteristic	Value	Method of standard
Methyl ester, wt%	>96.5	EN 14103
Density at 15 °C, kg/m^3	860-900	ASTM 1298
Viscosity at 40 °C, cSt	3.5-5.0	ASTM 445
Flash point, °C	>120	ASTM 93
Sulphur, wt%.	<0.0010	ASTM 2622
Carbon residue, on 10% distillation residue, wt%	<0.30	ASTM 4530
Cetane number	>51	ASTM 613
Sulfated ash, wt%	<0.02	ASTM 874
Water, wt%	<0.050	ASTM 2709
Total contaminate, wt%	<0.0024	ASTM 5452
Copper strip corrosion	<96.5	ASTM 130
Oxidation stability at 110 °C, hours	>6	EN 14112
Acid value, mg KOH/g	<0.50	ASTM 664
Iodine value, g Iodine/100g	<120	EN 14111
Lionlenic acid methyl ester, wt%	<12.0	EN 14103
Methanol, wt%	<0.20	EN 14110
Monoglyceride, wt%	<0.80	EN 14105
Diglyceride, wt%	<0.20	EN 14105
Triglyceride, wt%	<0.20	EN 14105
Free glycerin, wt%	<0.02	EN 14105
Total glycerin, wt%	<0.25	EN 14105
Group I metals (Na+K)	<5.0	EN 14108 and EN 14109

2.3 Biodiesel catalysts

Traditionally, catalysts are distinguished into 2 types, i.e. homogeneous and heterogeneous. This distinction is linked to the fact that the catalyst operates respectively in the same phase where the reaction occurs (homogeneous catalysts) or in a different phase (heterogeneous catalysts). In general, most of the processes using homogeneous catalysts occur in a liquid phase, whereas for the heterogeneous catalysts, the catalyst is usually in a solid form, and the reaction occurs either in the liquid or gaseous phase. In Table 2.4, advantages/disadvantages of homogeneous and heterogeneous catalysis are compared.

Table 2.4 The comparison of homogeneously and heterogeneously catalyzed transesterification [12]

Factors	Homogeneous catalysis	Heterogeneous catalysis
Reaction rate	Fast and high conversion	Slow
After treatment	Impossible or non-economic for recovery	Possible for recover
Processing methodology	Limited use of continuous	Continuous fixed bed operation possible
Presence of water/ free fatty acid	Sensitive	Less sensitive
Catalyst reuse	Not possible	Possible
Cost	Comparatively costly	Potentially cheaper

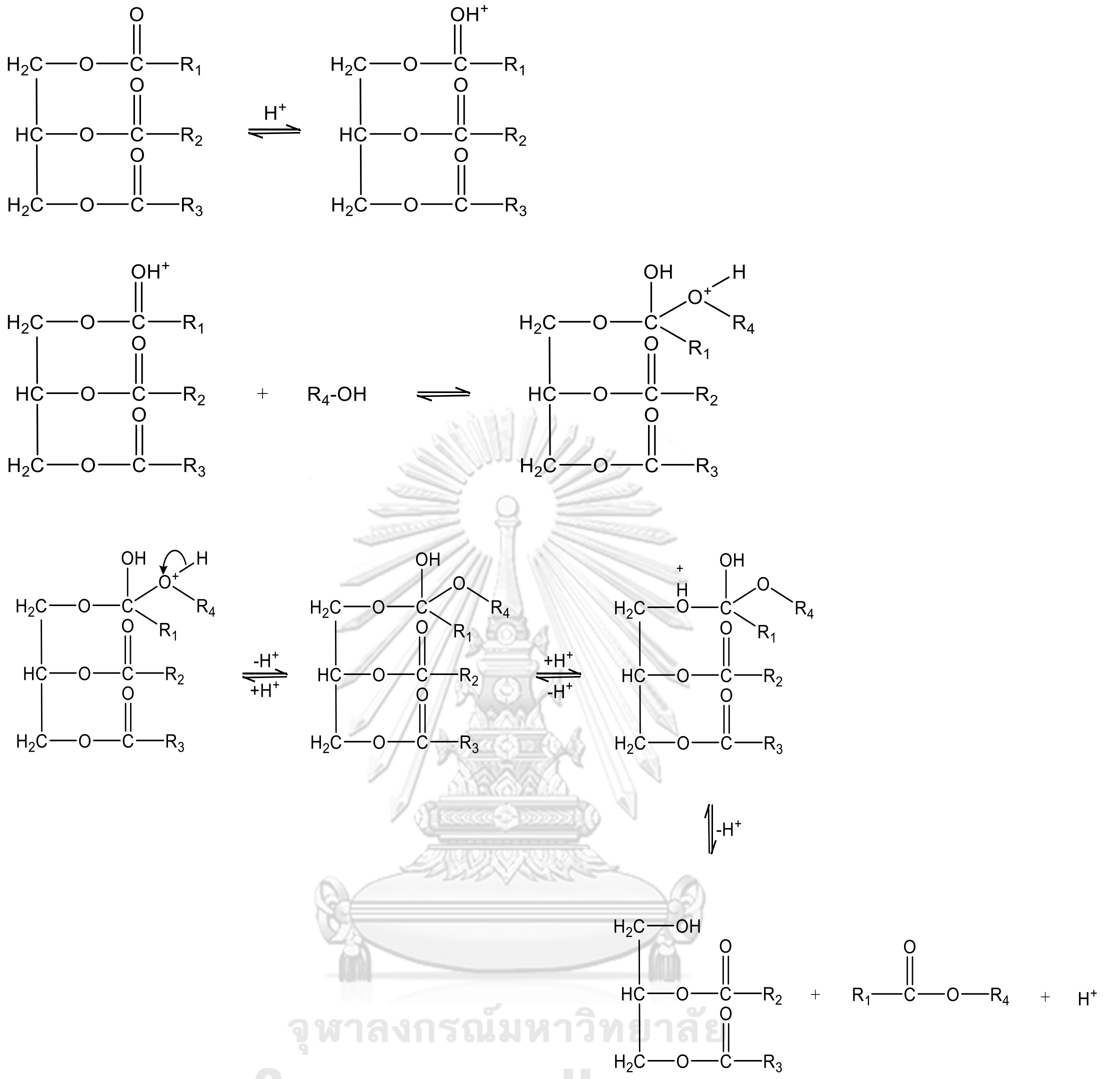
2.3.1 Homogeneous catalysis

2.3.1.1 Acid catalysis

Sulfuric, hydrochloric and sulfonic acids are the most popular homogeneous catalyst in the acid-catalyzed transesterification shown in Table 2.5 [12]. Generally, the reaction catalyzed by the acids are performed at height molar ratios of alcohol to oil, low to moderate temperatures and pressures, and high acid concentrations to obtain a high yield of methyl ester product. However, a large excess amount of alcohol makes the recovery of glycerol to be difficult. Mechanism of acid-catalyzed transesterification is shown in figure 2.7. This in turn increases the electrophilicity of the adjoining carbon atom, making it more susceptible to nucleophilic attack by alcohol [12].

Table 2.5 The examples of acid catalysis [12]

Type of catalyst	For example	Comments
Inorganic homogeneous	Conc. Sulfuric acid	Cheap, decomposition products, corrosion
Organic homogeneous	*p*-Toluene sulfonic acid	High price, recycling necessary
Organic heterogeneous	Acidic ion exchange resins	High price, continuous reaction possible, low stability



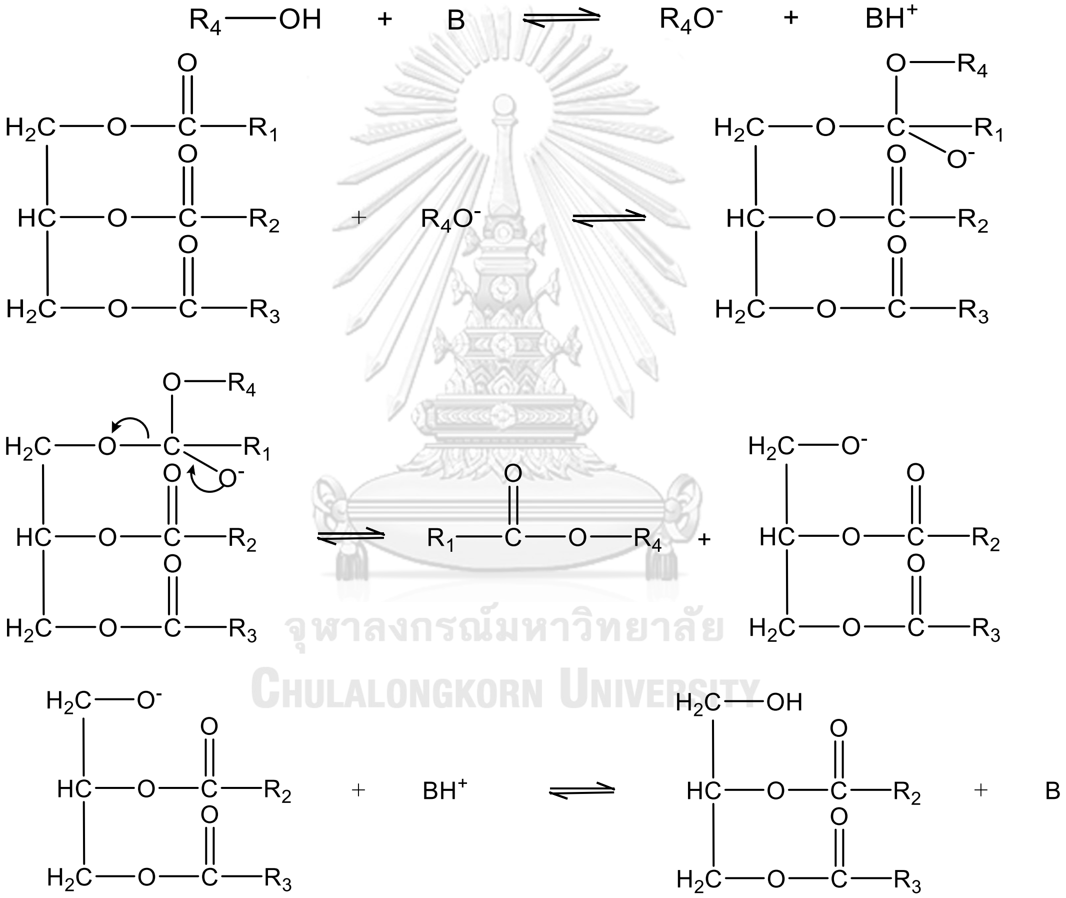
R_1, R_2, R_3 : Carbon chain of fatty acid

R_4 :   Alkyl group the alcohol

Figure 2.7 Mechanism of the acid-catalyzed transesterification of vegetable oils [12]

2.3.1.2 Base catalysts

Currently, most of biodiesel is produced in the presence of alkali catalysts, such as sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium methoxide and potassium methoxide. Industrially, NaOH and KOH are preferred due to their wide availability and low cost. In contrast, the base catalysis takes on a more direct route, creating firstly an alkoxide ion, which directly acts as a strong nucleophile, giving rise to a different reaction pathway shown in Figure 2.8. Even though the transesterification with homogeneous base catalysts is practical, the base-catalyzed process suffers from serious limitations that transform into high production costs for biodiesel. Strict feedstock specification is a main issue. In particular, the total FFA content associated with the lipid feedstock must not exceed 0.5 wt. %. Otherwise, soap formation seriously hinders the production of fuel grade biodiesel [12].



B : Base Catalyst

R_1, R_2, R_3 : Carbon chain of fatty acid

R_4 : Alkyl group the alcohol

Figure 2.8 Mechanism of the base-catalyzed transesterification of vegetable oils [12]

2.3.2 Heterogeneous catalysis

Whereas traditional homogeneous catalysis offers a series of advantages, its major disadvantage is the fact that homogenous catalysts cannot be reused. Moreover, catalyst residues have to be removed from the ester product, usually necessitating several washing steps which increase production costs. Thus, there have been various attempts at simplifying product purification by applying heterogeneous catalysts, which can be recovered by filtration or are alternatively used in a fix-bed catalyst arrangement. The most frequently cited heterogeneous alkaline catalysts are alkali metal-and alkali earth metal carbonates and oxides as shown in Table 2.6 [13].

Table 2.6 The sample of heterogeneous catalysts [13]

Catalyst type	**Examples**
Alkali metal carbonates and hydrogen carbonates	Na_2CO_3, $NaHCO_3$, K_2CO_3, $KHCO_3$
Alkali metal oxides	K_2O (produced by burning oil crop waste)
Alkali metal salts of carboxylic acids	Cs-laurate
Alkali earth metal alcoholates	Mixtures of alkali / alkali earth metal oxides and alcoholates
Alkali earth metal carbonates	$CaCO_3$
Alkali earth metal oxides	CaO, SrO, BaO
Alkali earth metal hydroxides	$Ba(OH)_2$
Alkali earth metal salts of carboxylic acids	Calcium and Barium acetate
Strong anion exchange resins	Amberlyst A 26, A 27
Zink oxides / aluminates	ZnO
Metal phosphates	Ortho-phosphates of aluminum, gallium or iron (III)
Transition metal oxides, hydroxides and carbonates	Fe_2O_3, $(^{+}Al_2O_3)$, Fe_2O_3, Fe_2O_3, Fe_3O_4, NiO, Ni_2O_3, $NiCO_3$ $Ni(OH)_2$, Al_2O_3
Transition metal salts of amino acids	Zn- and Cd- arginate
Transition metal salts of fatty acids	Zn- and Mn- palmitates and stearates
Silicates and layered clay minerals	Na- / K- silicate Zn-, Ti- or Sn- silicates and aluminates
Zeolite catalysts	Titanium-based zeolites, faujasites

2.3.2.1 Amberlyst-15

Amberlyst-15 resin is a macro reticular polystyrene based ion exchange resin with strongly acidic sulfonic group. Thus, it serves as an excellent source of strong acid and has been used in various acid catalyzed reactions. It is easy to measure, safe to use, and readily removed at the end of the reaction. An additional advantage is that the catalyst can be regenerated and can be used several times. Amberlyst-15 has also been used for production of biodiesel (BD). Pal and coauthors [14] reported that palm fatty acid distillate (PFAD), a byproduct from the palm oil refinery process, has been utilized as an alternative feedstock for biodiesel production via Amberlyst-15 catalyzed esterification. The biodiesel yield obtained using Amberlyst-15 is 97% [14].

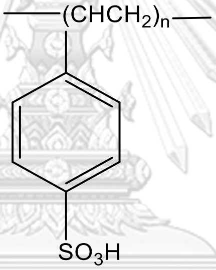


Fig 2.9 Amberlyst-15 [14]

2.3.3 Enzymatic catalysts

Although chemical transesterification using base catalysts gave high conversion levels of triglycerides to their corresponding methyl esters in short reaction times, the reaction has several drawbacks: energy intensive difficulty in recovery of glycerol, removed of the acid or base catalysts from the product, required treatment for alkali wastewater, and interference of free fatty acids and water with the reaction. Both extracellular and intracellular lipases are also able to effectively catalyze the transesterification of triglycerides in either aqueous or nonaqueous system. Enzymatic transesterification methods can overcome the problems mentioned above. In particular, it should be noted that the by-product, glycerol, can be easily recovered without any complex process, and free fatty acids contained in waste oils and fats can be completely converted to methyl esters. In general, the production cost of a lipase catalyst is significantly greater than that of an alkali one. A summary of the advantages and disadvantages of each technological possibility to produce biodiesel could be found in Table 2.7 [11].

Table 2.7 Comparison of the different technologies to produce biodiesel [11]

Variable	**Base catalyst**	**Acid catalyst**	**Lipase catalyst**	**Supercritical alcohol**	**Heterogeneous catalyst**
Reaction temperature (°C)	60-70	55-80	30-40	239-385	180-220
Free fatty acid in raw materials	Saponified products	Esters	Methyl esters	Esters	Not sensitive
Water in raw materials	Interfere with reaction	Interfere with reaction	No influence	No influence	Not sensitive
Yields of methyl esters	Normal	Normal	Higher	Good	Normal
Recover of glycerol	Difficult	Difficult	Easy	No influence	Easy
Purification of methyl esters	Repeated washing	Repeated washing	None	No influence	Easy
Production cost of catalyst	Cheap	Cheap	Relatively expensive	Medium	Potentially cheaper

2.3.4 Ionic liquids catalysts

As a new type of catalyst, ionic liquids (ILs) have been vigorously developing during the past few years, due to the wide liquid range, virtually negligible vapor pressure, recoverability, favorable solubility and low corrosively. In addition, they can be functionalized by different functional groups such as –OH, –COOH and –SO_3H

groups to catalyze different reaction systems. It has been proved that the acidic ILs are promising alternative to traditional transesterification catalysts. From the previous research, the investigation of 1,2,4-trizolium-based group as matrix for ILs is still insufficient, and further detail investigation is then needed to synthesize novel acid ILs catalyst with the high thermal stability and catalytic activity for the transesterification reaction. However, high cost and toxicity are the limitations of ILs [15].

