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Electrochemical synthesis of methoxide for transesterification of palm oil



Miss Apiruedee Juntuma

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering in Chemical Engineering

Department of Chemical Engineering

FACULTY OF ENGINEERING

Chulalongkorn University

Academic Year 2021

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การสังเคราะห์เมทอกไซด์ด้วยเคมีไฟฟ้าสำหรับปฏิกิริยาทรานส์เอสเทอร์ฟิเคชันของน้ำมันปาล์ม



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

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ปีการศึกษา 2564

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

Thesis Title	Electrochemical synthesis of methoxide for transesterification of palm oil
By	Miss Apiruedee Juntuma
Field of Study	Chemical Engineering
Thesis Advisor	Assistant Professor Palang Bumroongsakulsawat, Ph.D.

Accepted by the FACULTY OF ENGINEERING, Chulalongkorn University in
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อภิฤดี จันทุมมา : การสังเคราะห์เมทอกไซด์ด้วยเคมีไฟฟ้าสำหรับปฏิกิริยาทรานส์เอสเทอร์ฟิเคชันของน้ำมันปาล์ม. (Electrochemical synthesis of methoxide for transesterification of palm oil) อ.ที่ปรึกษาหลัก : ผศ. ดร.พลัง บำรุงสกุลสวัสดิ์

โซเดียมเมทอกไซด์เป็นตัวเร่งปฏิกิริยาเอกพันธ์ชนิดเบสที่นิยมใช้ในการเร่งปฏิกิริยาทรานส์เอสเทอร์ฟิเคชัน ได้เมทิลเอสเทอร์ของกรดไขมัน (Fatty acid methyl ester, FAME) เป็นผลิตภัณฑ์หลักและกลีเซอรอลเป็นผลิตภัณฑ์พลอยได้ แต่ปัญหาหลักของการใช้ตัวเร่งปฏิกิริยาแบบเอกพันธ์คือตัวเร่งปฏิกิริยาละลายลงในสารทำปฏิกิริยา จึงต้องเพิ่มขั้นตอนการปรับสภาพและกระบวนการล้างด้วยน้ำในการแยกผลิตภัณฑ์ออกจากตัวเร่งปฏิกิริยา งานวิจัยนี้ศึกษากระบวนการสังเคราะห์เมทอกไซด์ด้วยเคมีไฟฟ้า โดยใช้เรซินแลกเปลี่ยนประจุลบ แอมเบอร์ไลต์ ไออาร์เอ 402 (Amberlite IRA402 anion exchange resin) เป็นตัวดูดซับเมทอกไซด์ที่ถูกสังเคราะห์ขึ้นและยังเป็นตัวเร่งปฏิกิริยาเอกพันธ์สำหรับปฏิกิริยาทรานส์เอสเทอร์ฟิเคชันเพื่อดูความสามารถในการเร่งปฏิกิริยาของเรซิน ซึ่งแตกต่างจากหลายงานวิจัย การสังเคราะห์นี้ใช้เพียงเรซินแลกเปลี่ยนประจุลบป้อนอิเล็กโทรไลต์ในฝั่งแคโทดซึ่งเป็นที่ที่เมทอกไซด์ถูกสังเคราะห์ขึ้นและเก็บลงในเรซิน โดยไม่จำเป็นต้องสิ่งอื่นเพิ่มเข้าไป เช่น โซเดียมคลอไรด์ หรือน้ำ ซึ่งกำจัดขั้นตอนกระบวนการปรับสภาพและล้างด้วยน้ำ แผ่นใยไทเทเนียมเคลือบด้วยแพลทินัม (platinize titanium fiber felt) ถูกใช้เป็นทั้งขั้วแอโนดและแคโทด เมทอกไซด์ถูกสังเคราะห์ขึ้นด้วยการมีเยื่อแลกเปลี่ยนประจุลบที่ความหนาแน่นกระแสคงที่ที่ 8.25 mA cm^{-2} เป็นเวลา 4 ชั่วโมง เรซินจากการอิเล็กโทรไลซิสมีไฮดรอกไซด์ไอออน $0.00039 \text{ mol cm}^{-3}$ เทียบกับวิธีแลกเปลี่ยนประจุมีไฮดรอกไซด์ไอออน $0.00029 \text{ mol cm}^{-3}$ ผลการทดลองพบว่าเรซินที่ดูดซับไฮดรอกไซด์สามารถเร่งปฏิกิริยาทรานส์เอสเทอร์ฟิเคชันได้ดีกว่าเรซินที่ดูดซับเมทอกไซด์ ดังนั้นการรีเจนเนอเรชันเรซินที่ใช้แล้วด้วยเคมีไฟฟ้าไม่สามารถกู้คืนความสามารถในการเร่งปฏิกิริยาของเรซินกลับมาได้ ผลของปริมาณตัวเร่งปฏิกิริยา สัดส่วนโดยโมลของเมทานอลต่อน้ำมัน และอุณหภูมิของปฏิกิริยา ถูกวิเคราะห์ด้วยวิธีพื้นผิวผลตอบจากการออกแบบส่วนประสมกลาง การวิเคราะห์ทางสถิติแนะนำว่ามีเพียงปริมาณตัวเร่งปฏิกิริยา อุณหภูมิของปฏิกิริยา และความสัมพันธ์ระหว่างปริมาณตัวเร่งปฏิกิริยา อุณหภูมิ ที่ส่งผลอย่างมีนัยสำคัญต่อร้อยละผลได้ของ FAME

สาขาวิชา วิศวกรรมเคมี

ปีการศึกษา 2564

ลายมือชื่อนิสิต

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Apiruedee Juntuma : Electrochemical synthesis of methoxide for transesterification of palm oil. Advisor: Asst. Prof. Palang Bumroongsakulsawat, Ph.D.

Sodium methoxide (NaOCH_3) is commonly used as an alkaline homogeneous catalyst in transesterification to produce fatty acid methyl ester (FAME) and glycerol as a by-product. However, this conventional process requires a few steps to remove the homogeneous catalyst from the products by neutralization and washing, creating waste salts to be treated with additional cost. This study investigates the electrochemical synthesis of methoxide. Amberlite IRA402 anion exchange resin is used to adsorb the generated methoxide and subsequently as a heterogeneous catalyst for transesterification to observe its catalytic activity. In contrast to many other similar works, this synthesis was performed with anion-exchange resin as the only electrolyte in the cathode compartment where methoxide is synthesized electrochemically and stored in the resin without any other additives such as sodium chloride (NaCl) or water needed, eliminating the need for neutralization and washing. Platinized titanium fiber felt was used as electrodes. Methoxide ions can be generated with the presence of an anion-exchange membrane at a constant current density of 8.25 mA cm^{-2} for 4 h. The hydroxide equivalent of electrolyzed resin was $0.00039 \text{ mol cm}^{-3}$, compared with that from ion exchange of $0.00029 \text{ mol cm}^{-3}$. The results of the experiment suggest that hydroxide ions as base in the resin could better catalyze transesterification than methoxide ions; therefore, electrochemical regeneration did not restore its catalytic activity. The response surface methodology (RSM) from a central composite design (CCD) of experiments was conducted to analyze the effects of the catalyst loading, the methanol-to-oil molar ratio, and the reaction temperature. Statistical analysis suggested that only the catalyst loading, the reaction temperature, and the interaction between the catalyst loading and the reaction temperature affected the FAME yield significantly.

Field of Study: Chemical Engineering

Student's Signature

Academic Year: 2021

Advisor's Signature

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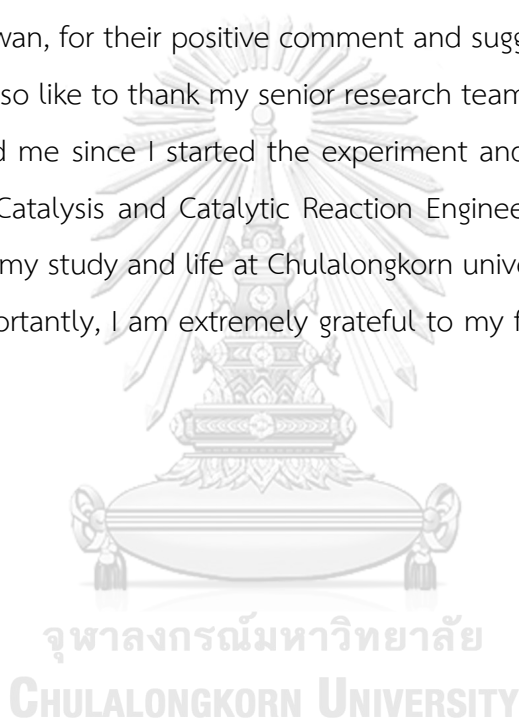


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Chapter I

Introduction

1.1 Motivation

Transesterification is the reaction between triglyceride that is present in vegetable oil and animal fat and short-chain alcohol such as methanol to produce fatty acid methyl ester (FAME) and glycerol as a by-product. FAME is used for both biodiesel and biosolvents applications due to its benefits such as biodegradability, low toxicity, low vapor pressure, non-inflammable and environmental friendliness. Even though in the near future the demand for biodiesel will likely decline following governments' policies on banning diesel engines, the biosolvent applications will still remain. For example, some conventional organic solvents such as toluene, methyl isobutyl ketone and trichloroethylene can be replaced by methyl soyate, a biosolvent, and toxic bis(2-ethylhexyl)-phthalate by ethyl oleate [1].

Alkaline homogeneous catalysts, such as potassium hydroxide (KOH), sodium hydroxide (NaOH) and metal alkoxide [2-5], are commonly used for the transesterification reaction in both laboratory and industrial scales due to their benefits such as short reaction time (30-60 min), high FAME yield (90-99%), and low costs [4, 6]. When NaOH or KOH is used in transesterification, it requires a pre-step to form alkoxide as the actual homogeneous catalyst for transesterification [7, 8]. In addition, the presence of free fatty acid (FFA) in the feedstock causes soap formation that results in decreased FAME yields and difficulties in separation [9]. Although acidic homogenous catalysts can be used with acidic feedstock, their properties cause equipment corrosion [6].

The most metal alkoxide used in transesterification is sodium methoxide (NaOCH_3) due to its high activity and no water formation in the reaction, which prevents the saponification reaction [4, 5]. However, the limitations of the

conventional transesterification process are difficulties in removing the homogeneous sodium methoxide from the products because it is miscible in the reaction mixture. Neutralization and washing of the mixture from the reactor are required for catalyst removal, creating waste, non-recyclable salts to be treated with additional cost [5, 10].

Anion-exchange resin can be used as a heterogeneous catalyst in transesterification to solve these problems associated with homogeneous catalysts, eliminating the need for neutralization and washing. The resin is easily separated from the product and can be regenerated and reused without any loss in catalytic activity [11]. In addition, glycerol [12, 13] as a by-product and some impurities of feedstock such as FFA, water and dark brown pigment [13, 14] are removed by being adsorbed in the resin. The extent of adsorption should also depend on resin to oil ratio. Regeneration of used resin with three steps: washing with citric acid, soaking with NaOH, washing with water and followed by methanol appeared to recover the resin's catalytic activity [11]. Nevertheless, this regeneration method generates wastes which will incur treatment cost.

Electrochemical processes are always involved in the production of NaOCH_3 ; sodium metal (Na) [15, 16], sodium amalgam (NaHg) [17], or NaOH [18], each of which must be synthesized electrochemically, is reacted with methanol to produce NaOCH_3 . From the standpoint of process intensification, electrochemical techniques may be employed directly during transesterification to generate methoxide in situ. Transesterification of triglyceride with alcohol can be performed by an electrocatalytic process with additives such as sodium chloride (NaCl) and water as a supporting electrolyte to increase the electrical conductivity [19-22]. However, this process still generates methoxide as a homogeneous catalyst and therefore catalyst separation is still an issue.

This research focuses on improving the electrochemical synthesis of methoxide. Amberlite IRA402 anion exchange resin was used to adsorb methoxide generated by electrolysis of pure methanol and also as the only electrolyte without any other additives such as water or NaCl, eliminating the need for neutralization and washing. Used resin was regenerated by electrochemical techniques and reused in

transesterification to observe the catalyst's reusability. The response surface methodology (RSM) based a central composite design (CCD) was used to design the experiment and analyzed the effects of catalyst loading, reaction temperature and methanol-to-oil molar ratio.

1.2 Research objectives

To investigate the synthesis of methoxide by electrolysis of methanol, Amberlite IRA402 anion exchange resin as an electrolyte and adsorbent for the generated methoxide.

To study the use of synthesized electrolyzed resin and ion-exchanged resin as a heterogeneous catalyst in the transesterification of refined palm oil and methanol.

To investigate the electrochemical regeneration of used ion-exchanged resin.

1.3 Research scope

1.3.1 Methoxide synthesis

1.3.1.1 Methoxide-resin is synthesized by electrolysis of methanol, with Amberlite IRA402 anion exchange resin as the only electrolyte added.

1.3.1.2 Electrochemical process is carried out in a two-chamber electrochemical cell with the presence of anion-exchange membrane at a constant current density of 8.25 mA cm^{-2} .

1.3.1.3 An anode compartment was filled with ion-exchanged resin in methanol, and cathode compartment was filled with resin in Cl form in methanol.

1.3.2 Transesterification

1.3.2.1 Ion-exchanged resin and electrolyzed resin were used as heterogeneous catalysts.

1.3.2.2 Refined palm oil and methanol were used as reactants.

1.3.2.3 Transesterification was carried out by catalyst loading of $0.1475\text{--}0.2949\text{ cm}^3\text{ g}_{\text{oil}}^{-1}$, methanol-to-oil molar ratio of 6:1-13:1, reaction temperature at 50-60 °C at a constant stirring speed of 1500 rpm for 4 h.

