# Fatty acid methyl ester production by transesterification of refined palm oil with methanol catalysed by anion-exchange resin with tetrahydrofuran as a co-solvent

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

น.ส.ซาร์กัล อามารา

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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| By | Miss Zargul Ammara |
| Field of Study | Chemical Engineering |
| Thesis Advisor | Associate Professor PALANG BUMROONGSAKULSAWAT, Ph.D. |

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ซาร์กัล อามารา : การผลิตเมทิลเอสเตอร์ของกรดไขมันด้วยทรานสเอสเตอรฟิเคชันของน้ำมันปาล์มผ่านกระบวนการด้วยเมทานอลเร่งโดยเรซิ่นแลกเปลี่ยนไอออนลบด้วยเทตระไฮโดรฟูรันที่เป็นตัวทำละลายร่วม. ( Fatty acid methyl ester production by transesterification of refined palm oil with methanol catalysed by anion-exchange resin with tetrahydrofuran as a co-solvent) อ.ที่ปรึกษาหลัก : พลัง บำรุงสกุลสวัสดิ์

เรซินแลกเปลี่ยนประจุลบอัลคาไลน์ โดยเฉพาะ AmberLiteTM IRA402 และ AmberLystTM A26 ที่มีรูพรุน ถูกนำมาใช้เพื่อศึกษาการเปลี่ยนสถานะเป็นเอสเทอริฟิเคชันของน้ำมันปาล์มและเมทานอล กระบวนการทางอุตสาหกรรมทั่วไปสำหรับการสร้างไบโอดีเซลหรือตัวทำละลายสีเขียว คือ ทรานส์เอสเทอริฟิเคชัน แม้ว่าตัวเร่งปฏิกิริยาที่เป็นเนื้อเดียวกัน เช่น โซเดียมเมทอกไซด์และโซเดียมไฮดรอกไซด์จะถูกใช้ในโรงงานทรานส์เอสเทอริฟิเคชันส่วนใหญ่ แต่ตัวเร่งปฏิกิริยาต่างชนิดกันมีประโยชน์ในการแยกออกจากผลิตภัณฑ์สำเร็จรูปได้ง่ายกว่า เป้าหมายของการศึกษานี้คือเพื่อทำความเข้าใจให้ดียิ่งขึ้นว่าน้ำมันปาล์มและเมทานอลรวมตัวกันเพื่อผลิตกรดไขมันเมทิลเอสเทอร์ (FAME) ซึ่งเป็นไบโอดีเซลชนิดหนึ่งที่แพร่หลายได้อย่างไรการศึกษาก่อนหน้านี้ส่วนใหญ่ตรวจสอบการผลิตกรดไขมันเอทิลเอสเทอร์ (FAEE) โดยการเปลี่ยนน้ำมันปาล์มด้วยเอทานอล อย่างไรก็ตาม เป้าหมายของงานวิจัยนี้คือการตรวจสอบการใช้อัลคาไลน์แอนไอออนแลกเรซินสำหรับการเปลี่ยนผ่านของน้ำมันปาล์มและเมทานอลด้วยการเติม THF เป็นตัวทำละลายร่วม ทรานส์เอสเทอริฟิเคชันจาก IRA402 ซึ่งเป็นตัวเร่งปฏิกิริยาที่หนาแน่น แนะนำว่าอัตราการผลิต FAME นั้นขึ้นอยู่กับความเข้มข้นของน้ำมันในเชิงเส้นตรง ในขณะที่เมทานอลไม่ส่งผลกระทบต่อเนื้อหา FAME มากนัก การเปลี่ยนแปลงตำแหน่งพื้นฐานของเรซิน ผลผลิตจะได้รับผลกระทบเช่นกัน ซึ่งหมายความว่าการถ่ายโอนมวลภายนอกจะถูกตัดออกเพื่อควบคุมปฏิกิริยา ขั้นตอนการกำหนดอัตราสำหรับ IRA402 เป็นไปได้มากที่สุดที่ปฏิกิริยาของอะซิลกลีเซอรอลและเมทอกไซด์ที่พื้นผิวของเรซิน ในกรณีของ A26 ปฏิกิริยาถูกควบคุมโดยการถ่ายโอนมวลภายนอกเนื่องจากผลผลิตไม่ได้รับผลกระทบจากการเปลี่ยนตำแหน่งพื้นฐานที่พื้นผิว แต่ปฏิกิริยาลดลงหลังจากผ่านไประยะหนึ่งเนื่องจากการก่อตัวของเฟสทุติยภูมิที่ปิดกั้นรูพรุนของเรซินในที่สุด เฟสที่สองถูกกระตุ้นโดยกลีเซอรอลซึ่งได้รับการยืนยันเมื่อมีการเติมกลีเซอรอลเมื่อเริ่มปฏิกิริยาทรานส์เอสเทอริฟิเคชัน มีการสร้างแบบจำลองอัตราการเกิดปฏิกิริยาสำหรับเรซินทั้งสองชนิด ค่าคงที่ของอัตราการเกิดปฏิกิริยาที่ได้รับจากการปรับข้อมูล

สาขาวิชา วิศวกรรมเคมี ลายมือชื่อนิสิต ...............................................
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# # 6470373121 : MAJOR CHEMICAL ENGINEERING
KEYWORD: Transesterification, Biodiesel, Anion exchange resin, Glycerol, Reaction rate

Zargul Ammara : Fatty acid methyl ester production by transesterification of refined palm oil with methanol catalysed by anion-exchange resin with tetrahydrofuran as a co-solvent. Advisor: Assoc. Prof. Dr. PALANG BUMROONGSAKULSAWAT, Ph.D.

Alkaline anion exchange resins, specifically dense AmberLite$^{TM}$ IRA402 and porous AmberLyst$^{TM}$ A26, are used to study the transesterification of palm oil and methanol. A common industrial process for creating biodiesel or green solvents is transesterification. While homogeneous catalysts like sodium methoxide and sodium hydroxide are used in most transesterification facilities, heterogeneous catalysts have the benefit of being simpler to separate from the finished product. The goal of this study was to better understand how palm oil and methanol combine to produce fatty acid methyl ester (FAME), a prevalent kind of biodiesel. Previous studies mainly investigated the production of fatty acid ethyl ester (FAEE) by trans esterifying palm oil with ethanol. However, the goal of this research was to examine the utilization of alkaline anion exchange resins for the transesterification of palm oil and methanol with addition of THF as co-solvent. Transesterification from IRA402, which is a dense catalyst, suggested that rate of FAME production is linearly dependent of concentration of oil. While the methanol does not affect the FAME content much. By varying the basic sites of resin, the yield also gets affected which means external mass transfer is ruled out for controlling reaction. The rate determining step for IRA402 is most likely the reaction of acylglycerol and methoxide at the surface of resin. In case of A26, the reaction was controlled by external mass transfer as yield did not get affected by changing the basic sites at the surface. But the reaction fell after some time due to the formation of secondary phase that eventually blocks the pores of resins. The secondary phase is triggered by presence of glycerol which was confirmed when glycerol was added at the start of transesterification reaction. Reaction rate modelling has been done for both resins. The reaction rate constants obtained through data fitting.

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Zargul Ammara

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# CHAPTER I

## Significance of problem

Both industry and academia have been compelled to produce more efficient power with less environmental harm because of rising fossil fuel prices and the grave consequences of toxic emissions[1]. The last several years have seen increased interest in biodiesel as a renewable and environmentally friendly fuel because of limited petroleum reserves and the harmful effects of petroleum diesel exhaust fumes on the environment. Biodiesel is sustainable and biodegradable because it is made entirely from oil or animal grease.[2] Free fatty acids, water, aromatic oils, phospholipids, sterols, and other contaminants are typically present in plant oils. These prohibit the oil from being employed promptly as an energy source. Transesterification, pyrolysis, and emulsification are the key chemical transformations that the oil needs to undergo to solve these issues. Transesterification is the first and most significant process among these to create cleaner and safer fuel from vegetable oils.[3] The process of transesterification of animal or plant-based fats like sunflower, palm oil with alcohol which are short chained, for example, ethanol and methanol results for the production of biodiesel, an alkyl ester of fatty acids. Resultantly, the synthesis of biodiesel produces glycerin as a byproduct. [4]

The benefits of biodiesel over petroleum diesel (PD) in decreasing exhaust emissions might be summed up as possessing a high flash point and being made from renewable sources. Since biodiesel contains more oxygen than PD, it reduces emissions of particulates, carbon monoxide, hydrocarbons, sulfur, polyaromatic compounds, noise and smoke when used in diesel engines.[5]

The yield of biodiesel can be enhanced by using suitable catalysts. Due to their high catalytic activity, homogeneous base catalysts, such as $CH_3ONa$, $NaOH$, $CH_3OK$, and $KOH$ are most generally utilized for the commercial process to synthesize biodiesel.[6] In the homogeneous catalyst-catalyzed transesterification, the reactant, oil, must have an acid value less than one and be essentially dehydrated. Moreover, saponification, an unwanted side reaction, happens and an additional procedure is compulsory to recover these homogeneous catalysts, leading to a high manufacturing expense. On the contrary, using other types of catalysts referred to as heterogeneous catalysts such as ion exchange resins (IE) and zeolite have obvious benefits because they are not corrosive, simple to remove from the ion mixture, and do not need product washing.[7]

This research will focus on transesterification of palm oil and methanol by using Amberlyst A26 and Amberlite IRA402 as heterogenous catalyst. Among different choices of alcohol, methanol is foremost the better choice in terms of availability and cost. Moreover, due to higher reactivity of methoxide intermediate, methyl ester is likely to form faster than ethyl ester. Nevertheless, methanol is less miscible in oil but to enhance the miscibility, tetrahydrofuran was used as co-solvent. Additionally, ethyl ester tends to form stable emulsion at the end of reaction, which makes it difficult to extract, while methanol is feasible to extricate. IE resins are promising as heterogenous catalysts, but there have not been many publications on their usage in the synthesis of biodiesel with methanol. This represents an evolution at the use of the catalysts Amberlyst-A26 and Amberlyst-IRA402 for palm oil transesterification to biodiesel.

## 1.1 Objectives

To investigate the effects of anion exchange resin types (IRA402 and A26) on FAME generation rates with tetrahydrofuran (THF) as a co-solvent in the transesterification of refined palm oil with methanol.

## 1.2 Research scope

1. Dense IRA402 and porous A26 were used as heterogeneous catalysts.
2. Methanol and refined palm oil were used as reactants.
3. Cosolvent THF was used to enhance the solubility of methanol in oil.
4. Standard transesterification conditions: molar ratio of 9.5:1, anion exchange resin as catalyst at 60 °C with 1500 rpm.

## 1.3 Expected outcomes

1. Study of heterogenous catalysts to improve the yield of FAME content.
2. Comparison of the performance of IRA402 and A26 in transesterification.
3. Reaction rate modelling for transesterification of refined palm oil with methanol and THF as cosolvent and anion exchange resins as heterogenous catalysts.

# CHAPTER II

# Theories and literature review

## 2.1 Biodiesel

The main physicochemical processes that may be used to make biodiesel include transesterification, esterification, pyrolysis, and supercritical fluids. The most popular technique of producing biodiesel out of all of them is transesterification, which involves reacting triglycerides and alcohol with catalysts to form fatty acid and glycerin.

Depending on the manner of processing, a variety of raw materials, animal greases, vegetable oils, algal oils and waste oils are just a few of the possible kinds of oils that can serve as raw material for biodiesel production. Additionally, using biodiesel made from oil derived from plants, an ideal supply for biodiesel production, demonstrates how using biodiesel may significantly cut greenhouse gas emissions while also being economically advantageous.[8-10]

The amount of biodiesel produced worldwide has grown recently. A 7.5% growth from 2015 to 2016 was reported as the production was more than 30.8 million $m^3$ ($Mm^3$). In 2016, the United States, Germany, Argentina, Brazil, and Indonesia were top producers. The European Union's member states generated 10.7 $Mm^3$, or 34.7% of the world's biodiesel synthesis, in 2016.[11]

## 2.2 Transesterification reaction

Transesterification is a process which uses alcohol to replace one ester's alcohol with another. Transesterification is a reversible process, and it mostly entails mixing the reactants. A catalyst, such a strong basic or acid, has the effect of speeding up the conversion of reactants to product.[3, 12]

$$R'COOR + 3CH_3OH \leftrightarrow 3RCOOCH_3 + C_3H_8O_3 \quad (1)$$

The transesterification mechanism consists of three phases, each of which is a reversible reaction. In each step out of three, alcohol and fatty acid, in glyceride form are combined in each step to create one mole of water and an ester. Three fatty acids make a triglyceride, or TAG, molecule, therefore three moles of alcohol are needed to completely convert each TAG molecule into an ester as in Figure 1. A stoichiometric excess of alcohol makes the transesterification process more effective because it shifts reaction equilibrium in favor of esters. Another technique to keep the reaction going is to constantly remove one of the intermediates from the mixture. [13]