As a new green type of ILs, deep eutectic solvents (DESs), have emerged recently. DESs contain large, asymmetric ions that have low lattice energy and hence low melting points. They are usually obtained by the complexation of a quaternary ammonium salt with a metal salt or hydrogen bond donor (HBD). The charge delocalization occurring through hydrogen bonding between for example a halide ion and the hydrogen-donor moiety is responsible for the decrease in the melting point of the mixture relative to the melting points of the individual components. For example, DESs have been used in organic transformations as eco-friendly solvent/catalyst systems. And the DESs based on the combination of ChCl and $ZnCl_2$ can be used as the Lewis acidic catalyst in the methanolysis of soybean oil. With the demand for development of higher efficient acidic DES catalysts, the DES based on ChCl and *p*-toluenesulfonic acid has been also prepared and applied in the esterification reaction of acidic crude palm oil and other type of reactions [15].

2.4 Glycerol

Glycerol is the simplest trihydric alcohol which has IUPAC name of propane-1,2,3-triol [16]. It is also commercially known as glycerin, 1,2,3-propanetriol, 1,2,3-trihydroxypropane, glyceritol or glycyl alcohol. As shown in Figure 2.9, glycerol has three hydrophilic hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature [17].

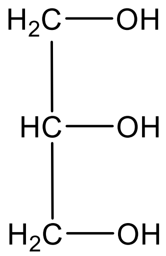


Figure 2.10 Structure of glycerol [17]

2.4.1 Glycerol properties

Pure glycerol is colorless, odorless, viscous liquid with syrupy and sweet taste. Pure glycerol has a specific gravity of 1.261, a melting point of 18.2 °C and a boiling point of 290 °C under normal atmospheric pressure, accompanied by decomposition. At low temperatures, glycerol may form crystals which melt at 17.9 °C. Physical and chemical properties of glycerol are shown in Table 2.8 [16].

Table 2.8 Physical and chemical properties of glycerol [16]

Chemical formula	$C_3H_5(OH)_3$
Molecular mass	92.09382 g/mol
Density	1.261 g/cm^3
Viscosity	1.5 Pa.s
Melting point	18.2 °C
Boiling point	290 °C
Food energy	4.32 kcal/g
Flash Point	160 °C (close cup)
Surface tension	64.00 mN/m
Temperature coefficient	-0.0598 mN/(mK)

2.4.2 Applications of glycerol

Currently, the amount of glycerol is expected to grow at an annual rate of 2.8%. The applications of glycerol, either directly as an additive or as a raw material, range from its use as a food, tobacco and drugs. The remainder being used in the manufacture of lacquers, varnishes, inks, adhesives, synthetic plastics, regenerated cellulose, explosives and other miscellaneous.

Abdullah *et al*. (2010) [17], review potential technologies for glycerol transformation, for example, the products from glycerol such as 1,3-propanedieol, propylene glycerol, docosahexaenoic acid (DHA), glycerol carbonate, polyglycerol, dichloropropanol (DCP), butanol, ethanol, hydrogen, acrolein, succinic acids, dihydroxyacetone etc. Another way, glycerol reacts with other ingredients formed as products such as *tert*-butyl glycerol ether, acetyl glycerol, acetal glycerol etc.

2.4.3 Fuel additive

Fuel additive which could be classified into gasoline/petrol and diesel additive is a chemical substance that assists the cleanliness of engine part, i.e. carburetor, intake valve and fuel injector, prevent incomplete combustion, temper fuel gelling and nozzle choking, as well as protect engine parts from corrosion which leads to better engine performance and acceleration, improve fuel economy and reduce emissions of greenhouse gas. Fuel additive likewise could indigenously reduce the particulate emissions while addition of additive to marine diesel fuel could significantly reduce particulate emission, emission concentration of CO_2 and NO, in the meantime improve the emission concentration of oxygen and excess air quantity [17].

2.4.3.1 *tert*-Butyl glycerol ethers

Figure 2.11 is a representation of the etherification of glycerol with isobutylene, showing the main etherification product: mono-*tert*-butylglycerols

(MTBG), di-*tert*-butylglycerols (DTBG), and tri-*tert*-butylglycerol (TTBG). Note that MTGB and DTBG can include several isomers depending upon the etherification position within the glycerol molecule. Hence, the terms MTBG and DTBG are intended to embrace all the embrace all the possible mono- and di-*tert*-butyl-ethers, respectively. Being undesired the presence of MTBG in the final product, reaction conditions must be established with the purpose of maximizing the production of the di- and tri-derivatives. Tables 2.9 and 2.10 show di-*tert*-butylglycerol ether and tri-*tert*-butylglycerol ether which have shown as valuable fuel additive to enhance cold properties for biodiesel [17].

Table 2.9 Comparison of additive blends used for the characterization [17]

Additive Blend	Compositions
Diesel	Diesel (D2)
Biofuel	80% biodiesel + 20%D2
Additive	Glycerol Ethers (GE)
ME* & additive	80% ME + 20% GE
Diesel & additive	95% D2 + 5% GE
Biofuel & additive	95% B20* + 5% GE

*B20=biodiesel 20%, ME=methyl ester

Table 2.10 Physical properties of additive blends [17]

Additive Blend	DVPE* (Psi)	Cloud point (℃)	Pour point (℃)	Specific gravity
Methyl ester	1.50	0	-3	0.8786
Diesel	0.20	-11	-33	0.8501
Biofuel	0.99	-10	-21	0.8502
Additive	6.21	N/A	N/A	0.8680
ME & additive	2.27	-5	-6	0.8823
Diesel & additive	0.52	-11	-33	0.8419
Biofuel & additive	1.10	-10	-21	0.8541

* DVPE = dry vapor pressure equivalent

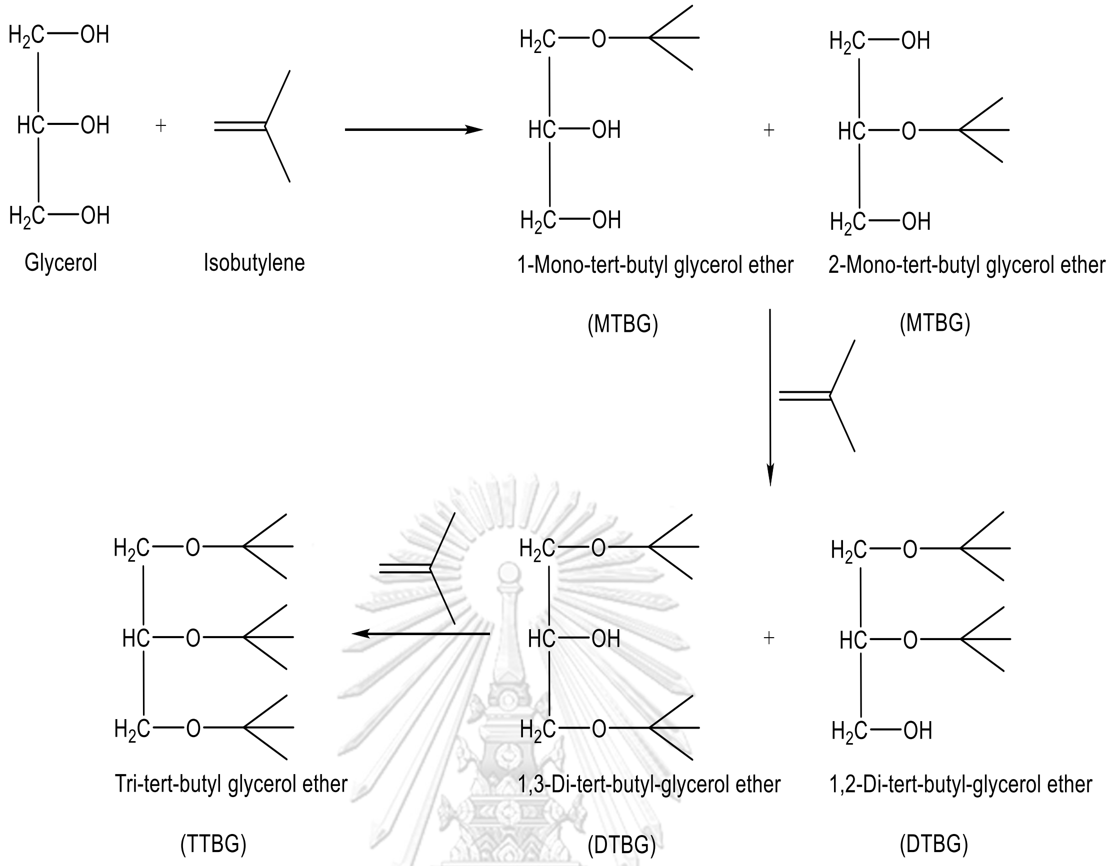


Figure 2.11 Etherification of glycerol with isobutylene [17]

2.4.3.2 Solketal

Acetalization is suitable technique for the value-added of glycerol. Acetalization reaction between glycerol and acetone over acid catalyst results in 2, 2-dimethyl-1,3-dioxolane-4-methanol (solketal) as the condensation product (Fig 2.12). Solketal, an oxygenated fuel additive, could reduce the particulate emission and improve the cold flow properties of liquid transportation fuels. It helps to reduce the gum formation, improves the oxidation stability, and enhances the octane number when added to gasoline. More importantly, the aquatox fish test on the toxicity of the solketal showed that solketal (with a LC_{50} for fish to be as high as 3,162 ppm) has demonstrated much less environmental toxicity than the common fuel additive, (MTBE; methyl *tert*-butyl ether), with a LC_{50} of 1,000 ppm. Other application of solketal such as mono-acetin, STBE (solketal *tert*-butyl ether) formation and benzyl solketal ether have been synthesized by different reactants, kind of catalyst and different type of process [18, 19].

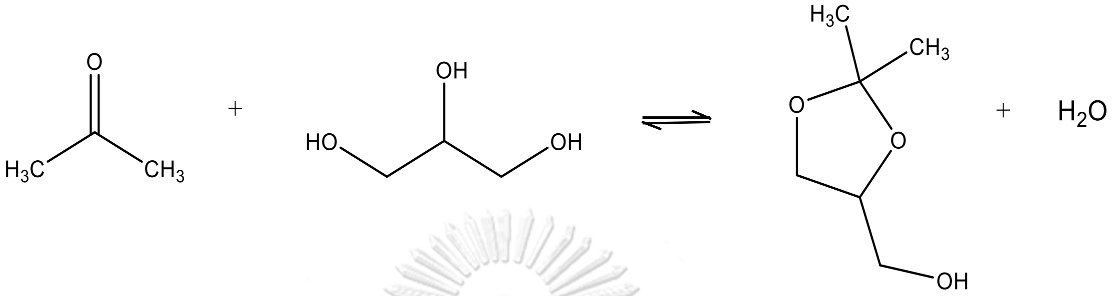


Figure 2.12 Acetalization reaction between glycerol and acetone [18]

2.5 Literature review

2.5.1 Acid-catalyzed biodiesel production

Freedman *et al.* [6] reported that the transesterification of soybean with methanol using 1 wt% sulfuric acid with methanol/oil 30:1, 65 °C at 69 h gave fatty acid methyl ester over 99%yield.

Kusakabe *et al.* [5] studies transesterification of vegetable oil with methanol in the presence of dimethyl ether (DME) as co-solvent. The *p*-toluenesulfonic acid (TsOH), benzenesulfonic acid and sulfuric acid were used as catalysts. TsOH showed highest catalystic activity. The yield of FAME reached 97.1% when 4wt% of TsOH base on the oil weight was used at 80 °C and reaction time 2 h in the presence of DME. The reaction rate was greatly improved by addition of DME as a co-solvent because of disappearance of mass transfer resistance between the two phases.

Hayyan *et al.* [20] studied esterification of sludge palm oil (SPO) with methanol. The *p*-toluenesulfonic acid (TsOH) was used as catalyst. The optimum conditions for esterfication process used 0.75wt% TsOH to SPO, 10:1 molar ratio, 60 °C reaction temperature, and 60 minutes reaction time resulted in 96% yield of crude biodiesel and 90.93% conversion of free acid (FFA) to free fatty acid methyl ester (FAME).

Encinar *et al.* [21] studied transesterification and esterification of animal fats with methanol. The three different types of FFA (fats A = 10.7%, fats B = 4.9% and fats C = 13.5%) in animal fats were used to produce biodiesel. The sulfuric acid, phosphoric acid, *p*-toluenesulfonic acid monohydrate and potassium hydroxide were used as catalysts. Biodiesel with 89.0 wt% ester content was obtained by acid-transesterification (9 wt% sulfuric acid, 6:1 methanol:fats molar ratio, 60 °C and 48h). The pre-esterification conditions were 0.5 wt% sulfuric acid or 1.0 wt% *p*-toluenesulfonic acid, 6:1 methanol : fats A (FFA = 10.7%) mmolar ratio, 65 °C and 4 h made it possible to obtain fats with acid value less than 0.5% FFA. Biodiesel of 97.3 wt% ester content was obtained by alkali transesterification.

Calgaro *et al.* [22] studied heterogeneous for biodiesel production. KSF clay and amberlyst 15 catalysts were selected as acid catalysts for the optimization study of the transesterification of *Jatropha curcas* oils into biodiesel, in presence of different co-solvents. The optimum parameters for both catalysts were 1:12 M ratio, 5 wt% of catalyst, 160 °C and 6 h of reaction with a FAME yield of 70 wt%. A kinetic study was experimentally investigated by using a semi-empirical model to represent the experimental data. Furthermore, catalyst reusability was successfully maintained in its transesterification activity for five cycles at the optimized condition.

2.5.2 Acid-catalyzed *tert*-butyl glycerol ether production

Klepcova *et al.* [3] studied etherification of glycerol with *tert*-butanol at the presence of Amberlyst -15 as catalyst. The maximum conversion of glycerol near 96% was reached at the temperature 90 °C and at the molar ratio *tert*-butanol/glycerol = 4:1 after 180 min. Catalytic activity of Amberlyst-15 was compared with two large-porous zeolites (H-Y and H-BEA). The final conversion of glycerol was comparable with amberlyst-15, but H-BEA was more active (twice amount of formed di-ethers near 45% against 25% with Amberlyst-15 was reached at 360 min of reaction).

Melero *et al.* [23] studied etherification of glycerol with isobutylene. The propylsulfonic-acid-functionalized mesostructured silica (Pr-SBA-15), arenesulfonic-acid-functionlized mesostructured silica (Ar-SBA-15), acidic macroporous resins (Amberlyst-15), acidic macroporous resins (Amberlyst-36), Purolite (CT-275) and Nafion-SiO_2 composite (SAC-13) were used as catalysts. The *tert*-butylated derivates, di-*tert*-butylglycerols (DTBG) and tri-*tert*-butylglycerol (TTBG) has shown to be valuable fuel additives leading to decrease in the emission of particulate matter, hydrocarbon, carbon monoxide and unregulated aldehydes. Likewise, said ethers can also act as cold flow improvers for use in biodiesel. The optimal conditions have been found to be 75 °C and isobutylene to glycerol molar ratio of 4/1. Using these reaction conditions, glycerol conversions were up to 100% and combined selectivities towards di- and tri-*tert*-butylglycerol over 92% were achieved after 4 h of reaction over arenesulfonic-acid-modified SBA-15 [23].

Filimonov *et al.* [4] studied etherification of glycerol with isobutylene. The *p*-toluenesulfonic acid (TsOH) amberlyst-15, 1-(4-sulfobutyl)-3-hexylimidazolium trifluoromethanesulfonate (IL-6), Keggin unit of silicotungstic acid $H_4SiW_{12}O_{40}$ (HSiW) were use as catalysts. The optimum condition for etherification process was TsOH 7.5 wt% base on glycerol, mole ratio of isobutylene : glycerol = 4:1, 60 °C reaction temperature, and 5 h reaction time to obtain 99% conversion and 70% yield of di and tri glycerol ether.