1.3.3 Electrochemical regeneration

1.3.3.1 The used resin was washed with methanol for the pre-steps to clean the resin.

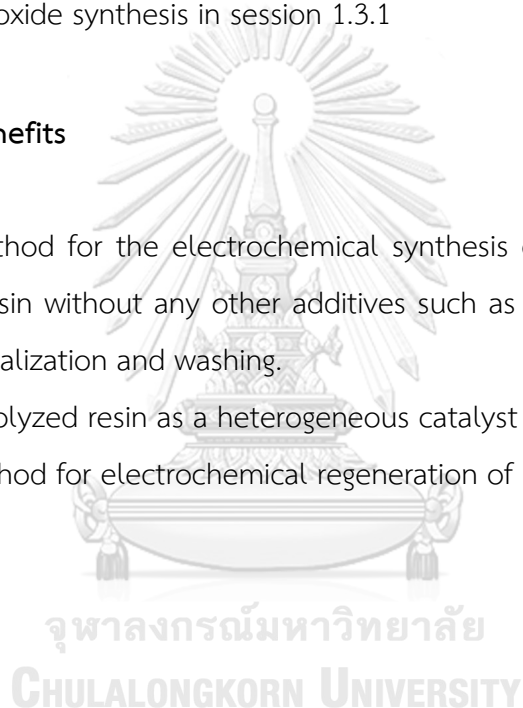
1.3.3.2 Electrochemical regeneration is carried out with similar condition of methoxide synthesis in session 1.3.1

1.4 Expected benefits

14.1 A method for the electrochemical synthesis of methoxide adsorbed in anion-exchange resin without any other additives such as NaCl or water, eliminating the need for neutralization and washing.

14.2 Electrolyzed resin as a heterogeneous catalyst for transesterification.

14.3 A method for electrochemical regeneration of used ion-exchanged resin



Chapter II

Theory and literature reviews

2.1 Transesterification

Transesterification is a reaction between triglycerides, as present in vegetable oils and animal fats, and short-chain alcohol such as methanol and ethanol to produce FAME or FAEE (fatty acids ethyl ester) and glycerol as a by-product. In Thailand, palm oil is usually used as a feedstock because Thailand is the third-largest producer of palm oil in the world. Methanol is commonly used for transesterification due to its properties such as high reactivity, low cost, and availability [5, 23].

As shown in Eq. (1), the stoichiometry of the reaction is 1:3 triglyceride to alcohol, and the reaction is reversible. To force the reaction to generate the product side, a fatty acid ester and glycerol, requires an excess of alcohol. The mechanism of transesterification is presented in Eqs. (2)-(4). It consists of three reversible reactions, and each step produces one mole of fatty acid ester. The intermediates in this process are diglycerides and monoglycerides [7, 8].



2.2 The catalysts

Alkaline homogeneous catalysts such as NaOH, KOH and NaOCH₃ are commonly used for transesterification [24]. The Industrial scale used the homogeneous alkaline catalyst for the reaction because of its benefits such as short reaction time (30-60 min), high FAME yield (90-99%), and inexpensive [4, 6]. However,

the purity of the feedstock is a limitation of the alkaline homogeneous catalyst for transesterification. As demonstrated in Eq. 6, alkaline soap formation (RCOONa), which is miscible in the products and results in decreased FAME yields and difficulties in separation, is prevented when the FFA of the feedstock is less than 0.5 % [6, 13, 24]. The active intermediate methoxide was suppressed by water that presents in feedstock [13]. In addition, the glycerol produced contains 5-7% salts, as a result, the cost of the purification step is increased [25].



Acidic homogenous catalysts such as sulfuric acid (H_2SO_4), hydrochloric acid (HCl), sulfonic acid ($\text{H}_2\text{O}_3\text{S}$) and phosphoric acid (H_3PO_4) have low susceptibility to FFA in the feedstock, and it can simultaneously catalyze both esterification of FFA and transesterification of triglycerides. Therefore, acid catalysts can solve the limitation of alkali catalysts [6, 24]. Nevertheless, the weaknesses of the acid catalysts are slow reaction rate, the long reaction time (50 h), requiring the high molar ratio of alcohol to oil (30:1) and corrosive of a reactor [6, 26, 27].

Furthermore, the drawback of the conventional process is difficulties in removing the homogeneous sodium methoxide from the products because it is miscible in the reaction mixture. Neutralization and washing of the mixture from the reactor are required for catalyst removal, creating waste, non-recyclable salts to be treated with additional cost [5, 10].

As a result, the heterogeneous catalyst can overcome the drawbacks of homogeneous catalysts. The heterogeneous catalyst can be easily separated from the product eliminating the need for neutralization and washing, which reduces the amount of wastewater generated, and it can be reused. Furthermore, it does not produce soap throughout the process and can be used in continuous processing [10, 24, 28].

2.2.2 Ion exchange resin

Ion exchange resin is one kind of heterogeneous catalyst. There are two types: (a) anion-exchange resin and (b) cation-exchange resin

Anion-exchange resins may be either strongly or weakly basic, which differ in their functional groups. The Strongly basic are of quaternary amino groups ($-N^+(CH_3)_2C_2H_4OH$), but the weakly basic are of amino groups ($N^+(CH_3)_3$). Both types are formed in gel or macroporous structures. The resins consist of a polymer matrix with functional groups such as OH^- , RO^- or HCO_3^- [20]. Due to the anion-exchange resin with a lower crosslinking density and a smaller particle size than the cation exchange resin caused a high reaction rate and conversion. Therefore, the anion-exchange resins have a greater potential than the cation-exchange resin from the viewpoint of catalytic activities [11].

Anion-exchange resin is commonly supplied in two forms: chloride and hydroxide. Because of its highly porous structure, the resin may hold a huge amount of liquid phases, such as water molecules. For transesterification, the resin requires pretreatment steps for removing the water, which could deactivate the resin's activity, by washing with the same solvent used in transesterification [28, 29].

In the case of resin Cl form used in transesterification, it is necessary to displace Cl^- ions with OH^- ions by mixing with a base solution such as 1M NaOH or 5% NaOH. Subsequently, the resin is washed with DI water to remove the excess NaOH, and ethanol is then used to remove water [11, 13, 30]. The resin should be stored by soaking with alcohol to prevent the active site (OH^-) of the resin reacting with carbon dioxide (CO_2) in the air, which forms hydrogen carbonate (HCO_3^-) [29, 30]. The mechanism pathway for transesterification of methanol with Amberlyst A26OH and triglycerides with/without FFA is described in Figure 1. The OH^- presented in the resin reacts with methanol to form CH_3O^- , and the CH_3O^- is adsorbed in the basic resin surface as a heterogeneous catalyst. After that, triglyceride reacts with resin surface bond CH_3O^- to produce FAME and glycerol [31].

The mechanism for transesterification using anion-exchange resin OH^- form is proposed in Eqs. (6)-(9). The resin OH^- form reacts with methanol to form an alkoxide ion and H^+ ion. The formed alkoxide attacks the carbonyl carbon atom of

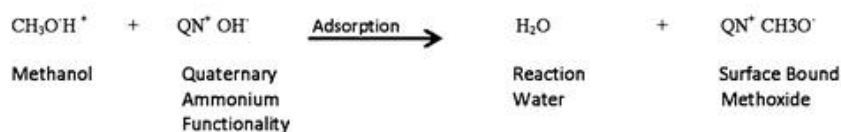
the triglycerol (TG) molecule, which produces methyl ester (ME) and an ionized diglyceride(D⁻).



The impurities of the feedstock, FFA, water and dark brown pigment, were removed by the adsorption on the resin [13, 14]. The Amberlyst A26OH [29] and Doaion PA306 [14], anion-exchange resin, were used in transesterification. There has a good performance for FFA removal, and the FAME purity was close to 100% at molar ratio of oil:methanol of 3:1 due to no soap formulation during the process [14]. As shown in Figure 1 [31], the glycerol as a by-product was also removed by the adsorption on the resin. No glycerol was detected at molar ratio of waste cooking oil:methanol of 3:1 [13] and soybean oil: methanol below 9:1 [12]. However, the extent adsorption should also depend on resin-to-oil ratio.

In addition, 0-1.0 wt.% water that is produced from a reaction between hydroxide ion and methanol affects the transesterification because the catalytic active site (OH⁻) of the resin was deactivated by water because of bonding of water molecules more efficiency than methanol. When the water was fully absorbed on the active site, more water content was not affected on the FAME conversion [12, 31]. However, water formation in the reaction and water presented in oil should be removed to prevent triglyceride hydrolysis as a side reaction, and oil without FFA as reactants in transesterification over the anion-exchange resin as a catalyst can be prevented the deactivation of the catalytic active site.

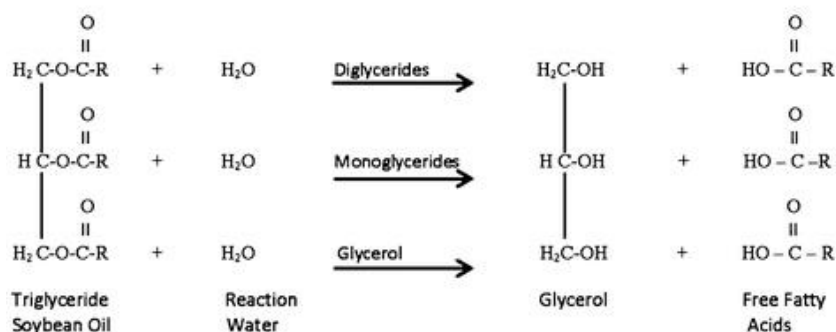
Step 1. Methanol adsorption by ion exchange on basic resin surface.



Step 2. Fatty acid (Oleic Acid) adsorption by ion exchange on basic resin surface.



Step 3. Hydrolysis of glycerides (Tri, Di, Mono) from soybean oil.



Step 4. Transesterification of glycerides (Tri, Di, Mono) with basic resin surface bound methoxide.

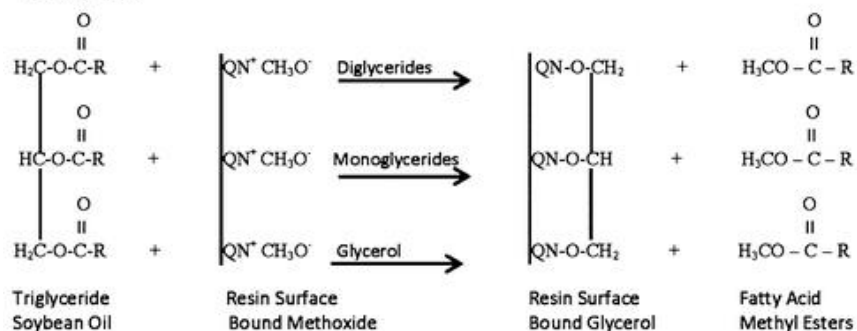


Figure 1 Transesterification pathway of triglycerides that present in soybean oil with/without oleic acid (free fatty acids) over Amberlyst A26OH basic ion-exchange resin. (R = alkyl group) [31]

Ferreira et al.[30] used the Purolite A503s anion exchange resin, ethanol and palm olein and achieved a conversion of 98.10% in ethyl ester using a jacketed batch reactor to perform at optimal parameters that using oil: ethanol

molar ratio of 1:12.85, 17.6% catalyst. stirring at 400 rpm for 10 h, and a thermostatic bath was used to control the reaction temperature at 49.4 °C, the schematic of transesterification is shown in Figure 2. Furthermore, High FAME conversion (>90%) was obtained in transesterification with anion-exchange resin as the catalyst [11, 12, 28-30].

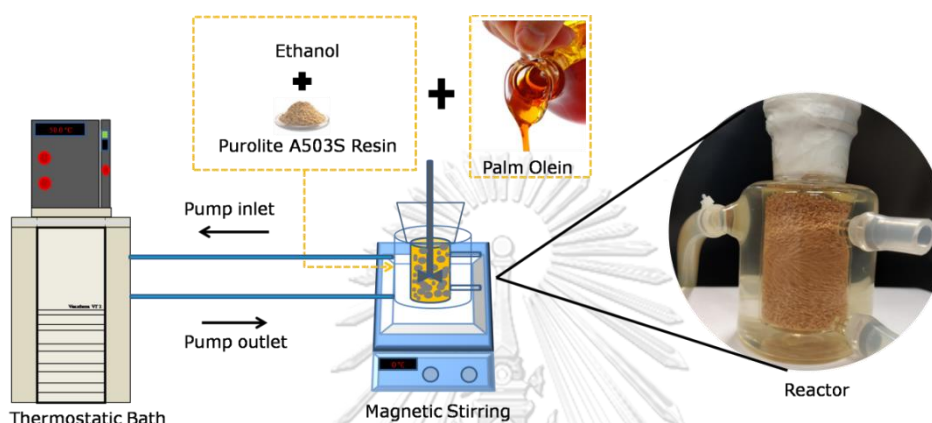


Figure 2 The schematic of transesterification [30]

2.2.2.1 Regeneration method of the resin used.

After the end of the experiment, the resin is easily separated by filtration, and it was regenerated by the following three steps: (1) the used resin was washed with acidic solution such as 5 v/v % citric acid in ethanol [11] or 0.43 M acetic acid in methanol [13] to remove the organic substances such as the fatty acid ions or glycerol that cover the active sites of the resin; (2) the resin was replaced the acetic ion with the OH^- ion by a 1M NaOH solution, and then it was washed with the water to remove the NaOH aqueous solution; (3) restoring the initial swelled condition by washing with ethanol or methanol.

After the transesterification of waste cooking oil with ethanol, used PA306S anion exchange resins were treated with various combination steps and repeated for transesterification to observe the catalytic activity which was compared with the original experiment. The results are shown in Figure 3. The catalytic activity of the resins treated by only the third step and combining first with the third step are found to significantly decrease after the original experiment. But the catalytic activity increases by adding the second step for replacement with OH^- ions. The OH^- ion

reacts with ethanol to form ethoxide, which is the active species, for transesterification of triglyceride to produce the ethyl oleate. Therefore, the absence of the second step leads to decreasing ethyl oleate conversion. Furthermore, the conversion of the resin treated with all three steps and the conversion of the original experiment remained almost constant at 5 h for four times [11]. Besides, Naomi Shibasaki-Kitakawa et al. [13] founded the used resin that was regenerated by all three steps to repeat for transesterification without any loss in catalytic activity.

