Application of co-solvent for biodiesel production in ultrasound-assisted reactor.

Miss Panidaporn Ritprasert

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 2019

การประยุกต์ใช้ตัวทำละลายร่วมสำหรับการผลิตไบโอดีเซลในเครื่องปฏิกรณ์ที่ใช้คลื่นเหนือเสียงร่วมด้วย

น.ส.พนิดาภรณ์ ฤทธิ์ประเสริฐ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2562

Thesis Title	Application of co-solvent for biodiesel production in ultrasound-assisted reactor.
By	Miss Panidaporn Ritprasert
Field of Study	Chemical Engineering
Thesis Advisor	Professor Suttichai Assabumrungrat, Ph.D.
Thesis Co Advisor	Assistant Professor Kanokwan Ngaosuwan, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirement for the Master of Engineering

.... Dean of the Faculty of Engineering
(Professor SUPOT TEACHAVORASINSKUN, Ph.D.)

THESIS COMMITTEE

.... Chairman
(Professor Bunjerd Jongsomjit, Ph.D.)
.... Thesis Advisor
(Professor Suttichai Assabumrungrat, Ph.D.)
.... Thesis Co-Advisor
(Assistant Professor Kanokwan Ngaosuwan, Ph.D.)
.... Examiner
(Pimporn Ponpesh, Ph.D.)
.... External Examiner
(Assistant Professor Worapon Kiatkittipong, Ph.D.)

พนิดาภรณ์ ฤทธิ์ประเสริฐ : การประยุกต์ใช้ตัวทำละลายร่วมสำหรับการผลิตไบโอดีเซลในเครื่องปฏิกรณ์ที่ใช้คลื่นเหนือเสียงร่วมด้วย. (Application of co-solvent for biodiesel production in ultrasound-assisted reactor.) อ.ที่ปรึกษาหลัก : ศ. ดร.สุทธิชัย อัสสะบำรุงรัตน์, อ.ที่ปรึกษาร่วม : ผศ. ดร.กนกวรรณ ง้าวสุวรรณ

ไบโอดีเซลเป็นหนึ่งในพลังงานที่ได้รับความสนใจเป็นอย่างมากในปัจจุบัน เนื่องจากเป็นพลังงานหมุนเวียนและลดการปล่อยแก๊สพิษ เช่น คาร์บอนมอนอกไซด์ น้อยกว่าเมื่อเปรียบเทียบกับเชื้อเพลิงดีเซลจากปิโตรเลียม ไบโอดีเซลนิยมผลิตผ่านปฏิกิริยาทรานส์เทอริฟิเคชันโดยจำเป็นต้องใช้ตัวเร่งปฏิกิริยาในการเร่งอัตราการเกิดปฏิกิริยาให้เร็วขึ้น อย่างไรก็ตามปัญหาด้านการถ่ายเทมวลระหว่างสารตั้งต้นทั้งสองชนิดที่ไม่ละลายเข้าด้วยกันซึ่งเป็นอุปสรรคต่อการผลิตไบโอดีเซล การใช้เครื่องปฏิกรณ์อาศัยคลื่นเหนือเสียงร่วมด้วยและการใช้ตัวทำละลายร่วมสามารถลดปัญหาด้านการถ่ายโอนมวลได้ ในงานวิจัยนี้ได้มีการผลิตไบโอดีเซลจากน้ำมันปาล์มด้วยเครื่องปฏิกรณ์ที่อาศัยคลื่นเหนือเสียงแบบไหลเวียน โดยใช้ปฏิกิริยาทรานส์เอสเทอริฟิเคชันที่อุณหภูมิ 60 องศาเซลเซียส ความดันบรรยากาศ ปริมาณตัวเร่งปฏิกิริยาร้อยละ 10 โดยมวล และอัตราส่วนโดยโมลระหว่างเมทานอลและน้ำมันเท่ากับ 9 ต่อ 1 พบว่าที่อัตราส่วนโดยปริมาตรระหว่างเมทานอลและตัวทำละลายร่วมเมทิลไมริสเตทเท่ากับ 1 ต่อ 0.1 จะให้ปริมาณผลได้ของไบโอดีเซลสูงที่สุด (ร้อยละ 95.31 ของผลได้) นอกจากนี้การใช้ตัวทำละลายผสมระหว่างอะซิโตนและเมทิลไมริสเตทจะช่วยเพิ่มประสิทธิภาพการผลิตไบโอดีเซลได้ยิ่งขึ้นเนื่องจากช่วยเพิ่มการละลายของสารตั้งต้นและเพิ่มตำแหน่งว่องไวของตัวเร่งปฏิริยาแคลเซียมออกไซด์ด้วย ผลจากการใช้คลื่นเหนือเสียงที่ความถี่และพลังงานสูงที่สุดร่วมกับตัวทำละลายผสมทำให้ปริมาณผลได้ของไบโอดีเซลเพิ่มขึ้นจากร้อยละ 14.07 เป็น 91.75 ดังนั้นการประยุกต์ใช้ตัวทำละลายร่วมสำหรับการผลิตไบโอดีเซลในเครื่องปฏิกรณ์ที่อาศัยคลื่นเหนือเสียงร่วมด้วยแบบไหลเวียนสามารถเพิ่มปริมาณผลผลิตไบโอดีเซลสำหรับการผลิตไบโอดีเซล องค์ความรู้ที่ได้จากการวิจัยครั้งนี้สามารถนำไปต่อยอดเป็นระบบที่มีกำลังการผลิตที่สูงขึ้นในลำดับต่อไป

สาขาวิชา วิศวกรรมเคมี
ปีการศึกษา 2562

ลายมือชื่อนิสิต ....
ลายมือชื่อ อ.ที่ปรึกษาหลัก ....
ลายมือชื่อ อ.ที่ปรึกษาร่วม ....

5871009521 : MAJOR CHEMICAL ENGINEERING

KEYWORD: biodiesel, co-solvent, Heterogeneous catalyst, transesterification, Ultrasonic reactor

Panidaporn Ritprasert : Application of co-solvent for biodiesel production in ultrasound-assisted reactor.. Advisor: Prof. Suttichai Assabumrungrat, Ph.D. Co-advisor: Asst. Prof. Kanokwan Ngaosuwan, Ph.D.

Biodiesel has been a promising alternative energy due to its renewability and lesser emissions of harmful gases such as carbon monoxide in comparison to traditional petroleum diesel fuel. Mostly, biodiesel production via transesterification requires catalyst to achieve faster reaction rate and complete the reaction. However, mass transfer between two immiscible reactants are obstacle to the biodiesel production. In this work, ultrasound-assisted (US) reactor and addition of co-solvent were used to overcome mass transfer limitation. The condition for biodiesel production from transesterification of palm oil using a circulated US reactor and addition of co-solvent was operated at 60°C, 1 atm, calcium oxide loading (10 %wt), and methanol to oil molar ratio of 9:1. It was found that using methanol to methyl myristate (co-solvent) volume ratio of 1:0.1 gave the highest biodiesel yield (about 95.31 %). Moreover, using the mixture of acetone and methyl myristate as a co-solvent can improve the biodiesel production efficiency because it can increase the solubility of reactants and active sites of calcium oxide catalyst. The results also reported that the higher ultrasound frequency and power combined with co-solvent provides increasing biodiesel yield from 14.07 to 91.75 %. Therefore, the application of co-solvent for biodiesel production in the circulated US reactor can improve biodiesel yield. The knowledge from this study can be developed for the further process scale up.

Field of Study:	Chemical Engineering	Student's Signature ....
Academic Year:	2019	Advisor's Signature ....
		Co-advisor's Signature ....