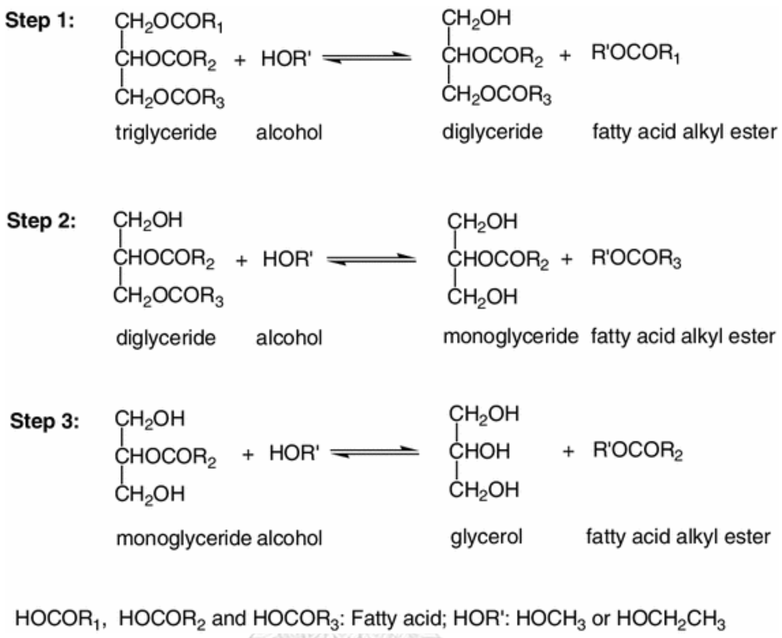

*Figure 1: Mechanism of Transesterification* [13]

## 2.3 Catalysts for transesterification:

Different types of catalysts are used to convert fats into FAMEs. They are broadly categorized as homogeneous and heterogeneous catalysts. Homogeneous catalysts offer faster kinetics, but catalyst separation is an issue. In practice, the catalysts are neutralized and separated as salts.[14]

NaOH, KOH, $CH_3ONa$, and $CH_3OK$ are common homogenous catalysts for transesterification. The most effective of these sodium methoxide $CH_3ONa$, which yields biodiesel exceeding 98 wt.% in a matter of minutes (30 min).[15] In a study, researchers trans esterified seed oils with methanol utilizing alkaline catalysts to produce biodiesel. According to the authors, KOH increased the reaction's seed oils' catalytic activity. During this study, reaction conditions used were, molar ratio of methanol to oil was 6:1, a 1 weight percent loading quantity of catalyst, at 65 °C reaction temperature, for 3 h. At these experimental parameters, the biodiesel contents of the Camellia and Vernicia seed oils were 97.7 % and 96.1 %, respectively, on KOH catalyst.[16]

For homogenous catalysts, Na-based catalysts are endorsed over K-based catalysts due to their molecular weight, a lower weight of the catalysts is needed for the same number of moles.[17] Nonetheless, the resultant biodiesel as well as glycerin must be extracted by washing with hot distilled water at least twice in order to neutralize the basic catalyst.[18]

The main advantage of homogeneous catalysts is that they react in the identical phase of the reaction mixture.[19] The most apparent downside of adopting alkaline homogeneous catalyst is how fast the saponification process might start, particularly for feedstocks which contain high free fatty acid (FFA) concentrations. Biodiesel, wastewater and glycerin used for washing cannot be separated from each other when soap is formed.[20]

In contrast, heterogeneous catalysts provide us with a range of benefits, including rapid glycerol recovery, efficient catalyst recovery, better product purification, cheap catalyst reuse, and less energy and water usage. Additionally, while having a leaching issue, the majority of heterogeneous catalysts, particularly solid alkaline catalysts, have made excellent rates.[21] Enzyme catalysts tolerate free fatty acid and water concentrations, making it simple to purify biodiesel and glycerol. This has made the application of enzyme catalytic synthesis of biodiesel a popular topic in recent years. Unfortunately, because of its massive cost and prolonged residence time, this category of catalyst is not much cost efficient for commercial purposes to make biodiesel.[22]

On the other hand, the entire synthetic cycle for heterogenous catalyst is economically and ecologically sustainable since they may be used and recycled several times without adversely affecting their efficiency.[23] Ion exchange resins (IERs), an example of heterogenous catalysts, which are copolymers of styrene and divinylbenzene with quaternary ammonium or sulfonic acid functional groups on their backbone.[24]

### 2.3.1 Heterogenous anion exchange catalysts:

There are two categories for ion exchange resin are anion-exchange and cation exchange, resins. Former resin mentioned typically include a polymeric matrix comprised of multiple functional groups. Whilst strongly basic anion exchange resins contain quaternary ammonium groups, the majority of weak basic are made of amino groups. The two both take the shape of gel or macroporous beads. Standard anion-exchange resins sold in the market are classified as type 1 or type 2 resins, which are strongly basic or weakly basic resins, respectively. On the other hand, cation exchange resins are composed of cross-linked polymer charged functional groups capable of exchanging ions with the surrounding solution $H^+$, $Ca^{2+}$, $Na^+$ $K^+$ .[25] Acidic cation exchange resins can be used to catalyze feedstock with higher FFA content for biodiesel production.

The intensity of the alcohol's adsorption on the resin was found to be substantially more than that of the ester, according to Mazzotti et al (1997). The anion-exchange resins displayed more activity than the other one, because of this. High conversion as well as higher reaction rate were produced by these resins with reduced cross-linking density and small size particle. [26]

Ramon Sousa Barros Ferreira et al. discussed the mechanism of anion exchange resin in Figure 2 during transesterification. Alcohol (A) gets adsorbed on the active site of resin($S(OH^-)$), in the first step, which results in an alkoxide ion $A^-$ and an $H^+$ ion. A fatty acid alkyl ester (E) molecule and an ionized diacylglycerol ($D^-$) molecule are created when the produced alkoxide attacks the triacylglycerol (T) molecule. To generate neutral diacylglycerol, negatively charged diacylglycerol is electrophilically attached to the $H^+$ ion (D). The production of the second alkyl ester molecule originates from the nucleophilic attacks of A to on the diacylglycerol in the second phase, alongside the creation of the monoacylglycerol (M) molecule and the alkyl ester. The third stage entails the formation of a glycerol (G) molecule coupled with the generation of the third alkyl ester molecule.[27]

**1° step** $A + S(OH^-) \rightleftarrows A^- + S(OH)^- - H^+$

$$A^- + T \rightleftarrows AT^-$$

$$AT^- \rightleftarrows E + D^-$$

**2° step** $D^- + S(OH^-) - H^+ \rightleftarrows D + S(OH)^-$

$$A^- + D \rightleftarrows AD^-$$

$$AD^- \rightleftarrows E + M^-$$

**3° step** $M^- + S(OH^-) - H^+ \rightleftarrows M + S(OH)^-$

$$A^- + M \rightleftarrows AM^-$$

$$AM^- \rightleftarrows E + G^-$$

$$G^- + S(OH^-) - H^+ \rightleftarrows G + S(OH)^-$$

Figure 2: Mechanism for anion exchange resin [27]

Research by N.jaya et al. (2015) revealed that pongamia oil can be trans esterified using heterogenous catalyst. Heterogeneous catalyst-based biodiesel synthesis decreases sludge output and production costs by roughly 5%. In the ideal conditions of molar ratio of 9:1 at 75 °C with 2 wt.% anion heterogeneous catalyst and 270 rpm, pongamia oil delivers a higher yield of fatty acids ethyl esters (FAEE). The ASTM fuel criteria are met by trans esterified pongamia oil. With permissible emission standards, this diesel mix was sufficient for transportation at 48% load.[7]

The study by Ramon (2021) showed the strong effect of resin Purolite A503S on transesterification of palm oil for ethyl esters. By utilizing 17.6 % catalyst with molar ratio 1:12.85 at 49.4 °C temperature, an approximated conversion of 98.10 % in FAEE was achieved from the optimized variables. The resin Purolite A503S is a prospective catalyst used in transesterification reaction despite the prolonged reaction time.[28]

Isabel J. et al. (2020) presented a study for trans-esterification of palm oil and ethanol using the strong heterogenous anion exchange resin. Catalysis reaction was done in a glass reactor at 400 revolutions per minute with a suspended magnetic bar on a magnetic stirrer. Anhydrous ethanol and Amberlyst A26OH, a resin that had previously undergone pretreatment, were added to the reactor in known amounts. To measure the content of FAEE with ongoing transesterification procedure, samples were taken at predetermined intervals of time. This study emphasizes how crucial resin preparation is. The ideal operating conditions, which can ensure a high conversion to FAEE in 8 hours, are catalyst amounts of 6% and 10%, temperatures between 55 °C and 60 °C, and molar ratios ranging from 3.5:1 to 6.0:1as shown Figure 3.[29]

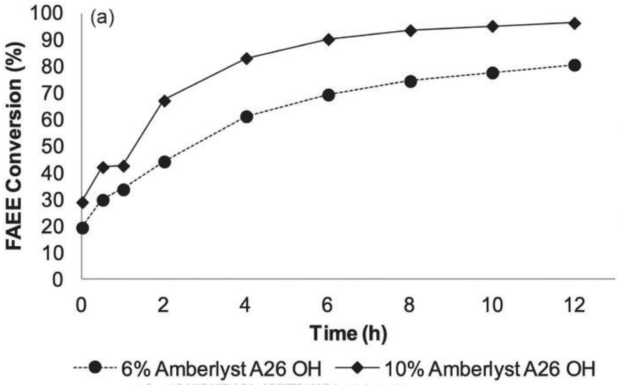

Figure 3: Effect on FAEE with different wt.% of A26 resin[29]

### 2.3.2 Methods to prepare heterogenous catalysts for FAME:

Biodiesel can be prepared by using many types of heterogenous catalysts and raw materials as well. Few of the studies are mentioned which showed the production of biodiesel by different heterogenous catalyst.

Tongxin et al. (2021) elaborated a study which used Cao modified Zn-Ce/$Al_2O_3$ as a heterogenous catalyst prepared by hydrothermal method. With the molar ratio of Ca: Zn: Ce: Al being 4:4:1:1, the following substances are dissolved in DI water for the hydrothermal (HT) method: Ca $(NO_3)_{24}H_2O$, Al $(NO_3)_{39}H_2O$, Ce $(NO_3)_{36}H_2O$ and Zn $(NO_3)_{26}H_2O$. The urea co-precipitator is then slowly added to the nitrate solution at a molar ratio of 1:2, and the mixture is continuously agitated for one hour. The mixture was autoclaved at 120 °C for a day. The solution was desiccated at 105 °C temperature and then was calcined at 850 °C in order to activate this catalyst after being chilled to ambient temperature. Because of its extensive surface area, fine pore structure, optimal uniformity, and excellent stability, heterogenous catalyst has the best catalytic capability, with a biodiesel yield of 85.34 %. The catalyst wt% used is 8% for 3 hr at temperature of 65 °C. [30]The problem with using this catalyst is that it requires high temperature for activation and crude biodiesel has to be washed to remove residual glycerol and then vaporize it at 80 °C, which increase the overall production cost.

In a study conducted in 2013 by Nyoman et al., it showed that $CaO/KI/\gamma\text{-}Al_2O_3$ heterogenous catalyst can be used in transesterification of palm oil with methanol. The catalyst was prepared by precipitation and impregnation method. Supported CaO by alumina roughly took 8-9 h to prepared at high temperature. After that catalyst was dried at 105 °C overnight to remove water content. This study found the optimum condition for transesterification by varying temperatures, molar ratio, weight of catalyst and reaction time. Reaction pressure was kept at 4-12 MPa at reaction temperature of 210-290 °C. This process gave the FAME yield 81% for 30 min at temperature 290 °C using sub-supercritical methanol. [31]

In another process, sulfonated graphene was reported as a potential heterogenous catalyst for trans-esterification of palm oil and methanol. Palm oil was made at lab scale by collecting fine palm fruits. A procedure was utilized for the synthesis of graphene oxide (GO) and reduced graphene oxide (r-GO) from graphite powder and various chemical reagents. The GO was subjected to sonication in DI water followed by treatment with $Na_2CO_3$ and hydrazine hydrate to produce r-GO. The r-GO was subsequently filtered, washed with 1 N HCl and acetone, and dried under vacuum. For trans-esterification, palm oil and methanol were stirred for 24 h at 100 °C. Reaction time for this study was 10 h at a higher temperature of 100 °C with catalyst loading 10%. [32]

The procedures to prepare the catalyst for transesterification are quite complex and time consuming. So, this study will use commercially available anion exchange resins to determine the behavior of fatty acids methyl esters. In addition to that, heterogenous catalysts are easy to recover from the product. The overall cost of this process will be reduced as compared to a system using homogenous catalyst, as it eliminates the need for soap washing step.