The Used D261 anion exchange resin as a catalyst in the reaction between soybean oil and methanol was regenerated by flushing with methanol to remove the organic substance such as esters or glycerol covered on the resin surface and washing with 5 wt.% of KOH in methanol to activate the resin as the fresh resin. Although this regeneration contains only two steps, the FAME conversion can keep above 90% of each run for five cycle experiments [12]. Therefore, the anion-exchange resin has the potential for continuous biodiesel production and excellent catalytic reusability.

Nevertheless, these regeneration methods generate wastes which will incur treatment cost.

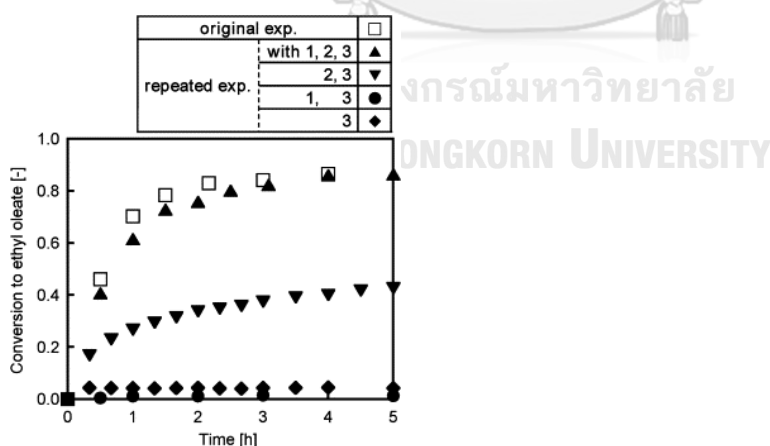


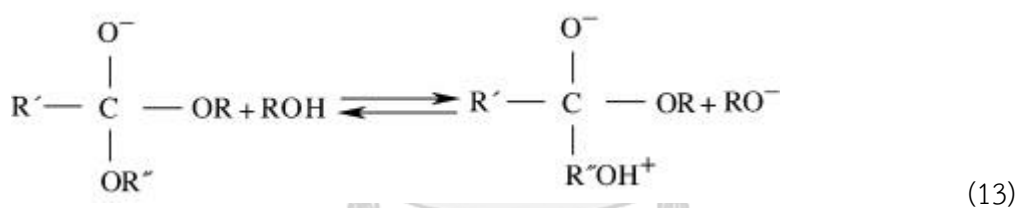
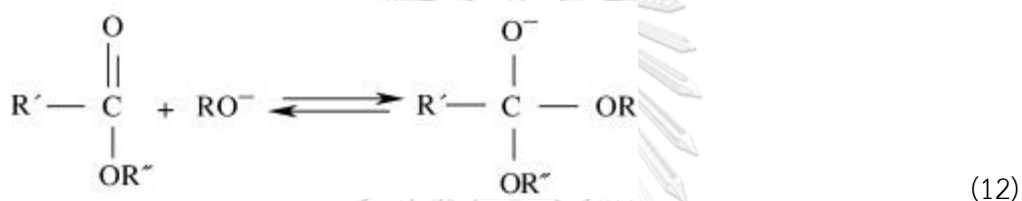
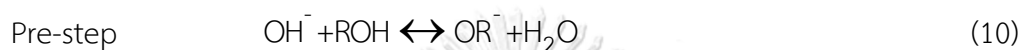
Figure 3 The effect of each trigeneration step of the used resin on conversion to ethyl oleate [11]

2.2.1 Methoxide

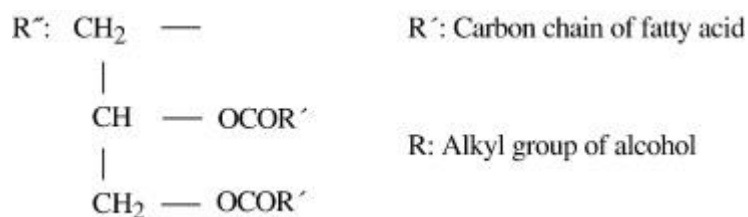
NaOH or KOH was used in transesterification, it is necessary to replace the base form with alkoxide (RO^-), as shown in Eq. (10). As indicated in Eq. 11, when

NaOCH₃ is employed, it converts to RO⁻ and Na⁺ ions. Eqs. (12)-(14) illustrate three steps in the mechanism of alkaline catalyzed transesterification [7, 8]. First, RO⁻ ion attacks the carbonyl carbon atom of ester to produce a tetrahedral intermediate. The intermediate is then reacted with alcohol to generate the RO⁻ ion. Finally, a tetrahedral intermediate is rearranged to produce a fatty acid ester and a diglyceride.

Therefore, alkoxide is an actual homogeneous catalyst for transesterification reaction.



where



Alkoxide in form of NaOCH_3 is usually used as homogeneous catalyst in transesterification and no water formation in the reaction which prevent saponification as a side reaction [5]. Several studies investigated using 25-30% of NaOCH_3 in methanol as a homogeneous catalyst to improve the FAME yield for transesterification [4, 32, 33]. Lin et al.[4] obtained 99.7% biodiesel yield at 0.75 wt.% NaOCH_3 , palm oil to methanol molar ratio of 1:6 and reaction time of 3 min. However, after the end of the transesterification, the catalyst was removed by adding the silica gel [4].

2.2.1.1 Routes for synthesis of sodium methoxide

The four routes to produce NaOCH_3 are described in terms of raw materials [32]. In process I, sodium metal (Na) which is produced by electrolysis of molten sodium chloride deposited at the cathode [15] or NaOH with the Castner cell [16] is the raw material for NaOCH_3 production. Na is melted and reacted with methanol in a jacketed reactor with an agitator. The process is simple and high yield and purity of NaOCH_3 . Nevertheless, close control is required to avoid the risk of explosion due to the high reactivity of Na, the release of hydrogen (H_2) and the highly exothermic reaction. In addition, the cost of Na as a raw material is expensive [34].

In process II, NaOCH_3 is generated from sodium amalgam (NaHg) which is the product of NaCl brine in mercury cathode cells [16]. The chlorine gas formed at the anode, while the sodium metal formed at the cathode dissolves in the mercury to generate the NaHg . This NaOCH_3 process is simple, low operating and raw material costs. Although NaHg is employed as a reactant to slow down the interaction of an alkaline metal with alcohol, the final product contains poisonous mercury, which is a source of concern for the environment [17].

In process III, NaOCH_3 is produced from NaOH as inexpensive raw material and methanol by a relative stripping column. The concentration of NaOCH_3 is 20-40 wt.% in methanol. Although this process is safe to operate, it requires a separation unit to separate methanol from water because of the methanol in vapor distillates contaminating with 3-10% water [18]. Moreover, the Industrial

scale of NaOH production is produced from the electrolysis of sodium chloride solution which is the chloralkali process [35].

In process IV, methanol solution of sodium acetate (NaOOCCH_3), which is the product from NaOH and acetic acid, is used to form NaOCH_3 and acetic acid (CH_3COOH) by electrodialysis. 11 wt.% of sodium acetate in methanol was entered through the anode, and it releases the Na^+ ions. These ions pass through a cation exchange membrane and react with methanol to form NaOCH_3 and release H^+ . Methanol is generated by H^+ ions crossing a bipolar membrane and reacting with acetate ions. This process obtains pure NaOCH_3 in methanol. However, it requires an additional step to produce the dilute from the acetic acid exiting of the electrodialysis-cell stack and is difficult to scale up [36].

The routes for producing NaOCH_3 for transesterification all have two steps. The electrochemical processes produce raw materials: Na, NaHg, or NaOH and reacts with methanol to generate NaOCH_3 in a difference of ways.

Therefore, this research studies the process intensification for the synthesis of methoxide and then adsorbing the created methoxide in the anion-exchange resin by electrochemical for transesterification, removing the salt washing step and reducing the cost and procedure.

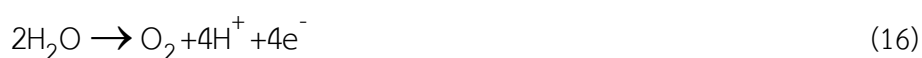
2.2.1.2 Electrochemical synthesis of methoxide

Electrochemical techniques may be employed directly during transesterification to generate methoxide which is the active species in the production of FAME in situ. Eqs. (15)-(19) show the mechanism of electrocatalytic transesterification. NaCl and water are introduced in an electrolysis cell. The Cl^- ions and water are oxidized into chloride (Cl_2) and oxide (O_2) on the anode, Eqs. (15)-(16). The OH^- ions are generated from water on the cathode, Eq. (17), and then OH^- ion reacts with methanol to form CH_3O^- ion, which is a strong nucleophilic active species, Eq. (18). The CH_3O^- ion then attacks the carbonyl moiety in glyceride molecules, resulting in FAME and glycerol as a by-product, Eq. (19) [19, 20].

Water [37], NaCl or both water and NaCl [19, 21, 22] are used as supporting electrolytes to increase the electrical conductivity. The resistance of

the system is reduced by increasing the total concentration of ions in the electrolyte by NaCl [38]. However, this process involves free electrolytes which can be formed NaOCH₃ in methanol as a homogeneous catalyst, as a result, a few steps are required to remove the catalyst by neutralization and washing.

Anodic reaction



Cathodic reaction



Proton transfer reaction



Transesterification



2.3 Reaction parameters affecting transesterification

The transesterification of triglycerides with alcohols to create FAME or FAEE and glycerol is influenced by several parameters. Table 1 shows the optimal condition of each major reaction parameter that affects yield (%) using anion-exchange resin as a heterogeneous catalyst.

2.3.1 Oil to alcohol molar ratio

Transesterification is a reversible equilibrium reaction, and excess alcohol can be shifted the equilibrium toward the product side [8]. The stoichiometry of transesterification of triglyceride, 3 mol of fatty acid ester and 1 mol of glycerol are produced from 1 mol of triglycerides and 3 mol of alcohol. Moreover, the alcohol to oil molar ratio is related to the type of catalyst [27]. For the Purolite A503S anion exchange resin as a heterogeneous catalyst, an increase of oil to alcohol

molar ratio from 1:7.96 to 1:16 increases the yield and purity of FAEE [30]. However, the FAME conversion dropped when excess alcohol due to the dilution of triglyceride molecules and a decrease in driving force between ethanol and triglycerol [12, 30]. The range of palm oil to ethanol molar ratio between 1:3.5 and 1:6 using in transesterification over Amberlyst A26OH catalyst was achieved high conversion to FAME over 96% [28].

In addition, glycerol was adsorbed on the resin when the molar ratio of methanol to soybean oil is below 9:1 [12].

2.3.2 Reaction Temperature

One of the parameters affecting FAME conversion and reaction rate is reaction temperature. Low reaction temperature (33.12 °C) is related to low FAME conversion due to a decrease in the fluidity of the reaction mixture, an increase in viscosity of palm olein and the reduction in mutual solubility of palm olein and ethanol, that affects the mass transfer inside pores and an increase in the reaction time [28, 30]. However, the reaction temperature at 60 °C is limited by the property of the OH⁻ form of the anion-exchange resin such as Purolite A503S [30], and the temperature should be maintained below the boiling point of alcohol to prevent alcohol evaporation. In addition, at 60°C temperature, the reaction equilibrium changed and reversed because of the glycerol present in the mixture [39]. Therefore, the optimal reaction temperature range is between 45 and 60 C, which depends on the type of triglyceride [9, 28, 30].

2.3.3 Catalyst content

The most important variable that affects FAME yield is the amount of catalyst. A decrease in the catalyst content is related to a decrease in FAEE conversion because of the lower availability of the active site reacting with ethanol to form ethoxide which is the active species for transesterification [30]. Ferreira et al. [30] studied the FAEE conversion using the Purolite A503S anion exchange resin with palm olein and ethanol. The amount of catalyst increased from 12.5 to 17.5% and

consequently increased the FAEE conversion from 87.7% to 97.59%. However, an excess of the catalyst (19.2%) can increase the effective resistance between the reactants and the catalyst, increasing the viscosity of the mixture, which results in a decrease in the FAME conversion [30, 39].

2.3.4 Reaction time

The reaction time for transesterification is also important. An increase in reaction temperature leads to an increase in the reaction rate and short reaction time. Therefore, the FAME conversion increases with increased reaction time. However, the FAME conversion decreases with increased reaction time beyond the point that obtains optimal conversion due to soap formation [9].

2.3.5 Stirring speed

The stirring speed affects product formulation. When the heterogeneous catalyst is used for transesterification, the suspension and precipitation of the catalyst are considered. If the case of some catalyst particles is not suspended and remains at the bottom, the stirring speed needs to be increased [30].

Table 1 Summary of some studies for transesterification using anion-exchange resin as a heterogeneous catalyst

Feedstock	Alcohol	Catalyst	Catalyst, wt. %	oil:alcohol molar ratio	Temperature, °C	Time, h	Stirring speed, rpm	Yield, %	Ref.
Palm olein	Ethanol	Purolite A503s	17.5	1:13	50.1	10	400	98.1	[30]
Palm olein	Ethanol	Amberlyst A26OH	11.36	1:6.8	55	8	400	>96	[28]
Acid soybean oil	Ethanol	Amberlyst A26OH	20	1:9	50	6	500	>90	[29]
Acid soybean oil	Methanol	Amberlyst A26OH	20	1:10	50	-	550	0.008 ^a	[31]

^a Concentration of esters (mol L⁻¹)

Chapter III

Materials and methods

The experiments are divided into three parts. In the first part, electrochemical conversion of anion-exchange resin (Amberlite IRA402) from chloride form to methoxide form without any additional electrolyte is demonstrated. The second part proves that transesterification with the resin prepared by both non-electrochemical means, i.e. ion exchange, and electrochemical means can be achieved. The last part shows the electrochemical regeneration of used ion-exchanged resin to restore its catalytic activity for transesterification.

3.1 Materials

Amberlite IRA402 anion exchange resin in chloride form (Sigma-Aldrich) was employed as an electrolyte and adsorbent for synthesizing methoxide-resin. The characteristics of Amberlite IRA402 resin are shown in Table 2. Pure palm oil (Morakot) and Methanol (Merck) were used as the reactants for transesterification. Methanol from the source was also used for methoxide-resin synthesis. Sodium chloride (Merck) was used for the determination of methoxide content in resin by the ion exchange.