ACKNOWLEDGEMENTS

I would like to express appreciation to my advisor, Professor Dr. Suttichai Assabumrungrat, for sharing experience and expertise, and sincere and valuable guidance and encouragement to me. In addition, I wish to express my sincere thanks to Dr. Kanokwan Ngaosuwan, her co-advisor, for her kind assistance and suggestions for my project. I would grateful to thank to Professor Dr. Bunjerd Jongsomjitas the chairman, Dr. Pimporn Ponpesh and Assistant Professor Dr. Worapon Kiatkittipong as the members of the thesis committee for their kind.

Finally, I also would like to acknowledge with gratitude, the continuous support and love of my family – my parents, Mr. Prapat Ritprasert and Mrs. Wimon Ritprasert. They kept me going, and this dissertation would not have been possible without them.

Panidaporn Ritprasert

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

Chapter 1

Introduction

1.1 Introduction

Nowadays, energy issue related to the carbon emission from burning fossil fuels has been found to be an environmental problem as a global warming. This problem has also been increased due to the continuous growth of energy demand from fossil fuels. The rapid increases in the number of industries and vehicles also give rising in the petroleum price. Therefore, many researchers have been encouraged to investigate the possibility of using alternative sources of energy instead of energy from fossil sources [1-3].

Biodiesel has been a promising alternative fuel due to its renewability, biodegradability, and lesser emissions of harmful gases such as sulfur dioxide, carbon monoxide and unburnt hydrocarbons in comparison to petroleum diesel fuel. Mostly, biodiesel production via transesterification requires catalyst to produce the faster reaction rate and completion reaction. The conventional homogeneous catalyst is used for biodiesel production such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) etc. Using this catalyst requires the washing step to separate catalyst from biodiesel affecting the environment problem. Heterogeneous catalyst gains more advantages including easy separation of catalyst from reactant and product, reducing washing procedure, decreasing amount of waste water, reusability and long life catalyst[4, 5]. The disadvantages of biodiesel production via transesterification using heterogeneous catalyst are 2 major issues including of (I) mass transfer limitation between reactant and active site of catalyst and (II) insolubility of oil and alcohol phase.

Nevertheless, the disadvantage is mass transfer limitation and hence ultrasound-assisted reactor was used to overcome this disadvantage [6]. Ultrasonic or ultrasounds wave is a mechanical wave in the range of 20–1000 kHz. Ultrasound wave can apply to investigate the deep measuring of sea and find object under water etc. Ultrasound assisted reactor provides great mixing because it can increase the interfacial area of mixture via cavitation and micro bubble formation. Thus, mass transfer limitation for biodiesel production can decrease and enhance the reaction rate [7]. Our previous work studied biodiesel production via transesterification of palm oil using a circulated continuous flow ultrasound assisted reactor (US) and compared with mechanical stirred reactor (MS). The reaction was carried out at 60°C, 1 atm and methanol to oil molar ratio of 9:1 using 2% of CaO catalyst loading. The results were found that biodiesel yield was increased in the shorten time with the assistance of US. Moreover, ultrasound frequency and power also have effect on degree of mixing of reactant [8]. However, the maximum biodiesel yield obtained from CaO catalyzed transesterification in this US was about 80% which did not conform to EN standard as 96.5% of fatty acid methyl ester (FAME). Therefore, this research is focusing on the improvement of efficiency for biodiesel production in flow US.

The addition of co-solvent can increase reaction rate and reduce reaction time. Various co-solvents for transesterification such as acetone, hexane, diethyl ether (DEE), tetrahydrofuran (THF) and carbon dioxide (CO_2) were used to increase the yield of biodiesel [9-12]. The main advantage is to increase the miscibility between oil and methanol because of their disappearance of inter-phase mass transfer resistance in the heterogeneous two-phase reaction system by enhancing the rate of reaction. Moreover, Hashemzadeh and Sadrameli [13] used biodiesel as a co-solvent to improve the mutual solubility of the oil and methanol for CaO catalyzed transesterification to produce biodiesel at a yield of 89.72%.

The aim of this investigation is to improve the efficiency of biodiesel production by addition of co-solvent in transesterification from palm oil in the flow US. Acetone, THF and FAME (biodiesel product) are chosen as co-solvent, due to their properties which can enhance the solubility of transesterification mixture. This approach could be applied to industrial scale.

1.2 Research objective

To improve the efficiency of biodiesel production by investigation of the suitable co-solvent via transesterification of palm oil using CaO catalyst in the ultrasound assisted-reactor.

1.3 Scope of work

1.3.1 Select suitable co-solvent (Acetone, THF and FAME) to mix with reactants in transesterification of palm oil with methanol via ultrasound probe reactor. The chosen operating condition is the methanol to oil molar ratio 9:1, the methanol to co-solvent volume ratio 0.5:1, the reaction temperature of 60°C and 10 wt% based on oil.

1.3.2 Choose the suitable co-solvent and investigate the effect of adding co-solvent amount on the efficiency for biodiesel production via transesterification of palm oil with methanol in ultrasound probe reactor. The methanol to co-solvent volume ratio was varied as 1:0.1, 1:0.25, 1:0.5 and 1:1. While the operating condition was controlled by using the methanol to oil molar ratio 9:1, the reaction temperature of 60°C and 10 wt% of CaO catalyst based on oil.

1.3.3 To investigate effect of operating parameters on ultrasound assisted reactor including ultrasound frequency (20, 50 and 20 & 50 kHz), power (400 and 800 W) and feed flow rate (35 to 100 mL/min) in the ultrasound assisted reactor for biodiesel production from transesterification of palm oil with methanol under optimum condition.

1.4 Expected outputs

The improvement of biodiesel production efficiency by adding co-solvent to reduce the reaction time for transesterification from palm oil in the flow US is expected.

Chapter 2

Theory and literature reviews

2.1 Biodiesel

Biodiesel or chemically known as fatty acid methyl ester (FAME) is an alternative fuel that can be produced from renewable natural resources such as vegetable oils, animal fats, and oil from alga or used cooking oils. It can be substituted or mixed to petroleum diesel without modification of diesel engine. The various feedstocks for biodiesel production are shown in Table 1.

Table 1 Feedstocks for biodiesel production.

Non-edible oil	Edible oil	Other sources
Jatropha oil	Palm oil	Algae
Neem	Rapeseed oil	Waste cooking oil
Karanja oil	Peatnut oil	Animal fats
Eucalyptus oil	Castor oil	Beef tallow
Linseed	Soybean oil	Fish oil
Rubber seed	Canola oil	Chicken fat
Polanga	Sunflower oil	
Rubber seed	Coconut oil	
Yellow oleander	Cottonseed oil	
	Corn oil	

Generally, biodiesel production can be obtained from the chemical reaction of vegetable oils or animal fats and short chain alcohol such as methanol using homogeneous or heterogeneous catalyst through transesterification. Therefore, it can convert a vegetable oil to form fatty acid alkyl ester (FAAE) and glycerol.

Moreover, physical and chemical properties of biodiesel was according with American Society for Testing and Materials (ASTM) D6751 or The European EN14214 biodiesel international standard were shown in Table 2.

Table 2 Specification of ASTM and EN standard for biodiesel.