### 2.3.3 Previous Studies with Amberlyst A26-OH:

Numerous studies have reported the application of A26 for synthesis of biodiesel, summarized in Table 1. Some of these studies observed the general behavior of Amberlyst A26-OH and others tried to optimize the yield of FAME or FAEE. Oguzhan (2008) trans-esterified the canola oil using ethanol, isopropanol and methanol in presence of two different cosolvents. The findings of this study suggested that it not economically possible for this resin with canola oil for production of biodiesel as highest recorded yield was only 67%.[33] Yousaf and coauthors (2015) carried the methanolysis of soybean oil by using strong anion exchange resin. They explained the reaction mechanism by Eley-Rideal occurring of surface of resin. [34] Vafakish and Barari (2016) used Amberlyst A26 for trans-esterification of animal fat with methanol. Range of reaction time and catalyst loading were investigated for this study. The biodiesel obtained met the fuel standards and yield was about 95%. [35] Other study by Tiana et. al. (2018) tested the production of FAEE and deacidification of soybean oil at the same time to enhance the application of transesterification. [36]

*Table 1: Studies with A26 anion exchange resin*

| ***Resin*** | ***Type of alcohol*** | ***Reaction temperature*** | ***Type of oil*** | ***Reaction time*** | ***Stirring speed*** | ***Molar ratio*** | ***Reference*** |
|---|---|---|---|---|---|---|---|
| *Amberlyt-A26 OH* | Ethanol, isopropanol, and methanol | 45 ºC | Canola oil | 0-8 h | 1000rpm | 6:1 | [33] |
| *Anion exchange A26* | Methanol | 50 ºC | Soybean oil | 0-18 h | 550 rpm | 10:1 | [34] |
| *Amberlyst-A26* | Methanol | 65 ºC | Tallow fat | 1-8 h | NA | 6:1 | [35] |
| *A26-OH form* | Ethanol | 60 ºC | Soybean oil | 0-15 h | 500rpm | 9:1 | [36] |

## 2.4 Effect of alcohol type on transesterification:

The kind of alcohol used and the molar ratio to oil greatly influence the production and characteristics of biodiesel. At optimized reaction conditions, the yield of biodiesel produced with Karanjna oil was 91.05% for methanolysis and 77.4% for ethanolysis. The lower yield may be a result of ethanol's lower reactivity as contrasted to methanol and the challenge of purifying it from glycerine. The optimal reaction conditions for ethanolysis were 8.42:1 molar ratio, at 61.3 °C, 1.21 wt.% of catalyst, and 2 hr to generate 77.4% yield. For methanolysis, 91.05% yield was reached by maintaining a molar ratio of methanol of 10.44:1 for 1.5 hr at 66.8 °C.[37]

Idris and coauthors (2016) discussed the results of alcohol used on yield and quality of biodiesel. The most common usage for alcohol in transesterification is methanol, as it’s a short chain alcohol and less expensive as compared to ethanol. An alcohol's moisture concentration is crucial for its optimal use in the synthesis of biodiesel. This is related to the hydrolysis of triglycerides to fatty acid that proceeds when water is present during the transesterification process, which results in the creation of soap and low yield. Regrettably, all short-chain alcohols are hygroscopic and are capable of readily absorbing water from the surrounding environment. On the other hand, ethanol can be suggested as a better alternative because of its less toxic nature. But ethanol in transesterification is much less reactive. In addition to that methanol does not make azeotrope with water and easily recoverable, while ethanol makes complex organic compound. Other choices of alcohols like propanol, tert-butanol, butanol, octanol and other branched alcohols can also be utilized but they are quite expensive as compared to methanol and ethanol.[38]

H Sanli and coworkers (2008) presented a study where the different types of oil were checked against the various types of alcohol for transesterification reaction. Different temperatures for reaction were set according to the type of alcohol, few were conducted at room temperature and others were below the boiling temperature of alcohol. The lab scale reactor was used with a water-cooled condenser. All the experiments were conducted at the same speed, 1000 rpm. For acid and alkaline catalyst, when ethanol was used in reaction at 75 °C for 48 h, product obtained did not match the quality required for biodiesel standard. However, during the reaction of methanol as reactant, the yield obtained was 97.85% with reaction condition 6:1 molar ratio for 1h, 1% wt. KOH. But when molar ratio was changed to 3:1 the quality of fuel dropped.[39]

**2.5 Cosolvents for transesterification:**

Yanbiao and others (2012) investigate the effect of various cosolvents on trans-esterification of soybean oil with methanol with heterogenous catalyst, anion exchange resin D26. This resin was identified to have a better catalytic activity. The FAME conversion may be substantially increased where n-Hexane was used as co-solvent. Under ideal circumstances, the conversion of FAME measured was 96%. According to GC-MS results, the product is simplex and mostly made up of methyl esters. Due to resin absorbing glycerol, it was not detected, which is favorable for product extraction.[40]

Nichaonn and coworkers (2017) conducted the research to make biodiesel by waste cooking oil and methanol and calcium methoxide catalyst. The pace of the reaction can also be increased by enhancing the oil and methanol solubility and mass transfer by adding a cosolvent to the reaction media, such as tetrahydrofuran (THF). Research studies involving a complicated variable process have been subjected to the use of the response surface methodology (RSM). The study examined how the concentrations of the catalyst and THF affect the conversion of FAME after 1.5 hours at a 10:1 methanol to oil molar ratio. The outcomes demonstrated that higher levels of both catalyst and THF concentrations were associated with greater FAME conversion rates.

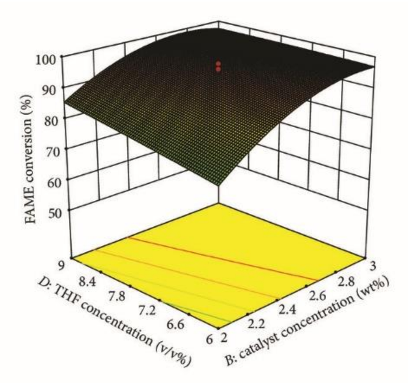

*Figure 4: RSM for FAME conversion w.r.t THF and catalyst concentration* [41]

In the absence of THF, a 99.06% FAME conversion rate was achieved at specific reaction conditions, including a 12:1 molar ratio, 65C temperature, and 3% catalyst for a duration of 3 hours. However, when THF was utilized to decrease molar ratio, a similar FAME conversion rate of 99.06% was obtained with a lower catalyst loading of 2.83% and a shorter reaction time of 1.669 hours mentioned in Figure 4. The findings suggested that the presence of THF expedited the catalytic process by improving the mixing of methanol and the $Ca(OCH_3)_2$ catalyst. [41]

M Taherkhani (2018) did research on transesterification of linseed oil with methanol where THF as cosolvent in presence of KOH as catalyst was used. When co-solvent was not utilized, the greatest yield percentage was 84.3%; whereas, by adding cosolvent, the highest FAME yield was 93.15%. Biodiesel from linseed is substitute fuel for extremely cold climates since it has a low pour point of -17 °C and a low cloud point of -7 °C. The optimal conditions (7.30 wt% catalyst, 750 rpm, 50 °C for 2 hr) allowed for the production of biodiesel with a yield of 84.3% and FAME purity of 99.7% without requiring the use of a co-solvent. Conversely, when THF was employed as a co-solvent (6.80 wt% catalyst, 700 rpm, 40 °C for 1.5 hr), the biodiesel yield was 93.15%, and the FAME purity was 99.8%. [42]

Simone et al. (2005) performed the transesterification by using different vegetable oils in presence of short chained alcohol methanol with cation exchange resin Amberlyst A15 in presence of THF as cosolvent. A two-necked reactor with a reflux condenser was used over a magnetic stirrer for constant stirring in each experiment. Various molar ratios of methanol to oil and same amount of resin were utilized in the reactions, which were performed at 60 °C for 2–8 h with the help of a co-solvent (THF). They demonstrated that fatty acid content of the oil influences the transesterification of methanol with vegetable oil catalyzed by ion-exchange resins as shown in Figure 5. Higher methyl esters yields are generated by vegetable oils with short chain FA, most likely so because the polar resin phases have active sites which are more accessible.[43]

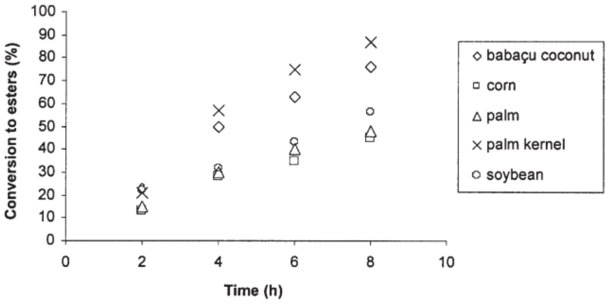

Figure 5: Effect on FAME for different type of oil over time [43]

## 2.6 Parameters affecting transesterification reaction:

The trans-esterification process, which entails the combination of an ester functional group with an alcohol to produce a different ester and alcohol, can be affected by a variety of variables. The reactants, the catalyst employed, the alcohol-to-oil ratio, the reaction temperature, and the reaction duration are a few examples of these factors. To obtain a high yield of the desired product with excellent quality, as well as to reduce the manufacturing cost and process's effect on the environment, it is vital to optimize these factors. Therefore, for the effective implementation of this chemical reaction in different industrial and research uses, a comprehensive knowledge of the parameters influencing transesterification reaction is required.

### 2.6.1 Oil to alcohol molar ratio:

The molar ratio of oil to alcohol has subsequent effect on conversion of FAME. In general, more methanol should be employed during the transesterification process than is necessary for mixing with the oil. The extra methanol acts as a catalyst to speed up the process and increase the biodiesel output. The output of biodiesel will be reduced if the oil to methanol ratio is too low because there might not be enough methanol to completely react with all the oil. On the other hand, if the percentage is too high, there might be too much methanol, which could cause unwanted side effects like the production of soap, which would reduce the output of FAME. For transesterification reaction to complete, 3 mol of alcohol is necessary to reaction with 1 mol of oil.[44] The surplus amount of methanol is added to make sure that reaction is completed without formation of soap. A range of molar ratio of alcohol to oil is tested from 3:1 to 24:1 , it was observed that yield spiked up to a certain ratio and started to decrease when there is too much alcohol. [45] when using dolomite catalyst the FAME yield increased upto 15:1 molar ratio and then started decline. [46]

### 2.6.2 Stirring speed:

Stirring speed during reaction affects the yield of biodiesel. A study in 2021 reported the influence of stirring speed on FAME yield when using palm oil and a strong anion exchange resin. [28] At low speed some resin beads may be stay at bottom of reactor which will eventually reduce the reaction rate. For all the experiments conducted for this study, the stirring speed was constant at 1500rpm.

### 2.6.3 Reaction temperature:

One of the most important parameters that affects the yield and quality of biodiesel is reaction temperature. Reaction temperature decreases the impulsive potency of the resin $OH^-$ due to which temperature is kept constant at 50 ºC. Temperature below 50 ºC does not produce the required yield of FAME. [47] The conversion of FFA was investigated in range of 50-60 ºC with Amberlyst-15 anion exchange resin. Catalyst loading in sink to reaction temperature is crucial. More yield of FAME was observed when reaction temperature is less than boiling temperature of methanol. [48] The catalytic activity of heterogenous catalyst has an impact on the reaction time and temperature. Higher temperature can lead to less activity of the A26 resin. The ideal range to conduct reaction for A26 resin is 45-60 ºC. [36]

### 2.6.4 Reaction time:

The duration of reaction is also vital for the trans esterification reaction. In general, the methyl or ethyl ester contents increase over longer periods of time while reaction temperature is even lower. But at higher temperature when equilibrium established quickly the FAME conversion decreases at longer time. [49] In other study it was observed that longer reaction time has not have significant effect on yield of biodiesel. [50]

From literature review, it has been explained that the transesterification reaction is the process by which triglycerides (such as those found in palm oil) react with an alcohol (such as methanol) to produce esters, the main element of biodiesel. In this reaction, a catalyst is typically used for reaction rate enhancement and improving the yield of the desired product. Ion exchange resins are a type of solid catalyst that have the potential to be effective in transesterification reactions. However, despite their potential advantages, and as per our best knowledge, there hasn't been a lot of research published on their use as catalysts for production of biodiesel using methanol. By using Amberlyst A26 and Amberlite IRA402 as heterogenous catalysts in the transesterification of palm oil to make biodiesel, this research aims to investigate the effectiveness of these anion exchange resins and provide new insights into their potential use in this application. This could represent an evolution in the use of these catalysts for biodiesel, as it expands our understanding of their capabilities and could lead to improved processes for producing biodiesel.

# CHAPTER III

# Materials and Methodology

## 3.1 Materials

The AmberLite$^{TM}$ IRA402 & AmberLyst$^{TM}$ A26 (Sigma-Aldrich) were acquired from a local supplier. Commercially available palm oil (Morakot) was bought from a grocery store in Bangkok, Thailand. Merck’s ACS reagent Tetrahydrofuran (THF) was added to the reaction mixture as a co-solvent. Thermo Fisher’s analytical reagent Methanol (Merck) was utilized as the primary alcohol for transesterification reaction. As the resin IRA402 was originally supplied in its chloride form, sodium hydroxide (Merck) was used to convert the resin into its hydroxide form by ion exchange. Hydrochloric acid was used to decrease the hydroxide contents of both types of resin in some experiments.

## 3.2 Methods

### 3.2.1 Preparation of resin by ion exchange:

The AmberLite$^{TM}$ IRA402 & AmberLyst$^{TM}$ A26 are in Cl and OH form as supplied. The IRA402 resin needs to be converted into the OH form, whereas the A26 resin can simply be washed with methanol. To change the resin IRA402 into the OH form, 4 mL resin needs to be stirred in volume of 32 mL of 1.5 M NaOH solution for 30 min. The excess sodium hydroxide replaces the chloride ions on the resin with hydroxide ions, effectively converting the resin from the Cl form to OH. The 30 min stirring time is typically sufficient to ensure that all of the chloride ions on the resin have been replaced by hydroxide ions. After the resin has been stirred in the NaOH solution, it needs to be washed with methanol until the pH of washing methanol becomes stable to remove any residual sodium hydroxide and other impurities not adsorbed and, importantly, to convert hydroxide into methoxide, which is the active catalytic species for transesterification with methanol. The ion exchange process is summarized for IRA402 in Figure 6 and Figure 7 for A26 resin.