2.5.3 Acetalization of glycerol

Smirnov *et al.* [18] studied the acetalization of glycerol with aldehyde (ketone). 79% glycerol conversion was obtained with H_2SO_4 1 mol% of glycerol as catalyst.

Suriyapradilok and Kitiyanan [19] studied the synthesis of solketal from glycerol and acetone using TsOH as catalyst. The reaction progressed successfully when using the acetone in excess. Subsequently, the prepared solketal is used for synthesizing benzyl solketal ether by reaction with benzyl alcohol. The optimal condition at 12 hours, 1:6 molar ratio of glycerol to acetone gave the highest conversion (82.7%). The solketal to benzyl alcohol molar ratio was set at 1:1 solketal to benzyl alcohol molar ratio and converts to 92.9% after 12 hours. The selectivity of dibenzyl ether was very high at 2 hours (59.4%).

CHAPTER III

EXPERIMENTAL

3.1 Material and Equipments

3.1.1 Chemicals

1. Palm oil was purchased from Morakot industries PCL, Thailand
2. Methanol (MeOH), analytical grade and gas chromatography grade, were purchased from Sigma-Aldrich
3. *p*-Toluenesulfonic acid (TsOH) was purchased from Sigma-Aldrich
4. Conc. Sulfuric acid (H_2SO_4) was purchased from Merck
5. Amberlyst 15 (dry) was purchased from Sigma-Aldrich
6. Isobutylene (C_4H_8), 99% purity certified pure grade, was purchased from Linde (Thailand) Company Limited
7. Choline chloride (ChCl: $C_5H_{14}ClNO$)
8. Glycerol, anhydrous 99.5%, was purchased from Merck
9. Acetone (C_6H_6O) was purchased from Sigma-Aldrich
10. Standard FAME were purchased from Sigma-Aldrich
11. Chloroform-d ($CDCl_3$)

3.1.2. Equipments

1. Parr® reactor
2. Hotplate stirrer
3. Thermometer
4. Volumetric flask
5. Vial
6. Beaker
7. Condenser
8. Silicone oil bath

9. Rotary evaporator

10. Desiccator

11. Pipet

12. NMR tube

13. Magnetic stir bar

14. Gas chromatography (GC)

15. Nuclear magnetic resonance spectrometer (NMR); for ^{1}H NMR, chemical shift (δ_H) of the residual solvents at 7.26 and 3.31 ppm for $CDCl_3$ and CD_3OD, respectively, were used as reference.

3.2 Determination of molecular weight of palm oil and acid value

3.2.1 Fatty acid methyl ester compositions

Fatty acid methyl ester composition of biodiesel produced from palm oil was determined by GC-MS Agilent using HP-5 column stationary phase polyethylene glycol (column 35 m x 0.32 mm x 0.25 µm). To prepare the sample, 250 mg of sample and 5 mL of methylheptadecanoate solution (10 mg/mL) were added into a 10 mL vial. Helium gas was used as carrier gas and the temperature of the injector was set at 290 °C. The oven temperature was retained at 50°C for 5 min and increased to 240°C with ramping rate of 20 °C /min. The molecular weight of palm oil was calculated from fatty acid methyl ester composition (see detail in Appendix A-2).

3.3 Homogeneous catalyst

3.3.1 Biodiesel production

p-Toluenesulfonic acid (TsOH) and conc. sulfuric acid (H_2SO_4) were used as catalyst. TsOH was dried in oven at 100°C for 24 h. and then kept in the desiccator prior to use. Palm oil, acid catalyst and methanol were added into a three neck round bottom flask connected with a condenser and moisture trapping system (using an acid flask containing conc. sulfuric acid (H_2SO_4)). The reaction was carried out in a constant temperature silicone oil bath with a magnetic stir bar.

Transesterification of PO with methanol using a mixture of TsOH and H_2SO_4 (TsOH-H_2SO_4) as catalyst was carried out in a three-neck round bottom flask equipped with a reflux condenser, a moisture trapping system and a temperature-controlled magnetic stirrer, and a sampling port. 10 grams of PO and desired amounts of methanol and catalyst were used and the reaction was performed at temperature ranging from 50 °C to 90 °C, molar ratios of methanol and PO ranging from 6:1 to 15:1, amount of catalyst ranging from 5 wt % to 15 wt % of PO and reaction time from 2 to 8 h. After the reaction, the products were extracted by n-hexane from the reaction mixture, and the n-hexane layer (biodiesel layer) was washed with distilled water for three times to remove water-soluble substances. Then *n*-hexane and the residual trace water were removed by rotary evaporator under reduced pressure before the products were analyzed. The reactions were monitored by the proton nuclear magnetic resonance spectroscopy (^1H NMR).

3.3.2 *tert*-butyl glycerol ether process

To a Parr® reactor (show in figure 3.1) glycerol, catalyst and isobutylene were added. The required amount of isobutylene was then added into the reactor and the reaction was performed at 70°C for 4 h.

Figure 3.1 Parr® reactor

3.3.3 TsOH-H_2SO_4 catalyzed etherification

3.3.3A Etherification of commercial glycerol

Etherification of commercial glycerol (99%, analytical grade) with isobutylene was performed in Parr® reactor, equipped with thermocouples. In typical conditions, 0.125 mol of glycerol, 7.5 wt% TsOH- H_2SO_4, 6:1 molar ratios of isobutylene and glycerol at 70°C and reaction time of 4 h were used [4]. The prepared glycerol ethers were characterized by GCMS and used as reference for GC-FID analysis.

3.3.3B Etherification of crude glycerol from biodiesel production

After the transesterification, methanol was removed from the reaction mixture under reduced pressure. The lower phase comprising of glycerol and catalyst was separated and glycerol then being used as starting material for the etherification. The molar ratios of isobutylene and the residue glycerol (estimated by mole of PO) ranging from 6:1 to 15:1 and temperature ranging from 70 to 90°C were performed. The reaction mixtures were analyzed by GC-FID.

3.3.3C Etherification of crude glycerol in a presence of biodiesel as co-solvent

After the removal of methanol from the transesterified product, a residue containing biodiesel, glycerol and catalyst was etherified with isobutylene in Parr® reactor. The reaction mixtures were analyzed by GC-FID.

3.4 Heterogeneous Catalyst

3.4.1 Catalyst preparation and characterization

Amberlyst 15 (dry) was used as catalysts. Modified Amberlyst 15 catalysts were prepared by soaking Amberlyst 15 in MeOH at room temperature for different durations (1, 7, 15 and 30 day) followed by evaporation, oven-drying at 105°C and keeping in desiccator prior to use. We have demonstrated that porosity of catalyst at several time using Scanning Electron Microscope (SEM).

3.4.2 Biodiesel production using modified Amberlyst 15 as catalysts

The transesterification reaction between palm oil and methanol in the presence were performed in batch reactor. The reaction equipment consisted of a 100 ml three neck round bottom flask equipped with a water reflux condenser, a temperature-controlled magnetic stirrer and sampling port. For the transesterification a 10 g of palm oil was charged to the three necked round bottom flask and heated up to the desired temperature, while stirring at 400 rpm.

All experiments were varied molar ratios of methanol/palm oil between 6:1, 9:1, 12:1 and 15:1, a reaction time between 2 to 24 h, temperature ranging from 50 °C to 90 °C, molar ratios of methanol and amount of catalyst ranging from 5 wt % to 15 wt % of PO and reaction time from 2 to 24 h. After the reaction, the products were extracted by *n*-hexane from the reaction mixture, and the *n*-hexane layer (biodiesel layer) was washed with Sat. $NaHCO_3$ and distilled water for three times to remove water-soluble substances and a residual trace water was dried over anhydrous Na_2SO_4. Then *n*-hexane were removed by rotary evaporator under reduced pressure before the products were analyzed. The reactions were monitored by the proton nuclear magnetic resonance spectroscopy (^{1}H NMR).

The Etherification of crude glycerol from biodiesel production

After the transesterification, methanol was removed from the reaction mixture under reduced pressure. The glycerol phase comprising of catalyst was then used for the etherification. The molar ratios of isobutylene and the residue glycerol (estimated by mole of PO) ranging from 6:1 to 15:1 and temperature ranging from 70 to 90°C were performed. The reaction mixtures were analyzed by GC-FID.

3.5 Deep Eutectic solvent (DESs)

3.5.1 Preparation of DESs

Deep eutectic solvent [(*p*-toluenesulfonic acid and choline chloride (ChCl-TsOH)] were used as catalyst for biodiesel and *tert*-butyl glycerol ether production. ChCl-TsOH were dried in vacuum oven at 60°C for 12 h. DESs were prepared by heating, ChCl and TsOH with different molar ratios in an oil bath at 80°C with continuously stirring, until forming an uniform and transparent liquid. The prepared ChCl-TsOH DESs were listed in Table 2.1. To be noted, ChCl is playing the role of hydrogen bond acceptor (HBA), while TsOH is role as the hydrogen bond donor (HBD).

Table 3.1 The used DESs in this work.

Abbreviation	ChCl:TsOH (mol/mol)
DESs-1	1:1
DESs-2	1:2
DESs-3	1:3
DESs-4	2:1
DESs-5	2:3

3.5.2 Synthesis of biodiesel using DESs as catalyst

PO, methanol and catalyst were added into a Parr® reactor. 10 grams of PO and desired amounts of methanol and catalyst were used and the reaction was performed at temperature ranging from 70 °C to 120 °C, molar ratios of methanol and PO ranging from 6:1 to 15:1, amount of catalyst ranging from 4 wt % to 12 wt % of PO and reaction time from 2 to 10 h. After the reaction, the products were extracted by n-hexane from the reaction mixture, and the n-hexane layer (biodiesel layer) was washed with distilled water for three times to remove water-soluble substances. Then n-hexane and the residual trace water were removed by rotary evaporator under reduced pressure before the products were analyzed. Finally, the obtained products were analyzed by gas chromatography (GC-FID).

3.5.3 Etherification of glycerol

Etherification of glycerol (99%, analytical grade) with isobutylene was performed in Parr® reactor, equipped with thermocouples. In typical conditions, the molar ratios of isobutylene/glycerol ranging from 6:1 to 15:1, temperature ranging from 70 to 90°C, amount of catalyst 4 to 8 wt% and reaction time 3 to 8 h were investigated. The reaction mixtures were analyzed by GC-FID.

3.6 Determination of fuel properties

In comparison of fuel properties between biodiesel production from transesterification and a mixture of biodiesel and the etherified product acid value, pour point and iodine value were determined. The results compared to fuel properties based on biodiesel standard are shown in Table 3.2.

Table 3.2 Biodiesel standard

Fuel properties	Biodiesel
Acid value, mg KOH/g oil	<0.5
Pour point (°C)	-15 to 10
Iodine value (g iodine/100g)	120 - >103

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of palm oil

Molecular weight of PO (858.77 g/mol) was estimated by fatty acid compositions obtained by gas chromatography-mass spectrometry (GC-MS) analysis in table 4.1. PO in our study comprised of saturated fatty acids, with 33.4% palmitic acid (C16:0), 8.1% stearic acid (C18:0) and 0.7% myristic acid (C14:0). The unsaturated fatty acids are approximately 57.5% oleic acid (C18:1) and 0.2% linolenic acid (C18:3). The AV of PO was 0.4, which was suitable as a substrate for investigating transesterification of vegetable oil for biodiesel production.

Table 4.1 Fatty acids composition of palm oil

Fatty acids	Structure	Type of fatty acid	Fatty acids (wt%)
Lauric acid	C13:0	Saturated	0.1
Myristic acid	C14:0	Saturated	0.7
Palmitic acid	C16:0	Saturated	33.4
Stearic acid	C18:0	Saturated	8.1
Oleic acid	C18:1	Unsaturated	57.5
Linoleic acid	C18:2	Unsaturated	0.04
Linolenic acid	C18:3	Unsaturated	0.2

4.2 Transesterification using TsOH, H_2SO_4 and TsOH-H_2SO_4 as catalyst

4.2.1 Effects of TsOH, H_2SO_4 and TsOH-H_2SO_4 as catalyst

Theoretically, a stoichiometric ratio for the transesterification requires three moles of alcohol per mole of triglyceride to yield three moles of fatty acid ester and one mole of glycerol. However, the molar ratio of MeOH/oil used in the transesterification depends on feedstock and catalyst [5-7]. Kusakabe and coworker [5] studied transesterification of corn oil with methanol in the presence of dimethyl ether (DME) as co-solvent. The *p*-toluenesulfonic acid (TsOH) and sulfuric acid were used as catalysts. TsOH showed highest catalytic activity. The yield of FAME reached 97.1% when 4wt% of TsOH base on the oil weight was used at 80 °C and reaction time 2 h. In our study, transesterification of PO using 5wt% of TsOH as catalyst and MeOH/oil with different molar ratio (6:1, 9:1, 12:1 and 15:1) at 80 °C was carried out. The results (Fig 4.1) have shown that 6:1, 9:1, 12:1 and 15:1 molar ratios of MeOH/oil gave the conversion within 8 hours for 98.2, 99.7, 99.6 and 99.6%, respectively. In comparison with previous research [5], this study without co-solvent in the process using higher amount of TsOH and higher temperature gave the conversion of biodiesel up to 99%. Although the molar ratio of 9:1 or above gave over 99% of conversion within 5 hours, molar ratios 12:1 and 15:1 produced some difficulty on separation of the biodiesel phase and glycerol phase due to the lowered density of the glycerol phase through the high amount of remaining methanol in the glycerol phase. After the transesterification, methanol was thus removed and then 2 phases of the biodiesel and glycerol were appeared. In addition, 5 wt% H_2SO_4 was used for the transesterification at 80 °C with the different MeOH/oil ratios 6:1, 9:1, 12:1 and 15:1 yielding the conversion of the transesterification 65.9, 67.1, 67.2 and 67.4%, respectively, within 8 h.

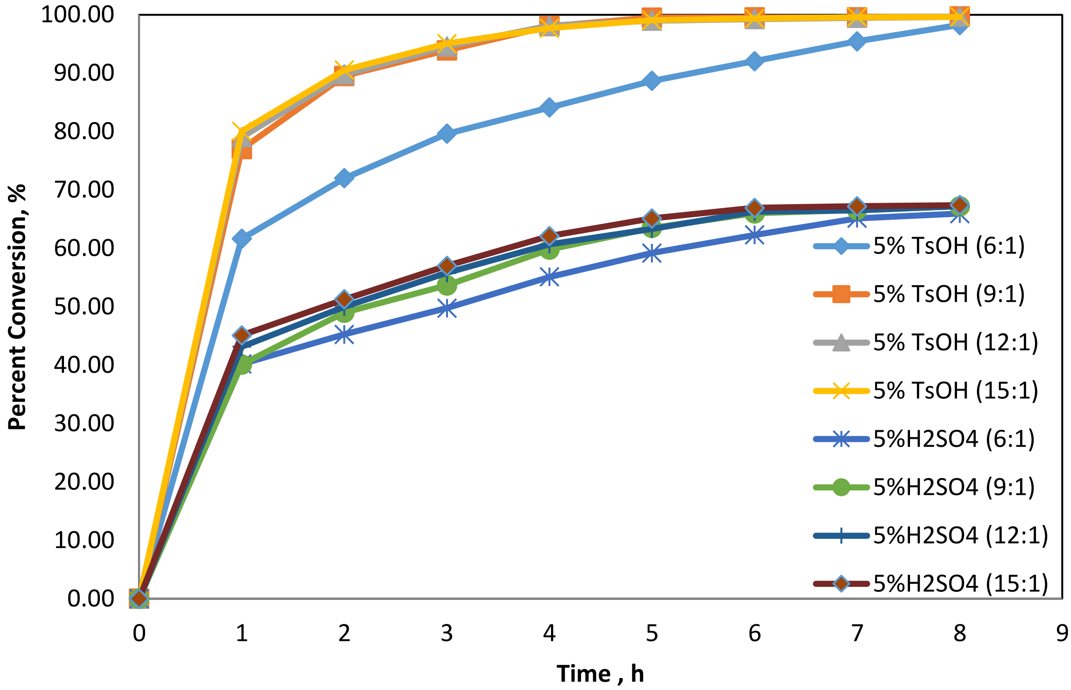


Fig 4.1 Conversion of the transesterification at 80 ℃ using 5% TsOH and 5 wt% H_2SO_4 as the catalyst and different MeOH/PO molar ratios

Furthermore, the results showed that TsOH, an organic acid, as the catalyst exhibited higher potentiality in transesterification than H_2SO_4, due to its solubility in glycerol as it is more soluble in triglyceride compared to H_2SO_4, an inorganic acid. Thus, TsOH resulted in faster transesterification and higher conversion. After a reaction period of 5 h at 80 °C, the yield of FAME reached 99% when using the TsOH catalyst while 5% H_2SO_4 resulted in about 50%.