Property/units	ASTM test method	ASTM limits	EN test method	EN limits
Oxidation stability at 110°C (h)	EN 14112	Min 3 h	EN-ISO 14112	Min 6 h
Cloud point (°C)	D-2500	-	EN-ISO 23015	-
Pour point (°C)	D-97	-	EN-ISO 3016	-
Cold filter plugging point (°C)	D-6371	-	EN 116	Variable
Cold soak filterability (s)	D-7501	360 (max)	-	-
Viscosity at 40 °C (cSt)	D-445	1.9-6.0	EN-ISO 3104	3.5-5.0
Sulfated ash (%mass)	D-874	0.02 (max)	EN-ISO 3987	0.02 (max)
Sulfur (%mass)	D-5453 / D-4294	0.0015 (S15, max) 0.05 (S500, max)	EN-ISO 20846/ 20884	0.0010 (max)
Sodium and potassium (mg kg^{-1})	-	-	EN 14108/ 14109	5 (max)
Calcium and magnesium (mg kg^{-1})	-	-	EN 14538	5 (max)
Flash point (°C)	D-93	130 (min)	EN-ISO 3679	120 (max)
Cetane number	D-613	47 (min)	EN-ISO 5156	51 (min)

Table 2 Specification of ASTM and EN standard for biodiesel (continued).

Property/units	ASTM test method	ASTM limits	EN test method	EN limits
Methanol or ethanol (% mass)	-	-	EN 14110	0.20%
Copper strip corrosion	D-130	3 (max)	EN-ISO 10370	1 (max)
Phosphorus (% mass)	D-4951	0.001 (max)	EN 14107	0.001 (max)
Conradson carbon residue (100%/ % mass)	D-4530	0.05 (max)	EN-ISO 10370	0.3 (max)
Ester content (% mass)	-	-	EN 14103	96.5 (max)
Distillation temperature (°C)	D-1160	90% at 360 °C	-	-
Total contamination (mg kg^{-1})	-	-	EN-ISO 12662	24 (max)
Water and sediment (% vol.)	D-2709	0.05 (max)	-	-
Neutralization value (mg, KOH per gram)	D-664	0.5 (max)	EN-ISO 14104	0.5 (max)
Free glycerin (% mass)	D-6584	0.02 (max)	EN-ISO 14105/ 14106	0.02 (max)
Total glycerin (% mass)	D-6584	0.24 (max)	EN-ISO 14105	0.25 (max)
Monoglyceride content (% mass)	-	-	EN-ISO 14105	0.8 (max)
Diglyceride content (% mass)	-	-	EN-ISO 14105	0.2 (max)
Triglyceride content (% mass)	-	-	EN-ISO 14105	0.2 (max)
Density (kg m^{-3})	-	-	EN 3675	860-900
Lubricity at 60 °C (WSD/μm)	-	-	-	-

2.2 Production of biodiesel

Biodiesel can produce via various processes. Mostly, it can be divided four methods as direct use and blending, micro-emulsion, thermal cracking or pyrolysis and transesterification. Mostly, the conventional process is transesterification process. This is because of the fact that this process is relatively easy, carried out at normal conditions, and gives the best conversion efficiency and quality of the converted fuel [8].

2.2.1 Direct use and blending (Dilution)

In direct use and blending or dilution, vegetable oil can be directly used as diesel fuel without any modified engine. Nevertheless, it has some problems for long run due to its unacceptable properties like higher viscosity of vegetable oil, acid value, FFA content, and gum formation. Thus, it is difficult to use as engine fuel. Dilution or blending method can reduce the viscosity and density of vegetable oils. The dilution of vegetable oils can be mixed with such material as diesel fuels, solvent or ethanol in certain proportion[14]. The advantage and disadvantage of blending method are shown in Table 3.

Table 3 The advantages and disadvantages of blending method

Advantages	Disadvantages
High heat content (80% of diesel fuel)	Thickening and gelling
Renewability	Carbon deposits in engine
Easy for used	Cocking and trumpet formation

2.2.2 Micro-emulsions

Micro-emulsions are defined as transparent, thermodynamically stable colloidal dispersion in immiscible two phases. It can be obtained from mixing vegetable oils in immiscible phase solvent. The droplet diameters of micro-emulsions are in the range from 2 to 200 nm[15]. Micro-emulsion method can overcome the problem derived from high viscosity of vegetable oil[16].

2.2.3 Thermal cracking (Pyrolysis)

Thermal cracking or pyrolysis defined, is the conversion of one substance into another various chemical compound by using heating or by heat with a catalyst. Pyrolysis consists of thermally decomposing of chemical complex compounds in the limits amount of oxygen or any other oxygenating compounds to prevent the complete combustion. The thermal cracking material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The process is conducted at high temperature about 450-600°C. Consequently, the quantity and quality of the product is similar to diesel fuel. Nevertheless, chemical compound from thermal cracking is difficult to characterize because the several of reaction path ways and the several of reaction products may be obtained from the reactions[17]. Thermal cracking of triglycerides mechanisms is shown in Fig. 1.

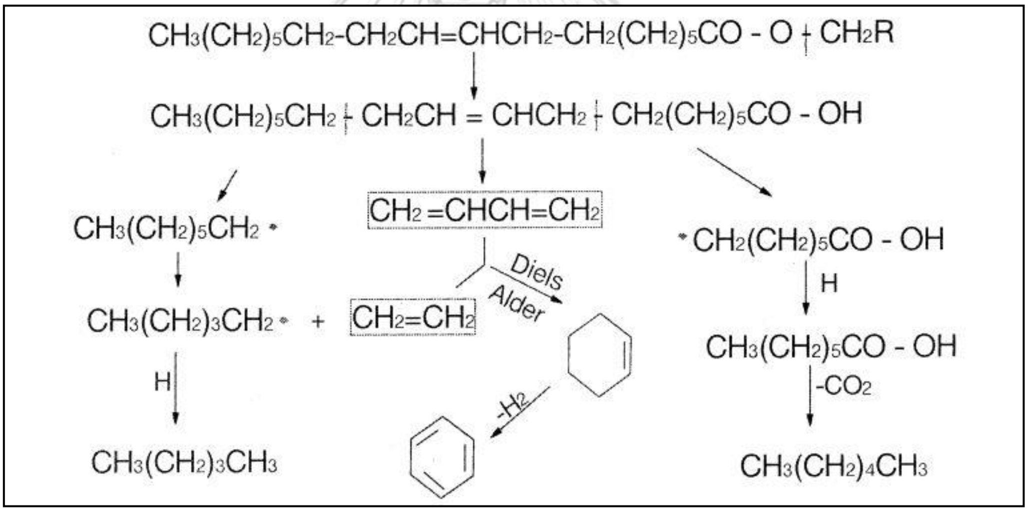


Fig. 1 Thermal cracking of triglycerides mechanisms [19].

2.2.4 Transesterification

Transesterification is the most commonly and widely used for biodiesel production derived from the reaction of oil or triglycerides with short chain alcohol such as methanol or ethanol using base or acid as catalyst at mild condition. The stoichiometry of the reaction requires 1 mole of triglyceride and 3 moles of methanol to provide 3 moles of fatty acid methyl ester as product and 1 mole of glycerol as by product. The overall transesterification of triglyceride is shown in Fig. 2.

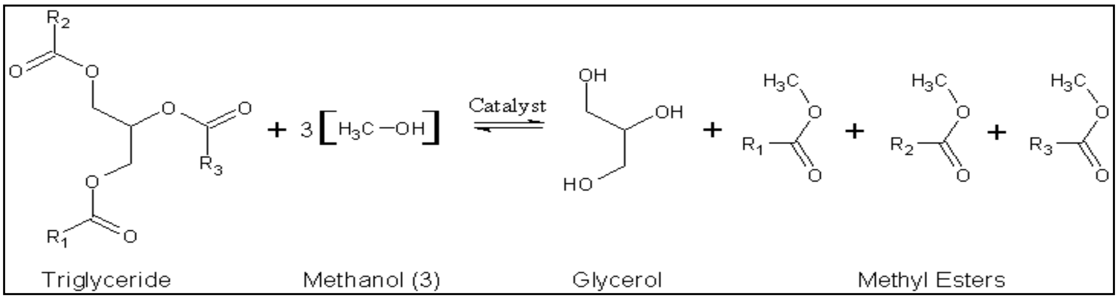


Fig. 2 Transesterification of triglyceride.