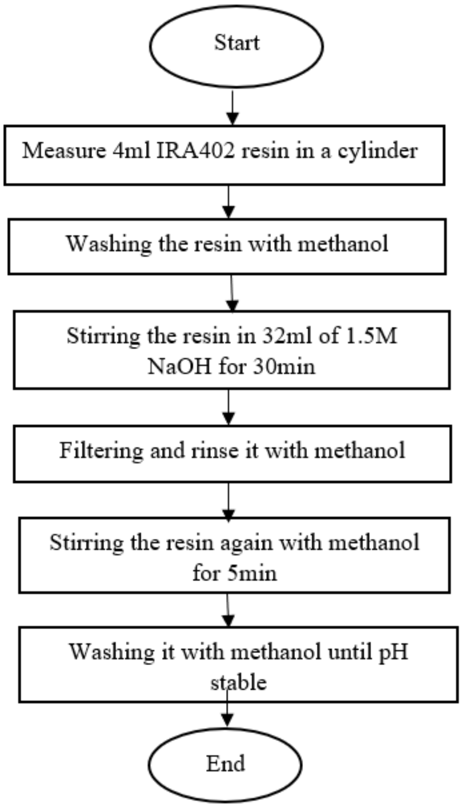

*Figure 6: Method for preparation of IRA402 resin*

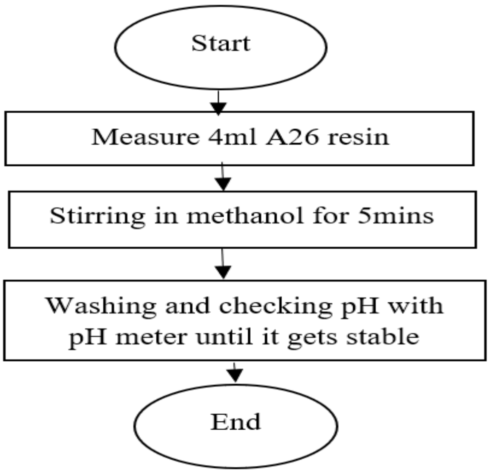

*Figure 7: A26 resin preparation*

### 3.2.2 Resin characterization:

Bothe resin IRA402 and A26 were characterized by SEM (Hitachi S-3400N) for their morphology.

Resin A26 was washed with methanol whereas resin IRA402 was converted into OH form by using 1.5M NaOH solution and then washed with methanol. Washed resin was dried in oven overnight before testing. It can be observed that A26 OH is porous but IRA402 OH is quite dense.

Pore volume and surface area of resins were estimated by $N_2$ physisorption with Brunauer-Emmett-Teller (BET) isotherm.

### 3.2.3 Transesterification reaction

A three-neck jacketed reactor with a thermostatic water bath was used to conduct transesterification experiments. A magnetic stirrer with a magnetic bar was used to agitate the reaction mixture during the experiment at 1500 rpm. A thermometer was positioned within the reactor to monitor the temperature of the reaction. Methanol and THF that evaporated during reaction and heating was recovered to the reaction mixture with a glass reflux condenser. The reactor was filled with 13.9 g of palm oil and 20.89 mL of THF, the flow of reaction is mentioned in Figure 8, which were then preheated to the desired temperature, 60 °C, which was kept constant for all experiments. Then, 6.309 mL of methanol was poured into the reactor along with 4 mL of anion-exchange resin. The reaction time was then initiated after heating the mixture of anion-exchange resin, methanol, and palm oil to the reaction temperature. These amounts resulted in a total liquid volume of ca. 42 mL and a molar ratio of methanol to oil of 9.5:1.

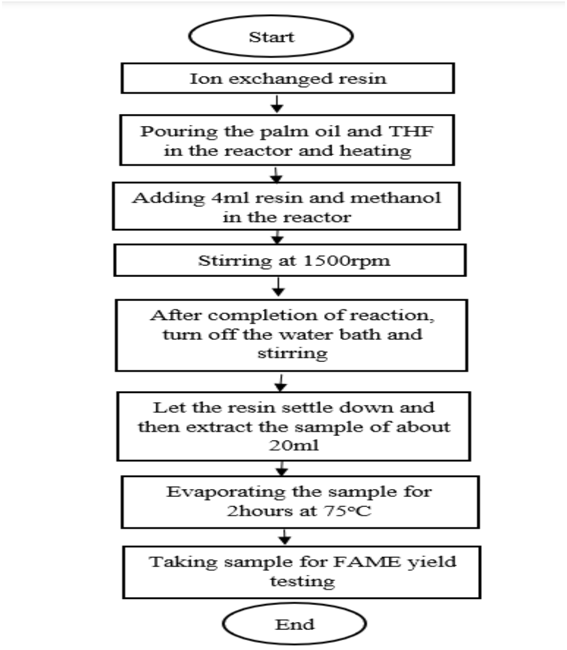

*Figure 8: Transesterification for biodiesel production*

The following Figure 9 illustrates the setup used for the transesterification of methanol and palm oil.

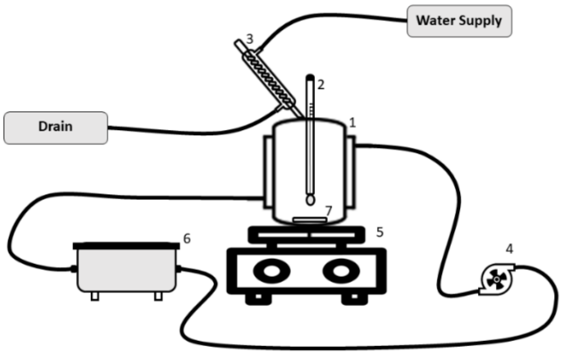

*Figure 9: Experimental Setup for transesterification (1) jacketed reactor (2) thermometer (3) condenser (4) pump (5) magnetic stirrer (6) water bath (7) magnetic bar*

### 3.2.4 Analysis of FAME:

After completion of reaction, 20 mL of the reaction mixture without resin was collected and heated to 75 °C for 2 h in a jacketed vessel for evaporation of unreacted methanol and THF. The remaining liquid was centrifuged for 2 min. Only the top oily phase was analyzed for its FAME yield.

To evaluate the FAME yield percentage, Gas Chromatography (GC) was employed. The GC system was equipped with a DB-WAX column measuring 29.9 m in length, 0.32 mm (about 0.01 in) in diameter, and 0.25 µm in thickness, in addition to a flame ionization detector (FID). A sample with a weight of 0.25 ± 0.015 g was prepared and mixed with an internal standard of methyl heptadecanoate, which weighed 0.050 ± 0.005 g. The resultant mixture was diluted to a volume of 5 ml (about 0.17 oz) in n-heptane. The GC system was programmed to inject 1 µL of the sample, with an injection temperature of 250 °C. The temperature was then kept at 150 °C for 5 min before being raised at a rate of 3 °C $\text{min}^{-1}$ to 190 °C and maintained at 220 °C for the following 5 min.

The GC showed five peaks and yield for FAME was calculated by following formula.

$$\text{FAME yield\%} = \left\{\frac{A_{\text{FAME}}}{A_{\text{IS}}} \times \frac{m_{\text{IS}}}{m_{\text{S}}}\right\} \times 100\% \qquad (2)$$

$A_{\text{FAME}}$ is the total Area of FAME peaks.

$A_{\text{IS}}$ is the area of internal standard.

$m_{\text{IS}}$ is the mass of the internal standard in the diluted sample.

$m_{\text{S}}$ is mass of the sampled oily phase containing FAME.

The FAME content obtained from analysis by GC is:

$$\text{FAME content} = \frac{m_{\text{FAME}}}{m_{\text{FAME}} + m_{\text{MG}} + m_{\text{DG}} + m_{\text{TG}}}$$

Only the oil phase after solvent/methanol evaporation was injected to the GC. Therefore, glycerol and methanol could be assumed not to exist in any GC samples.

The exact way to determine the actual mass of FAME generated from a given mass of oil is to multiply the FAME content by the mass of the oil phase remaining after solvent evaporation, which is very difficult to measure due to the coexistence of two phases after transesterification.

An approximate method is to multiply the FAME content by the initial mass of oil used in the experiment. This is plausible because both FAME and glycerides share the same large numbers of carbon atoms in the acyl groups. It could be shown that:

$$\frac{3m_{\mathrm{FAME}}}{m_{\mathrm{TG}}} = \frac{3 \times 289.8\ \mathrm{g\ mol^{-1}}}{847.3\ \mathrm{g\ mol^{-1}}} = 1.03$$

$$\frac{2m_{\mathrm{FAME}}}{m_{\mathrm{DG}}} = \frac{2 \times 289.8\ \mathrm{g\ mol^{-1}}}{595.5\ \mathrm{g\ mol^{-1}}} = 0.97$$

$$\frac{m_{\mathrm{FAME}}}{m_{\mathrm{MG}}} = \frac{289.8\ \mathrm{g\ mol^{-1}}}{343.8\ \mathrm{g\ mol^{-1}}} = 0.84$$

In other words, glycerides could be considered as multiples of FAME molecules. Therefore, the mass gain from methanol or loss in glycerol in the oil phase after transesterification and solvent evaporation could be neglected. This ultimately led to the assumption that the mass of the oil phase after solvent evaporation was the same as the initial mass of oil used in that experiment. Hence, the mass of FAME generated could be obtained by multiplying the FAME content by the initial mass of oil.

## 3.3 Calculations used in this study:

### 3.3.1 The calculation for concentration of FAME by A26 resin:

To calculate the concentration for FAME by A26 resin, the following values were used in the designed model.

$$c_{TG,b} = c_{TG,b}\,|_{t=0\ s}\; e^{\frac{-t/V}{\frac{1}{kxv+k_S x a_S}+\frac{1}{k_C a_S}}} \qquad (35)$$

V is the total volume of reactor including oil, THF and methanol which approximately sum up to 42ml.

$a_S$ is the surface area of resin beads which is equal to

$$a_s=\frac{submerged\ density}{particle\ density}\times\frac{amount\ of\ resin}{1000}\times\frac{3}{radius\ of\ resin}\qquad(36)$$

$c_{TG}$ at t=0 is

$$c_{TG}=\frac{\left[\frac{amount\ of\ oil\ used}{molar\ mass\ of\ palm\ oil}\right]}{total\ volume\ of\ reaction\ mixture}\qquad(37)$$

total volume of resin beads is.

$$V=\frac{submerged\ density\ of\ resin\ bed}{particle\ density\ of\ resin}\times\frac{amount\ of\ resin}{1000}\qquad(38)$$

Modelling has been done on Microsoft excel for ease of calculations.

### 3.3.2 The calculation of amount of HCl used to remove basic sites on resin surface:

As in some experiments, basic sites of resin were replaced from $OH^-$ to $Cl^-$, 37% of HCl solution was used for this process. First resin was washed with methanol to remove any moisture and then stirred in HCl solution for 30mins.

Below are the calculations to get the 50% basic sites of resin.

$$=\frac{amount\ of\ resin\times exchange\ capacity\ of\ resin\times relative\ hydroxide\ conten\ needed\ to\ remove\times molar\ mass\ of\ HCl}{\frac{percentage\ of\ HCl\ used}{density\ of\ HCL}}\qquad(39)$$

$$\text{Volume of HCl used}=\frac{(0.0004\ L\ resin)(0.73\ mol/L)(0.5)(36.46\ g/mol)}{(0.37)/(1.19\ g/ml)}\qquad(40)$$

Volume of HCl used= 0.00012ml

As this is a very small amount, the volume was measured using a micropipette.

### 3.3.3 The calculation of FAME yield by GC:

After completion of reaction and removing THF through evaporation, sample is collected and analyzed through GC. The sample in GC has three components, internal standard methyl heptadecanoate, biodiesel and n-heptane.

The GC showed five peaks in Figure 10. The first highest peak is n-heptane followed by methyl palmitate, methyl heptadecanoate, methyl linoleate and methyl oleate.

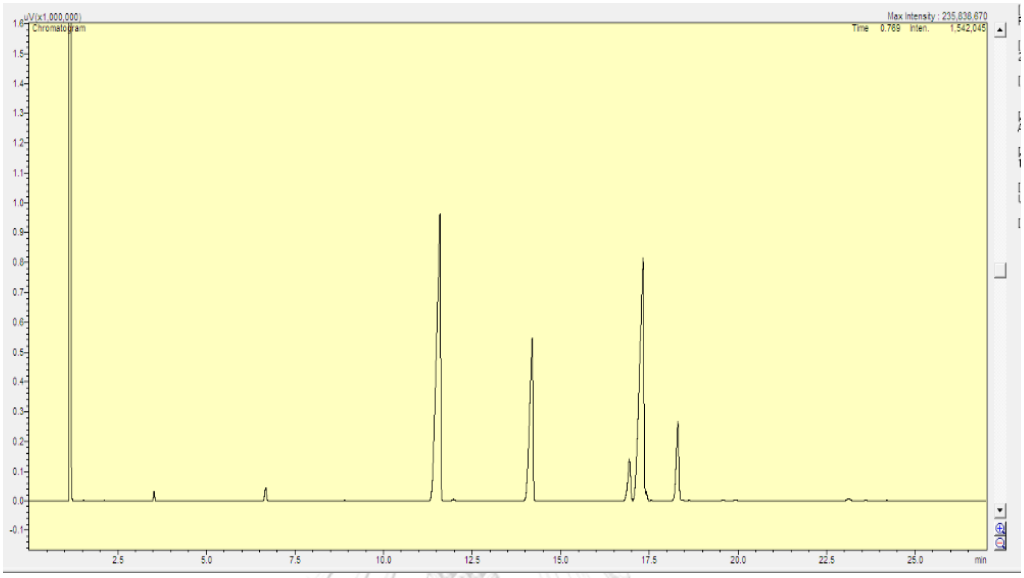

*Figure 10: Sample peaks in GC analysis*

The yield for FAME was calculated by the following formula.