Since TsOH and H_2SO_4 alone effected on transesterification, it was speculated whether a mixture of TsOH- H_2SO_4 accelerated this reaction. Thus effect of TsOH-H_2SO_4 as a catalyst on transesterification of PO with MeOH (9:1 molar ratio of MeOH:PO) at 80°C was investigated and the results were shown in Fig 4.2. When TsOH was kept at 2.5wt% and H_2SO_4 were varied by 2.5, 5 and 7.5 wt%, respectively, the results showed that conversion has reached 89.8, 95.0, 95.5 wt%, respectively after 6 h of reaction. When TsOH was kept at 5wt% and H_2SO_4 were varied by 2.5, 5 and 7.5 wt% conversion has reached 92.5, 98.0 and 99.2%, respectively after 4 h and the conversion at 6 h has reached 98.1, 99.6 and 99.8%, respectively. When TsOH was kept at 7.5wt% and H_2SO_4 were varied by 2.5, 5 and 7.5 wt%, the conversion has reached 92.3, 99.5 and 99.5%, respectively after 4 h. According to the results, the mixture of TsOH-H_2SO_4 accelerated the reaction faster than the single catalyst.

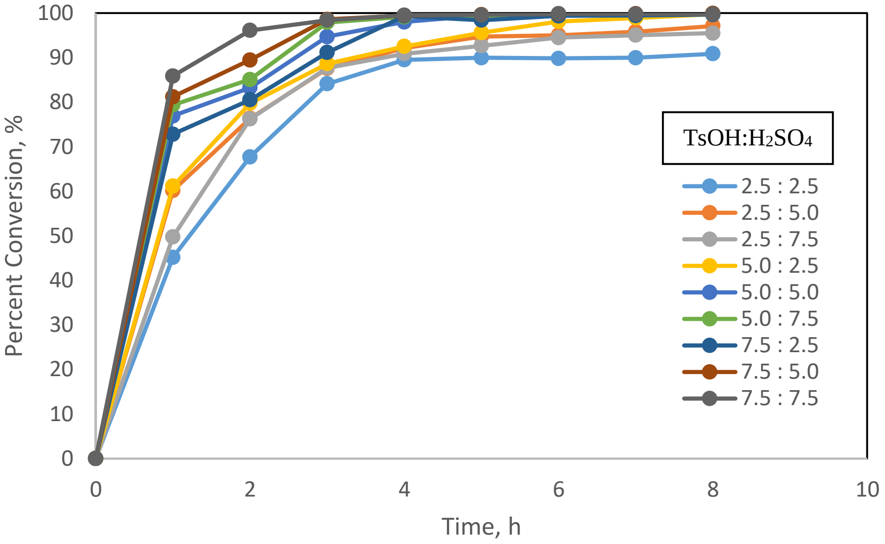


Fig 4.2 Effect of amount of the acid catalysts on transesterification using TsOH-H_2SO_4 as a catalyst at 80 °C and MeOH/oil molar ratio 9:1

After transesterification, distribution of the catalyst in the lower phase (glycerol) and the upper phase (biodiesel) was examined by ^1H NMR analysis. In biodiesel phase (Fig 4.3a-b), chemical shift (δ_H) of TsOH at 2.27, 7.24 and 7.56 ppm indicated that TsOH was presented in glyceride phase with and about 20%mol compared to fatty acyl moiety for 3 h transesterification using TsOH and about 2%mol compared to fatty acyl moiety using TsOH-H_2SO_4, respectively. In Figure 4.4, ^1H NMR results of the transesterification indicated a presence of TsOH when TsOH alone was used while no signal of TsOH was shown in the biodiesel phase when

$TsOH-H_2SO_4$ (7.5:5) was used. For the crude glycerol obtained by using $TsOH-H_2SO_4$ (7.5:5) for the transesterification with >99% conversion, the ^1H NMR (Fig 4.5) showed that a large amount of the acid catalysts was remained. It was obvious that most of catalyst was presented in the crude glycerol and the combined TsOH and H_2SO_4 was dissolved in the glycerol phase better than a single catalyst. Therefore, it was explained that increased solubility of TsOH in glycerol was caused by addition of H_2SO_4.

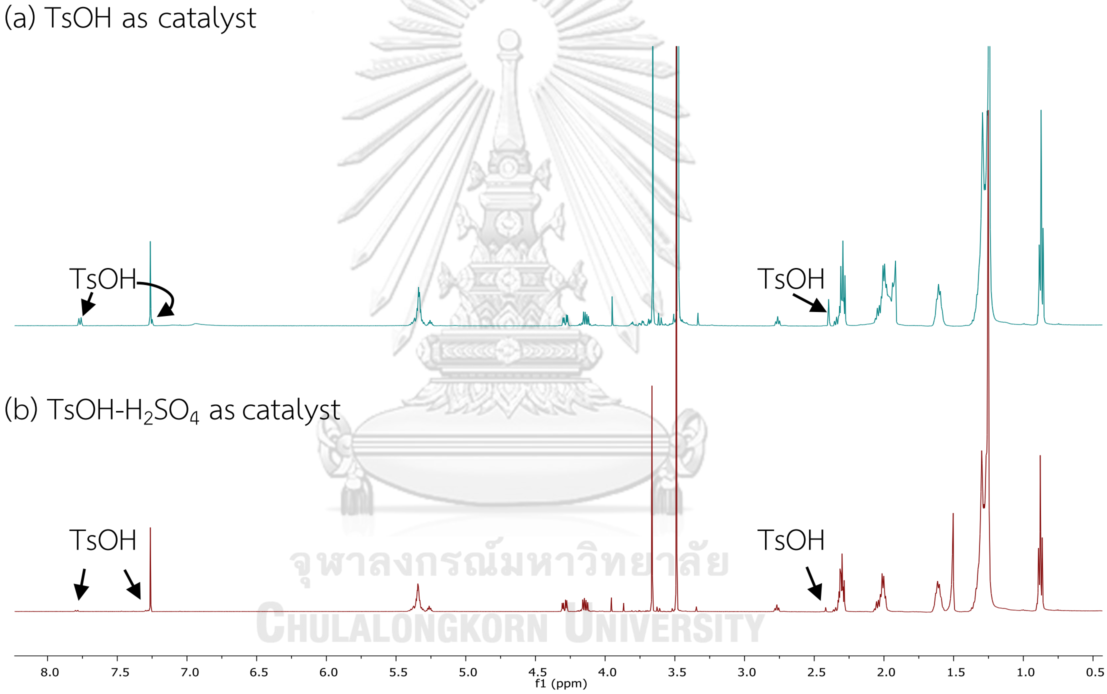


Fig. 4.3. ^1H-NMR spectra of 9:1 MeOH/oil molar ratio, and the product from transesterification at 80°C for 3 h (a) biodiesel using 7.5% TsOH as catalyst (b) biodiesel using $TsOH-H_2SO_4$ (7.5:5) as catalyst

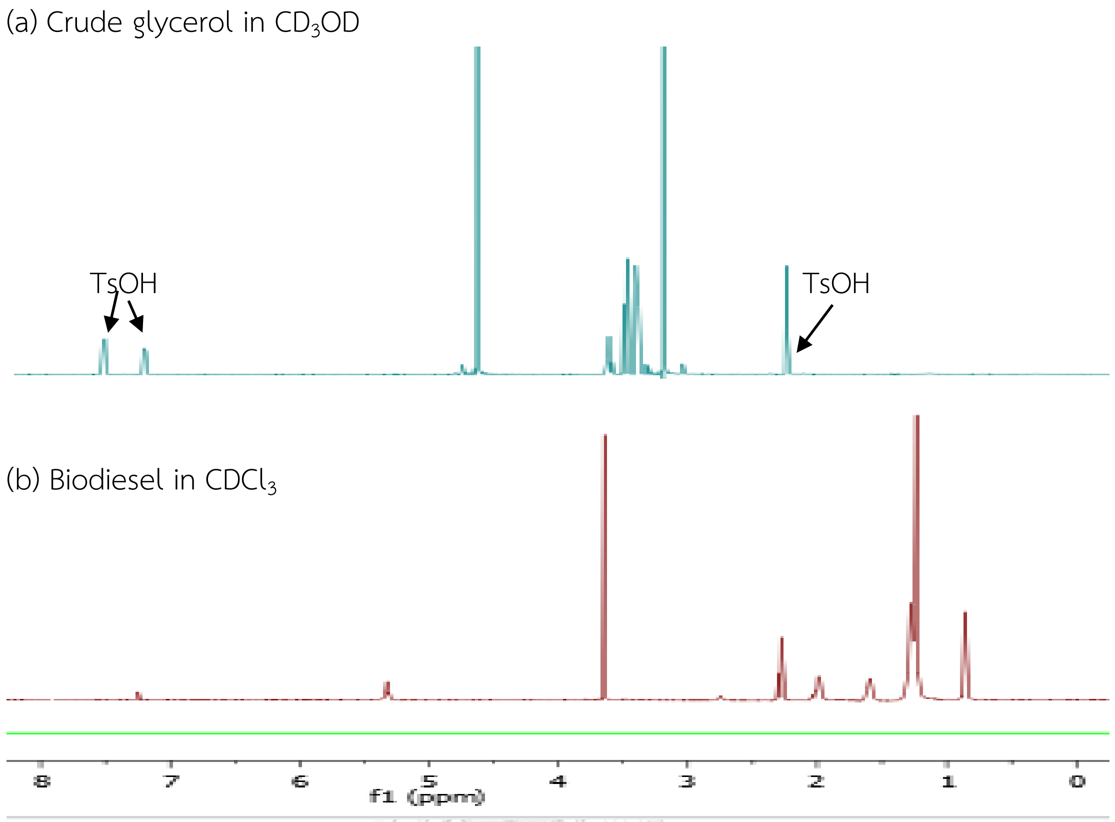


Fig. 4.4. ^{1}H-NMR spectra of crude glycerol obtained by using TsOH-H_2SO_4 (7.5:5) for the transesterification with >99% conversion 9:1 MeOH/oil molar ratio at 80°C for 6 h

4.2.2 Effects of reaction temperature

Using TsOH/H_2SO_4 (7.5:5) as a catalyst, 9:1 ratio of MeOH/PO, and an 8 h reaction time, a set of temperature experiment (50, 60, 70, 80 and 90°C) were investigated; The conversion (Fig 4.5) has reached 80.6, 85.1, 96.5, 99.8 and 99.1 wt%, respectively. The conversion of the reaction at 80 and 90°C were increased up to 99% within 6 hours. Reaction temperature 80 and 90°C did not result in a significant difference in the conversion. The results indicated that the increase of reaction temperature resulted in the increase of conversion as the higher temperature could improve the miscibility of oil and methanol and increase the reaction rate [5].

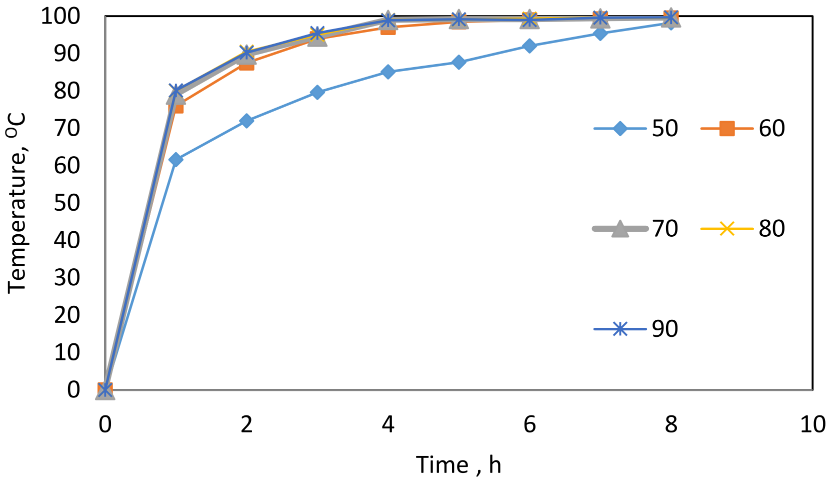


Fig 4.5 Effect of reaction temperature on transesterification using TsOH-H_2SO_4 (7.5:5) and 9:1 ratio of MeOH/PO

4.3 *tert*-butyl glycerol ethers from crude glycerol containing TsOH-H_2SO_4 as catalyst

Etherification of pure glycerol with isobutylene was shown in Fig 4.6. The sequence of *tert*-butyl glycerol ether from GC-FID chromatogram, compared with *tert*-butyl glycerol ethers from GC-MS chromatogram, were approved at retention time 18.5 min for 3-*tert*-butoxy-1,2-propandiol or mono-*tert*-butyl ether of glycerol 1 (MTBG: A), 27.0 min for 1,3-di-*tert*-butoxy-2-propanol or di-*tert*-butyl ethers of glycerol 1 (DTBG1: B), 28.5 min for 1,2-di-*tert*-butoxy-3-propanol or di-*tert*-butyl ether of glycerol 2 (DTBG2: C) and 34.5 min for tri-*tert*-butoxy-propane or tri-*tert*-butyl ether of glycerol (TTBG: D).

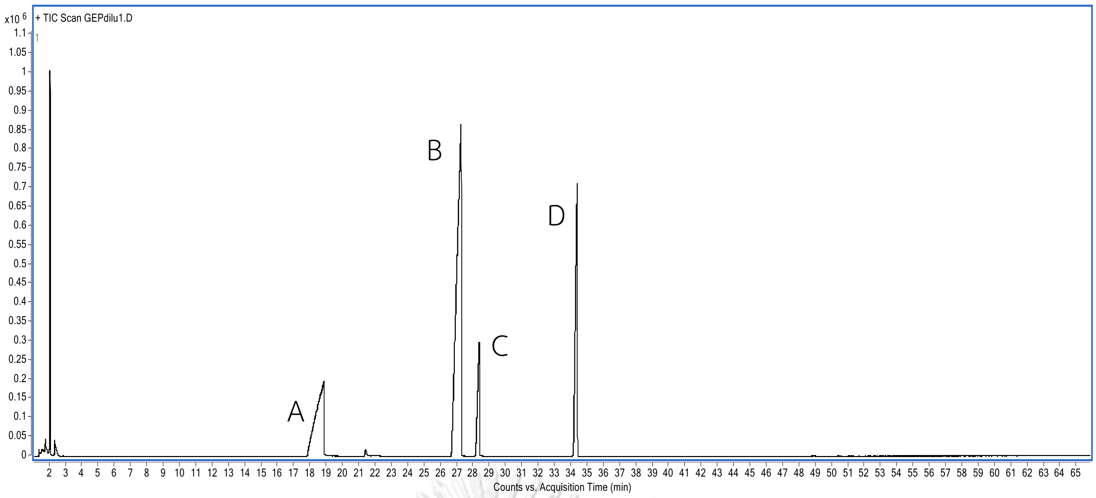


Fig. 4.6 The GC chromatogram of *tert*-butyl glycerol ethers from pure glycerol using 7.5%TsOH base on palm oil weight, 4:1 molar ratio of isobutylene and glycerol, 70°C for 4 h

4.3.1 Characterization of *tert*-butyl glycerol ethers

For the interpretation of GC-MS results, the products A, B, C and D were identified as mono, 1,3-di, 1,2-di and tri-*tert* butyl glycerol ether, respectively, according to Jamroz *et al.* [24].