Table 2 Amberlite IRA 402 anion exchange resin's physical and chemical characteristics

Characteristics	Details
Copolymer-matrix	Styrene-divinylbenzene (gel)
Type	Strong base anion, Type I
Functional group	Trimethylammonium
Ionic form as shipped	Cl ⁻
Total exchange capacity	≥1.2 eq/L (Cl ⁻ form)

Characteristics	Details
Particle density	1.07 g/mL
Particle diameter	600-750 μm
Temperature limit. OH^- form	5-60 $^{\circ}\text{C}$
Temperature limit. Cl^- form	5-100 $^{\circ}\text{C}$

3.2 Methods

3.2.1 Electrochemical synthesis of methoxide

Methoxide was generated by electrolysis of methanol in a two-compartment electrochemical cell 3D-printed from polypropylene filament to withstand methanol. The printed cell can be assembled with or without an anion-exchange membrane (Figure 4). The volume of the cathode compartment where methoxide was generated was $1 \times 2 \times 2 \text{ cm}^3$. Two pieces of platinized titanium fiber felt with the same active geometric area of $2 \times 2 \text{ cm}^2$ were used as both the anode and the cathode.

Amberlite IRA402 anion exchange resin in chloride (Cl^-) form is pretreated by washing with methanol to remove water adsorbed inside. The procedures to produce electrolyzed resin are shown in Figure 5. The cathode compartment of the electrochemical cell was filled with 4 cm^3 of the resin in Cl^- form. The anode compartment contains ion-exchanged resin, and it was added until its height match that of the resin on the cathode side. Ion-exchanged resin was used to lower the cell potential. Methanol was added in the cathode and anode compartments until the resin was fully submerged. Methanol was constantly added to make up the amount evaporated during electrolysis.

Electrolysis was carried out in the presence of anion exchange membrane at a constant current density of 8.25 mA cm^{-2} , which was an absolute current of 33 mA for this cell, for 4 h to observe the behaviors that occur in the cell. The electrolysis current was supplied by a direct current (DC) power supply.

Appendix A1 shows the calculation of the reaction time to create methoxide to the maximum capacity of the resin at the electrolysis current of 33 mA.

In addition, electrolysis (blank) was carried out with a similar condition as described previously, but it does not apply the electrical current.

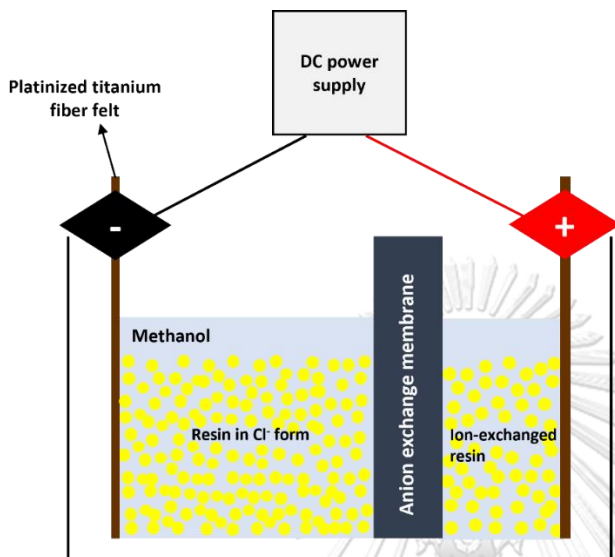
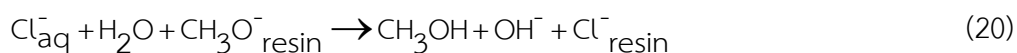


Figure 4 Electrolysis cell with presence of the anion exchange membrane

3.2.2 Analysis of hydroxide

The electrolyzed resin was washed with methanol. Then, the resin was stirred and left in 64 ml of 0.75 M NaCl solution for 5 min to displace adsorbed CH_3O^- ions in the resin with Cl^- ions. This procedure was carried out at a constant ratio of resin to NaCl of 1 cm^3 resin to 0.012 mol of NaCl. The pH of the resulting aqueous solution was measured using pH indicator strips or a pH meter. The reaction pathway of this method is shown in Eq. (20).



The procedures for analysis of methoxide are shown in Figure 6.

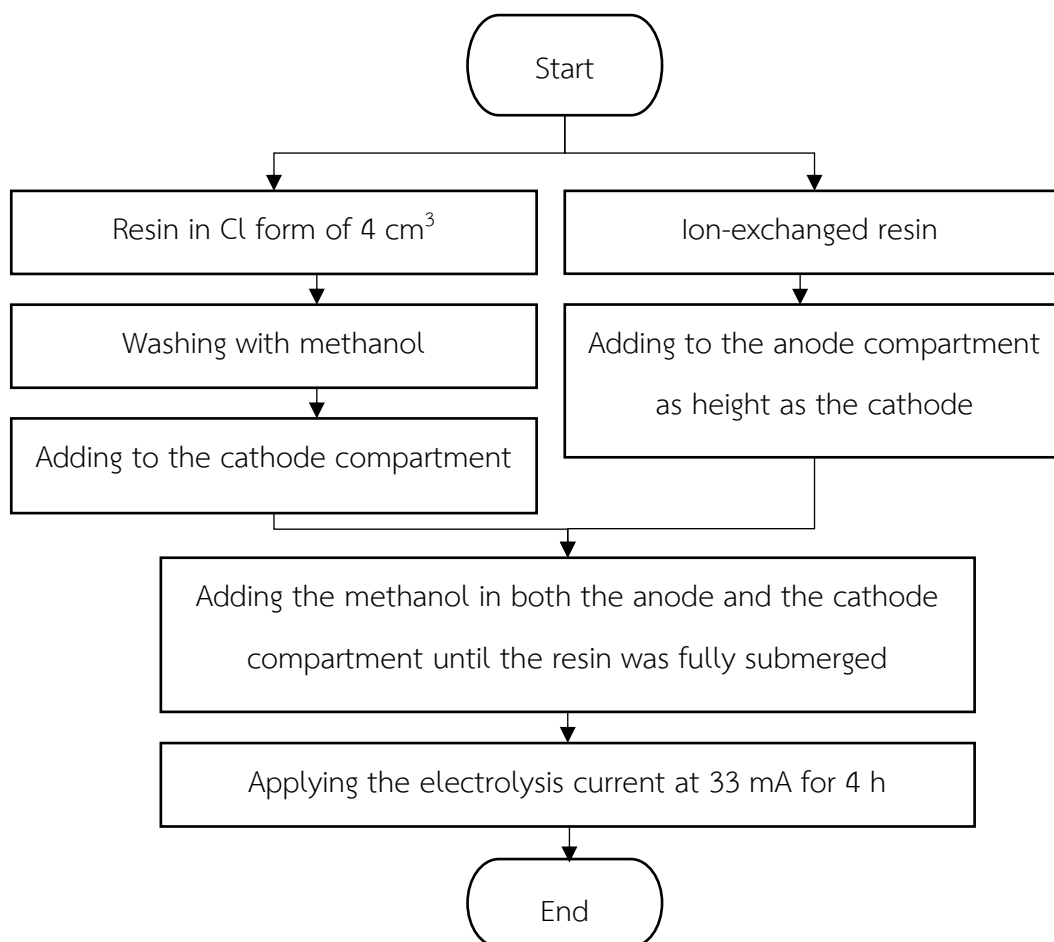


Figure 5 Flowchart of electrochemical synthesis of methoxide

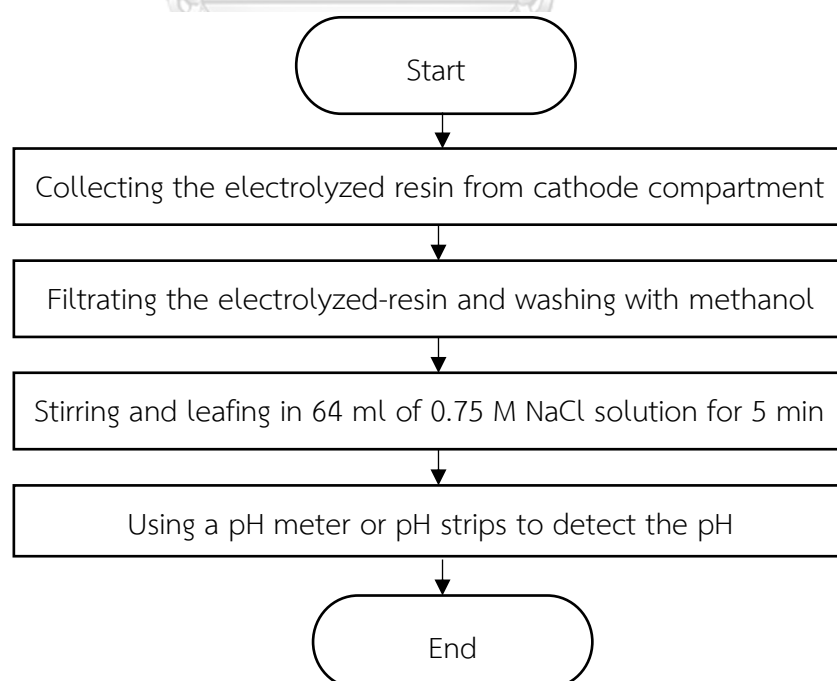


Figure 6 The procedures for analysis of hydroxide equivalent

3.2.3 Resin activation by ion exchange

For the first runs of transesterification, the Cl^- ion of the resin is replaced with OH^- ion by stirring with 1.5 M NaOH aqueous solutions for 5 min, the resin was washed with deionized (DI) water to withdraw the excess NaOH and then washed with methanol to remove water.

3.2.4 Transesterification reaction

The experiment set up is shown in Figure 7. The transesterification reaction of palm oil with methanol was performed by a three-neck jacketed reactor with a thermostatic water bath to control temperature. The reactor was placed on a magnetic stirrer with a magnetic bar for mixing the mixture solution. A thermometer was placed inside the reactor to monitor the reaction temperature. A condenser was used to recondense evaporated methanol back to the reaction mixture.

The procedures to produce FAME are shown in Figure 9. First, palm oil was placed inside the reactor and heated until the desired reaction temperature was reached. After, the methoxide-resin and methanol were mixed and added to heated palm oil in the reactor. Then, the mixer solution of methoxide-resin, methanol and palm oil was heated to the reaction temperature, and the reaction time was started.

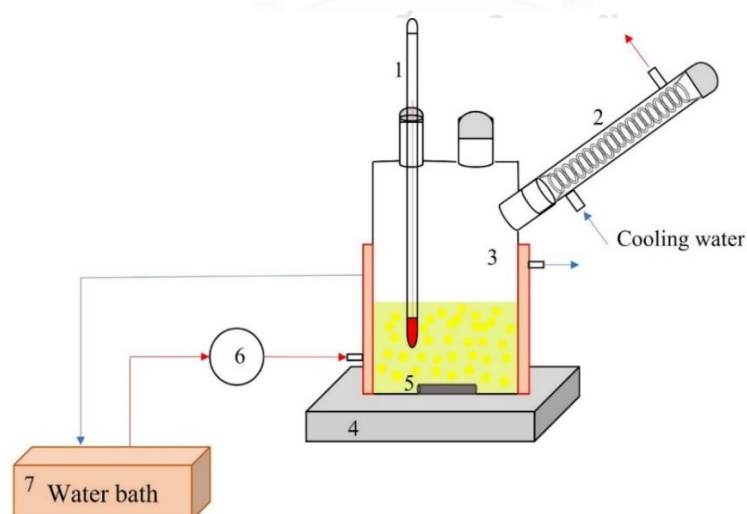


Figure 7 Schematic reaction apparatus in transesterification: (1) thermometer, (2) Condenser, (3) a three-neck jacketed reactor, (4) magnetic stirrer, (5) magnetic bar, (6) pump, (7) water bath

3.2.6 Experimental design

The effects and interaction of the catalyst loading, methanol-to-oil molar ratio and reaction temperature on FAME yield were evaluated by the response surface methodology (RSM) to design the experiment runs. The type of design is a central composite with two levels, three factors (factorial design ($\text{Level}^{\text{factor}}$) + axial points ($2 \times \text{factor}$), Figure 8 and Table 3), six axial points and three repetitions at the central point, totaling 17 experiments as presented in Table 4.

The second order polynomial model was fitted with the result of experiment data, and T-test was used to assess significant variables and the coefficient of the regression equation.

The reaction time and stirring speed were fixed as 4 h and 1500 rpm, respectively.