Methanol is the most commonly used in biodiesel production due to there are low cost, availability and shorten chain molecule that was rapidly reacted with oil or fatty acid. Glycerol as a by-product is separated from product and it can be used as a raw material for cosmetic and pharmaceutical industries. The reversible transesterification composes of three steps. Triglyceride (TG) is transformed to diglyceride (DG) then diglyceride (DG) is also transformed to monoglycerid (MG). Finally, monoglyceride is converted to glycerol (GL). Fatty acid methyl esters (FAMEs) are obtained from each transesterification steps as shown in Fig. 3.

$$\textbf{Triglyceride (TG)} + R'OH \xrightleftharpoons{\text{Catalyst}} \textbf{Diglyceride (DG)} + R'COOR_1$$

$$\textbf{Diglyceride (DG)} + R'OH \xrightleftharpoons{\text{Catalyst}} \textbf{Monoglyceride (MG)} + R'COOR_2$$

$$\textbf{Monoglyceride (MG)} + R'OH \xrightleftharpoons{\text{Catalyst}} \textbf{Glycerol (GL)} + R'COOR_3$$

Fig. 3 Three steps of reversible transesterification

For transesterification, the various parameters are influenced for conversion of vegetable oil or lipid such as

- Water or moisture

The water or moisture can react to form a soap in the system and induce the hydrolysis of triglycerides instead of the transesterification. Due to it may interact with high content of free fatty acid (FFA) in feedstocks. Therefore, it results in low conversion and low yields [18].

- Catalyst classified

Generally, the catalyst type was divided two mainly type; heterogeneous catalyst and homogeneous catalyst. The homogeneous and heterogeneous catalyzed transesterification to obtain suitable condition for both catalysts. Usually, the homogeneous catalyst provides the higher yield than heterogeneous catalyst because of no mass transfer limitation between reactant and active site. However, homogeneous catalyst cannot reuse, difficult separation of catalyst and glycerol and require the washing step [19].

- Reaction time

Reaction time is the most important parameter for reaction conditions for production of biodiesel. The induction period can observe during transesterification at the initial stage. This was due to the incomplete miscibility of the reactants resulting to enhance mass transfer resistance. Thus, an appropriate reaction time is required for the reactants to overcome the inter and intra molecular forces between them[9]. Moreover, the reversible reaction for transesterification might not allow the longer reaction leading to decrease product due to its reversible.

- Proportion of alcohol per oil (Methanol to oil ratio)

In general, increasing methanol to oil molar ratio can shift the reaction equilibrium toward the formation of biodiesel. Yield of biodiesel was increased when methanol to oil molar ratio was increased. For example, Roschat et al. [2] found that the increasing of the ratio to 15:1 did not change in biodiesel yield and further increase methanol to oil ratio to 18:1 tended to decrease %FAME yield. In this case, glycerol by-product may dissolve in the excessive methanol and thereby inhibit the mixing between methanol with the catalysts and oil.

- Reaction temperature

The FAME yield gradually increased with increasing the temperature from 25 to 65°C. Thereafter, a decrease in the FAME yield was observed when the temperature was increased to 75°C. The boiling point of methanol was below this temperature leading to vaporization of methanol and the FAME yield was also decreased [20].

- Catalyst loading

Generally, increasing amount of catalysts enhance biodiesel production However, the biodiesel yield did not increase when the catalyst loading amount was further increased. Such this limitation may be related to the phase mixing between palm oil, methanol and solid catalyst in terms of high viscosity of slurry limited mass transfer of reactants to catalysts [2].

2.3 Catalyst

A catalyst is a matter used to reduce the reaction time by increasing of chemical reaction rate due to it can decrease activation energy (E_a) of chemical reaction as presented in Fig. 4.

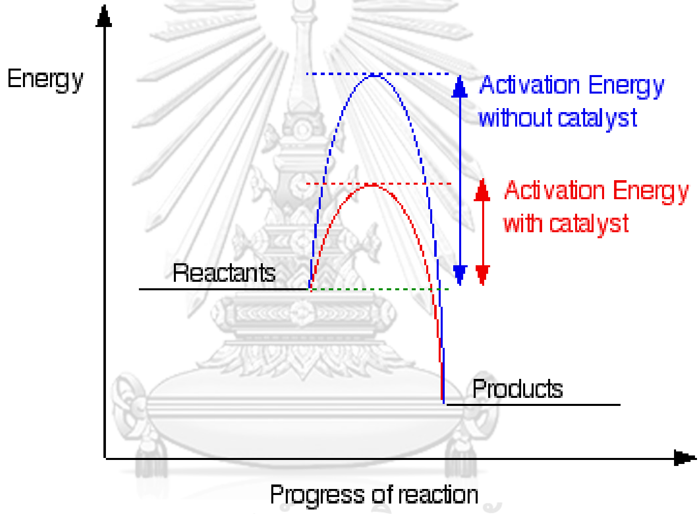


Fig. 4 Relation of activation energy and progress of reaction with catalyst and without catalyst [23].

Catalysts can be divided mainly two types as either homogeneous or heterogeneous catalyst. A homogeneous catalyst is one which molecules are dispersed in the same phase with the reactants. The commonly homogeneous catalyst is used in transesterification such as potassium hydroxide (KOH), sodium methoxide ($NaOCH_3$), potassium methoxide ($KOCH_3$) and sodium hydroxide (NaOH). They provided biodiesel yield higher than that of heterogeneous catalyst.

Nevertheless, this catalyst is required separation and washing processes to separate catalyst from product [12]. Therefore, a heterogeneous catalyst is one which molecules are different phase with the reactants. Using heterogeneous catalyst instead of homogeneous catalyst gains more advantages including of easy separation of catalyst from reactant and product, reusability and long life catalyst. Moreover, using this catalyst in biodiesel production process can reduce washing process resulting to decrease the volume of waste water and water pollution.

Mostly, the heterogeneous catalyst is used in transesterification such as calcium oxide (CaO) [8], zinc oxide (ZnO) [21], magnesium oxide (MgO) [22] and catalyst derived from nature source such as calcium oxide from eggshell [23], river snail shell [2], waste bone etc.

In addition, category of catalyst can be divided as base or acid catalyst. The advantages and disadvantages of base and acid catalysts for biodiesel production via transesterification are summarize in Table 4.

Table 4 The summarization of advantages and disadvantages of base and acid catalysts for transesterification [19].

Type of catalyst	Advantages	Disadvantages
Base catalyst	-Reaction rate is faster than acid-catalyst. -Reaction can carry out at mild condition. -Price of catalyst is cheap.	- Sensitive to FFA content in oil - Sensitive to ambient air - Soap will be easy formed. If the FFA content in oil higher than 2 wt%
Acid catalyst	-Insensitivity to FFA and water or moisture.	- Using high reaction temperature, high alcohol to oil molar ratio - Slow rate reaction - Energy intensive - Corrosion on reactor - Long time for reaction

Generally, the mechanism of the base-catalyst transesterification of oils/lipids including four steps as follow

(1) The first step is the reaction of base catalyst with alcohol by given the protonated catalyst and an alkoxide.

(2) The second step is the alkoxide attached at the carbonyl group of the triglyceride by the nucleophilic to generate a tetrahedral intermediate.

(3) The third step relates to the formation of the alkyl ester and the corresponding anion of diglyceride.

(4) The final step involves the deprotonating the catalyst. Therefore, the regenerating of active species, which is now able to react with a second molecule of the alcohol and starting another catalytic cycle.