A: mono-*tert*-butyl glycerol ether (MTBG)

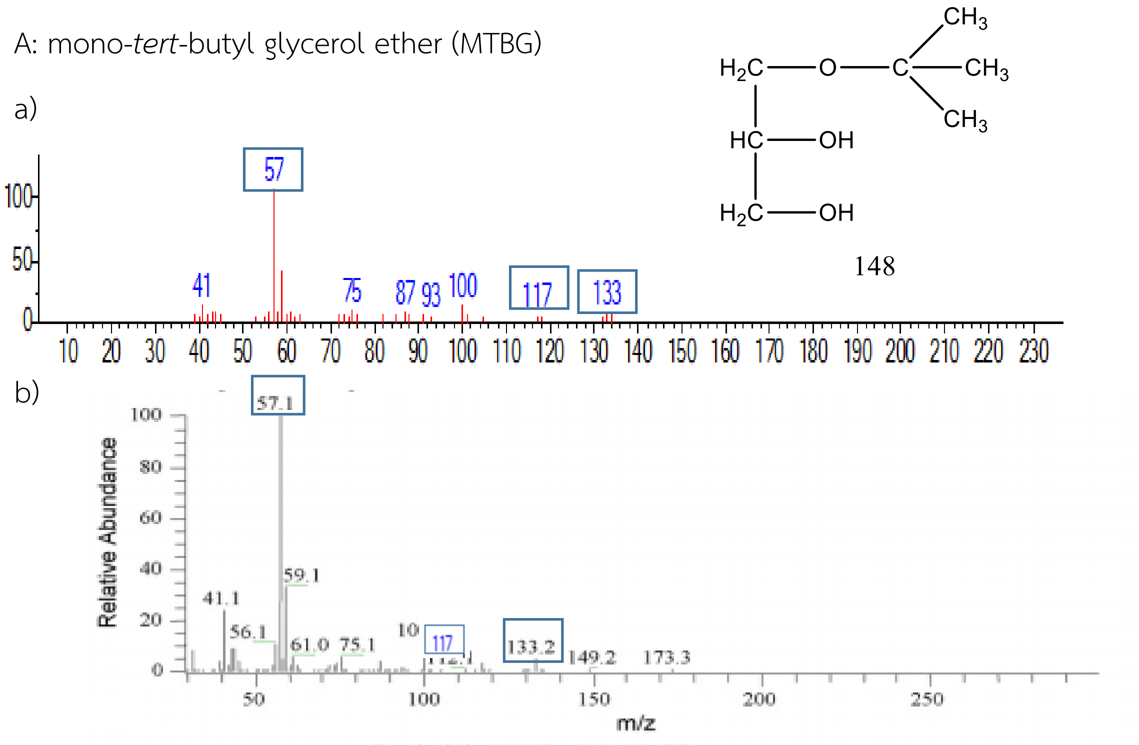


Fig. 4.7 Mass spectrum of mono-*tert*-butyl glycerol ether from a) GC-MS analysis b) literature (Jamroz *et al* [24]).

The EI mass spectrum of mono-*tert*-butyl glycerol ether (Fig 4.7) shows a base peak at *m/z* 57 corresponding to the ion of the *tert*-butyl group. The fragment ion observed at *m/z* 133 arising from the subtraction of the methyl group $[M\text{-}CH_3]^+$ and at *m/z* 117 from substraction of the $[M\text{-}CH_2O]^+$ hydroxymethyl group from molecular ion.

B: 1,3-di-*tert*-butyl glycerol ether (DTBG1)

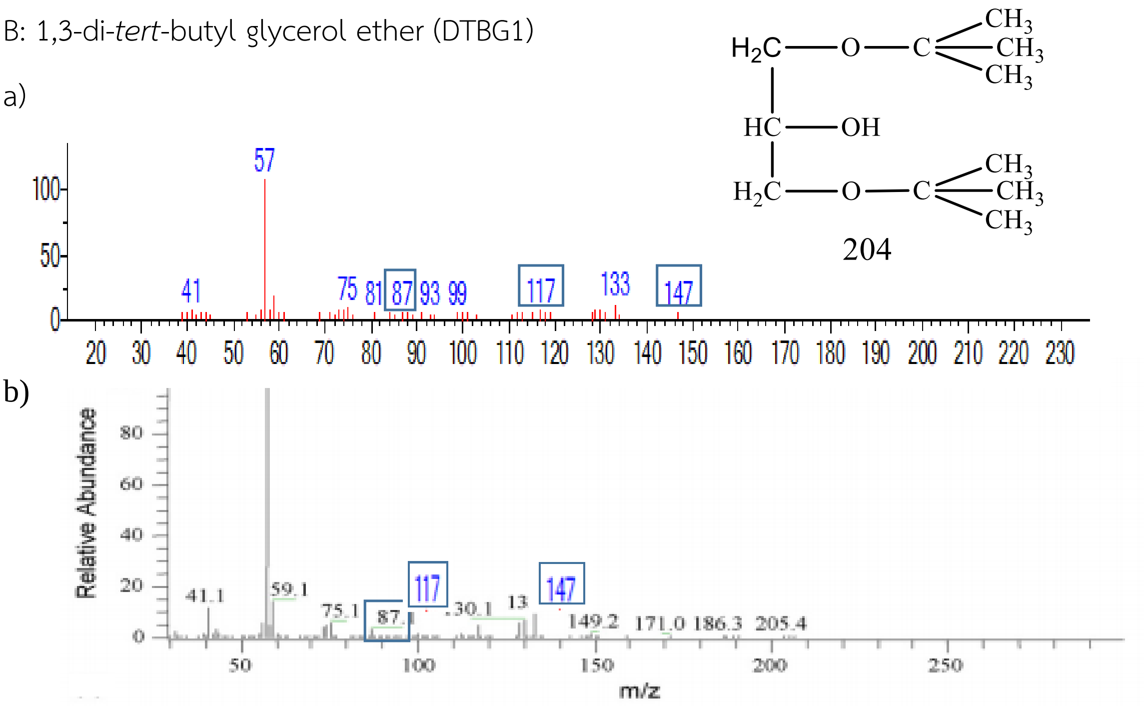


Fig. 4.8 Mass spectrum of 1,3-di-*tert*-butyl glycerol ether from a) GC-MS analysis b) literature (Jamroz *et al* [24]).

The EI mass spectrum of 1,3-di-*tert*-butyl glycerol ether (Fig 4.8) shows the presence of peak at *m/z* 117 corresponding to elimination of butoxymethyl moiety $[M\text{-}CH_2O^tBu]^+$ and that of ion at *m/z* 147 arising from the elimination of butyl group $[M\text{-}^tBu]^+$. The fragment is located at *m/z* 147 where it will not be observed in the spectrum of mono-*tert*-butyl glycerol ether.

C: 1,2-di-*tert*-butyl glycerol ether (DTBG2)

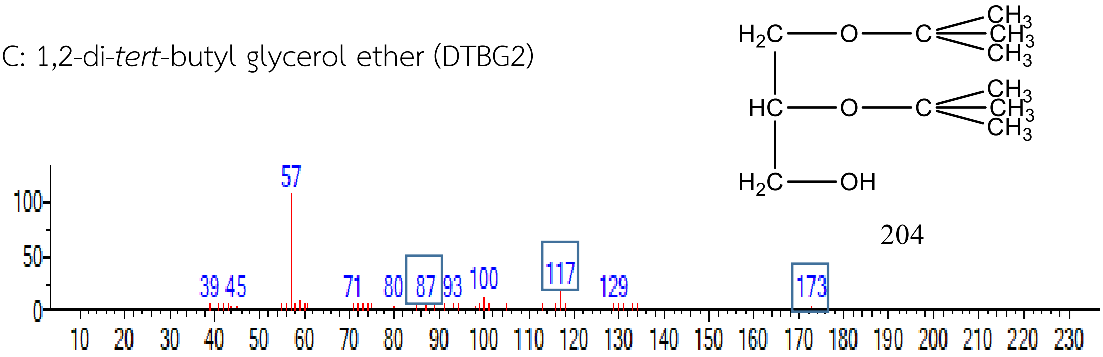


Fig. 4.9 Mass spectrum of 1,2-di-*tert*-butyl glycerol ether

The EI mass spectrum of 1,2-di-*tert*-butyl glycerol ether (Fig 4.9) shows the presence of peak at *m/z* 117 corresponding to elimination of butoxymethyl moiety [M-CH_2O^tBu]$^+$ and that of ion at *m/z* 173 arising from the elimination of hydroxyl methyl group [M-CH_2OH]$^+$. The fragment is located at *m/z* 173 where it will not be observed in the spectrum of mono-*tert*-butyl glycerol ether and 1,3-di-*tert*-butyl glycerol ether.

D: tri-*tert*-butyl glycerol ether (TTBG)

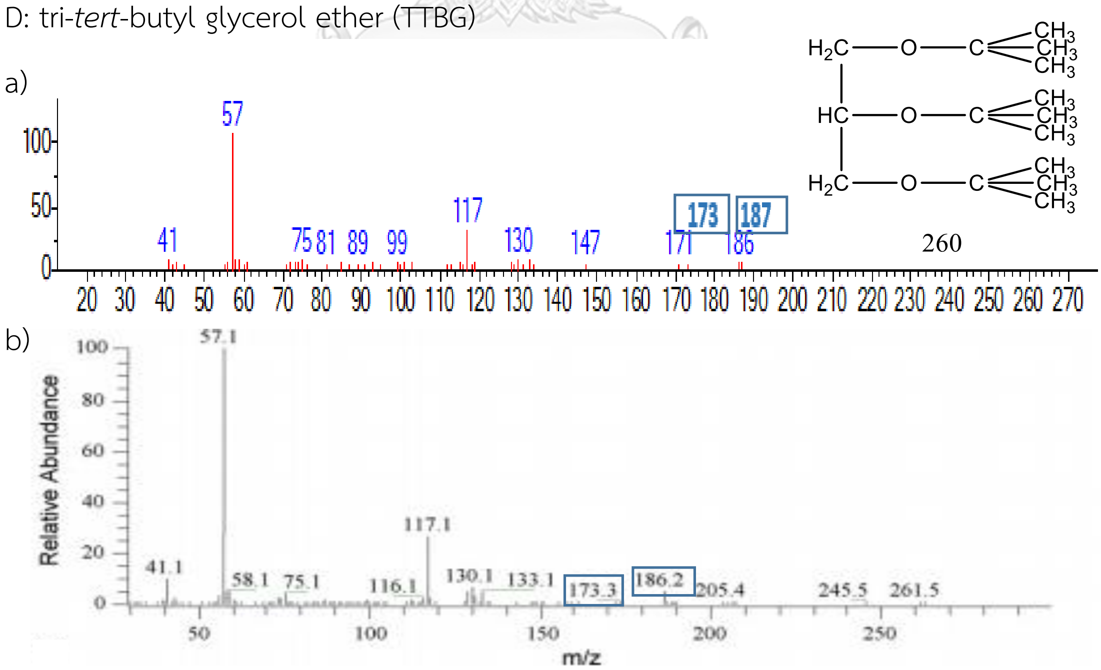


Fig. 4.10 Mass spectrum of tri-*tert*-butyl glycerol ether from a) GC-MS analysis b) literature (Jamroz *et al* [24]).

The EI mass spectrum of tri-*tert*-butyl glycerol ether (Figure 4.10) shows the presence of peak at *m/z* 173 corresponding to elimination of butoxymethyl moiety $[M\text{-}CH_2O^tBu]^+$ and that of ion at *m/z* 187 arising from the elimination of butoxy group $[M\text{-}O^tBu]^+$. The fragment is located at *m/z* 187 and 173 where it will not be observed in the spectrum of mono-*tert*-butyl glycerol ether, 1,3-di-*tert*-butyl glycerol ether and 1,2-di-*tert*-butyl glycerol ether.

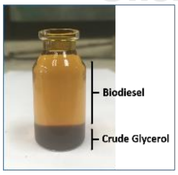
Biodiesel production with >99% conversion was obtained when the TsOH-H_2SO_4 with 7.5:2.5, 7.5:5 and 7.5:7.5 weight ratios and single TsOH were used. Thus, effect of those catalysts on etherification of the crude glycerol under isobutylene/glycerol molar ratio 6:1 at 70°C was investigated. After separation of glycerol from the transesterification using TsOH-H_2SO_4 as a catalyst and removal of methanol, the crude glycerol together with the remaining catalyst was subjected to etherification. Results (Table 4.2) showed that those catalysts resulted in 100% conversion of glycerol and amount of H_2SO_4 in TsOH-H_2SO_4 had a significant influence on the selectivity of the glycerol ethers. TsOH-H_2SO_4 with 7.5:5 ratio gave the highest yield of (DTBG+TTBG) with 80.3% and MTBG yield was increased when H_2SO_4 in TsOH-H_2SO_4 was increased.

Furthermore, effect of isobutylene/glycerol molar ratio (4:1, 6:1, 9:1, and 12:1) and of temperature (60°C, 70°C, 80°C and 90°C) were studied on the TsOH-H_2SO_4 (7.5:5) catalyst. On etherification for 5 h, results (Table 4.2) showed that the 100% conversion of glycerol was obtained by using 6:1 isobutylene/glycerol ratio at 70°C and DTBG+TTBG were obtained in 80.3%. When the molar ratio of glycerol and isobutylene was 6:1, the etherified yield was increased obviously. Higher amount of isobutylene in the reaction system (12:1) led to a slightly decrease of the yield due to dilution of the catalyst and substrates.

Since etherification in the presence of dioxane and sulfolane as a solvent gave a higher yield of DTBG and TTBG [3], we expected that biodiesel itself could be used as a solvent in etherification and the final product could be also used as biodiesel fuel. After transesterification using TsOH/H_2SO_4 (7.5:5) as a catalyst and removal of MeOH, the crude glycerol in a presence of biodiesel as obtained was etherified with isobutylene (isobutylene/glycerol molar ratio 6:1) at 70°C for 5 h. The conversion of glycerol has reached ~100% and DTBG+TTBG were obtained in 81.4%. It can be observed that better yields and higher selectivity of DTBG and TTBG were obtained when biodiesel was used as the reaction medium. It was probably caused by the addition of biodiesel resulting in a homogeneity of glycerol and isobutylene or better solubility of isobutylene in the reaction mixture. The TsOH-H_2SO_4 catalyst showed a good catalytic performance in the etherification similar to TsOH and it could be recovered for reuse while TsOH could not be recovered.

Since the crude glycerol could be directly used for the etherification, we expected that TsOH-H_2SO_4 could be reused for transesterification and etherification or through continuous synthesis.

Table 4.2 The effect of isobutylene/glycerol molar ratio and temperature (°C) *tert*-butyl glycerol ethers production

Feed stock[a]	Catalyst presented in crude glycerol* (TsOH: H_2SO_4)	Temperature, °C	I/G	Reaction time (h)	Amount of *tert*-butyl glycerol ethers, %[b]			
					M	D	T	D+T
Crude glycerol 	7.5:0	70	6:1	5	15.2	60.9	23.9	84.8
	7.5:2.5	70	6:1	5	26.9	59.3	13.8	73.1
	7.5:5	70	6:1	5	19.7	62.3	18.0	80.3
		60	6:1	5	19.9	60.6	19.5	80.1
		80	6:1	5	29.1	60.0	10.9	70.9
		90	6:1	5	30.1	60.7	9.2	69.9
		70	4:1	5	23.5	58.4	18.1	76.5
		70	9:1	5	20.3	55.4	24.3	79.7
		70	12:1	5	35.2	53.4	11.4	64.8
	7.5:7.5	70	6:1	5	40.1	46.3	13.6	59.9
Biodiesel + Glycerol	7.5:5.0 	70	9:1	5	18.6	63.3	18.1	81.4

[a] Crude glycerol was by-product from biodiesel 99%

[b] Amount of G, M, D and T (%) were calculated from GC-FID chromatogram and G = glycerol; M = MTBG; D = DTBG; T = TTBG, I = isobutylene

* wt % TsOH-wt % H_2SO_4 (on the basis of the oil)

4.4 Reusability of TsOH-H_2SO_4

Reusability of the TsOH-H_2SO_4 catalyst was investigated in the continuous synthesis. After transesterification, biodiesel was extracted (x3) with hexane, and the crude glycerol remained was etherified with isobutylene (9:1 ratio) at 70°C for 8 h. followed by extraction with *n*-hexane. The left over catalyst was used for the next cycle and the process was then repeated. For each cycle of the reaction, biodiesel and selectivity for glycerol ethers were examined.

The results showed that the catalyst can be reused for at least of 6 cycles until the reaction cannot be resumed and activity of the catalyst was less for 90% after 6 cycles. TsOH was considered as a homogeneous catalyst to organic synthesis. When TsOH was combined with H_2SO_4 through formation of hydrogen bond to producing mixing of TsOH-H_2SO_4, TsOH-H_2SO_4 would become a “homogeneous” catalyst at the moment. Owing to polarity of TsOH-H_2SO_4, they were not only the catalyst of transesterification reaction, but also they were increased polarity of glycerol. This is because TsOH-H_2SO_4 and glycerol could form a new ternary TsOH-H_2SO_4–glycerol. The ternary TsOH-H_2SO_4–glycerol was easy to separate from the products, making the overall operation convenient. Moreover, the recyclability experiments of the catalyst were conducted and the results showed that the sixth catalyst recycling run showed a slight reduction in the transesterification yield (78.58%) (>99% for the first run). From acid value test of glycerol phase in 1-6 cycle of catalyst, result showed 3.31, 2.63, 1.47, 1.01, 0.57 and 0.32 g KOH/ g of oil, respectively. The above results indicated that TsOH-H_2SO_4 containing the reaction would decrease the activity of the acidic TsOH-H_2SO_4 catalyst in the transesterification process was decreased.