FAME yield% = $\left\{\frac{A_{\mathrm{FAME}}}{A_{\mathrm{IS}}} \times \frac{m_{\mathrm{IS}}}{m_{\mathrm{S}}}\right\} \times 100\%$

$A_{\mathrm{FAME}}$ is the total Area of FAME peaks

$A_{\mathrm{IS}}$ is the area of internal standard.

$m_{\mathrm{IS}}$ is the mass of the internal standard in the diluted sample.

$m_{\mathrm{S}}$ is mass of the sampled oily phase containing FAME.

The sample of FAME yield by A26 for 4h contains:

mass of the internal standard= 0.05g

mass of biodiesel= 0.25 g

n-heptane volume= 5ml

*Table 2: Elemental composition of GC analysis*

| **Peak no** | **Ret. time** | **Area** |
|---|---|---|
| 1 | 1.091 | 235825331 |
| 2 | 13.291 | 4864566.6 |
| 3 | 16.172 | 3975176.2 |
| 4 | 19.311 | 6366314.8 |
| 5 | 20.357 | 1339474.6 |

Formula of calculation of FAME yield for A26 for 4h:

$$FAME\ content\% = \frac{(4864566.6 + 6366314.8 + 1339474.6) \times 0.05 \times 1000 \times 100}{3975176.2 \times 0.25 \times 1000}$$

$$FAME\ content\ \% = 63.37$$

# CHAPTER IV

# Results and discussion

## 4.1Physiochemical properties of resins:

Some physiochemical properties of both resins are listed in Table 3 below. Brunauer-Emmett-Teller (BET) theory is used to find surface area and pore volume for both resins. Nitrogen physisorption was unable to predict the results for IRA402 because this resin is not porous at all, and rather unusual data was obtained. Amberlyte-A26 has less surface area but more pores than Amberlite-IRA402 which has large surface area but dense without pores, revealed by characterization of both resins. Big pores are crucial in transesterification reactions containing large triglyceride organic molecules to facilitate reactant contact or collision and also for the optimum dispersion of the end products as surface area and particle size are key in catalysis overall.

Table 3:Physiochemical properties of anion exchange resin

| **Resin** | **Physical form** | **Chemical form** | **Surface area ($a/m^2g^{-1}$)** | **Exchange Capacity ($q$/eq $dm^{-3}$)** | **Submerged density ($\rho_b$/g $cm^{-3}$)** | **Dry particle density ($\rho_p$/g $cm^{-3}$)** | **Pore volume ($v/cm^3g^{-1}$)** |
|---|---|---|---|---|---|---|---|
| Amberlyte-A26 | Beads | $OH^-$ | 16.8 | 0.73 | 0.144 | 0.221 | 0.126 |
| Amberlite-IRA402 | Gel-type | $Cl^-$ | NA | 0.57 | 0.312 | 0.379 | NA |

### 4.1.1 Analysis of resin by SEM

The following are the scanning electron micrographs (SEM) of Amberlyst A26 and Amberlite IRA402 in Figure 11 & Figure 12.

The difference in porosity between Amberlyst A26 and Amberlite IRA402 in their OH form could be due to several factors, such as the type of resin beads and their manufacturing process, the degree of crosslinking, and the method of converting the resin into its OH form. Amberlyst A26 is a macroporous, weakly acidic resin. The resin beads have a highly crosslinked polymer matrix with large, interconnected pores that allow for rapid diffusion of ions and molecules. When the resin is converted into its OH form, the hydroxyl groups occupy the same sites as the previous acid groups, but with a different charge, making the resin basic. The conversion process does not significantly alter the porosity of the resin, which remains highly porous and suitable for ion exchange. On the other hand, Amberlite IRA402 is a strongly basic, gel-type anion exchange resin. The resin beads have a highly crosslinked polymer matrix that is denser and more uniform than that of Amberlyst A26. When the resin is converted into its OH form using NaOH, the hydroxyl groups replace the chloride ions on the resin, making it highly basic. However, the conversion process also causes some shrinkage of the resin beads and reduces their porosity. As a result, the OH form of Amberlite IRA402 appears denser than the OH form of Amberlyst A26 under SEM imaging. The conversion process to the OH form may also have an impact on the porosity of the resin, with Amberlite IRA402 being more susceptible to shrinkage and densification than Amberlyst A26.

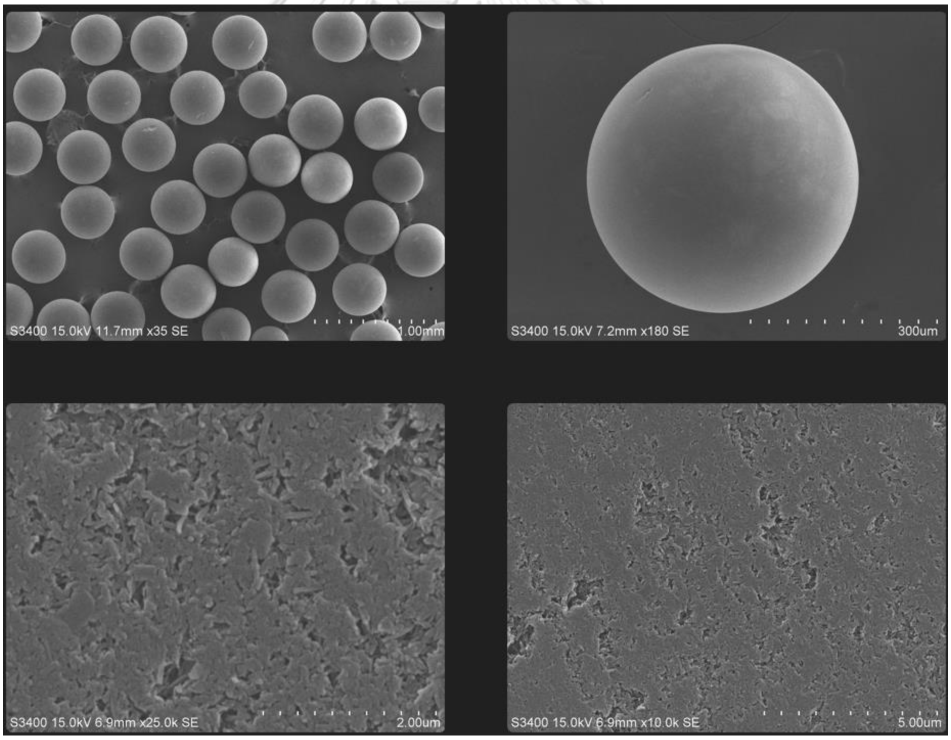

*Figure 11: SEM of surface of A26 OH form*

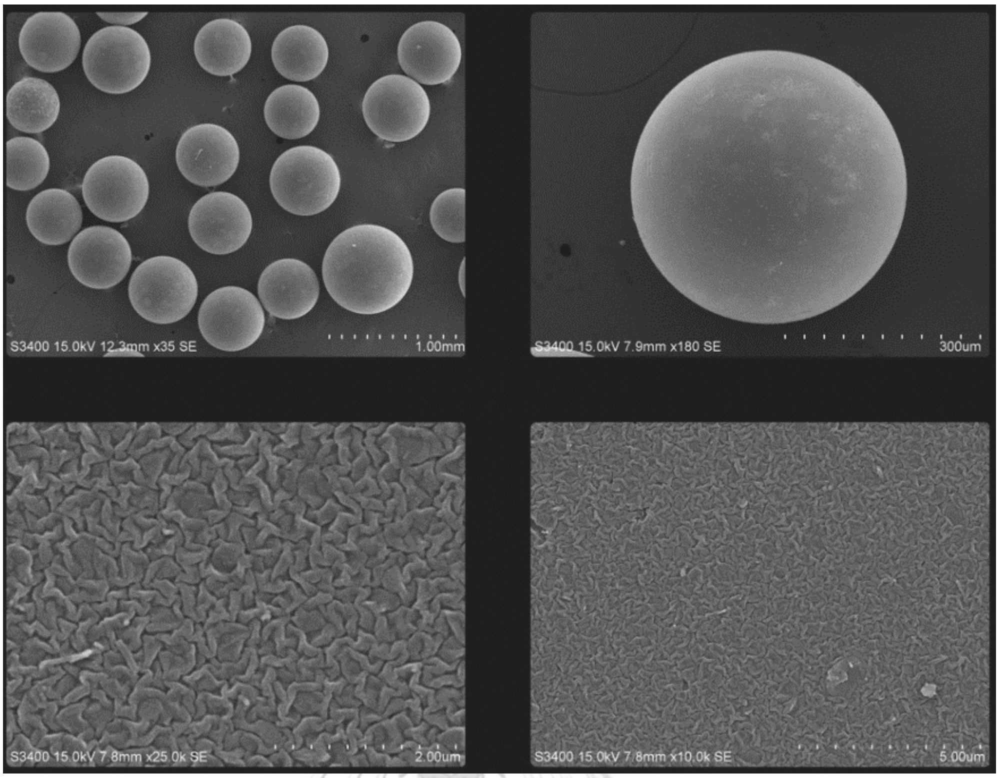

*Figure 12: SEM of surface of IRA402 OH form*

### 4.2 Transesterification with IRA402

Two different types of resins were used in this study. Anion exchange resin IRA402 has no pores on the surface. The kinetics of this resin was discussed. As IRA402 is dense, it is supposed that transesterification reaction is limited by external mass transfer.

Figure 13 below illustrates the FAME yield with and without the use of THF. As palm oil is viscous and immiscible with methanol, THF as cosolvent was used to dilute the reaction mixture and help form a single liquid phase. The Figure 13 shows that at standard conditions IRA402 has lower yield without THF.

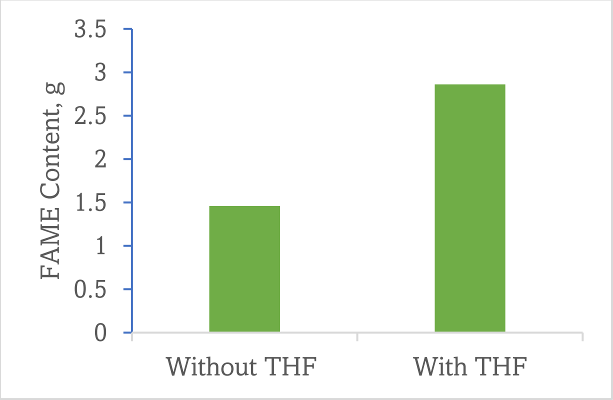

*Figure 13: FAME yield of IRA402 for 4h*

The reason behind the FAME yield difference with or without THF is the higher concentration of oil that is in contact with resin in the former case. Figure 14 below shows the comparison of physical appearance of both cases. Both pictures were taken after 4 h of transesterification reaction at standard reaction conditions. Without THF added, the resin IRA402 accumulates irregularly. It is clear from the picture that the resin beads showed a higher preference for the methanol phase while actively preventing the oil phase from forming a bond with the resin beads. This suggests that the oil must go through a transfer procedure to the methanol-rich phase to access the resin's catalytic sites and promote reactions at lower concentrations. Simply said, the oil must go to the methanol-rich phase due to the resin's preference for that phase in order to interact with it and take part in catalytic processes, especially when the resin is present in lower quantities. While on the other hand, reaction mixture with THF does not show any kinds of amassed resin beads. It can be inferred that in case of single phase when THF is added, the concentration of oil in contact with the resin beads is higher and the mass transfer of reactants to the surface of resin for reaction is much easier. These result in higher FAME yields when THF is added.

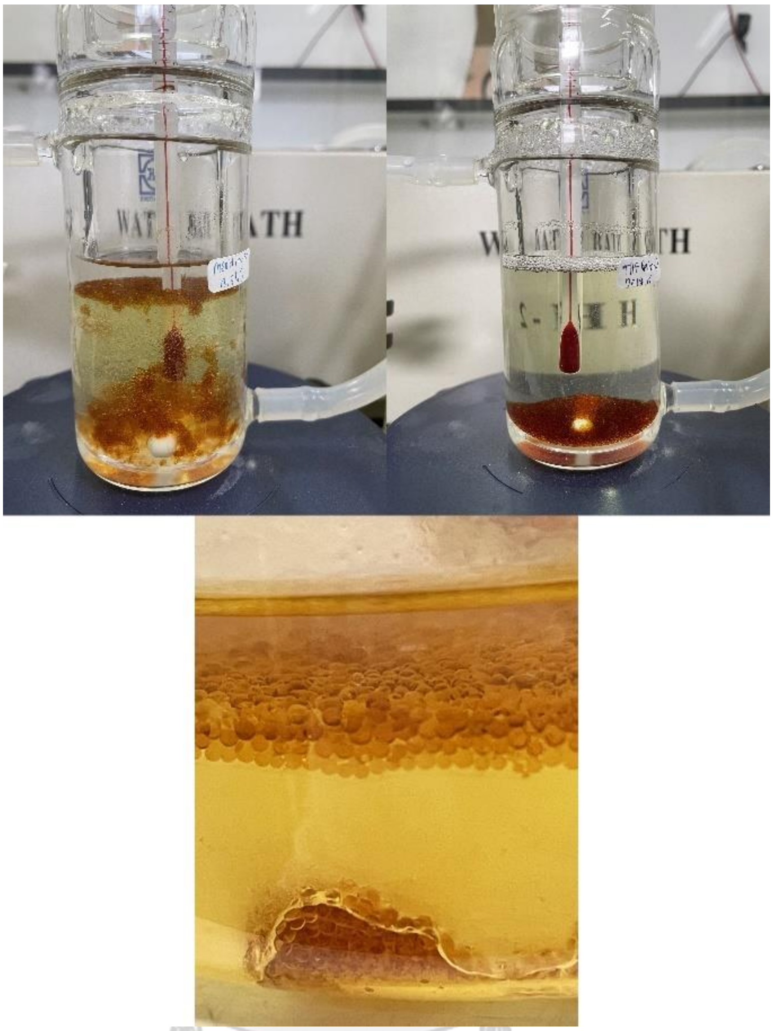

Figure 14: Reaction mixture without (left) and with THF (right) at bottom is close-up of resin agglomeration without THF

To investigate the kinetics of this resin, different experiments were conducted by changing the amount of oil, amount of methanol and varying the basic content sites of resin.