Overall mechanism of base catalyst transesterification process is shown in Fig. 5. Using sodium or potassium catalysts or any base catalyst were found soap formation generated from saponification [2]. Wu et al. [12] found that if there is water content in reaction, the soap formation will easily and quickly occur. The saponification is shown in Fig. 6.

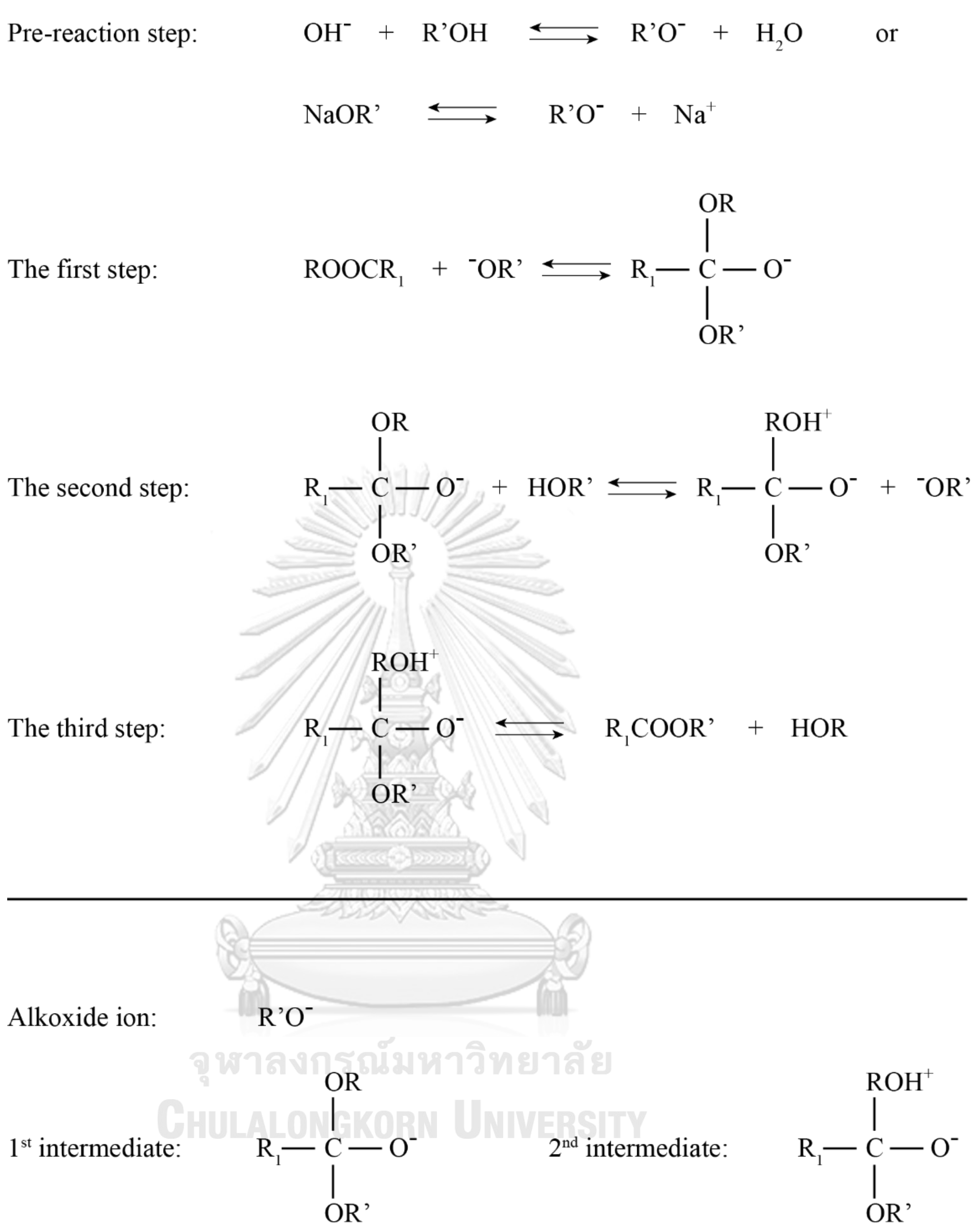


Fig. 5 Overall mechanism of base catalyst transesterification process [19].

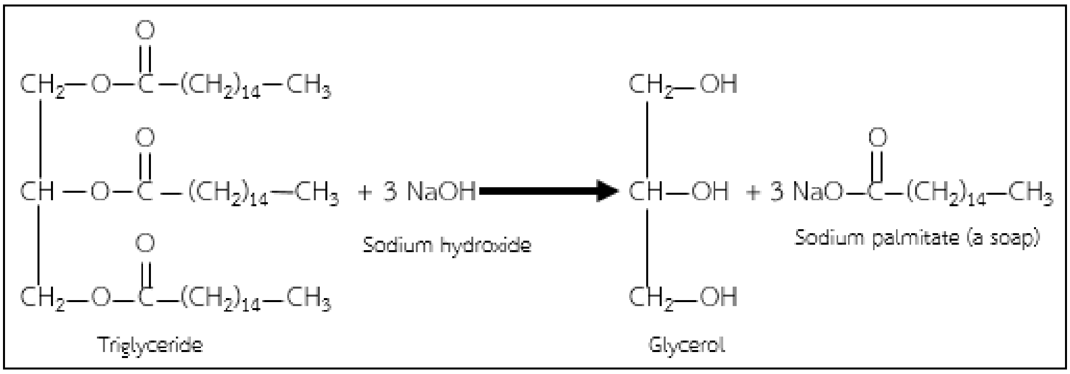


Fig. 6 Saponification.

To resolve the saponification reaction, acid catalysts were used in transesterification of oils/lipid [11]. The mechanism of the acid-catalyzed transesterification of oils/lipid is shown in Fig. 7 including three steps as follow:

(1) The protonation of the carbonyl group of the ester leads to generate the carbocation after a nucleophilic attack of the alcohol to produce the tetrahedral intermediate.

(2) The tetrahedral intermediate reacts with alcohol to produce anion of methoxide ion.

(3) Finally, tetrahedral intermediate is converted to ester, diglycerides and hydrogen proton. Then, diglycerides reacts to the protonation of the carbonyl group. The repeated of first step is observed to produce monoglyceride as product and glycerol as by-product.

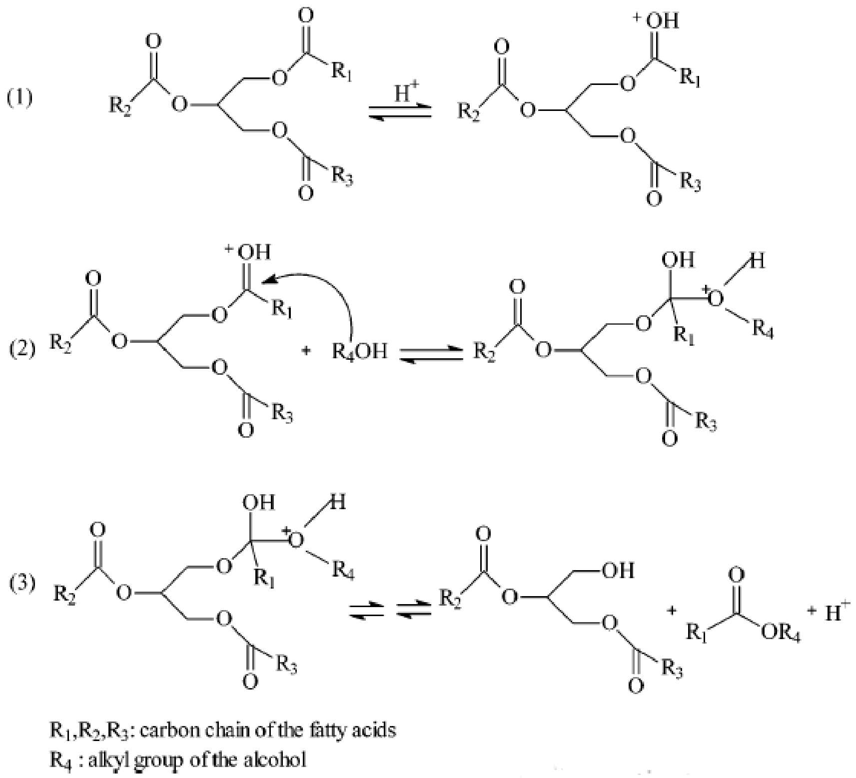


Fig. 7 Mechanism of the acid-catalyzed transesterification of oils/lipid [11].