4.5 Evaluation of TsOH-H_2SO_4 in synthesis of Solketal

Solketal, another fuel additive derived from glycerol, can be utilized by blending it with gasoline or biodiesel. [10,11]

In this work, the crude glycerol was subjected to the acetalization process with acetone catalyzed by the remaining catalyst (TsOH-H_2SO_4 (7.5:5)). The highest glycerol conversion (90.0%) was observed at 110°C, reaction time 8 hours and 6:1 of acetone/glycerol molar ratio. Since water was formed during the reaction, 100% conversion of glycerol could not be achieved. These results indicated that the catalyst remaining in crude glycerol could be used as catalyst in similar catalytic ability in the transesterification process, glycerol ether production and acetalization.

4.6 Catalytic effect of DESs on biodiesel production

DESs (choline chlorine–TsOH system) were prepared as shown in Table 3.1. TsOH was the HBD, and ChCl was the HBA. The transesterification of PO using 10 %ChCl-TsOH as catalyst, 8:1 molar ratios of MeOH/oil, at 110°C for 4h was carried out [15]. The results (Table 4.3) have shown that DESs-3 (ChCl:TsOH=1:3) gave the highest conversion (99.1 %). In comparison of molar ratio of TsOH in DESs, when the molar ratio of TsOH in ChCl:TsOH DESs was increased (1:1 to 1:3), the catalytic effect of TsOH-based DESs on transesterification was increased. Comparing with increased molar ratio of ChCl in the DESs, the catalytic effect was decreased. It indicated that the catalytic effect of TsOH was depended significantly on the combination of ChCl-TsOH. Obviously, the amount of TsOH in ChCl-TsOH played an important role on the outcome of palm oil biodiesel production (Table 4.3). When the amount of TsOH in the DESs was increased, the transesterification yields were increased rapidly until decreased in the presence of more amount of ChCl. The suitable ratio of ChCl-TsOH was 1:3, the transesterification yield was the highest. Considering catalytic effect and cost, ratio of ChCl-TsOH was 1:3 was chosen as an optimum amount of catalyst for biodiesel production.

Table 4.3 The effect of catalytic DESs on biodiesel production

Abbreviation	ChCl:TsOH (mol/mol)	%Conversion
DESs-1	1:1	81.3
DESs-2	1:2	90.4
DESs-3	1:3	99.1
DESs-4	2:1	90.5
DESs-5	2:3	87.2

4.6.1 Effect of MeOH/PO, reaction temperature, amount of catalyst and reaction time

Effect of methanol and PO ranging from 6:1 to 15:1 temperature ranging from 80°C to 120°C, amount of catalyst ranging from 4 wt % to 12 wt % of PO and reaction time ranging from 1 to 5 h was studied. Result, (table 4) indicated that the highest conversion of biodiesel (99.8%) were obtained from the condition of 10:1 methanol/PO ratio at 110°C and reaction time 4 h using ChCl:TsOH=1:3. Since, biodiesel was produced the maximum yield in this condition, ChCl:TsOH (1:3) was used in further step as catalyst for *tert*-butyl glycerol ethers production.

Table 4.4 The Effect of MeOH/PO molar ratio, reaction temperature(°C), amount of catalyst and retention time (h)

Condition using ChCl:TsOH (1:3) as catalyst		Biodiesel[a], %
MeOH/PO (10 %TsOH in DESs, at 110°C for 5h)	6:1	97.3
	8:1	99.4
	10:1	99.5
	12:1	99.1
	15:1	99.0
Temperature, °C (10 %TsOH in DESs, 10:1 MeOH/PO for 5h)	80	80.2
	90	91.3
	100	97.6
	110	99.8
	120	99.7
Amount of catalyst (wt%) (At 110°C 10:1 MeOH/PO for 5h)	4	83.6
	6	90.4
	8	98.5
	10	99.2
	12	99.0
Reaction time (h) (10 %TsOH in DESs, at 110°C 10:1 MeOH/PO)	1	85.7
	2	89.3
	3	95.6
	4	99.3
	5	99.1

[a] The %conversion were calculated from ^{1}H-NMR

The molar ratio of methanol to oil affected the process of transesterification reaction. The effect of molar ratio of methanol to oil was studied and the results were shown in Table 4.4. When the molar ratio of methanol to oil was increased from 6:1 to 10:1, the transesterification yield was increased obviously. Continuing adding methanol into the reaction system (12:1 and 15:1) led to a slightly decreasing of the yield of biodiesel due to dilution of the catalyst and substrates. Therefore, 10:1 was the optimum molar of methanol to oil, and the transesterification to give 99.2% yield of biodiesel.

Reaction temperature played a vital role in most of organic reactions. In order to study the effect of reaction temperature, a set of temperature experiments (80, 90 100, 110 and 120°C) were performed. The results (Table 4.4) indicated that when reaction temperature was increased, the higher transesterification yield (99.8%) was obtained at 110°C. Continuing increasing the reaction temperature (120°C) showed a slight decline. Therefore, 110°C should be the optimum reaction temperature for transesterification.

Since this type of reaction was a liquid-liquid reaction (PO and methanol), the contact area between catalyst and the substrates was a key role for to the transesterification. In Table 4.4, amount of ChCl:TsOH also played an important role on the outcome of palm oil biodiesel production. When the amount of ChCl:TsOH catalyst was increased, the transesterification conversion were increased rapidly at first, and then became stable in the presence of more amount of ChCl and the suitable amount of ChCl:TsOH (10%), gave the highest conversion (99.2%). Considering catalytic effect, 10% amount of ChCl:TsOH was chosen as an optimum amount of catalyst for biodiesel production.

Reaction time was one of the most important factors in various reactions. The effect of reaction time on transesterification reaction was investigated and results were shown in Table 4.4. As the reaction time was prolonged, the transesterification conversion was increased rapidly within 2 h, and then reached the highest yield of biodiesel 4 h. Therefore, 4 h was chosen as the optimum reaction time of transesterification reaction for biodiesel production.

4.6.2 *tert*-butyl glycerol ethers from crude glycerol using ChCl:TsOH as catalyst

After transesterification using ChCl:TsOH (1:3) as catalyst and removal of methanol, the crude glycerol together with the remaining catalyst was separated and then subjected to etherification process.

Effect of isobutylene/glycerol molar ratios (6:1, 9:1, 12:1 and 15:1) and temperature (80, 90, 100 and 110°C) were studied at 5 h reaction period. Results (Table 4.5) indicated that the highest conversion of glycerol were obtained from the condition of 12:1 isobutylene/glycerol ratio at 100°C and reaction time 5 h. The yield of DTBG+TTBG was 90%. The selectivity of DTBG+TTBG was increased by increasing molar ratios of isobutylene/glycerol and reaction temperature. When the molar ratio of glycerol and isobutylene was increased up to 12:1, the etherified yield was increased obviously. Continuing adding isobutylene into the reaction system (15:1) led to a slightly decreasing of the yield due to dilution of the catalyst and substrates.

Table 4.5 The effect of isobutylene/glycerol molar ratio and temperature (°C) *tert*-butyl glycerol ethers production

Feed stock[a]	Temperature, °C	I/G	Reaction time (h)	Amount of *tert*-butyl glycerol ethers, %[b]			
				M	D	T	D+T
Crude glycerol	80	6:1	5	14.4	71.6	14.0	85.6
	90	6:1	5	14.0	68.9	17.1	86.0
	100	6:1	5	13.4	68.7	17.9	86.6
	110	6:1	5	14.1	67.1	18.8	85.9
	100	6:1	5	13.4	68.7	17.9	86.6
	100	9:1	5	16.9	66.7	16.4	83.1
	100	12:1	5	16.6	72.5	10.9	83.4
	100	15:1	5	18.0	60.8	19.1	79.9
Biodiesel + Glycerol	100	6:1	5	10.1	77.7	12.2	89.9

[a] Crude glycerol was by-product from biodiesel 99%

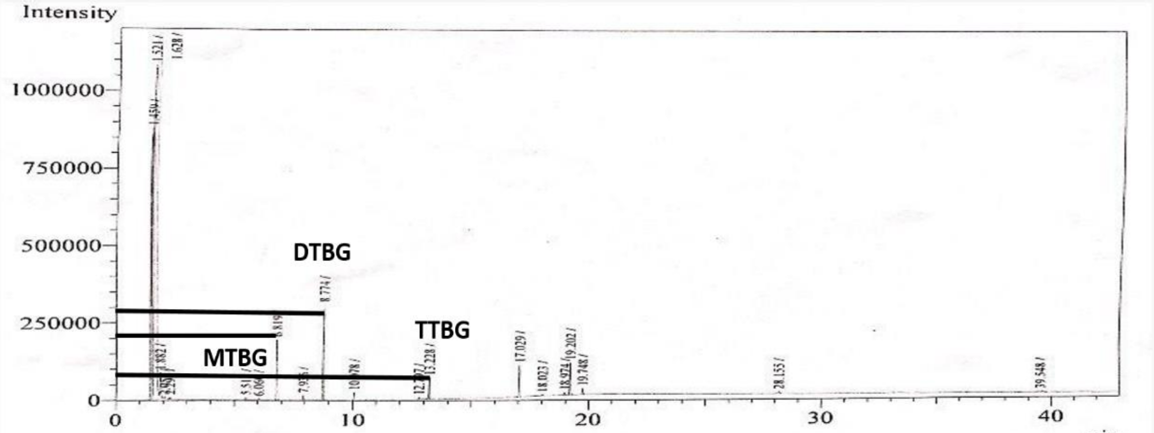
[b] Amount of G, M, D and T (%) were calculated from GC-FID chromatogram and G = glycerol; M = MTBG; D = DTBG; T = TTBG, I = isobutylene

According to the study on the effect of temperature, DTBG+TTBG (86.6%) was obtained at 100°C. At 6:1 isobutylene/glycerol molar ratio and the reaction temperature (100°C), the highest selectivity of DTBG+TTBG were achieved. When the temperature was increased up to 110°C, the etherified yield was decreased obviously.

4.6.3 Using TsOH-H_2SO_4 and ChCl:TsOH as catalyst for *tert*-butyl glycerol ethers from crude glycerol compare between

GC-MS result (Fig. 4.10) showed that those catalysts had a significant influence on the selectivity of MTBG and DTBG and TTBG. TsOH-H_2SO_4 with 7.5:5 ratio gave higher yield of MTBG than TTBG while ChCl:TsOH gave higher yield of TTBG than MTBG. Comparing yield of MTBG, ChCl:TsOH resulted in less MTBG than TsOH-H_2SO_4.

(a) TsOH-H_2SO_4 as catalyst



(b) ChCl:TsOH as catalyst

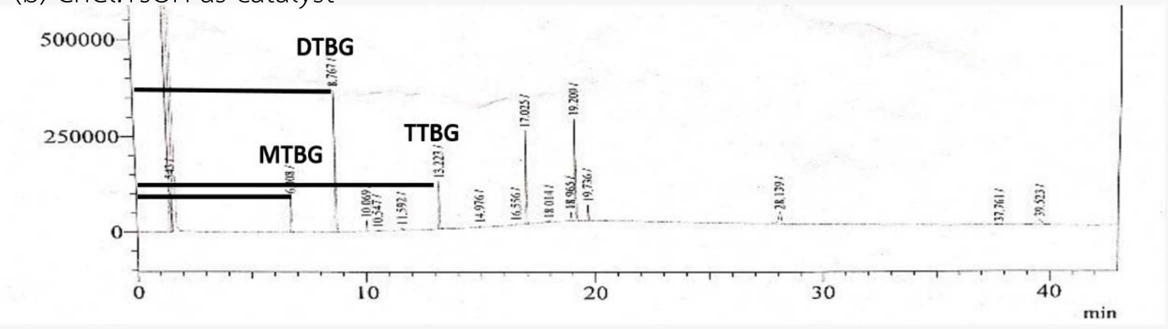


Fig. 4.11 Mass spectrum of *tert*-butyl glycerol ethers from crude glycerol compare between using TsOH-H_2SO_4 and ChCl:TsOH as catalyst

4.7 Reusability of ChCl-TsOH DESs

Reusability of the ChCl-TsOH catalyst was investigated in the continuous synthesis. After transesterification, biodiesel was extracted (x3) with hexane, and the crude glycerol remained was etherified with isobutylene (15:1 ratio) at 70°C for 8 h. followed by extraction with *n*-hexane. The left over catalyst was used for the next cycle and the process was then repeated. For each cycle of the reaction, biodiesel and selectivity for glycerol ethers were examined.

The result shown that the catalyst can be reused for a maximum of 4 cycles of continuous step of reaction until the reaction cannot be resumed and activity of the catalyst was less for 90% after 4 cycles. The reusability of the ChCl-TsOH catalyst (4 cycles) less than reusability of the TsOH-H_2SO_4 catalyst because the different amount of acid in catalyst system. Both of TsOH and H_2SO_4 were acid in TsOH-H_2SO_4 system which TsOH was an acid in ChCl-TsOH system.

4.8 Amberlyst-15

This research was studied the modification of Amberlyst-15 (dry) in 2 methods; heating Amberlyst 15 (dry) at 220°C for different durations (4, 24, and 48 h) and by soaking Amberlyst 15 (dry) into methanol in a different period of time to study its swelling rate for catalyst in continuous transesterification and etherification process.

From Fig 4.12, after performing a modification of Amberlyst-15 (dry) by heating Amberlyst 15 (dry) at 220°C, It was found that Amberlyst-15 (dry) was burnt. Since the Amberlyst 15 (dry) can be stable up to 120°C, the modification of Amberlyst-15 (dry) by heating at 220°C cannot be used for catalyst in continuous transesterification and etherification process.

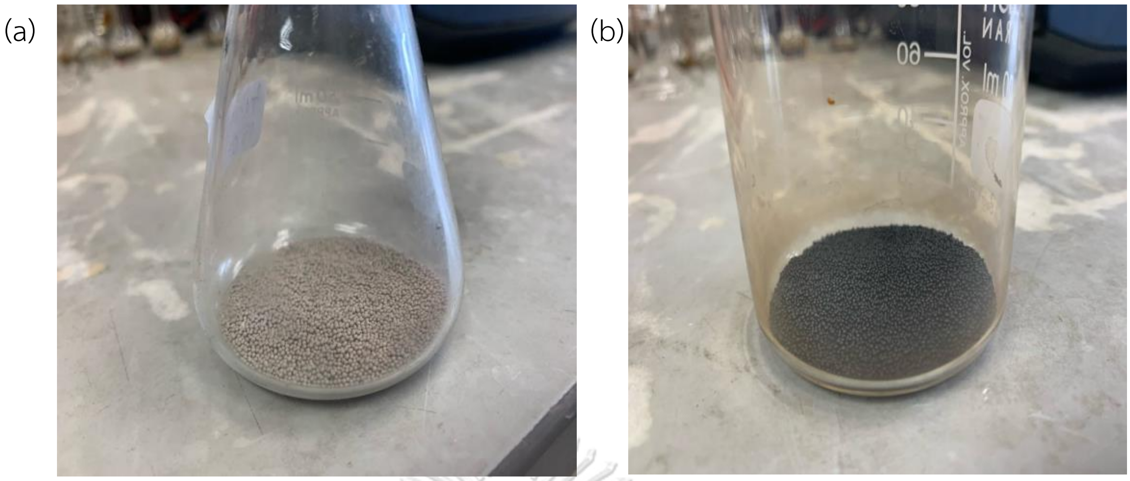


Fig. 4.12 The modification of Amberlyst-15 (dry) by heating Amberlyst 15 (dry) at 220°C (a) unmodified (b) heating at 220°C

In another method, Amberlyst 15 (dry) was soaking in methanol for a different period of time. The result showed that the rate of reaction was increased when soaking for a long time. In 4.13, fractures of the treated Amberlyst 15 were increased when time for soaking Amberlyst 15 (dry) in methanol was increased. Although longer soaking time provided higher catalytic effect of the catalyst, the formation of biodiesel was less than 90%. Thus, using the MeOH treated Amberlyst 15 for the study of the formation of glycerol ether from glycerol would not be continued.