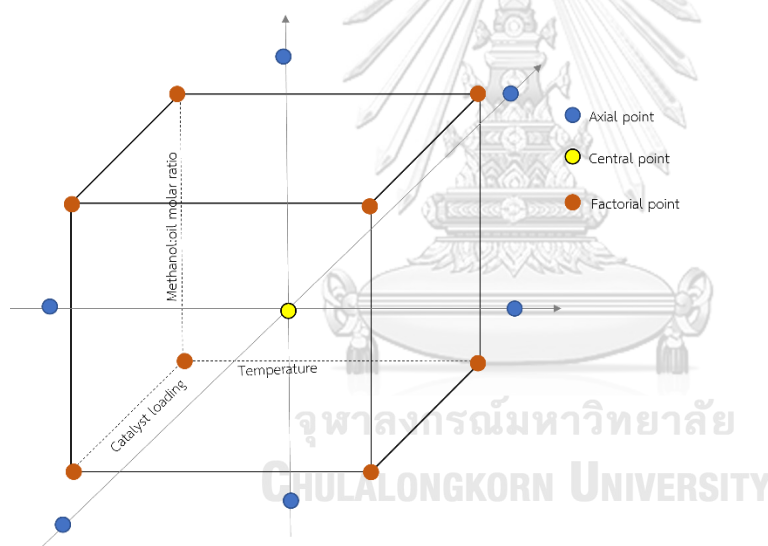


Figure 8 Central composite design (CCD)

Table 3 Factors and levels variables of the central composite design

Factors	Levels				
	-1.68	-1	0	1	+1.68
Catalyst loading ($\text{cm}^3 \text{g}_{\text{oil}}^{-1}$)	0.0972	0.1475	0.2212	0.2949	0.3452
Methanol to palm oil molar ratio	3.61:1	6:1	9.5:1	13:1	15.38:1
Temperature ($^{\circ}\text{C}$)	46.59	50	55	60	63.40

Table 4 Design table for transesterification of palm oil with methanol over ion-exchanged resin as a heterogeneous catalyst

Test	Catalyst loading ($\text{cm}^3 \text{g}_{\text{oil}}^{-1}$)	Methanol-to-oil molar ratio	Temperature ($^{\circ}\text{C}$)
1	0.1475	6:1	50
2	0.2949	6:1	50
3	0.1475	13:1	50
4	0.2949	13:1	50
5	0.1475	6:1	60
6	0.2949	6:1	60
7	0.1475	13:1	60
8	0.2949	13:1	60
9	0.0972	9.5:1	55
10	0.3452	9.5:1	55
11	0.2212	3.61:1	55
12	0.2212	15.39:1	55
13	0.2212	9.5:1	46.59
14	0.2212	9.5:1	63.41
15(CP)	0.2212	9.5:1	55
16(CP)	0.2212	9.5:1	55
17(CP)	0.2212	9.5:1	55

CP=central point

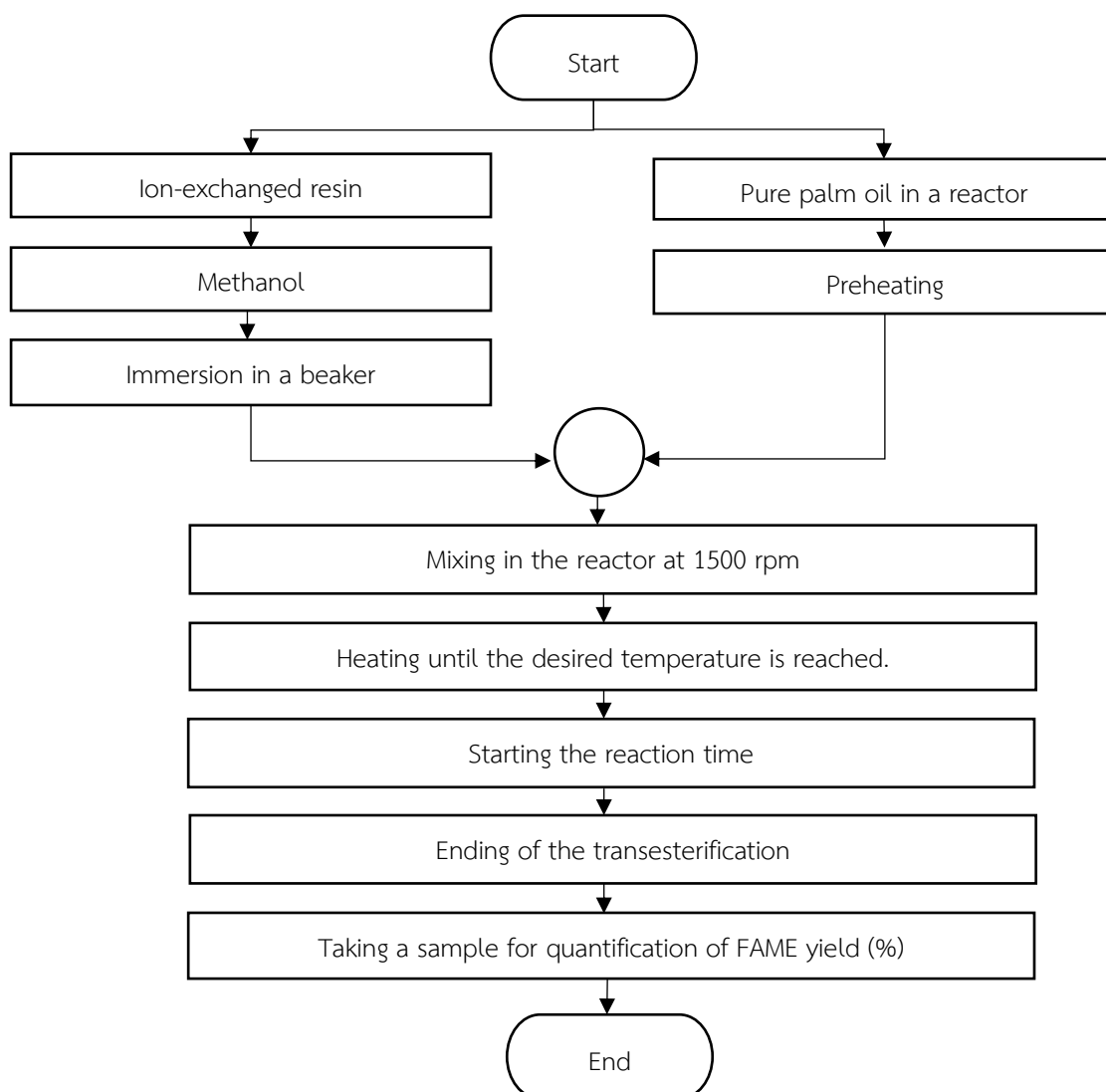


Figure 9 The procedures for transesterification of palm oil with methanol

3.2.7 Catalyst stability and regeneration test

The catalyst stability test was carried on by using the catalyst loading of $0.1475 \text{ cm}^3 \text{ g}_{\text{oil}}^{-1}$, methanol-to-oil molar ratio of 9.5:1, the reaction temperature at 65°C , stirring speed at 1500 rpm and the reaction time of 4 h. After each batch experiment ends, the used resin is recovered by filtration, and methanol is added in the reactor to remove the residual resin. The resin was washed with methanol following the pre-steps to clean the resin. The used resin was repeated until it is FAME yield $\leq 70\%$ of fresh resin and then it was regenerated by electrolysis. Electrochemical regeneration was carried out with the similar condition as previously

described in section 3.2.1 by replacing resin in Cl form in the cathode compartment with the used resin. After each regeneration, the regenerated resin is repeated for the next run to observe its activity. The procedures of catalyst stability and regeneration test are shown in Figure 10.

3.2.8 Analysis of FAME

The phases of the reaction mixture sample were separated by centrifuge for 10 minutes. A sample consists of three phases: the top phase containing methanol; the middle phase containing FAME; and the bottom phase containing the catalyst. The FAME phase was collected to determine the FAME yield (%).

The FAME yield (%) was analyzed by gas chromatography (GC). The sample and methyl heptadecanoate as biodiesel standard were weighted to 0.25 ± 0.0015 g and 0.05 ± 0.0005 g, respectively, and then the solution was diluted with 5 ml of n-heptane. After that, the sample solution of approximately 1 μ L was injected into a GC. The GC equipped with a flame ionization detector (FID) and a DB-WAX column, length of 29.9 m, an internal diameter of 0.32 mm and film thickness of 0.25 μ m. The operating conditions of GC for FAME analysis are shown in Table 5. The temperature starts at 150 $^{\circ}$ C and holds time for 5 min, and it was increased to 190 $^{\circ}$ C for 5 min. and 220 $^{\circ}$ C for 5 min. by an increased rate at 3 $^{\circ}$ C min^{-1} . Equation Eq. (21) is FAME content (%), which was used as FAME yield (%).

$$\text{FAME yield (\%)} = \frac{\left(\sum A_{\text{FAME}} \right)}{A_{\text{Ref}}} \times \frac{m_{\text{Ref}}}{m_{\text{FAME}}} \times 100\% \quad (21)$$

Where $\sum A_{\text{FAME}}$ = Area of FAME

A_{Ref} = Area of methyl heptadecanoate (Biodiesel standard)

m_{FAME} = Mass of FAME sample (g)

m_{Ref} = Mass of methyl heptadecanoate (Biodiesel standard) (g)

Table 5 The operating conditions of GC for FAME analysis

Parameters	Condition
Injection port	
Injection mode	Split
Carrier gas	He
Temperature	250 °C
Pressure	122.1 kPa
Column	
Temperature	150 °C
FID	
Temperature	250 °C

3.2.9 FT-TR Characterization of glycerol adsorption

The used ion-exchanged resin from transesterification, glycerol, the liquid sample from anode compartment were characterized by Fourier transform infrared (FT-IR). The spectra of used ion-exchanged resin from transesterification and glycerol were recorded in the range of 1090-1000 cm^{-1} and liquid sample from anode compartment in the range of 4000-500 cm^{-1} at a resolution of 2 cm^{-1} .

3.2.10 Inductively coupled plasma - optical emission spectrometer (ICP-OES)

The generated some solid powder in anode compartment during the electrolysis was analyzed amount of Ti element by ICP-OES. The solid powder sample of 0.0052g was dissolved with 2ml of 65% nitric acid solution, and then the mixture was adjusted the volume to 10 ml by adding DI-water.

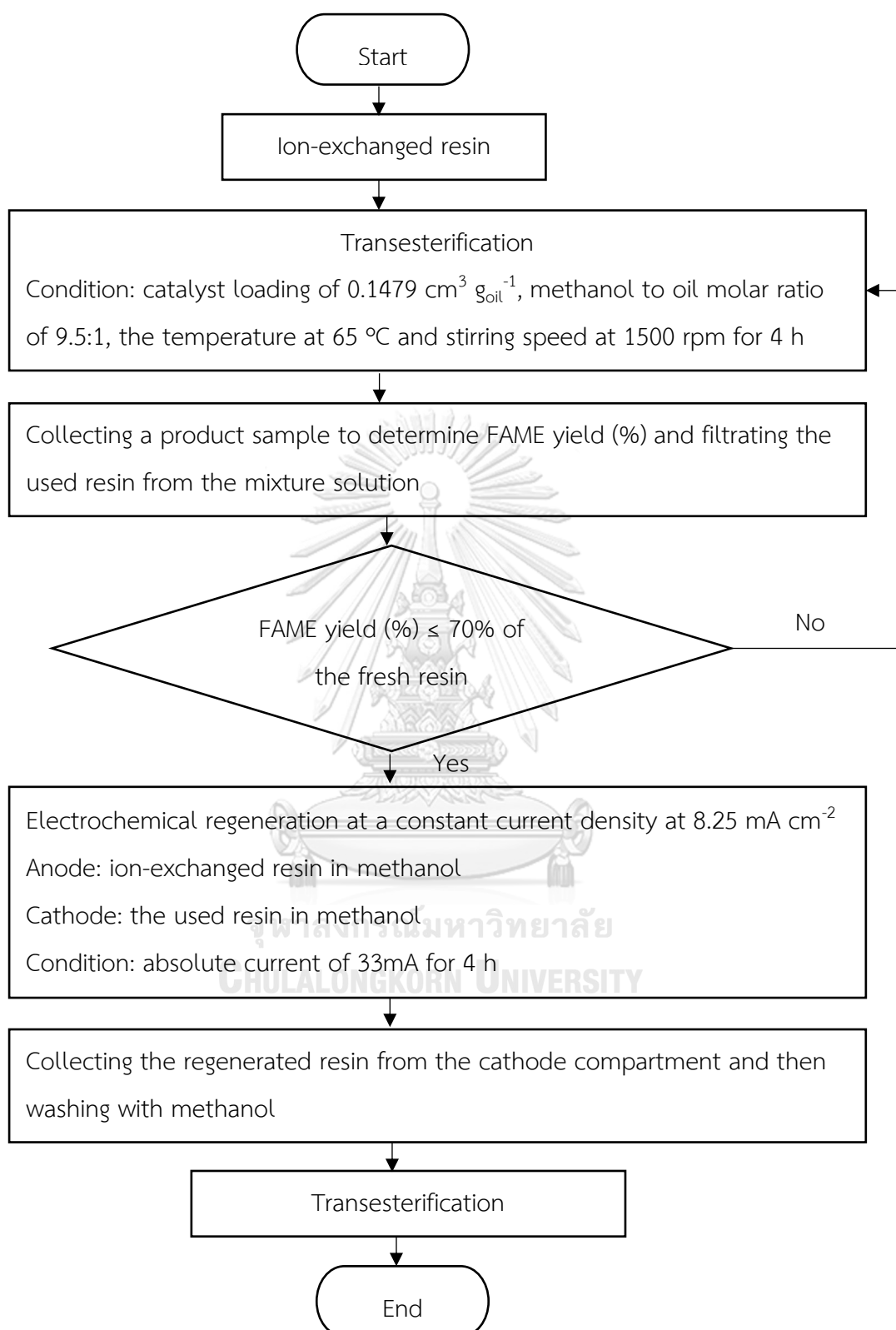


Figure 10 Flowchart of catalyst stability and regeneration test

Chapter IV

Result and discussion

The experiments are divided into three parts. In the first part, electrochemical conversion of anion-exchange resin (Amberlite IRA402) from chloride form to methoxide form without any additional electrolyte is demonstrated. The second part proves that transesterification with methoxide-resin prepared by both non-electrochemical means, i.e. ion exchange, and electrochemical means can be achieved. The last part shows the electrochemical regeneration of used ion-exchanged resin to restore its catalytic activity for transesterification.

4.1 Electrochemical synthesis of methoxide

Methoxide ion was generated by electrolysis of methanol in the cathode compartment, and hydrogen gas also was generated, as shown in Eq. (22). On the other hand, after the end of electrolysis, observing platinized titanium fiber felt as an electrode at the anode was shorter and thinner than initial, indicating that titanium (Ti) was oxidized to Ti^x , as shown in Figure 11 and Eq. (23). Ti^x ion reacted with hydroxide ion, and then titanium hydroxide ($Ti(OH)_x$) was formed, as shown in Eq. (24). Some white solid powder was observed at the anode compartment that shows in figure 14. The solid powder was analyzed Ti element in the sample by ICP-OES, solid powder 0.0052 g containing 33.8077% Ti. Therefore, the solid powder might be $Ti(OH)_x$. In addition, observing solid black power was deposited on the surface of the electrode as shown in Figure 12. It was analyzed by EDX and found that carbon element which the carbon might be generated by oxidation of methanol, as shown in figure 13 and Eq. (24), respectively.