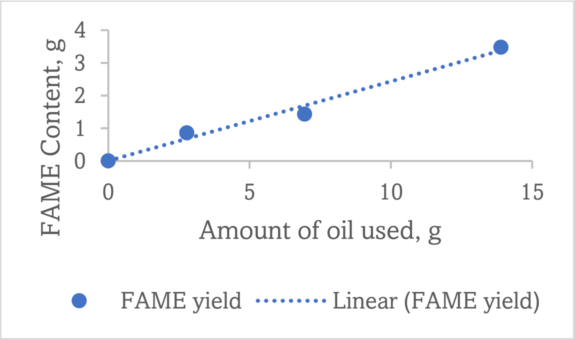

Figure 15: FAME yield of IRA402 with different amount of oil for 4h

Figure 15 showed that the amount of oil used in reaction linearly affects the FAME yield. These findings demonstrated that, with respect to oil concentration, the reaction was first order.

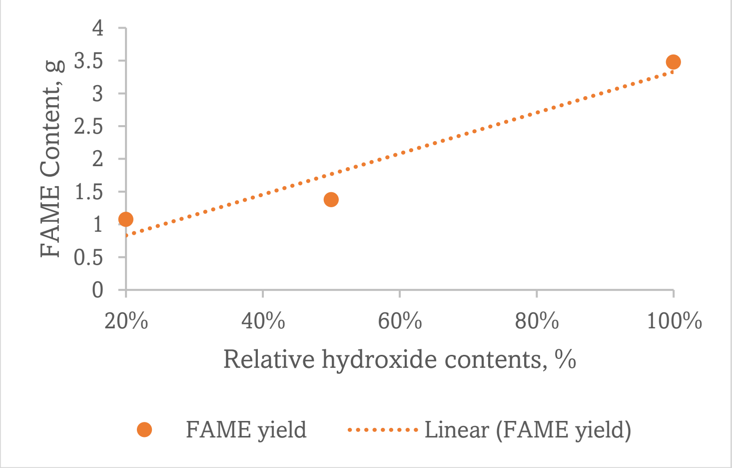

*Figure 16: FAME yield of IRA402 with different basic sites for 4h*

Figure 16 above shows the effects of the basic sites on the surface of resin on the FAME yield. The results suggested that relative hydroxide content linearly affected the FAME yield and therefore the reaction rate was also first order with respect to the basic site content. Also, as IRA402 has no pores, it can be concluded that external mass transfer limitation is basically nonexistent.

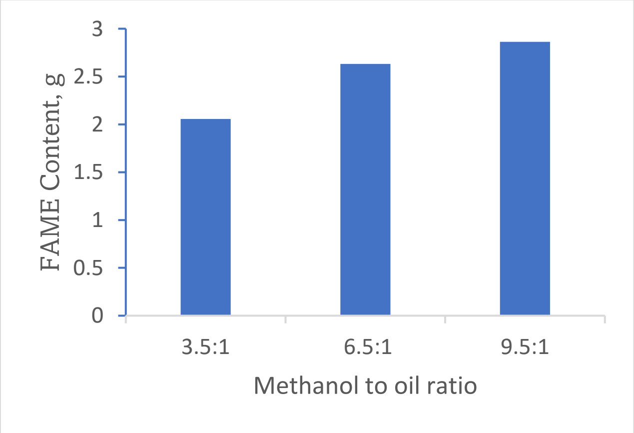

*Figure 17: FAME yield of IRA402 with different amount of methanol for 4h*

Figure 17 shows the biodiesel content with 9.5:1 to 3.5:1 methanol to oil ratio in reaction mixture. As per the results, a significant decrease in the methanol amount from 6.3 mL to 2.3 mL resulted in only a little decrease in the FAME yield. It can be concluded that the step involving methanol is unlikely a rate-determining step. Based on the behaviors depicted in the figures mentioned, it can be inferred that the interaction between acylglycerols, which are present in palm oil, and adsorbed methoxide at the surfaces of the resin catalyst is what determines the rate of the transesterification process. This reaction leads to the production of fatty acid methyl ester and alkoxides derived from acylglycerols.

### 4.2.1 Kinetic model for anion exchange resin IRA402

The behaviors discussed in the above figures showed that methanol concentration does not affect the FAME yield but in literature a study by Jamal et. al presented that methanol adsorption on the surface of resin is rate-determining step. [34] However, in this work, by all the results discussed earlier it was revealed that the slowest reaction in transesterification of palm oil is reaction of glyceride and methoxide at the resin surface to produce FAME. In another study the mechanism of transesterification was explained by Eley-rideal method by using heterogeneous catalyst MgZnAlO for Jatropha oil with methanol. [51] This study took in account all the steps of reaction and did sensitive analysis as well.

In this work, reaction rate modelling is presented to help to understand the reaction mechanism which is different from case which studied the same system but without THF. In this study, a simple reaction rate model was created that was especially suited to the system being studied. However, THF does not participate in the reaction and does not impact the reaction mechanism, it means that THF role is solely limited to being a passive solvent. It does not interact directly with the reactants, intermediates, or transition states involved in the process or go through any chemical changes.

For reaction rate modelling, it was assumed that all the triglycerides are converted into esters and glycerol and no side reaction occurred.

$$R'COOR + 3CH_3OH \leftrightarrow 3RCOOCH_3 + C_3H_8O_3 \qquad (3)$$

The rate of generation or consumption of a chemical species in the forward direction per unit IRA402’s geometric external surface area was written as:

$$r_{i,s} = \nu_i x_{\mathrm{site}} k_{\mathrm{f,s}} c_{\mathrm{TG}} \qquad (4)$$

where

$k_{\mathrm{f,\,s}}$ is rate constant for reaction occurring at the outer surfaces of resin beads in the forward direction [m s$^{-1}$]

$x_{\mathrm{site}}$ is relative basic site [dimensionless]

$\nu_i$ stoichiometric coefficient of species i in a chemical reaction [dimensionless]

The reaction law is written in accordance with results presented above. As transesterification is an equilibrium reaction with conversion of triglycerides exceeding 90%, only the forward reaction is used for modelling.

The rate constant for IRA402 could be estimated from the results presented in Figure 13, Figure 15, Figure 16 and Figure 17. The rate of change in the number of moles of TG according to the proposed rate law was:

$$\frac{dn_{TG}}{dt} = -\frac{x_{site}k_{f,s}n_{TG}}{V_{liq}} \times \left[\frac{\rho_b V_{resin,b}\left(4\pi R^2\right)}{\rho_P\left(\frac{4}{3}\pi R^3\right)}\right] \quad (5)$$

Simplifying the expression within the brackets:

$$\left[\frac{\rho_b V_{resin,b}\left(4\pi R^2\right)}{\rho_P\left(\frac{4}{3}\pi R^3\right)}\right] = \frac{3\rho_b V_{resin,b}}{\rho_P R} \quad (6)$$

Now, substituting this simplified expression back into the original equation:

$$\frac{dn_{TG}}{dt} = -\frac{x_{site}k_{f,s}n_{TG}}{V_{liq}} \times \frac{3\rho_b V_{resin,b}}{\rho_P R} \quad (7)$$

$$\frac{dn_{TG}}{dt} = -\frac{3\rho_b V_{resin,b}x_{site}k_{f,s}}{R\rho_P V_{liq}} \times n_{TG} \quad (8)$$

Suppose the constants are equal to α.

$$\frac{3\rho_b V_{resin,b}x_{site}k_{f,s}}{R\rho_P V_{liq}} = \alpha \quad (9)$$

The equation simplifies to

$$\frac{dn_{TG}}{dt} = -\alpha \times n_{TG} \quad (10)$$

$$\frac{dn_{TG}}{n_{TG}} = -\alpha dt \quad (11)$$

By integration using the appropriate limits

$$\int_{n_{TG}|_{t=0\,s}}^{n_{TG}} \frac{dn_{TG}}{n_{TG}} = -\alpha \int_0^t dt \qquad (12)$$

$$\ln(n_{TG})|_{n_{TG}|_{t=0\,s}}^{n_{TG}} = -\alpha t \qquad (13)$$

$$\ln(n_{TG}) - \ln(n_{TG}|_{t=0\,s}) = -\alpha t \qquad (14)$$

$$\ln\left(\frac{n_{TG}}{n_{TG}|_{t=0\,s}}\right) = -\alpha t \qquad (15)$$

$$\frac{n_{TG}}{n_{TG}|_{t=0\,s}} = \exp(-\alpha t) \qquad (16)$$

$$n_{TG} = n_{TG}|_{t=0\,s} \exp(-\alpha t) \qquad (17)$$

$$n_{TG} = n_{TG}|_{t=0\,s} \exp\left(-\frac{3\rho_b V_{resin,b} x_{site} k_{f,s}}{R\rho_P V_{liq}} t\right) (18)$$

$$m_{FAME} = n_{FAME} M_{FAME} \quad (19)$$

$$m_{FAME} = 3M_{FAME}(n_{TG}|_{t=0\,s} - n_{TG}) \ (20)$$

$$m_{FAME} = 3M_{FAME}/M_{TG}\left[1 - \exp\left(-\frac{3\rho_b V_{resin,b} x_{site} k_{f,s}}{R\rho_P V_{liq}} t\right)\right] m_{TG}|_{t=0\,s} \qquad (21)$$

By using the data with different amounts of oil in reaction in Figure 15, the slope obtained by regressing the data is 0.2426. Using this slope, rate constant obtained by above equation is 2.06e$^{-8}$ m s$^{-1}$.

## 4.3 Transesterification with anion exchange resin A26

Alkaline anion exchange resin A26 is a porous catalyst. In comparison to the dense IRA402, resin A26 was expected to offer high FAME yield. Figure 18 below shows the transesterification reaction at standard conditions; 9.5:1 oil to methanol ratio, reaction temperature 60 °C at 1500 rpm, over a course of period. As clear from the graph the FAME yield spikes up in 1st hour of reaction but somehow did not increase as much as expected from a porous catalyst. Reaction rate model for A26 resin will be discussed after experimental results. After 1 h the slower reaction rate somehow resembles IRA402, which has no pores. First 0.5 h, the biodiesel content came to 3.5 g. It was expected that at the end of 4h (14400 s) this amount would be at least 4 times but only 8.8 g of FAME yield was obtained from 4 h of reaction. Adding to that when reaction time was stretched up to 9 h (32400 s), the FAME yield only increased 6% from 4-9 h. This abrupt change in FAME content could be because of shift of rate limiting step or formation of secondary phase after certain time.

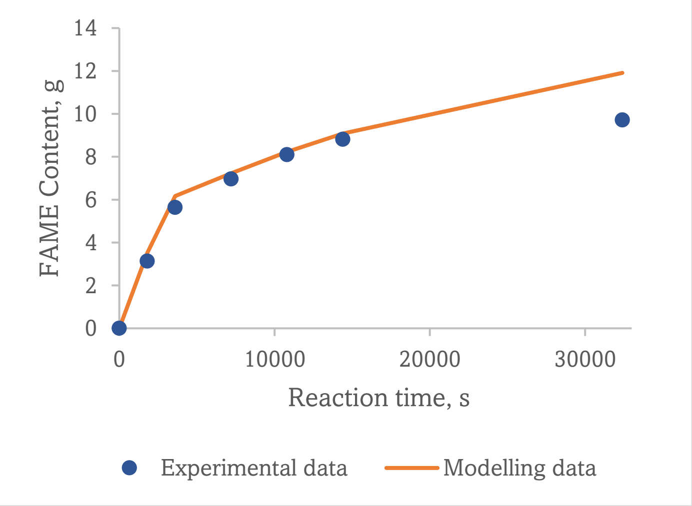

*Figure 18: FAME yield of A26 over different reaction time*

To determine what limited that transesterification reaction, many different reactions were conducted by varying the active site of resin for 0.5 h, 1 h and 4 h. The following are the results of resin A26 with relative basic sites. Nonlinear relations of reaction time for 0.5h, 1 h and 4h were quite different despite having same hydroxide basic sites. The FAME yield from Figure 19 revealed that for 10 to 100% relative sites, in 30 min reaction time did not vary much. Whereas for 4 h in Figure 20 and 1 h in Figure 21, the changes are prominent. For 4 h reaction with different basic site, swift change has been observed, it might verify that regime changes have occurred in this time. These profiles for A26 hinted that maybe the reaction is internal mass transferred. To verify that further investigation on A26 at different revolution per minute has been done.