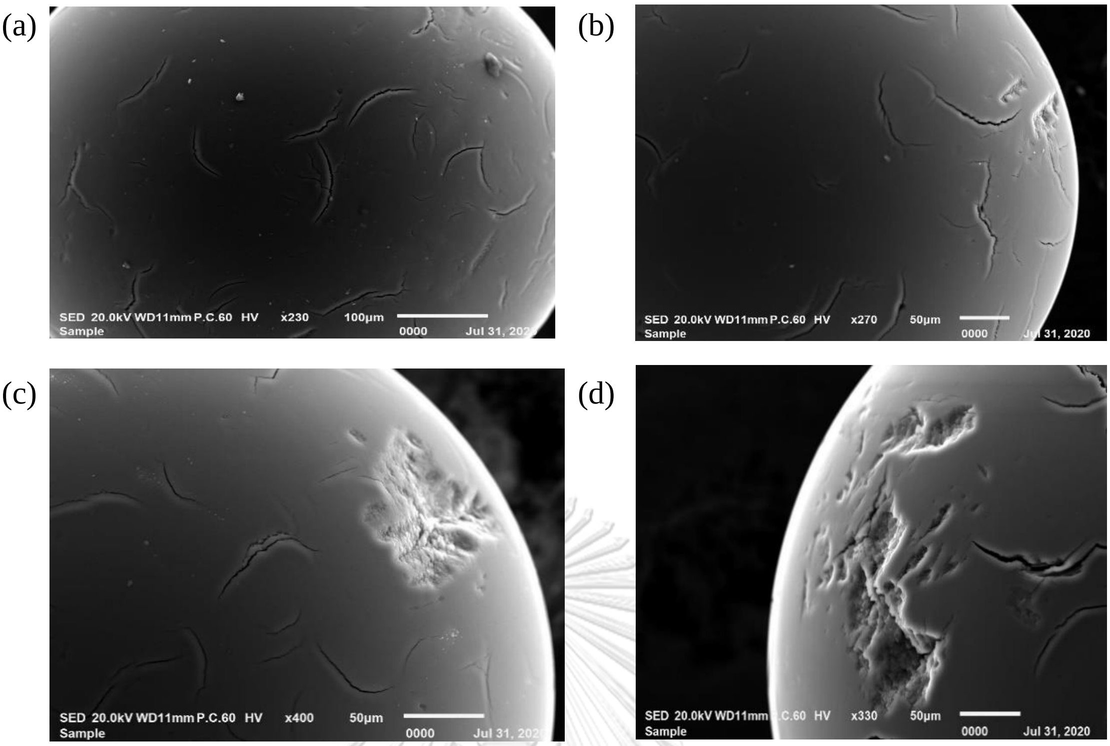


Fig. 4.13 Scanning electron micrograph (SEM) of the soaking Amberlyst 15 (dry) into methanol (a) unmodified (b) soaking in 7 days (c) soaking in 15 days (d) soaking in 30 days

4.9 Determination of fuel properties

In comparison of fuel properties between biodiesel production from transesterification and a mixture of biodiesel with the etherified product acid value, pour point and iodine value were analyzed. The results compared to fuel properties based on biodiesel standard were shown in Table 4.6. The additives decreased pour point of the palm biodiesel when blending TBGE in biodiesel. In comparison with previous research [23], acid value and pour point were higher than previous research but iodine value was less than.

Table 4.6 Biodiesel standard

Fuel properties	Standard	Biodiesel	10%TBGE Blending	From previous research
Acid value, mg KOH/g oil	<0.5	0.13	0.4	0.14
Pour point (°C)	-15 to 10	18	8	-6
Iodine value (g iodine/100g)	120 - >103	110	100	117.04

*Unpurified before testing

CHAPTER V
CONCLUSION AND SUGGESTION

5.1 Conclusion

In this study, the results showed that the mixture of TsOH-H_2SO_4 could be used in transesterification, etherification of glycerol with isobutylene and acetalization of solketal. For transesterification of PO, 7.5%wt TsOH and 5 wt% conc. H_2SO_4, 9:1 methanol: PO molar ratios after a reaction period of 4 hours at 80°C resulted in up to 99.9% conversion. It was found that the mixture of TsOH and H_2SO_4 could accelerated the reaction noticeably faster than the single catalyst, resulting in the enhancement of the transesterification rate and TsOH-H_2SO_4 as the catalyst for transesterification and etherification in continuous synthesis could be reused for 6 cycles, which would cause a reduction of waste and cost. When crude glycerol together with biodiesel was used the starting material in the production of *tert*-butyl glycerol ethers, the etherification in biodiesel resulted in higher selectivity of DTBG and TTBG (81.4%). In case of deep eutectic solvents, ChCl:TsOH (1:3), the highest conversion of biodiesel (~99.5%) were obtained by using of 10%wt ChCl:TsOH, 10:1 methanol/PO ratio at 110°C for 4 h and the further process (etherification) using isobutylene/glycerol molar ratio 6:1 at 100°C for 5 h gave high selectivity to produce DTBG and TTBG (86.6%). Furthermore, the catalyst can be reused for 4 cycles of continuous synthesis. The modification of Amberlyst 15 by soaking in methanol for a different period of time was studied and the rate of reaction was increased when increased soaking time for the treatment. However, the highest formation of biodiesel was less than 90%. Thus, the study of the continuous synthesis (transesterification and etherification) would not be studied. In comparison of fuel properties between biodiesel and biodiesel blending with *tert*-butyl glycerol ether, the glycerol ethers could improve; pour point from 18°C to 8°C iodine value from

110 to 100 (g iodine/100g) when 10% *tert*-butyl glycerol ether was blended in biodiesel.

5.2 Suggestion

In the part of heterogeneous catalyst, acid sites, pore sites, pore volume and surface area of Amberlyst 15 was unsuccessively modified by heating and soaking in methanol. I suggest that preparation of polysulfonic acid polymer will be an alternative method for improvement in synthesis of biodiesel and glycerol ethers.

REFERENCES

1. Gonzalez, L.R., Bolonio, D., Mazadiego, L.F., Silva, N.S. and Segovia, E.K. , *Long-term forecast of energy and fuels demand towards a sustainable road transport sector in ecuador (2016–2035): a leap model application.* Sustainability 2020. **12**: p. 472.
2. Kiakalaieh, A.T., Amin, N.A.S., Najaafi, N. and Tarighi, S., *A review on the catalytic acetalization of bio-renewable glycerol to fuel additives.* Frontiers Chemistry, 2014. **6**: p. 573.
3. Klepacova, K., Mravec, D., Kaszonyi, A. and Bajus, M., *Etherification of glycerol and ethylene glycerol by isobutylene.* Petroleum & Coal, 2003. **45**: p. 54-57.
4. Lee, H.J., Filimonov, I.N., Kim, H., Jung, K.S., and Seng, D. , *Etherification of glycerol by isobutylene: Tuning the product composition.* Applied Catalysis A:General 2010. **390**: p. 235-244.
5. Guan, G., Kusakabe, K., Sakurai, N. and Moriyama, K., *Transesterification of vegetable oil to biodiesel fuel using acid catalysts in presence of dimethyl ether.* Fuel, 2009. **88**: p. 81–86.
6. Freedman, B., Butterfield, R.O. and Pryde, E.H. , *Transesterification Kinetics of Soybean oil.* JAOCS, 1986. **63**: p. 1375-1380.
7. Idris, A.M., *The effects of alcohol to oil malar ratios and the type of alcohol on biodiesel production using transesterification process.* Egyptian Journal of Petroleum & Coal, 2016. **25**: p. 21-31.
8. *Palm oil [internet]*. 2002; Available from: http://en.wikipedia.org/wiki/Palm_oil.
9. Schuchardt, U., Sercheli,R. and Vargas, R.M. , *Transesterification of vegetable oils.* Journal of the Brazilian Chemical Society 1998. **9**: p. 199-210.
10. MA, F., and Hanna, M.A. , *Biodiesel production: a review.* Bioresource Technology 1999. **70**: p. 1-15.
11. Marchetti, J.M., Miguel, V.U. and Errazu, A.F., *Possible methods for biodiesel production.* Renewable sustainable Energy Review 2007. **11**: p. 1300-1311.
12. Lotero, E., Liu, Y., Lopez, D.E., Suwannakam, K., Bruce, D.A. and Goodwin, J.M.,

Synthesis of biodiesel via Acid Catalysis. Industry Engineering Chemical Resource, 2005. **44**: p. 5353-5363.

13. EPPO. *Heterogeneous catalysts [internet*. 2011; Available from: http://www.eppo.go.th.

14. Pal, R., Sarkar, T and Khasnobis S., *Amberlyst-15 in organic synthesis.* ARKIVOC 2012: p. 570-609.

15. Liu, W., and Wang, F., *p-Toluenesulfonic Acid-based deep eutectic solvent as Transesterification catalyst for Biodiesel Production.* Journal of Oleo Science 2018. **67**: p. 1163-1169.

16. *Glycerol [Internet]*. 2020; Available from: http://en.wikipedia.org/wiki/Glycerol.

17. Norhasyimi, R., Zuhairi, A.A. and Rahman, M.A., *Recent progress on innovative and potential technologies for glycerol transformation into fuel additives: A critical review.* Renewable & Sustainable Energy Reviews 2010 2010. **14**: p. 987-1000.

18. Smirnov, A.A., Selishcheva, S.A. and Yakovlev, V.A., *Acetalization Catalysts for synthesis of Valuable oxygenated Fuel Additives from Glycerol.* Catalysts 2018. **8**: p. 595.

19. Suriyaprapadilok, N.a.K., B., *Synthesis of Solketal from Glycerol and Its reaction with Benzyl alcohol.* Energy Procedia 2011. **9**: p. 63–69.

20. Hayyan, A., Alam, M.Z., Mirghani, M.E.S., Kabbashi, N.A., Hakimi,N.I.N.M., Siran,Y.M. and Tahiruddin, S., *Production of biodiesel from sludge palm oil by esterification process.* Energy and Power Engineering 2010. **4**: p. 11-17.

21. Encinar, J.M., Sanchez, N.,Martinez, G. and Garcia, L., *Study of biodiesel production from animal fats with high free fatty acid content.* Bioresource Technology 2011. **102**: p. 10907-10914.

22. Calgaro, C., Calaroto, S., Mazutti, M.A., Oliveira, D.D., Pergher, S. and Vladimir, I., *Production of biodiesel from soybean and Jatropha Curcas oils with KSF and amberlyst 15 catalysts in the presence of co-solvents.* Sustainable Chemical Process, 2013: p. 1-17.

23. Melero, J.A., Vicente, G., Morales, G., Paniagua, M., Moreno, J.M., Roldan, R., Ezauerro, A. and Perez, C., *Acid-catalyzed ethrification of bio-glycerol and*

isobutylene over sulfonic mesostructured silicas. Applied Catalysis A:General 2018. **346**: p. 44-51.

24. Jamroz, M.E., Jarosz, M., Jarosz, J., Benarek, E., Tecza, W., Jamroz, M.H., Dobrowolski, J.C. and Kijenski, J., *Mono-, Di-, and tri-tert-butyl ethers of glycerol A molecular spectroscopic study.* Spectrochimica Acta Part A, 2007. **67**: p. 980-988.

APPENDICES

APPENDIX A

CALCULATIONS

A-1 Characterization of palm oil

Amount of the methyl esters was examined on a GC-MS Agilent using HP-5 column stationary phase polyethylene glycol (column 35 m x 0.32 mm x 0.25 µm). To prepare the sample, 250 mg of sample was added into a 10 mL vial. Helium gas was used as carrier gas and the temperature of the injector was set at 290°C. The oven temperature was retained at 50°C for 5 min and increased to 240°C with ramping rate of 20°C /min.

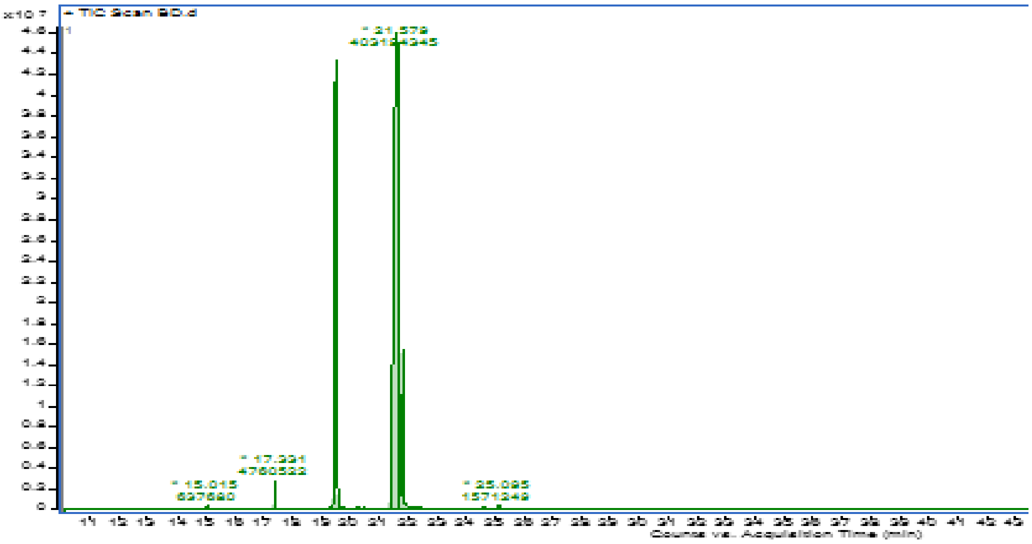
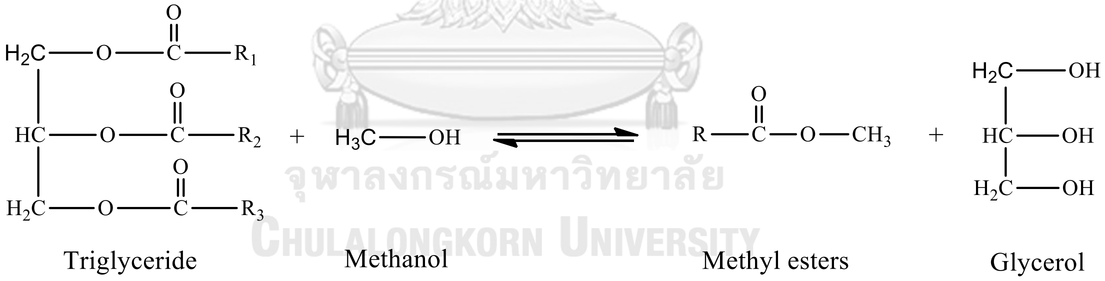


Fig A-1 GC chromatogram FAME composition of PO

Table A-1 Fatty acids composition of palm oil

Fatty acids	Fatty acids (wt%)	Molecular Weight (g/mole)	%Fatty acid x MW
Lauric acid	0.1	200.32	20.03
Myristic acid	0.7	228.47	159.87
Palmitic acid	33.4	256.43	8564.76
Stearic acid	8.1	284.48	2304.29
Oleic acid	57.5	282.47	16242.03
Linoleic acid	0.04	280.45	11.22
Linolenic acid	0.2	278.44	55.69
Average molecular weight of fatty acid			27,357.88/100=273.58



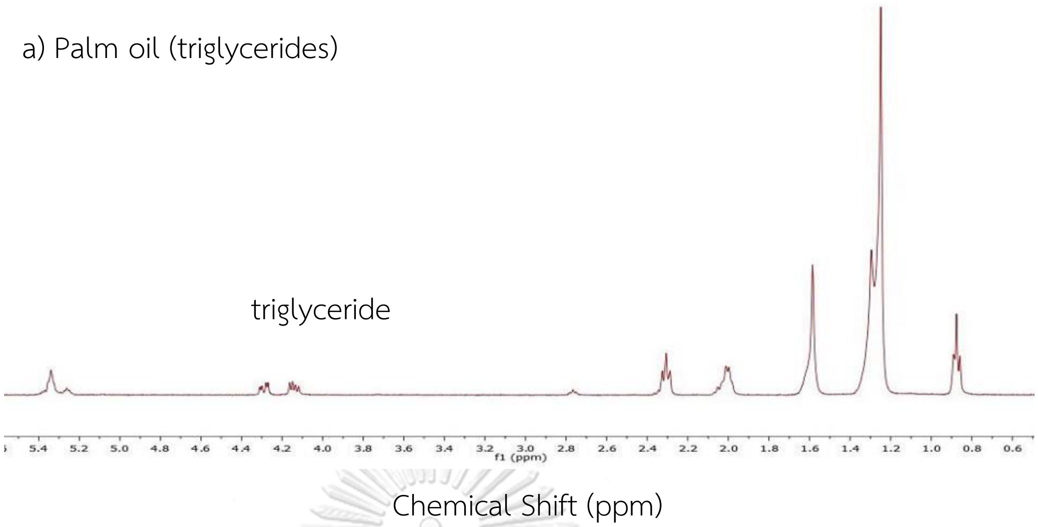
Molecular weight of palm oil = (273.58 – 17)(3) + (92.03-3)