Cathodic reaction



Anodic reaction

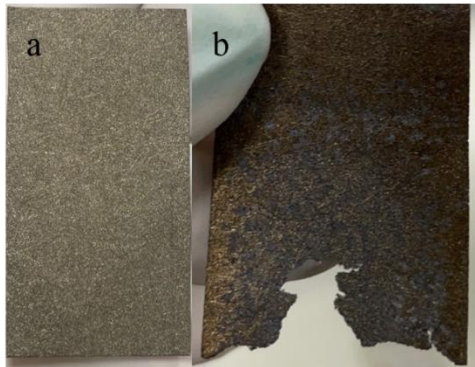


Figure 11 Platinized titanium fiber felt as electrode of anode a. before the electrolysis b. after the electrolysis



Figure 12 The electrode of anode was oxidized and deposited with carbon

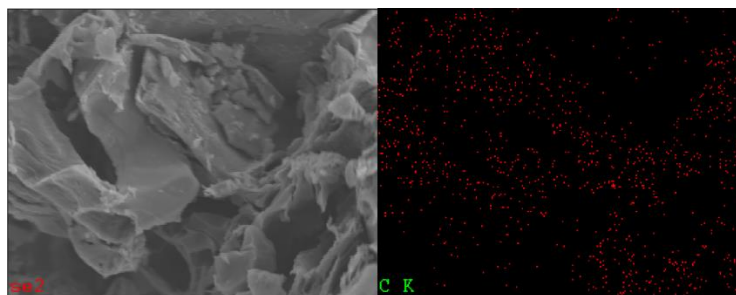


Figure 13 EDX of electrode of anode



Figure 14 Some solid powder was generated on anode compartment

No generated proton from the anode compartment was transported to the cathode due to separating with the anion-exchange membrane, which prevents the reaction between methoxide ion and proton to form methanol. Therefore, the generated methoxide ion was adsorbed in the ion-exchange site of resin, Cl^- ions of the resin were displaced with the generated methoxide ions, to form methoxide-resin in the cathode compartment.

Even though methoxide-resin was added in the anode compartment, diffusion of methoxide from anode to cathode compartment insufficient to replace Cl^- ion to methoxide ion in cathode. As shown in Figure 15, the hydroxide equivalent of ion exchange and electrolysis is 0.00029 and $0.00039 \text{ mol cm}^{-3}$, respectively. For electrolysis of methanol, generated methoxide was adsorbed in ion exchange site of resin by electrical force. On the other hand, Cl^- ion of the resin was displaced with OH^- ion by only the diffusion of NaOH for ion exchange. Therefore, the hydroxide equivalent of electrolysis was higher than ion exchange.

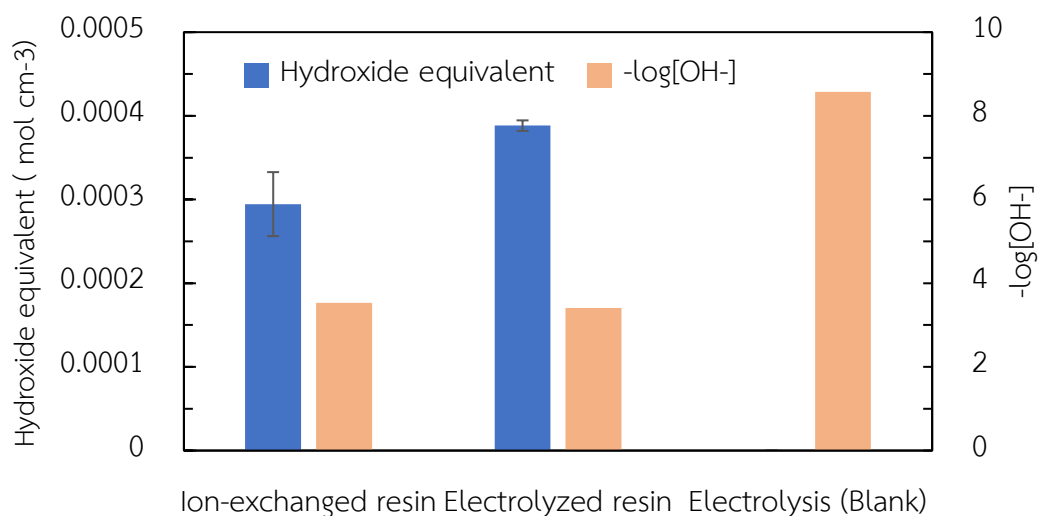


Figure 15 Hydroxide equivalent of difference method to prepared the resin as heterogenous catalyst.

4.2 Transesterification

4.2.1 Catalytic activity with statistical analysis

The results of the effect of catalyst loading, methanol-to-oil molar ratio and reaction temperature on FAME yield (%) were shown in Table 6. The second order polynomial model was used to describe the relationship between FAME yield and each term of variables which coefficient of each term and regression equation were showed in Table 7 and Eq. (27), respectively. Regressed yield (%) that show in Table 6 was calculated by this model and used to plot response surface with the experiment data as shown in Figure 16.

$$\text{FAME Yield (\%)} = -332.2129 + 542.7014(C) + 0.815(M:O) + 9.5456(T) - 147.6965(C^*C) - 0.0747(M:O * M:O) - 0.0623(T^*T) - 0.6518(C^*O:M) - 8.1398(C^*T) + 0.0152(O:M^*T) \quad (26)$$

Where C = Catalyst loading (ml g_{oil}⁻¹)
M:O = Methanol-to-oil molar ratio
T = Reaction temperature (°C)

Table 6 The result of experiment design and regressed yield (%) by the second order polynomial model

Test	Variables			Yield (%)	Regressed yield (%)
	Catalyst (ml g _{oil} ⁻¹)	M:O	Temperature (°C)		
1	0.1475	6:1	50	13.7200	12.4127
2	0.2949	6:1	50	19.5620	22.2129
3	0.1475	13:1	50	14.0900	12.8272
4	0.2949	13:1	50	21.6532	21.9545
5	0.1475	6:1	60	26.2253	28.2958
6	0.2949	6:1	60	22.4575	26.0921
7	0.1475	13:1	60	30.0541	29.7750
8	0.2949	13:1	60	23.2193	26.8985
9	0.0972	9.5:1	55	19.0439	20.6504
10	0.3452	9.5:1	55	31.4331	26.4732
11	0.2212	3.61:1	55	25.7717	22.7270
12	0.2212	15.39:1	55	24.0595	23.7542
13	0.2212	9.5:1	46.59	11.7562	12.6726
14	0.2212	9.5:1	63.41	34.4580	30.1882
15(CP)	0.2212	9.5:1	55	24.7943	25.8336
16(CP)	0.2212	9.5:1	55	27.4252	25.8336
17(CP)	0.2212	9.5:1	55	24.7117	25.8336

CP = Central point

M:O = Methanol-to-oil molar ratio

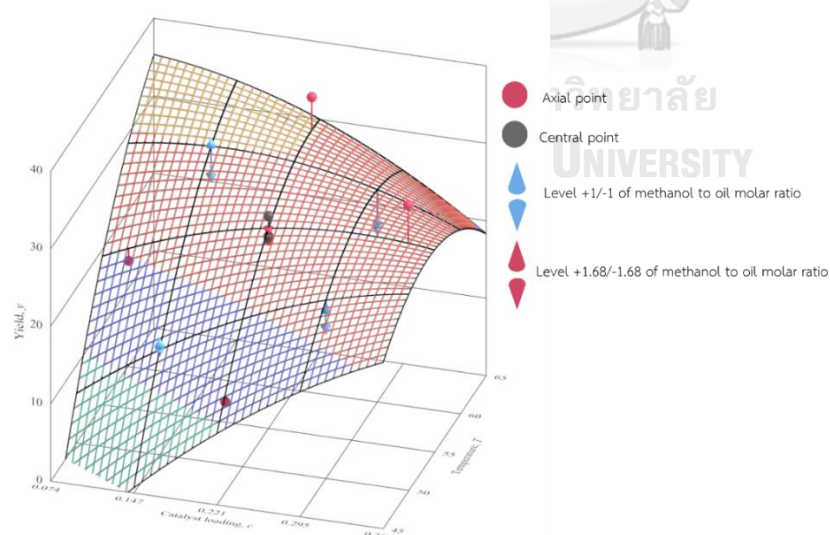
Table 7 Code coefficient for the second order polynomial model and p-value

Term	Coefficient	T-value	P-value
Constant	-332.2129	-2.1404	0.0696
Cat	542.7014	2.3852	0.0485
M:O	0.8150	0.1717	0.8685
T	9.5456	1.8628	0.1048
Cat ²	-147.6965	-0.7063	0.5028
M:O ²	-0.0747	-0.8060	0.4467
T ²	-0.0623	-1.3690	0.2133
Cat*M:O	-0.6518	-0.1246	0.9043
Cat*T	-8.1398	-2.2234	0.0616
M:O*T	0.0152	0.1972	0.8493

Cat=Catalyst loading ($\text{ml g}_{\text{oil}}^{-1}$)

M:O = Methanol-to-oil molar ratio

T=Reaction temperature ($^{\circ}\text{C}$)

**Figure 16** Response surface of interaction between catalyst loading and reaction temperature on FAME yield (%) using the second order polynomial model

The first response surface was constructed with a second order polynomial model to evaluate the significance of all regressors. The level of significance was set at 0.15 to minimize rejection of regressors; therefore, only the catalyst loading, reaction temperature and the interaction of catalyst loading and reaction temperature were significant to FAME yield as shown in Table 7. This leads to the simplified model with only three regressors. The lag of non-linear relation between the yield and the reaction temperature suggests that the reaction is not kinetically limited; mass transfer limitation is plausible.

The new regression equation using simplified model with the coefficient of each term, as shown in Eq. (27) and Table 8.

$$\text{FAME Yield (\%)} = -138.2920 + 471.1428(C) + 2.8418(T) - 8.1394(C*T) \quad (27)$$

When $C = \text{Catalyst loading (cm}^3 \text{ g}_{\text{oil}}^{-1}\text{)}$

$T = \text{Reaction temperature (}^{\circ}\text{C)}$

The results of FAME yield (%) from the experiment and regressed yield (%) by the simplified model were shown in Table 9. The range of FAME yield is between 11.7562% to 34.458%. Figure 17 shows the response surface plot between the effect of interaction of catalyst loading and reaction temperature on FAME yield (%) using the simplified model. The interaction between the catalyst loading and the reaction temperature is significant in the simplified model. This is interpreted as catalyst distribution becoming poorer at higher reaction temperature due to a currently unclear phenomenon. These results suggest that using low catalyst loading approximately $0.1475 \text{ cm}^3 \text{ g}_{\text{oil}}^{-1}$ at high reaction temperature to obtain the higher FAME yield.

An Increase in catalyst loading was an increase in the availability of active site reacting with methanol to form methoxide which catalyzes transesterification; therefore, FAME yield was increased by an increase in catalyst loading. However, excessive catalyst loading not only increased FAME yield but also increased glycerol as a by-product [40]. Glycerol adsorption in the resin might be another cause for low FAME yields. Glyceroxide ions were adsorbed at the ion-exchange sites of the resin [12, 13,

31, 41] which reduces the contact area between the active site and reactant. Therefore, glycerol adsorption in the resin occupied the active sites, where methoxide is preferably adsorbed, and led to low catalytic activity. From the experiment, observing partial catalyst particles hold with the edge of the reactor when using the catalyst loading more than $0.2949 \text{ cm}^3 \text{ g}_{\text{oil}}^{-1}$, as shown in Figure 18, this behavior may cause a reduction in FAME yield because the catalyst was inactive.

An increase in reaction temperature related to an increase in FAME yield, probably due to decrease in viscosity of reactants, increase in mutual solubility between methanol and palm oil and leading to increase in mass transfer [28]. However, the reaction temperature was limited by the specific manufacture of the resin in OH^- form at 60°C [42]. This might cause cracks in the resin beads as some solid powder was observed at the end of transesterification, as shown in Figure 19, and led to low FAME yields due to a currently unknown mechanism.

From Table 7, methanol-to-oil molar ratio is insignificant variable ($p\text{-value} > 0.015$) for the FAME yield. Comparing methanol-to-oil molar ratio at 3.61:1 (test 11) and 15.39:1 (test 12), the FAME yield was 25.7717% and 24.0595%, respectively, which yield did not change; therefore, an increase in the ratio of methanol in the system does not influence FAME yield. After each transesterification end, observing the surface of the used resin was covered with a thin film, as shown in Figure 20, which probably is methanol due to the polarity of the resin and methanol. Methanol which covers the surface of the resin is a barrier diffusion of oil into the resin that will react with methoxide to form FAME. Thus, the change in methanol molar ratio does not affect FAME yield because reaction rate was limited by mass transfer.