2.4 Improvement method for biodiesel production

At presently, biodiesel production via transesterification using heterogeneous catalyst instead of homogeneous catalyst was found to limit biodiesel yield due to it enhance the mass transfer resistance. The improvement of biodiesel production method to decrease mass transfer limitation can be classified as

2.4.1 Supercritical process [24-26]

Supercritical process is controlled by temperature and pressure. It requires high temperature and high pressure to form the single phase leading to obtain the homogeneous system. This process does not require catalyst as namely a non-catalytic biodiesel synthesis. Therefore, the high purity product was obtained from this process. Side reaction such as saponification in catalytic reaction does not generate in the supercritical process. The yield of product was only 72 % within 20 min. High temperature and high pressure operation can reduce the reaction time of transesterification. However, the reaction temperature of supercritical methanol process should not be higher than 350°C due to evaded unnecessary decomposition of fatty acid methyl esters or biodiesel. It should be noted that, using high temperature increases the energy consumption and operating cost. In addition, this method requires a high molar ratio of alcohol to oil to shift forward equilibrium and produce more biodiesel yield.

2.4.2 Intensification reactor

Intensification reactor is development of reactor which applied others technologies to improve the efficiency of reactor. The intensification reactor for biodiesel production via transesterification is used to shift equilibrium of reaction and increase mass transfer limitation such as homogenizer reactor [27], static mixer [28], micro channel reactor [29], cavitational reactor [30], membrane reactor [31] and reactive distillation [32] etc. There are a numerous of using intensification reactor to increase biodiesel yield. For instance, the maximum yield of biodiesel from waste cooking oil was obtained from hydrodynamic cavitation based on high speed homogenizer reactor was 97 % within 120 min using molar ratio of methanol to oil of 12:1, 3 wt% loading of KOH and temperature 50°C. High speed homogenizer is a technique of intensification for biodiesel production due to its generated hydrodynamic cavitation and it provided the higher biodiesel yield than that of the conventional method. The advantage of high speed homogenizer reactor is lower space and not found pressure drop in this system [27]. Hydrodynamic cavitation can improve the solubility of two immiscible reactants. In additional, a triple frequency ultrasound wave has also been used for the intensification process for produced biodiesel from palm oil. It obtained the highest yield 93 % within 15 min using methanol to oil molar ratio as 3:1, 1 wt% KOH. While the conventional stirring method was found the highest yield 75 % for 3 h reaction time [30]. Transesterification of refined palm oil in static mixer reactor, it showed 96.5% of FAME yield within 5 min using reaction temperature of 65°C, methanol to oil molar ratio of 10.5 and 1 wt% of KOH as catalyst [28].

For micro channel reactor with inner diameter 0.53 mm, the methanol to oil molar ratio was 6 and the KOH concentration was 1 % weight of the oil, over 95 % of methyl yield could be obtained with a residence time of about 6 min. The results indicated that the reaction time was shorter than that of a conventional batch reactor [29]. Furthermore, the biodiesel production from canola oil and methanol was carried out in a two-phase tubular membrane reactor. The pore size of the carbon membrane used in the reactor was 0.05 µm. The inner and outer diameters were 6 and 8 mm, respectively. Its length was 1,200 mm giving surface area of 0.022 m^2. The result was reported that 96 % of biodiesel yield was observed via 1 wt%, NaOH, reaction temperature 65°C, reaction volume 300 mL and flow rate 6.1 mL/min [31].

Finally, a process is combined both distillation and chemical reaction into a single unit that it called reactive distillation (RD). The advantage of using RD is to generate higher biodiesel yield, improve selectivity and lower cost. A reactive distillation (RD) column was long 4 m with inside diameter of 1–2 cm, connected with 2 L reboiler and 93 % volume of shred stainless steel as package with total reflux for biodiesel production. It was provided methyl ester purity of 92.27 % via the oil feed flow rate of 15 mL/min., methanol to oil molar ratio of 4.5:1, the optimal condition is at the reboiler temperature of 90°C using KOH of 1 wt% based on oil weight [32].

The development of intensification reactor for biodiesel production is to enhance the reaction rate extremely, therefore, the reaction time can be reduced and the important thing is to lower cost.

2.4.3 Using co-solvent

Transesterification consists of two immiscible phases that the solubility of vegetable oil or lipid in methanol are very low. As the results, the reaction rate is low. To overcome this problem by addition of co-solvent such as tetrahydrofuran (THF) [1], diethyl ether [9], hexane [33], acetone [34] or diesel [35] into the reaction mixture which can decrease insolubility of methanol into the oil [2]. The reaction can be accelerated by increasing of mass transfer of molecule-molecule of reactant resulting to complete in a shorter reaction time for either homogeneous catalyst or heterogeneous catalyst [10]. The comparison of reaction conditions and performance for various types of co-solvent used in transesterification is shown in Table 5.

The highest FAME yield was obtained using acetone as co-solvent for produced biodiesel from waste cooking oil (WCO) due to acetone as a polar aprotic solvent and it is classified as intermediate polarity. Thus, it can greatly dissolved in triglyceride as a low polarity and methanol as a high polarity [34]. Acetone can be extremely increased the transesterification reaction rate. Moreover, using WCO is cheaper raw material compared to refresh oils which can reduce the production cost of biodiesel. Besides, using other co-solvents were found lower FAME yields than that of acetone. Moreover, high molar ratio of methanol to oil, long reaction time and high temperature was also required for using the other solvent resulting to increase energy consumption.

Furthermore, the homogeneous alkali catalyzed transesterification of soybean oil using diesel as co-solvent in an ultrasound irradiation reactor was found excellent yields as 92 % within 45 min under optimum stoichiometric amount of alcohol as 3, 1.2 wt% NaOH loading catalyst, reaction temperature 50°C, ultrasound frequency of 20 kHz and 30 wt% of co-solvent (with respect to oil). Under similar reaction condition, it was found that the highest FAME yield of 45 % that obtained from the reaction without co-solvent (using only ultrasound irradiation) [35].

The yield of biodiesel was raised from 89.7 to 99.9 % with increasing in the volume of co-solvent from 5 to 10 mL due to the miscibility of the insoluble oil and alcohol layers was improved. Therefore, the both effect of using ultrasound irradiation and adding of co-solvent can overcame the mass transfer limitations which in turn enhances the reaction rate and consequently increase the product yield. In addition, using of ultrasound irradiation and co-solvent were found to improve the rate of in-situ transesterification of microalgae biomass. This process can be improved FAME yield 15-17 % compared to using stirrer method and decreased the molar ratio of reacting methanol to *Chlorella* oil from 26:1 to 79:1 [36]. Using ultrasound irradiation combined with co-solvent was significantly increased the conversion of microalgae lipids and reduced reacting methanol volumes. From now, literature review was found rarely using ultrasound irradiation combined with co-solvent to improve transesterification rate.

Table 5 Comparison of reaction conditions and performance for various types of co-solvent used in transesterification.