= 858.77

Fig A-2 Calculated molecular weight of palm oil

A-2 The calculated biodiesel conversion

a) Palm oil (triglycerides)



b) Fatty acid methyl ester of palm oil

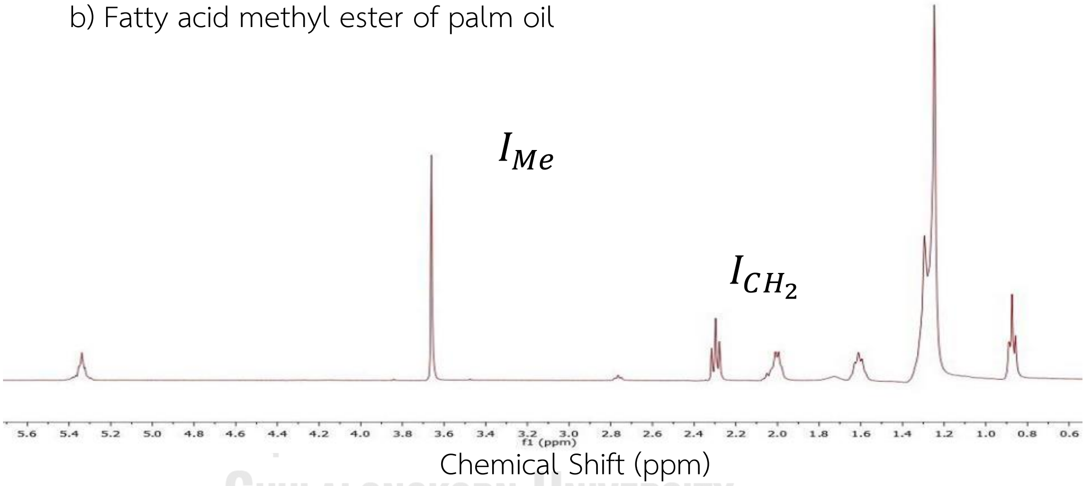


Fig A-3 ^{1}H NMR spectrum of the product from transesterification: (a) palm oil (triglycerides) (b) fatty acid methyl ester of palm oil

^{1}H NMR analysis

Each sample (about 10 mg) was dissolved with 0.7 mL of deuterated chloroform in a 5-mm NMR tube. Spectra were recorded on a Varian Mercury 400 MHz NMR spectrometer at 300 K.

The conversion was estimated by equation (1)

$$\text{Conversion (\%)} = \frac{2I_{\mathrm{Me}}}{3I_{\mathrm{CH_2}}} \times 100 \qquad (1)$$

Where I_{Me} is integral of a singlet signal at δ_{H} 3.65 ppm according to methoxy protons of fatty acid methyl esters (–OCH_3)

$I_{\mathrm{CH_2}}$ is integral of a triplet signal at δ_{H} 2.24-2.27 ppm corresponding to α–methylene protons of the fatty acyl moiety

The factors 2 and 3 were derived from the fact that methylene carbon and methyl carbon possesses two protons and three protons, respectively.

A-3 Preparation of *tert*-butyl glycerol ether

The *tert*-butyl glycerol ether profile was analyzed by GC-MS (Fig 3). Etherification of pure glycerol with isobutylene and *tert*-butyl glycerol ethers (mono-, di- and tri-glycerol ether) were used as reference for GC-FID analysis. Amount of the methyl esters was examined on a GC-MS Agilent using HP-5 column stationary phase polyethylene glycol (column 35 m x 0.32 mm x 0.25 μm). To prepare the sample, 250 mg of sample was added into a 10 mL vial. Helium gas was used as carrier gas and the temperature of the injector was set at 290°C. The oven temperature was retained at 50°C for 5 min and increased to 240°C with ramping rate of 20°C /min.

A-4 GC Chromatogram

Amount of glycerol ethers was performed on a gas chromatography GC-FID. The operating conditions were: The *tert*-butyl glycerol ethers profile was analyzed by GC-FID (Shimadzu 2010) gas chromatograph equipped with BP-20 column (column 30 m x 0.32 mm x 0.25 µm). To prepare the sample (10 mg/mL) were added into a 10 mL vial. Helium gas was used as carrier gas and the temperature of the injector was set at 250°C. The oven temperature was retained at 80°C for 5 min and increased to 210°C with ramping rate of 10°C /min.

Five abbreviations of the products are defined as follows: 3-*tert*-butoxy-1,2-propandiol or mono-*tert*-butyl ether of glycerol 1 (MTBG1), 2-*tert*-butoxy-1,3-propandiol, or mono-*tert*-butyl ether of glycerol 2 (MTBG2), 1,3-di-*tert*-butoxy-2-propanol, or di-*tert*-butyl ethers of glycerol 1 (DTBG1), 1,2-di-*tert*-butoxy-3-propanol, or di-*tert*-butyl ether of glycerol 2 (DTBG2), and tri-*tert*-butoxy-propane or tri-*tert*-butyl ether of glycerol (TTBG). The glycerol ethers were calculated using Equation (3).

$$\%\text{Yield} = \frac{Total\ peak\ area\ of\ MTBG+DTBG+TTBG}{Total\ peak\ area\ of\ MTBG+DTBG+TTBG+peak\ area\ of\ glycerol} \times 100 \quad (3)$$

$$\%\text{Selectivity of MTBG} = \frac{peak\ area\ of\ MTBG}{Total\ peak\ area\ of\ MTBG+DTBG+TTBG} \times 100$$

$$\%\text{Selectivity of DTBG} = \frac{peak\ area\ of\ DTBG}{Total\ peak\ area\ of\ MTBG+DTBG+TTBG} \times 100$$

$$\%\text{Selectivity of TTBG} = \frac{peak\ area\ of\ TTBG}{Total\ peak\ area\ of\ MTBG+DTBG+TTBG} \times 100$$

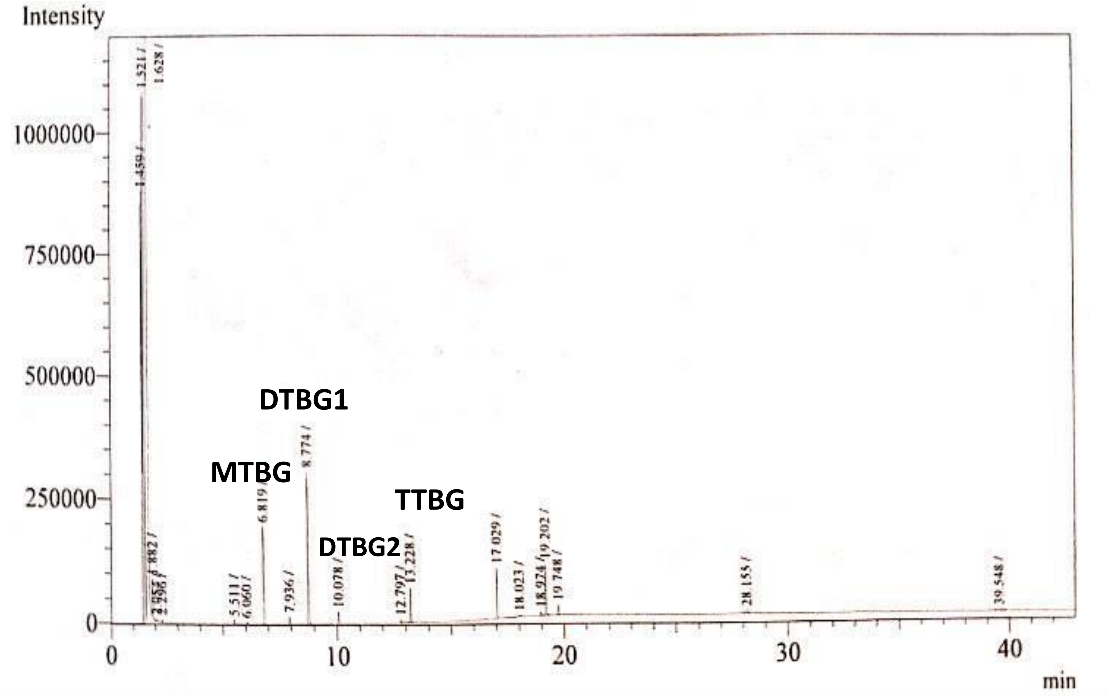


Fig. A-4 The GC chromatogram of *tert*-butyl glycerol ethers from crude glycerol using $TsOH-H_2SO_4$ as catalyst

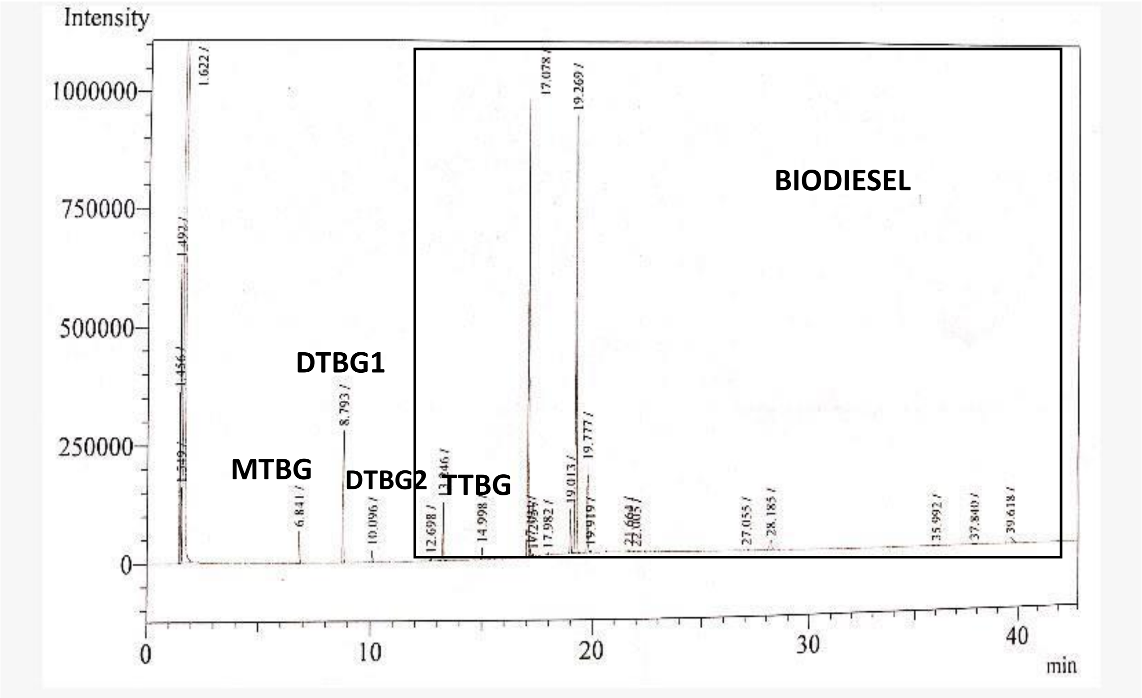


Fig. A-5 The GC chromatogram of *tert*-butyl glycerol ethers from biodiesel using TsOH-H_2SO_4 as catalyst

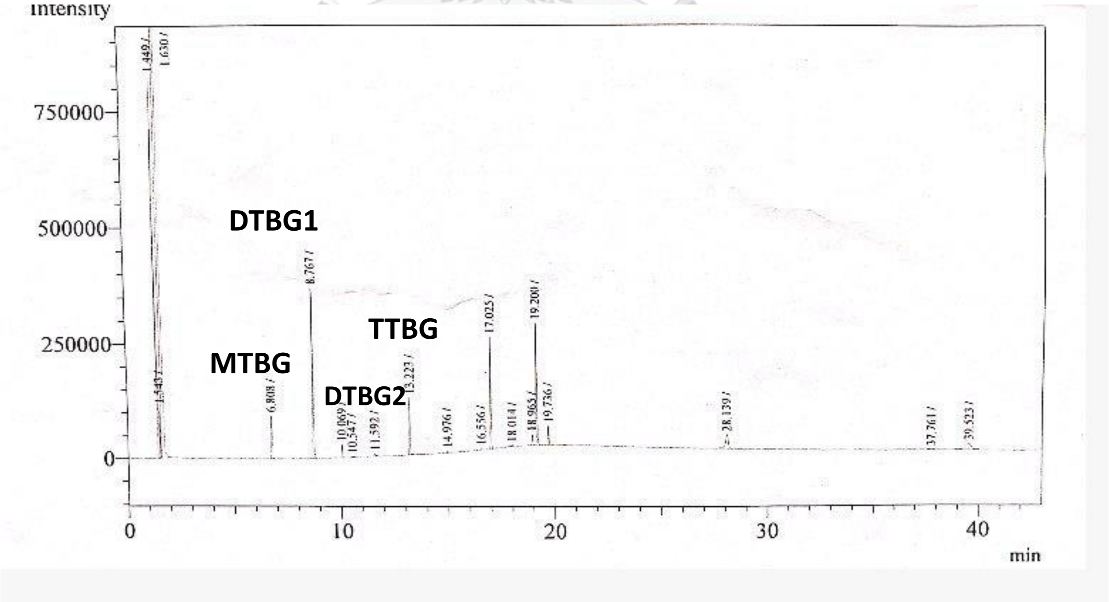


Fig. A-6 The GC chromatogram of *tert*-butyl glycerol ethers from crude glycerol using ChCl-TsOHas catalyst

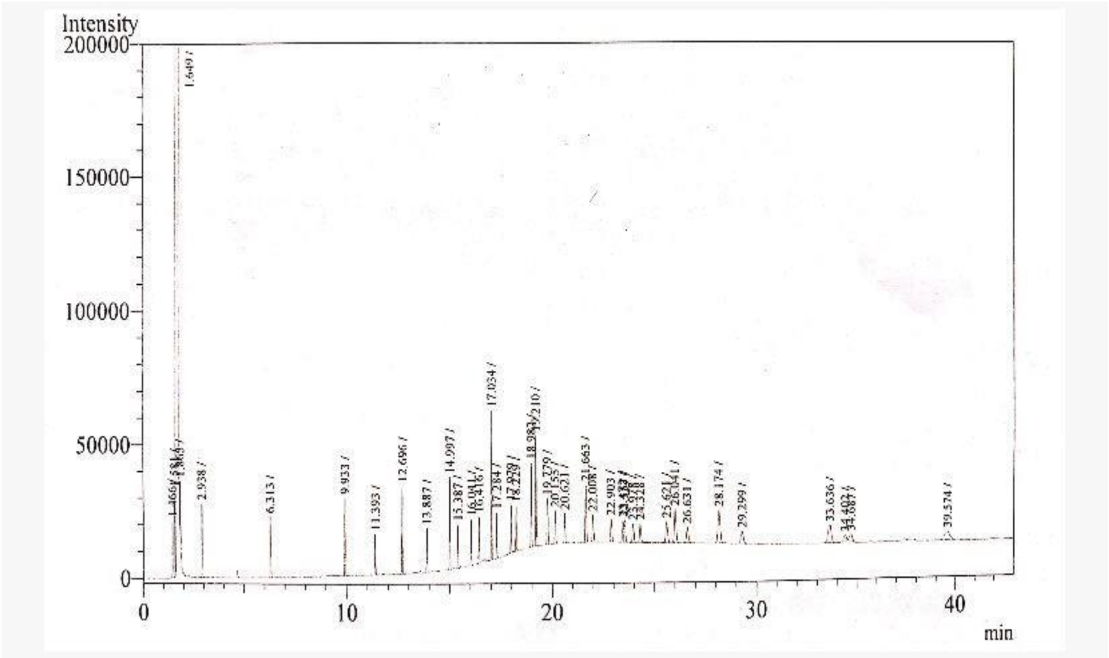


Fig. A-7 The GC chromatogram of FAME

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