Table 8 Code coefficient for the simplified model and p-value

Term	Coefficient	T-value	P-value
Constant	-138.2921	-3.5589	0.0035
Cat	471.1428	2.7681	0.0160
T	2.8418	4.0323	0.0014
Cat*T	-8.1394	-2.6365	0.0205

Cat=Catalyst loading ($\text{ml g}_{\text{oil}}^{-1}$)

M:O = Methanol-to-oil molar ratio

T=Reaction temperature ($^{\circ}\text{C}$)

Table 9 The result of experiment design and regressed yield (%) by the simplified model

Test	Variables			Yield (%)	Regressed yield (%)
	Catalyst ($\text{ml g}_{\text{oil}}^{-1}$)	O:M	Temperature ($^{\circ}\text{C}$)		
1	0.1475	1:6	50	13.7200	13.2637
2	0.2949	1:6	50	19.5620	22.7271
3	0.1475	1:13	50	14.0900	13.2637
4	0.2949	1:13	50	21.6532	22.7271
5	0.1475	1:6	60	26.2253	29.6789
6	0.2949	1:6	60	22.4575	27.1391
7	0.1475	1:13	60	30.0541	29.6789
8	0.2949	1:13	60	23.2193	27.1391
9	0.0972	1:9.5	55	19.0439	20.2906
10	0.3452	1:9.5	55	31.4331	26.1133
11	0.2212	1:3.61	55	25.7717	23.2019
12	0.2212	1:15.39	55	24.0595	23.2019
13	0.2212	1:9.5	46.59	11.7562	14.4442

14	0.2212	1:9.5	63.41	34.4580	31.9597
15(CP)	0.2212	1:9.5	55	24.7943	23.2019
16(CP)	0.2212	1:9.5	55	27.4252	23.2019
17(CP)	0.2212	1:9.5	55	24.7117	23.2019

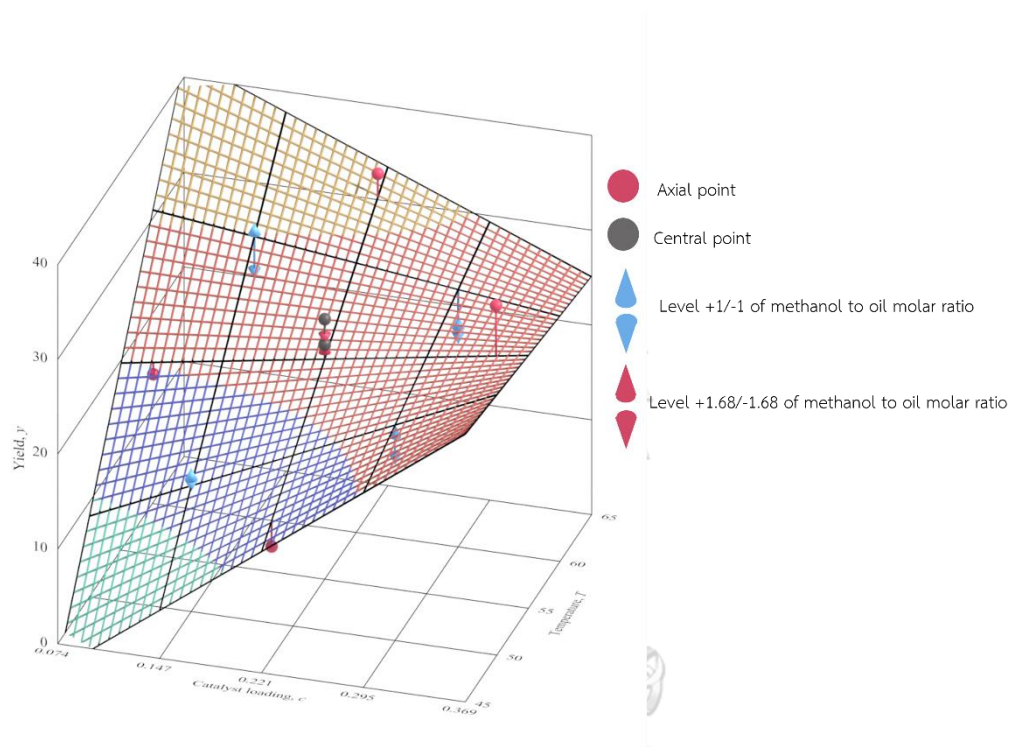


Figure 17 Response surface of interaction between catalyst loading and reaction temperature on FAME yield (%) using the simplified model



Figure 18 Partial the resin was edged of the reactor during transesterification



Figure 19 Some solid powder was generated during the transesterification

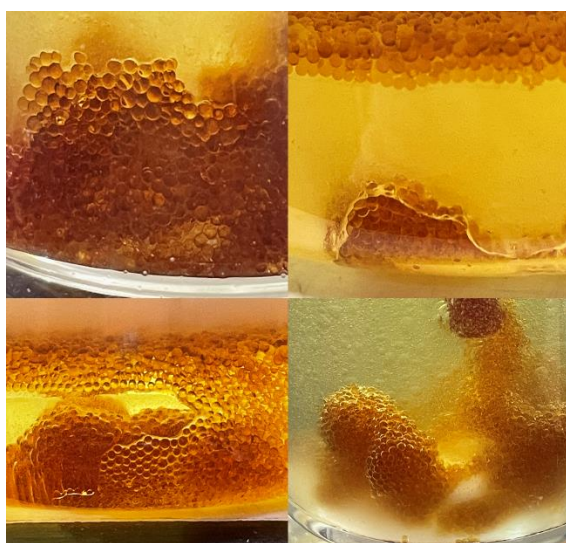


Figure 20 The surface of the resin was covered with film

Figure 21 shows the effect of the method for preparing the resin as the heterogeneous catalyst on FAME Yield (%). Methoxide ion was generated by electrolysis of methanol and adsorbed in the ion-exchange site of the resin. On the other hand, hydroxide ions were produced by ion exchange with 1.5 M of NaOH solution and adsorbed in the ion-exchange site of the resin. The FAME yield of transesterification using ion-exchanged resin as a heterogeneous catalyst was 19.31%, compared with that from electrolyzed resin of 5.6% which FAME yield using ion-exchanged resin was more than three times of the electrolyzed-resin. The type of base adsorbed in the ion exchange site of resin strongly influences FAME yield (%). These results suggest that transesterification is catalyzed better by hydroxide ions as the base in the resin. For electrolyzed resin, generated methoxide was adsorbed in an ion-exchange site and held tightly with amine, which might cause resin inactive and low activity for transesterification. In part of ion-exchanged resin, hydroxide ion

was adsorbed in ion-exchange site and then reacted with methanol to form methoxide during transesterification. Many studies used anion exchange resin in OH^- form as a heterogeneous catalyst in transesterification and obtained high catalyst activity of more than 90% of FAME yield [11, 13, 30]. Therefore, the hydroxide ion should be adsorbed in ion-exchange site with amine for preparing resin, and the hydroxide ion reacts with methanol during transesterification to increase its catalyst activity. In addition, Figure 21 indicates that the resin in Cl form cannot be catalyzed the transesterification.

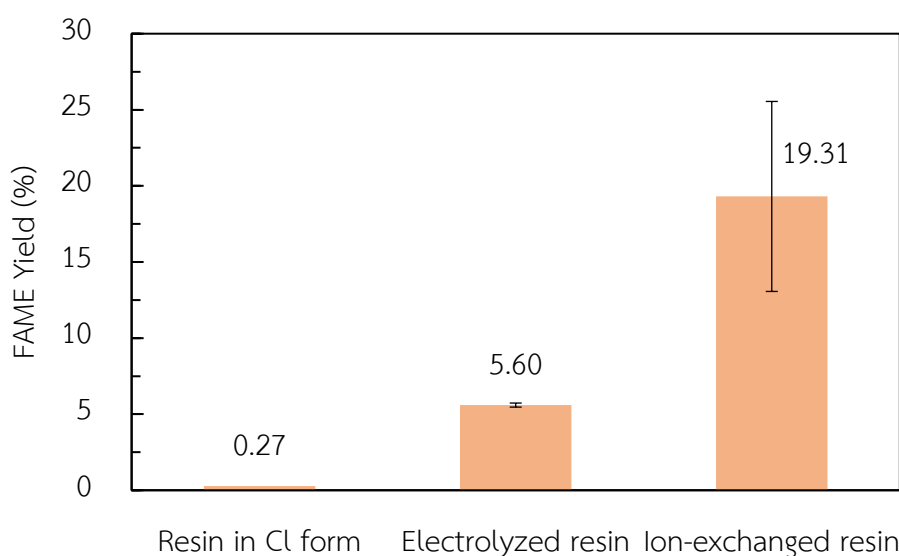


Figure 21 The effect of difference method to prepare the resin as a heterogeneous catalyst on FAME yield (%)

4.3 Catalyst stability and regeneration test

The Figure 22 presents catalytic stability of ion-exchanged resin at the reaction conditions: catalyst loading of $0.1475 \text{ cm}^3 \text{ g}_{\text{oil}}^{-1}$, methanol-to-oil molar ratio of 9.5:1, reaction temperature at 65°C and stirring speed at 1500 rpm for 4 h. Between fresh resin and reuse resin 1st time, the FAME yield plunged from 14.8915 % to 7.8794% which FAME yield of reused 1st resin dropped to 52% of fresh resin. After that, the FAME yield of reused resin 1st to 4th time was constant.

The anion exchange resin can adsorb glycerol which is a by product of transesterification in form of glyceroxide in ion-exchange site. As shown in Figure 23, a stretching vibration of the C-O in glycerol molecule presents at 1027.89 cm^{-1} . The wavenumber of C-O bond was shifted to 1033.67 cm^{-1} when glyceroxide was adsorbed in the active site of resin. According to Rong et al. (2018), the stretching vibration of C-O bond blue shift from 1037.5 cm^{-1} in glycerol to 1043.22 cm^{-1} in adsorbed glycerol strongly basic anion exchange-Cl resin, probably due to breaking of hydrogen bonds of glycerol molecules to glyceroxide ions. Not only glycerol that was adsorbed in the resin but also FFA that presents in refined palm oil [14, 29]. Therefore, glycerol and FFA adsorption in the resin occupied the active sites, where methoxide is preferably adsorbed, and led to decreased catalytic activity. In addition, a saturation of glyceroxide in the ion-exchange site may be the reason that the FAME yield was stable when used resin was repeat in 1st – 4th time for transesterification. Figure 24 shows the images of used 1st resin and used 5th resin (Reused 4th) time indicating that the resin was still a spherical shape, not fissures or break in the resin. The surface of reused 4th resin was covered which may be fatty compounds, as shown in Figure 24(b).

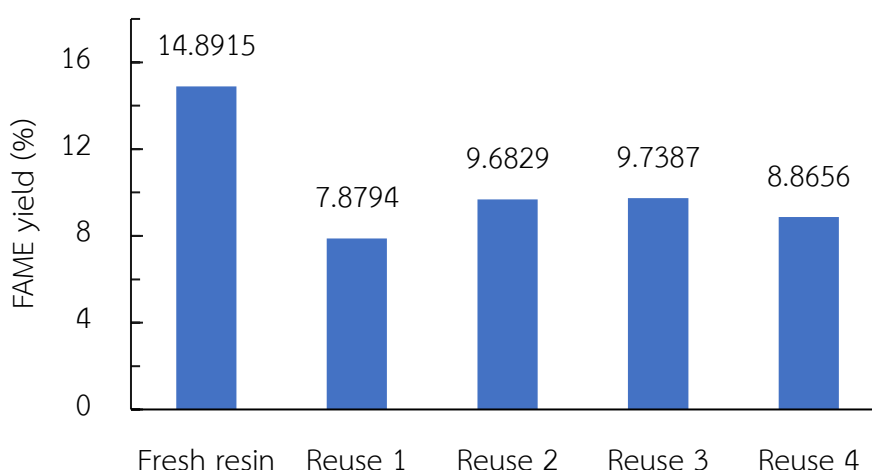


Figure 22 Catalyst stability test

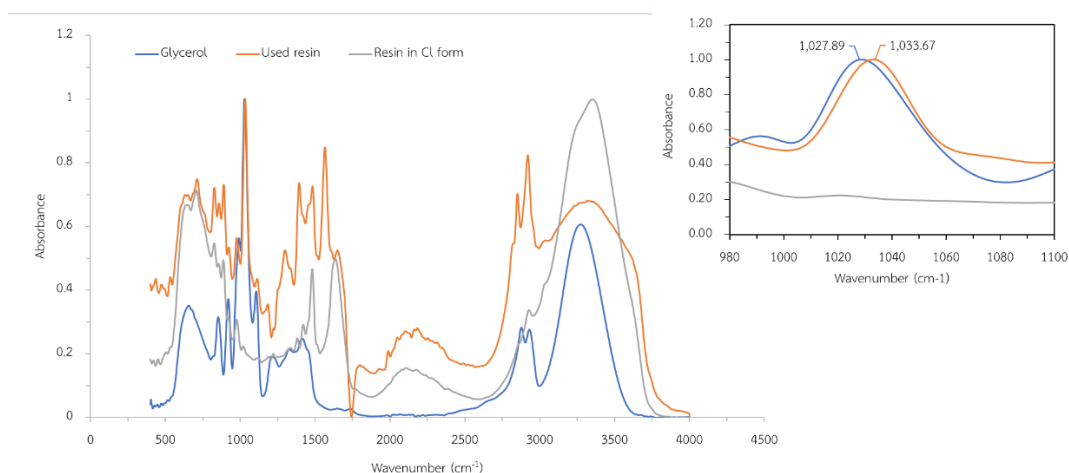


Figure 23 The blue shift of C-O of glyceroxide adsorbed in ion-exchange site of resin

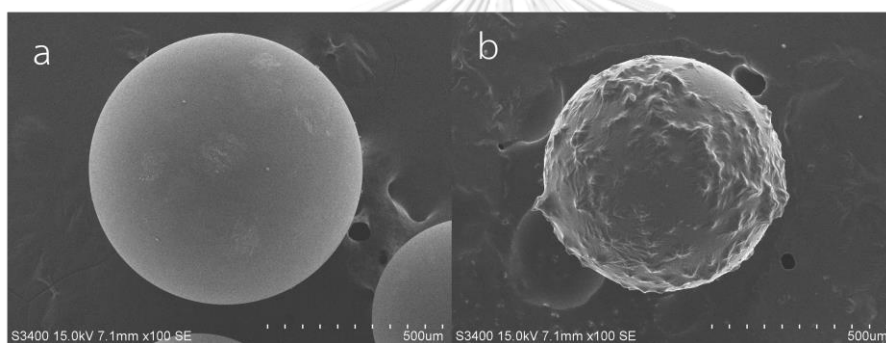


Figure 24 Images obtained by scanning electron microscopy (SEM) of a. used 1st resin b. used 5th resin (reused 4th)

As shown in Figure 25, the FAME yield (%) plunged from 23.7191% of fresh ion-exchanged resin to 11.5264% of reused resin 1st time which is less than 70% of fresh resin. The used resin was regenerated by electrolysis of methanol. The cathode compartment was filled with used resin, and the anode compartment was filled with ion-exchanged resin. Methanol was added to both cathode and anode compartments until the resin is fully submerged. The electrochemical regeneration was carried out in absolute current at 33 mA for 2 h and was stopped due to over cell potential at 45 V. During the electrolysis, some white solid powder and yellow cream were generated at the anode compartment, as shown in Figure 26. The white solid may be Ti(OH)_x which was described in session 4.1. The yellow cream that was

presented in anode compartment may be glyceroxide, conjugate of FFA or hydrocarbon from transesterification that was adsorbed in the resin. The Figure 27 shows analysis of some white solid powder and yellow cream indicating that powder might be Ti(OH)_x or compound of Ti-C. Both generated white solid and yellow cream might block flow of current between membrane and resin and causes over cell potential.