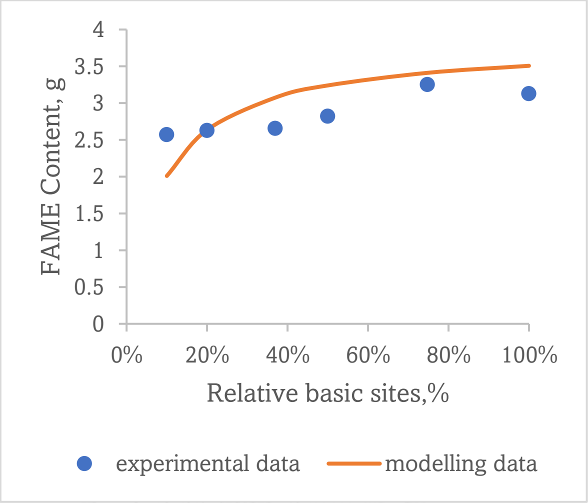

*Figure 19: FAME yield of A26 with different basic sites for 0.5h*

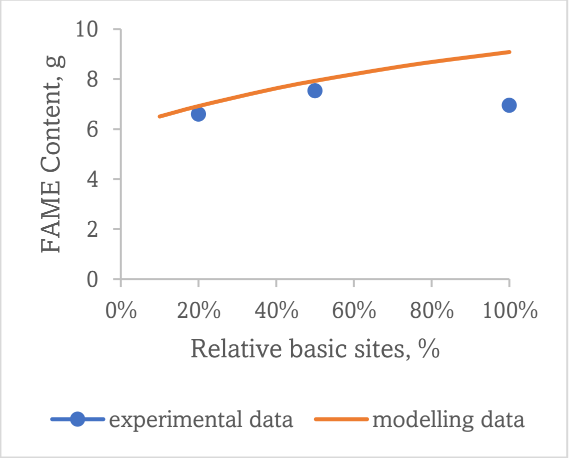

*Figure 20: FAME yield of A26 with different basic sites for 4h*

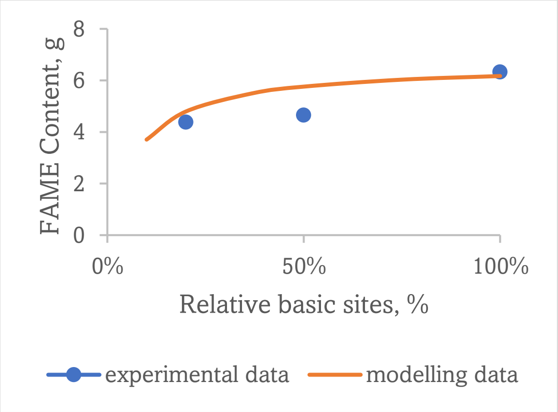

*Figure 21: FAME yield of A26 with different basic sites for 1h*

By looking at Figure 22 the FAME content decreases by increasing the agitation speed. It is because at higher agitation speed there is a higher vortex created between the resin beads and the stirring bar. As the speed increases so does the distance between bar and resin beads, all resins beads just follow the flow of vortex instead of getting stirred. In turn, this would result in a slower relative speed between the resin beads and the liquid, which would eventually lead to a decrease in the external mass transfer rate.

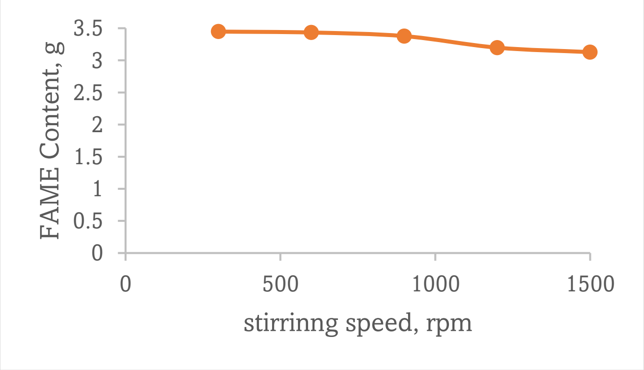

*Figure 22: FAME yield of A26 with different agitation speed*

Figure 23 shows the transesterification of 0.4 $cm^3$ of resin for 30 min with different hydroxide sites. 0.4 $cm^3$ resin with 100% basic sites means it has same active sites as 4 $cm^3$ resin with 10% basic sites. As mentioned earlier, transesterification might hold the internal mass transfer mechanism, keeping in that mind, both these reactions should give the same FAME yield. But it is revealed that only 0.39 g of FAME content was obtained from 0.4 $cm^3$ resin which is not even half of FAME yield obtained with 4 $cm^3$ of A26 resin at 100% basic content. So, this phenomenon rules out the internal mass transfer and rather points towards the external mass transfer which was discussed earlier with 4 $cm^3$ of resin A26 for 30 min at different rpms.

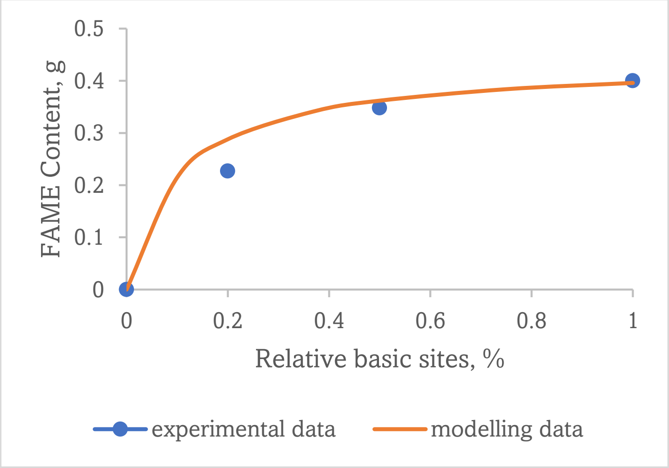

*Figure 23: FAME yield of 0.4$cm^3$A26 with different basic sites for 4h*

To check the effect of both reactants, oil and methanol, on the FAME yield, the transesterification reaction was studied by reducing the amount of oil and methanol to 25% of standard conditions. Figure 24 shows the FAME yield of reaction when 25% oil with 100% methanol as well as with both quantities reduced to 25% used. The plot revealed that approximately 94% of FAME contents were achieved in only 3h when 25% oil was used with 100% methanol. No sharp transition was observed to slower rates. In this instance, when the quantity of the oil and methanol are both cut by 25%. It suggests that compared to the conventional procedure, the reaction mixture has much less of both reactants. As a result, the total reaction kinetics and equilibrium was impacted by the reduced levels of oil and methanol. The reaction continued with a lower reactant concentration since the concentrations of both oil and methanol have decreased. As a larger concentration of reactants often results in a quicker reaction, this may impact the reaction rate. The Figure 24 represented that impact of reducing the oil concentration appears to have a more pronounced effect on the yield of FAME. Whilst, according to the findings of the studies, the reaction rates were not considerably impacted by decreased starting methanol concentrations. This result is consistent with the earlier discussion, which showed that methanol was not engaged in the reaction's phase that determined rate. The molar ratios of oil to methanol also stayed the same as in experiments with 100% oil and methanol when both the oil and methanol levels were decreased to 25%. This finding suggests that thermodynamic equilibrium was not the limiting factor in the low oil conversion reported with 100% oil and methanol.

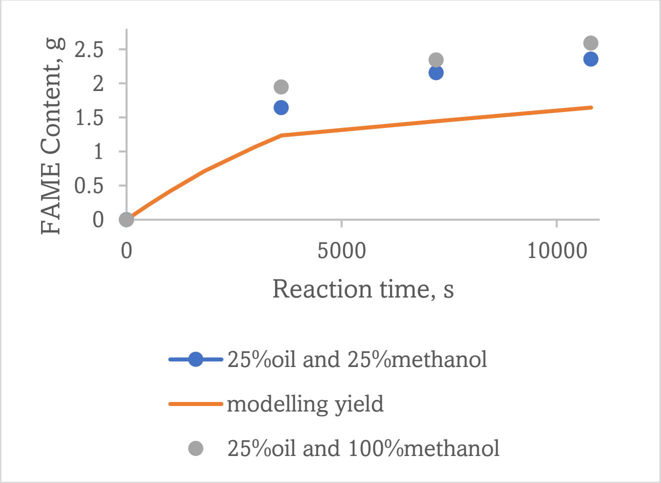

*Figure 24: FAME yield with different concentration of oil and methanol*

Heterogeneous catalyst utilization has several benefits, including simple catalyst separation and the possibility of reusing the catalyst. Experiments were carried out under ideal reaction circumstances, which included a stirring speed of 1500 rpm, a reaction temperature of 60 ºC, and a methanol to oil ratio of 9.5:1, to assess the reusability of catalyst A26. By recovering the resin used in a 3 h transesterification procedure and washing it with THF and methanol until all the biodiesel content was gone, the reusability of A26 was tested. After being cleaned, the resin was utilized once more for a 30-minute transesterification test. Figure 25 compares the yields of new and recycled A26 utilized in transesterification operations to produce fatty acid methyl ester. Interestingly, when the resin was reused, there was only a very minor drop in FAME production. These results show that after a straightforward cleaning procedure, the resin may be reused at least twice with a 10% decrease in FAME production. The washing procedure successfully removes the glycerol that has clogged the resin's pores, restoring its activity. Additionally, there was little hydroxide content leaking from the resin.

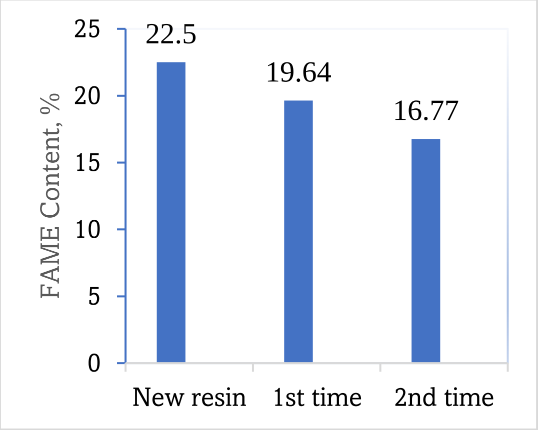

*Figure 25: FAME yield of used resin A26*

In conclusion, the findings in Figure 25 imply that A26 resin has good reusability, with just a little drop in FAME output after many applications. The usefulness and effectiveness of A26 as a heterogeneous catalyst in transesterification processes are further supported by its capacity to be regenerated by washing, which eliminates glycerol and restores activity. Also, these changes in reaction rate are not permanent and reversible with minor loss.

Figure 26 shows the FAME yield with and without glycerol added at the beginning of transesterification reaction. When glycerol was added at the start of reaction only 1.92 g of FAME yield was obtained in 0.5 h while without glycerol this number was 3.12 g. Glycerol, also a byproduct of the transesterification process, contributes to the development of the secondary liquid phase. When glycerol was present from the beginning of the process in the prior case, its concentration would initially be rather high. The rate of glycerol buildup in the resin bead's core would rise because of the greater concentration. Glycerol is higher in quantity and accelerates the creation of the secondary liquid phase. As previously indicated, this secondary phase's rapid development might impede the transesterification reaction by inactivating interior resin surfaces. As a result, the total FAME yield is decreased by the reaction being impeded on the resin surfaces.

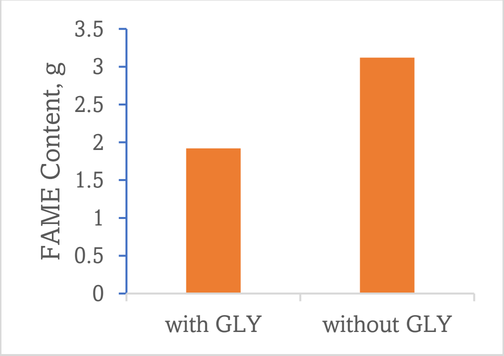

*Figure 26: FAME yield of A26 for 0.5h with and without glycerol (dark bar experimental data)*

### 4.3.1 Reaction rate modelling for resin A26:

A form of triglyceride from palm oil interacts chemically with an alcohol (in this case, methanol) to create FAME and glycerol. This process is known as transesterification. Only these three species were found to be crucial in characterizing the kinetics of the reaction in the preceding discussion of the transesterification reaction scheme using anion-exchange resin because as seen from the results that methanol does not affect the yield as well as there was no side reaction occurring, TG (triglyceride), GLY (glycerol), and FAME (fatty acid methyl ester). It is required to consider the concentrations or quantities of these important species throughout time in order to create a mathematical model to describe the kinetics of transesterification. The model may properly depict the behavior and progression of the transesterification process without needless complication by concentrating just on these species.

Making the model more straightforward by limiting the number of species to just these three makes it simpler to evaluate and comprehend the underlying kinetics and forecast how the reaction will behave in various situations. Additionally, focusing on the species that have the greatest influence simplifies the mathematical calculations and ensures a more accurate depiction of the reaction system.

The findings discussed earlier imply that internal mass transfer within A26's pores is substantially quicker than exterior mass transfer. In resin A26, it has pores, which are tiny openings or holes. Within A26, these pores establish a network of linked areas.