Co-solvent	Feedstock	Catalyst type	Catalyst (wt %)	Temperature (°C)	MeOH/oil molar ratio	MeOH/cosolvent ratio	Time (min)	Reactor type	Yield (%)	Reference
THF	Palm oil	CaO	5	65	12:1	10%	90	MS	95.03	[2]
1-	Palm oil	CaO	5	65	12:1	10%	90	MS	94.44	[2]
DEE	Rapeseed	KOH	0.7	27	9:1	1:1	120	MS	97.6	[1]
tBME	Rapeseed	KOH	0.7	30	9:1	1:1	120	MS	97.5	[1]
Acetone	WCO	$Ca_2Al_2O_5$	1.2	55	6:1	20%	25	MS	97.98	[34]
Acetone	Palm oil	CaO	5	65	12:1	10%	90	MS	90.23	[2]
Diesel	Soybean	NaOH	1	50	3:1	30%	45	US	92	[35]
Hexane	WVO	SnO_2-SiO_2	6	150	15:1	30%	90	MS	88.2	[33]

2.5 Ultrasound theory

2.5.1 Ultrasound wave

Sound with the frequency below the human hearing is refer as infrasound while sound waves that are above the frequency for human hearing is called ultrasonic or ultrasound wave as shown in Fig. 8. It is approximate 20 kilohertz (kHz), or 20,000 cycles per second which limits the range of high frequency to about 600 MHz. This ultrasound wave is a silent wave. Ultrasound wave is divided by its frequency (kilohertz) as well as by its intensity (W/cm^2). Ultrasound wave can be classified into two main groups corresponding with the frequency into (1) high-frequency and low power (2–10 MHz range) ultrasound wave, which is usually applied in medical imaging and chemical analysis and (2) low frequency and high-power (20–100 kHz) ultrasound that is used for cleaning, dispersing, and also for sonochemistry [37].

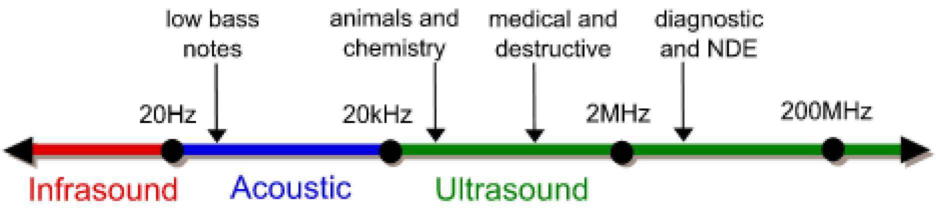


Fig. 8 Frequency range of ultrasound [41].

Ultrasound wave is used in wide ranges of application such as extraction and atomization. Ultrasound wave has three significant influence on reaction; Acoustic streaming mixing with variation of sonic pressure lead to rapidly movement of fluids. Finally, cavitation bubbles were formed by liquid breakdown that caused by the large negative pressure gradient application in fluid. The main effect of ultrasound wave on chemical reactions comes from the formation and collapse of micro bubble. The liquid jet effect is a cavity collapse that improves them as transfer by disrupting the interfacial boundary layer.

2.5.2 Ultrasound equipment

2.5.1.1 Ultrasound generator

Ultrasound generator converts the frequency of AC electric energy from power source (normal frequency of 50 or 60 Hz) into the ultrasound frequency before drive to ultrasound transducer. The most advanced ultrasound generator can adjust the frequency of the output wave to be suitable for use in various applications.

2.5.1.2 Ultrasound transducer

A transducer is a device used to convert the supplied electrical energy into mechanical energy in the form of vibrations finally occurring as ultrasound wave. The ultrasound wave dispersion into the liquid mixture creates the cavitation phenomena. Generally, transducer can divide to three main types that are liquid driven transducer, magnetostrictive transducer and the piezoelectric transducer [38]. The liquid driven transducer is mainly used for producing fine emulsion that it increases interfacial phenomena.

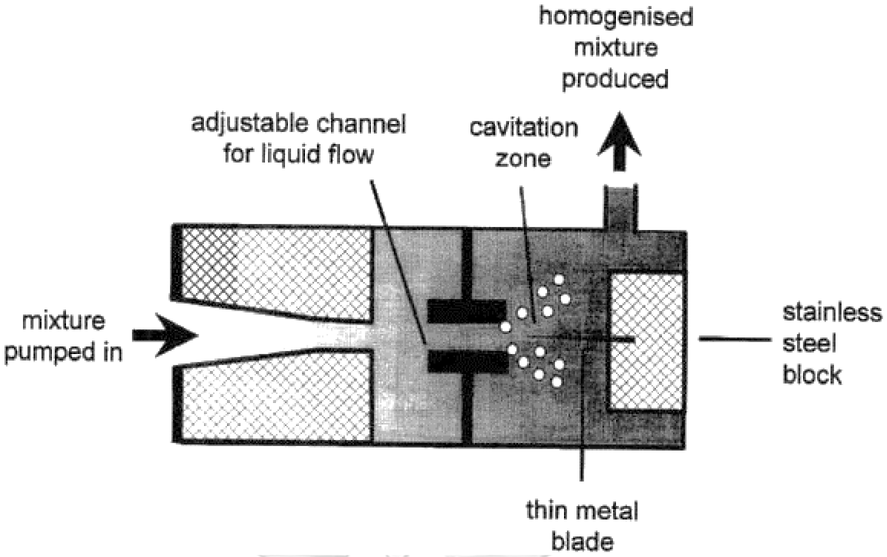
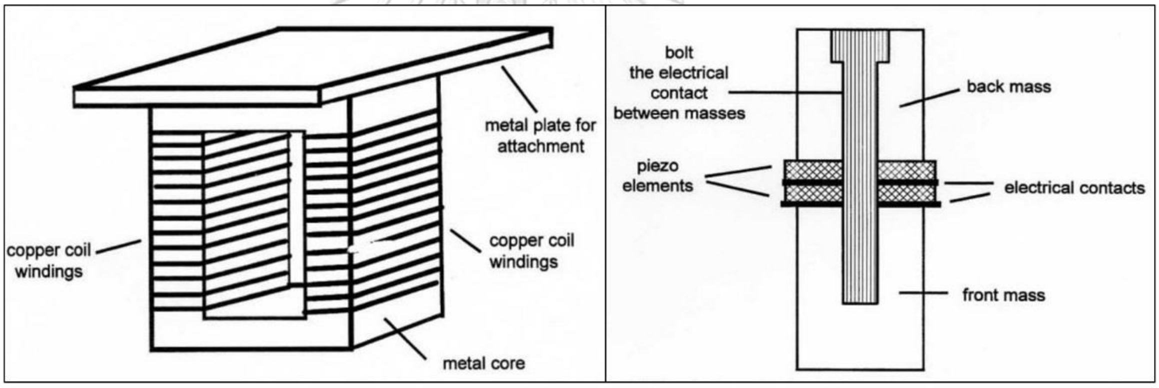


Fig. 9 Liquid driven transducer [40]



(A) Construction of magnetostrictive transducer (B) Construction of piezoelectric transducer

Fig. 10 Magnetostrictive and piezoelectric transducer [40]

Piezoelectric transducer is made from piezoelectric property of a material to convert electrical energy directly into mechanical energy. While magnetostrictive transducer is made from the magnetostrictive property of a material to convert the energy in a magnetic field into mechanical energy. However, the magnetostrictive transducers are limited the frequency range to below 100 kHz and lower electrical conversion efficiency than their piezoelectric transducers[37].