The electrolysis was continued again by replacing the used resin from anode compartment with fresh ion-exchanged resin and cleaning the membrane. The cell potential of electrolysis 2nd and 3rd times reach 45 V within 1.5h and 0.5h, respectively. However, several electrolysis batches until the total number of 4 hours reach. After regeneration, the regenerated resin was used in transesterification, and FAME yield is 9.9298%. Observing the FAME yield dropped from 11.5264% to 9.9298% when using reused 1st resin and regenerated resin, respectively, probably due to the hydroxide ion that was adsorbed in the resin by ion-exchange was displaced by methoxide ion from the electrolysis of methanol. This result is related to Figure 21 which showed the hydroxide catalyzing the transesterification better than methoxide.

When comparing the FAME yield of electrolyzed resin and regenerated resin by electrolysis, it was observed that FAME yield of regenerated resin is higher than electrolyzed resin as shown in Figure 21 and 25. Partial cross-linking of the resin might be destroyed, fissured, and broken by the high reaction temperature and long stirring, causing improving mass transfer and leading to high FAME yield (%) In addition, after the end of each transesterification, observing the volume of used resin more than initial volume is from 4 cm³ to approximately 4.8 cm³, which permanent swelling of the used resin related to destroying of partial cross-linking of the resin.

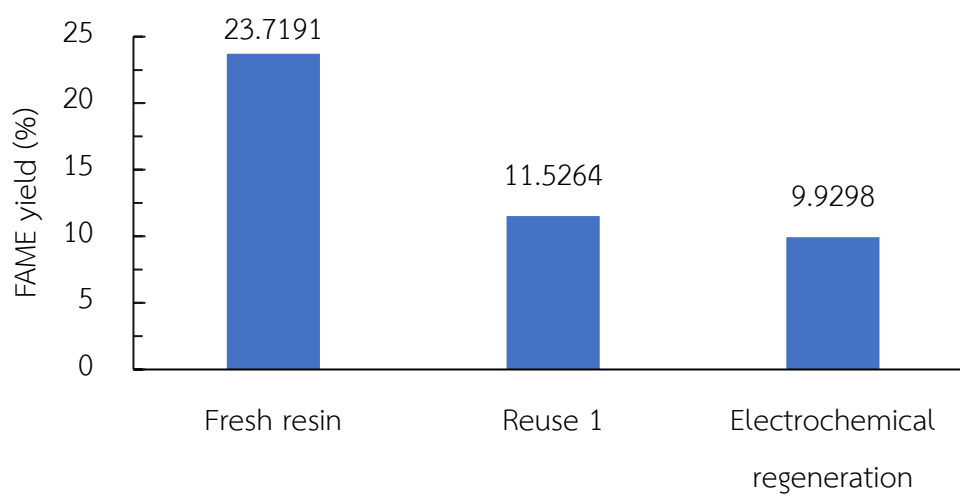


Figure 25 The effect of electrochemical regeneration on FAME yield (%)



Figure 26 Some solid in anode compartment during electrochemical regeneration

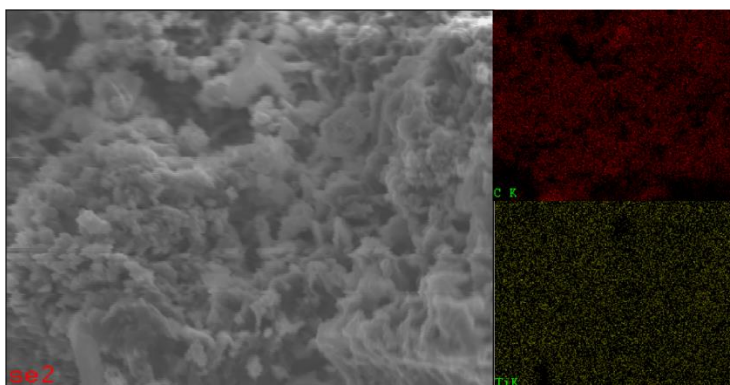


Figure 27 EDX formed some solid in anode compartment

Chapter V

Conclusion and recommendation

5.1 Conclusion

Methoxide can be generated by an electrolysis of methanol using Amberlite IRA402 anion exchange resin as the only electrolyte and subsequently as the adsorbent for generated methoxide. This synthesis without any additive such as NaCl or water needed, eliminating the need for neutralization, and washing step. The electrolyzed resin was used as a heterogeneous catalyst for transesterification of palm oil with methanol.

The electrolysis of methanol was carried out with presence of anion exchange membrane at current density of 8.25 mA cm^{-2} for 4 h. Methoxide ion was generated at cathode compartment and adsorbed in ion-exchange site of the resin. The electrolyzed resin had a hydroxide equivalent of $0.00039 \text{ mol cm}^{-3}$, compared with that from ion exchange of $0.00029 \text{ mol cm}^{-3}$ which hydroxide equivalent from electrolysis is more than ion-exchanged resin. However, the FAME yield when using electrolyzed resin as a catalyst at catalyst loading of $0.1475 \text{ cm}^3 \text{ g}_{\text{oil}}^{-1}$, methanol-to-oil molar ratio of 9.5:1, reaction temperature at 65°C , stirring speed at 1500 rpm and the reaction time for 4 h was 5.6% which is slightly less than 30% of FAME yield of ion-exchanged resin. The results of the experiment suggest that the type of base that was adsorbed in the ion-exchange site of resin strongly influenced FAME yield. Hydroxide ions as the base in the resin could better catalyze transesterification than methoxide ions. For electrochemical regeneration, hydroxide ions in used ion-exchanged resin was displaced with methoxide ions by electrolysis; therefore, the FAME yield of transesterification over regenerated resin not as well as fresh ion-exchange resin as a catalyst.

The response surface methodology based central composite design was useful for evaluation the effects of independent variables for transesterification. The first response surface was constructed with a second order polynomial model to

evaluate the significance of all regressors. Observing only catalyst loading, reaction temperature, and interaction between catalyst loading and reaction temperature were significant when the level of significance was set at 0.15. This leads to using the simplified model with only three regressors to create a new response surface which suggests that using catalyst loading is approximately $0.1475 \text{ cm}^3 \text{ g}_{\text{oil}}^{-1}$ at high reaction temperature will lead to high FAME yield. Furthermore, the lack of non-linear relation between the yield and the reaction temperature suggests that the reaction is not kinetically limited; mass transfer limitation is plausible.

5.2 Recommendation

5.2.1 The electrolysis of H_2O should be investigated to generate hydroxide ion and adsorb it in ion exchange site of the resin to compare the catalyst's activity of hydroxide-resin and methoxide-resin by electrolysis.

5.2.2 Ethanol should be investigated as short chain alcohol in transesterification of palm oil over the anion exchange resin as heterogeneous catalyst because the type of alcohol may affect mass transfer and FAME yield (%).

5.2.3 Condition at low catalyst loading of $0.1475 \text{ cm}^3 \text{ g}_{\text{oil}}^{-1}$ and high reaction temperature should be investigated to use for transesterification to obtain higher FAME yield (%).

Appendix A

A1. The calculation of the reaction time for an electrolysis

The reaction time for which the resin is saturated with methoxide generated by an electrochemical is estimated using the steps below.

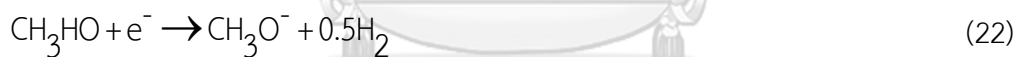
The total exchange capacity of the resin as shown in Table 2 = 1.2 eq L^{-1}

The volume of the resin that is used in the experiment = 4 cm^3

1.1 The quantity of the charge that 4 cm^3 of the resin can adsorb

$$= \left(1.2 \frac{\text{eq}}{\text{L}} \right) (4 \text{ cm}^3) \left(\frac{1 \text{ L}}{1000 \text{ cm}^3} \right) = 0.0048 \text{ mol}_{\text{CH}_3\text{O}^-}$$

As shown in Eq (22), an electron gives a CH_3O . So, the electrons of 0.0048 mol are used to saturate the resin.



1.2 Charge of these electrons

$$= (n \text{ electron})(F)$$

$$= \left(0.0048 \text{ mol}_{\text{e}^-} \right) \left(96,485 \frac{\text{C}}{\text{mol}} \right) = 463.128 \text{ C}$$

F is Faraday constant = $96,485 \text{ C mol}^{-1}$

The current density is constant at 8.25 mA cm^{-2}

The absolute current is 33 mA

1.3 The reaction time

$$= (\text{Total charge of the electron})(\text{The electric current})^{-1}$$

$$= \frac{463.182\text{C}}{0.033\text{A}} = 14035.82\text{s} = 233.93\text{min} \approx 4\text{h}$$

The reaction time at 4 h is used for the electrochemical synthesis of methoxide.

A2. The preparation of transesterification

At DOE 14: catalyst loading of $0.2211\text{ cm}^3\text{ g}_{\text{oil}}^{-1}$, methanol-to-oil molar ratio of 9.5:1

The volume of resin was measured to 5.8 cm^3

$$\text{Amount of palm oil} = \frac{5.8\text{cm}^3}{0.2211\text{cm}^3} = 26.232\text{g}$$

$$\text{The volume of methanol} = \frac{9.5 \times 32.04 \frac{\text{g}}{\text{mol}} \times 26.232\text{g}_{\text{oil}}}{847 \frac{\text{g}}{\text{mol}} \times 0.7981 \frac{\text{g}}{\text{cm}^3}} = 11.812\text{cm}^3$$

Table 10 The properties of resin, oil and methanol

Properties	
Bed density of resin	0.6781 g/cm ³
Average Oil Density	0.89 g/cm ³
Average Oil Molecular Weight	847 g/mol
Alcohol Density	0.7918 g/cm ³
Alcohol Molecular Weight	32.04 g/mol

A3. The calculation for FAME yield (%) by GC analysis

For example, DOE 14: catalyst loading of $0.2211\text{ cm}^3\text{ g}_{\text{oil}}^{-1}$, methanol-to-oil molar ratio of 9.5:1, the reaction temperature at 64°C , stirring speed at 1500 rpm and the reaction time of 4 h.

The sample contains

Standard weigh = 0.0513 g

Sample weigh = 0.25 g

n-Heptane = 5 ml

The calculation for FAME yield (%) was performed using Eq. (21)

$$\text{FAME yield (\%)} = \frac{\left(\sum A_{\text{FAME}} \right)}{A_{\text{Ref}}} \times \frac{m_{\text{Ref}}}{m_{\text{FAME}}} \times 100\% \quad (21)$$

Where $\sum A_{\text{FAME}}$ = Area of FAME

A_{Ref} = Area of methyl heptadecanoate (Biodiesel standard)

m_{FAME} = Mass of FAME sample (g)

m_{Ref} = Mass of methyl heptadecanoate (Biodiesel standard) (g)

$$\begin{aligned} \text{FAME yield (\%)} &= \frac{(2042432.9 + 58745.2 + 2504251.4 + 667843.3) \times 0.0513\text{g}}{3140629.3 \times 0.25\text{g}} \times 100 \\ &= 34.4541\% \end{aligned}$$

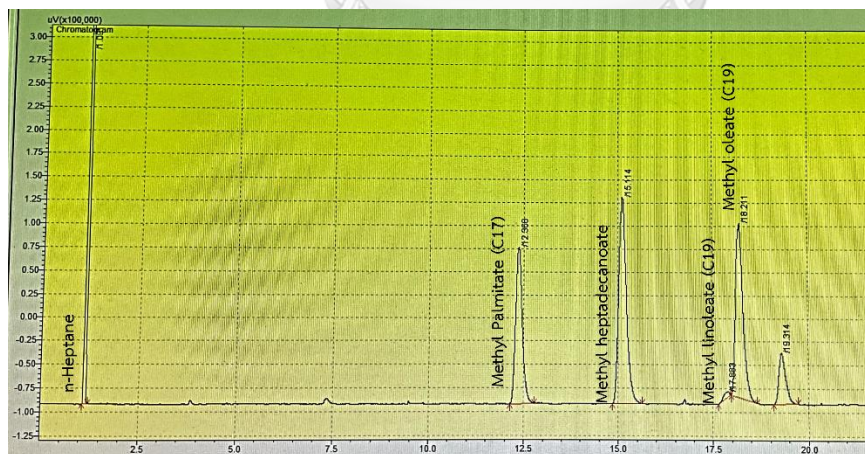


Figure 28 GC chromatogram of FAME sample (DOE14)

Table 11 Identification of compounds by GC

NO	Peak name	Ret.Time (min)	Area
1	n-Heptane	1.091	211067808.3
2	Methyl Palmitate (C17)	12.368	2042432.9
3	Methyl heptadecanoate	15.114	3140629.3
4	Methyl linoleate (C19)	17.883	58745.2
5	Methyl oleate (C19)	18.211	2504251.4
6	Methyl stearate (C19)	19.314	667843.3

A4. The determination of Ti content of solid powder from anode compartment during electrolysis

The solid sample of 0.0052 g was dissolved in 10 ml of total mixture solution
 From ICP analysis, the concentration of Ti in mixture solution is 1758 mg L⁻¹

The mixture solution is 10 ml

$$\text{Ti} = \frac{10\text{ml} * 1758\text{mg}}{1000\text{ml}} = 1.758\text{mg in } 0.0052 \text{ g of solid powder}$$

$$\text{Ti} = \frac{100 * 1.758 * 10^{-3}\text{g}}{0.0052\text{g}} = 33.8077\% \text{ of solid powder}$$

Therefore, solid powder of 0.0052g contains 33.8077% of Ti

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