The triglycerides move through the pores of A26 due to internal mass transfer, which enables molecules to diffuse or flow across the material's network of connected holes. External mass transfer, on the other hand, refers to the movement of methoxide between the surface of A26 and bulk.

With A26, it appears that external mass transfer is the main factor limiting the reaction rates, especially at high basic site contents.

In this simplified model we need only the kinetic model and the external mass transfer model.

The rate of generation or consumption of a chemical species in the forward direction per unit resin bead volume was required and written in accordance with transesterification reaction is:

Rate law for resin A26

$$r = kxc_{\mathrm{TG,s}} \qquad (22)$$

$$r_s = k_s x c_{\mathrm{TG,s}} \qquad (23)$$

where

$r$ is the reaction rate per volume of resin beads (not just volume of liquid inside beads) [mol m$^{-3}$ s$^{-1}$]

$r_\mathrm{s}$ is the reaction rate per outer surfaces of resin beads [mol m$^{-2}$ s$^{-1}$]

$c_{\mathrm{TG,s}}$ is the concentration of triglyceride at the outer surfaces of resin beads [mol m$^{-3}$]

$k$ is the volumetric rate constant [s$^{-1}$]

$k_\mathrm{s}$ is the area rate constant [m s$^{-1}$]

$x$ is the relative basic site content.

External mass transfer model: $$r_m = k_c\left(c_{\mathrm{TG},b} - c_{\mathrm{TG,s}}\right) \qquad (24)$$

where

$r_m$ is the external mass transfer rate between the outer surfaces of resin beads and the solution in the bulk.

$k_c$ is the mass transfer coefficient [m $s^{-1}$]

$c_{TG,b}$ is the concentration of triglyceride in the solution in the bulk [mol $m^{-3}$]

Both the volumetric reaction rate and the reaction rate area were included into model because the latter is needed to sustain the reaction rate when all the internal surface areas of resin beads are covered in glycerol phase.

Instead of relying exclusively on the reaction rate area, which only considers the reaction occurring at the accessible surface area, the volumetric reaction rate incorporates the reaction occurring across the entire area of the system. The pace at which the reaction occurs on the exposed surface area where the reactants come into contact is referred to as the reaction rate area. The surface area rate may not be enough to maintain the intended reaction rate when the surface area for the reaction is limited or covered, such as when interior surfaces are coated or deactivated. The overall reaction rate is maintained by the volumetric reaction rate, which considers the full reaction volume.

An expression for the concentration of triglyceride at the outer surfaces of resin beads can be obtained by equating the external mass transfer rate to the consumption rate of triglyceride:

$$r_m a_s = rv + r_s a_s \qquad (25)$$

$$r_m = r\frac{v}{a_s} + r_s \qquad (26)$$

$$k_c(\,c_{TG,b} - c_{TG,s}) = kxc_{TG,s}\frac{v}{a_s} + k_s x c_{TG,s} \qquad (27)$$

$$c_{TG,s} = \frac{k_c c_{TG,b}}{kx\frac{v}{a_s} + k_s x + k_c} \qquad (28)$$

where

$v$ is the total volume of resin beads [$m^3$]

$a_s$ is the outer surface areas of resin beads [$m^2$]

So, the total consumption rate of triglyceride expressed in relation to its concentration in the bulk is:

$$r_{total} = rv + r_s a_s \qquad (29)$$

$$r_{Total} = kxc_{TG,s}v + k_s x c_{TG,s} a_s \quad (30)$$

$$r_{Total} = \frac{(kxv + k_s x a_s) k_c c_{TG,b}}{kx\frac{v}{a_s} + k_s x + k_c} \qquad (31)$$

$$r_{total} = \frac{c_{TG,b}}{\frac{1}{kxv + k_s x a_s} + \frac{1}{k_c a_s}} \qquad (32)$$

where $r_{total}$ is the total consumption rate of triglyceride [mol s$^{-1}$]

The concentration of triglyceride at any time is:

$$r_{total} = -V\frac{dc_{TG,b}}{dt} = \frac{c_{TG,b}}{\frac{1}{kxv + k_s x a_s} + \frac{1}{k_c a_s}} \quad (33)$$

$$c_{TG,b} = c_{TG,b}\,|_{t=0\,s}\; e^{\frac{-t/V}{\frac{1}{kxv + k_s x a_s} + \frac{1}{k_c a_s}}} \quad (34)$$

where

$V$ is the total liquid volume, assumed to be constant, in the reactor [m$^3$].

The values used in this model are predicted by fitting the data into the above equation.

*Table 4: Parameters used in modelling of A26*

| **Parameters** | **Values** |
|---|---|
| k | 0.0251s$^{-1}$ |
| $k_s$ | 6.3×10$^{-8}$ ms$^{-1}$ |
| $k_c$ | 2×10$^{-7}$ ms$^{-1}$ |
| $M_{TG}$ | 847.78 gmol$^{-1}$ |
| $M_{FAME}$ | 289.8 gmol$^{-1}$ [52] |
| $c_{GLY\ lim}$ | 152 molm$^{-3}$ |

The process of fitting the model to the available experimental data led to the determination of the solubility limit of glycerol in the reaction mixture, indicated as $c_{GLY\ lim}$ which was found to be 152 mol $m^{-3}$. The number found here is the maximum amount of glycerol that will dissolve in the system under consideration. It is vital to acknowledge that the phase equilibrium system under investigation in this study lacks precise experimental data in literature. The literature's present knowledge mostly focuses on glycerol-oil systems, in which glycerol is dissolved in different kinds of oils. However, because THF is included in the reaction mixture as a co-solvent, the system being studied in this study is best categorized as a glycerol-THF system. For thermodynamic stimulation, Aspen Plus is the best option out there. The concentration limit of glycerol in a system using THF instead of oil may not be reliably predicted by a specific technique or model, according to Aspen Plus. The program normally considers glycerol-oil systems, which could not be immediately relevant to glycerol-THF systems, which would possibly lead to this shortcoming. Based on the assumption made in this case, it was concluded that Aspen Plus, a process simulation software, is likely to provide underestimated or overestimated predictions of the solubility of glycerol in an oil-containing phase. As a result, to obtain a more realistic estimate, a concentration limit value of 152 mol/$m^3$ for glycerol was determined using curve fitting in the study. This approach was considered more reliable as it accounted for the specific glycerol-THF system and provided a better representation of the solubility limit compared to the predictions made by Aspen Plus.

The rate constant, $k_{f,s}$, for reactions taking place at the outside surfaces of resin A26 was found to be $6.3\times10^{-8}$ $ms^{-1}$. The rate constant previously identified for resin IRA402 was $2.06\times10^{-8}$ $ms^{-1}$, and these numbers are in the same order of magnitude. This result is consistent with the theory that the slow second stage of the reactions only takes place at the resin's outside surfaces. The fact that A26's rate constant is higher than that of IRA402 suggests that A26's porosity helps to provide a bigger external catalytic surface area, which enables more effective reactions to take place at the resin's outside surfaces.

Previously, in literature review, many studies reported Eley-rideal mechanism to find the rate constant of heterogenous catalysts. Many of them found out that methanol adsorption is the rate limiting step for transesterification. Study by Tanguy used magnesium oxide catalyst to convert rapeseed oil and methanol into alkyl esters, reaction conditions were same as industrial conditions and rate constant determined for this reaction was $5.29\times10^{-3}$ $m^3$ $mol^{-1}$. [53] Another study converted soybean oil into biodiesel by using heterogeneous catalysts and biodiesel production yield obtained was 98% with methanol adsorption being the rate-limiting step. [54] Study by reported that conversion of Canola oil by using Amberlyst A26 resin at 45 ºC for 1.5 h is 66.67% without the addition of any co-solvent. [33] Asir and coauthor found out that the yield for methyl ester by palm oil and a heterogenous catalyst is 96.78% at reaction temperature of 60 ºC and 200 rpm. [14] But the highest yield obtained in this study is approximately equal to 94% when amount of oil was decreased from the standard conditions, it can be due to high rpm used in the study. Additionally, the rate constant obtained by reaction rate models of IRA402 and A26 are in same order proved the validity of observations made through experimentations.

The modelling values used in the above all figures, containing results, obtained from the equation are based on assumptions and are quite reasonably resonant with the experimental data. The predicted FAME yield from the model at different basic content sites showed the nonlinear trend. From 10% to 20% basic sites, the model predicted the internal mass transfer resistance for both 0.5 h and 1 h. But on the other hand, for 4h transesterification, model predicted that FAME yield abruptly changes from 10% basic sites to 20%, it is aligned with the fact of formation of secondary liquid phase. At higher basic sites, for all the reaction at 0.5 h, 1 h and 4 h, reaction is more likely controlled by external mass transfer because the trend is somehow linear. In Figure 18, the model overpredicted the FAME yield for 9 h transesterification, from experiment it was revealed that when secondary phase liquid covers the pores of resin, glycerides and methoxide cannot travel to the basic site eventually 9h of reaction only offers 6% higher content than 4h reaction. This effect is not included in the modelling equation therefore it predicted the FAME yield way higher than it is. This model is only accurate for up to 4h of transesterification reaction. Figure 23 presented the FAME yield for 0.4cm$^3$ resin for 0.5h, the values are close which means the model worked well for the designed system.

The model showed that lowering the initial amounts of oil or both oil and methanol to 25% of their standard values in Figure 24 would stop the development of the secondary liquid phase and allow oil conversions to approach 100%. The high concentration of glycerol, a byproduct of the transesterification reaction, near the core of the resin bead was attributed for the creation of the secondary liquid phase. The quantity of glycerol formed overall throughout the reaction would be reduced by reducing the starting concentration of oil or both oil and methanol to 25% of their standard values. Glycerol would accumulate less near the center of the resin bead at lower glycerol concentrations because the concentration gradient would be less pronounced.

# CHAPTER V

## Conclusion

Fatty acid methyl ester, commonly known as biodiesel, can be produced through transesterification of refined palm oil and alcohol in presence of THF as co-solvent. The palm oil and methanol combine to produce a homogenous solution with THF, increasing the amount of contact between the reactants otherwise resin form cluster surrounded by methanol. This enhances the molecular level mass transfer, enabling a quicker and more effective interaction between the palm oil and methanol. The problem of inadequate mass transfer between the immiscible liquid phases is resolved using THF as a co-solvent, resulting in increased reaction rates throughout the transesterification process.

Two heterogenous anion exchange resins were used as catalysts, IRA402 and A26. The effect of dense IRA402 and porous A26 on FAME yield was observed. The dense IRA402 resin employed in the study lacks channels that would allow reaction intermediates to reach the catalyst core. This implies that the only surface on which the reactants and products may interact is the resin's exterior. IRA402 resin severely restricts the mass transfer of reactants and products since there are no internal holes. As a result, both the removal of products from the catalyst's active sites and the diffusion of reactants toward those sites slow down and become less effective. The total reaction rate is impacted by this restriction on mass transfer inside the resin. Based on this understanding, it is predicted that employing the dense IRA402 resin will result in extremely little FAME content, which represents the desired outcome of the transesterification reaction. The FAME yields obtained with IRA402 resin were in fact quite low (20.6%) when compared to the yields obtained with porous A26 resin (63.4%), which was how this prediction was verified through experiments. The experiments also suggested that the reaction rate was discovered to be significantly influenced by the oil concentration, proving that the reaction rate rose according to the oil content. The rate-limiting stage of the transesterification reaction is most likely an interaction between oil molecules and the active sites on the IRA402 resin, according to the noted first-order dependence on oil concentration. A faster reaction rate is produced when the concentration of oil rises because there are more oil molecules available to interact with the catalyst. The excess availability of methanol confirms that the reaction is not constrained by the availability of methanol molecules, which explains the lack of dependency on the methanol concentration. Or, to put it another way, because the reaction mixture is already saturated with too much methanol, raising the concentration of methanol over a certain point does not considerably speed up the pace of the reaction.

For transesterification with A26 resin, internal mass transfer was anticipated to be the limiting factor in the transesterification process employing the porous A26 resin. This implies that the reactants would experience challenges diffusing into the resin's internal pores, resulting in slower reaction rates. However, the yields of FAME and the basic sites were not linearly related, according to experimental results using various basic sites of the A26 resin. This finding indicated that the reaction's behavior could not be explained only by internal mass transfer constraints. As more basic sites would offer more options for the reactants to access the active sites inside resin, one would anticipate a linear connection between the basic sites and the yields if internal mass transfer restrictions were the predominant concern.

In the transesterification process of A26, glycerol, a subsequent phase, was seen to bind to the pores of the resin. This adhesion prevented reactants from reaching the resin's interior pores, which constrained the reaction and reduced the FAME yield. Glycerol was purposefully introduced at the start of the process to confirm this theory. The fact that glycerol was present proved that it does, in fact, adhere to the pores of the resin, confirming the idea that the lower FAME output was caused by the glycerol phase obstructing the pores. However, it was noted that the glycerol's adhesion to the resin pores was not permanent. The results of subsequent tests showed that washing the resin to get rid of the glycerol that had stuck to it allowed for a partial recovery of the resin's activity.

A reaction rate model has been developed for IRA402 which yields the rate constant. Similar results were successfully achieved using a reaction rate model for the A26 resin that closely matched the experimental data. These models shed light on how each resin's transesterification process behaved. Along with the discovered kinetic parameters and rate constants, the successful regeneration of the experimental data using the reaction rate models offers evidence of the A26 resin's improved performance in terms of greater yields.

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