2.5.3 Types of ultrasound assisted reactor

2.5.3.1 Probe system

The ultrasound probe or ultrasound horn is generally used for experimental of laboratory scale. The transducer of probe system is directly immersed in liquid mixture. The advantage of using probe system is ability to deliver large amounts of power through a small transducer area to a small volume of reaction mixture in the nearly of ultrasound probe. The ultrasound probe or ultrasound horn shows in Fig. 11.

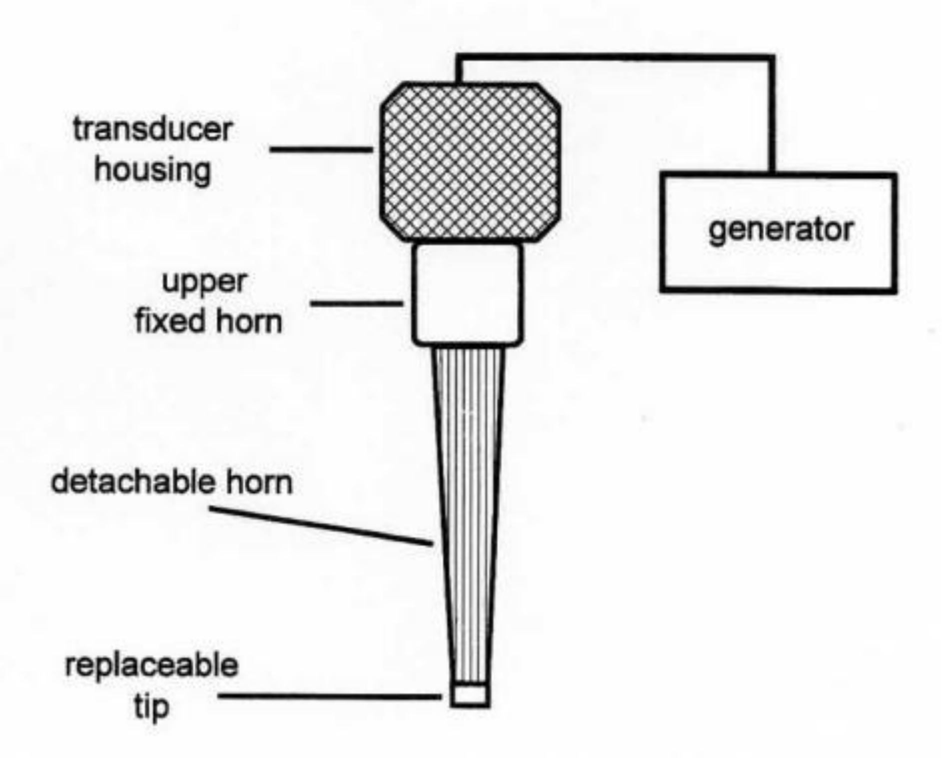


Fig. 11 Ultrasound probe system [40]

2.5.3.2 Ultrasound baths

Ultrasound bath composes of tank and transducer attached at bottom of tank. Ultrasound baths are indirectly sonication reactor due to liquid mixture is contained in tank and transducer is indirectly contacted with liquid mixture. However, the ultrasound power distributed into the liquid mixture is lower compared with other ultrasound reactor. Generally, ultrasound baths are usually used for cleaning applications.

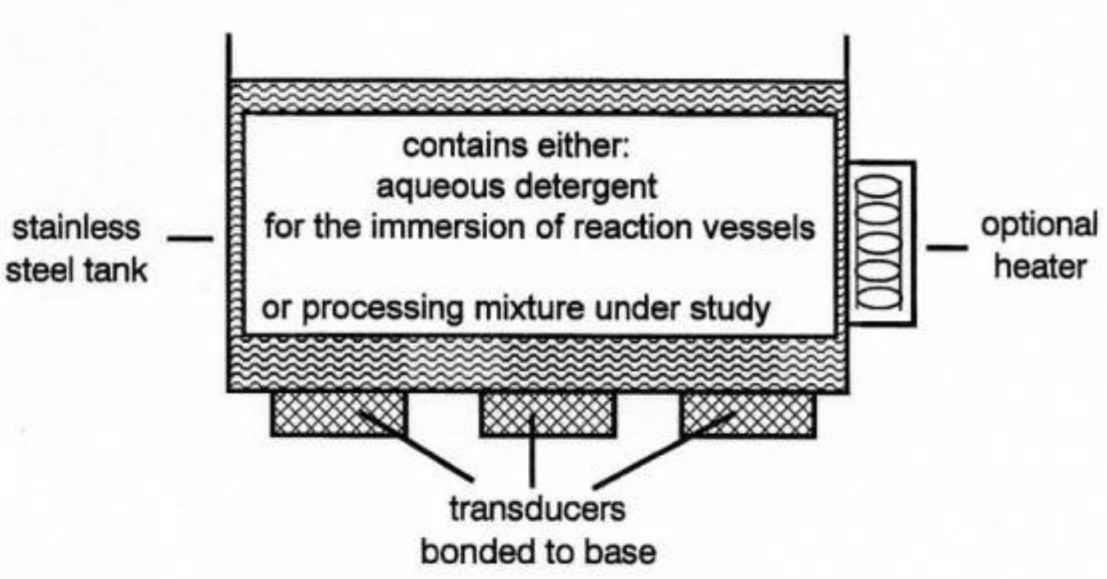


Fig. 12 Ultrasound bath [40]

2.6 Literature reviews

2.6.1 Conventional process and development for biodiesel production

In 1853, transesterification is developed by Duffy and Patrick. This process used to convert vegetable oil or animal fats to biodiesel by chemically break the molecule of triglyceride into methyl or ethyl esters of the renewable fuel with glycerol as a by-product. Nevertheless, this process requires catalyst to produce higher yield and completion reaction. Acid homogeneous catalyst was used to catalyze biodiesel forming reaction via esterification and transesterification such as sulfuric acid, hydrochloric acid and sulfonic acid [39].

The drawback of acid catalyst for transesterification is long reaction time, higher reaction temperature and corrosive. While homogeneous base catalysts can reduce the reaction time and lower reaction temperature to provide the high reaction rate. Homogeneous base catalyst is commonly using for biodiesel production via transesterification such as sodium hydroxide or potassium hydroxide [40]. Accordingly, the biodiesel production in the industrial process uses the homogeneous base catalyst in a batch or continuous process because they can be performed at low reaction temperature and atmospheric pressure with high conversion. Rashid et al. [41] studied the synthesis of biodiesel from crude sunflower oil via transesterification using alkaline catalyst. They found that the optimum conditions are agitator rate 600 rpm, methanol to sunflower oil molar ratio of 6:1, reaction temperature as 60°C, and 1 wt% NaOH catalyst concentration. The highest biodiesel yield of 97.1 % was achieved at 120 min and the fuel properties were found accordingly with ASTM D 6751 specifications.

Buasri et al. [22] reported that CaO can be synthesized from natural source such as a rock type dolomite. It can be encountered around the world which can be used as non-toxic base catalyst. It consists of calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$) are very less percentages of other compounds.

Thus, using heterogeneous catalyst is environmental friendly and decreased water volume from washing step because heterogeneous catalyst can be easy separation of biodiesel and glycerol, no water washing, and reusability of catalyst. Recently, heterogeneous base catalysts were widely used such as calcium oxide (CaO), magnesium oxide (MgO), mixed oxide and etc.

Kawashima et al. [42] studied the acceleration of transesterification using third different kinds of metal oxides containing calcium, barium, magnesium or lanthanum. They reported that calcium series catalysts showed the high basicity and higher catalytic activity of transesterification reaction. Moreover, Esipovich et al. [43] reported that the CaO fresh catalyst can produce 76.9 % FAME yield under the investigation conditions: a methanol to oil molar ratio of 9:1, a reaction temperature of 60°C, reaction time of 120 min with catalyst loading 1.3 wt% based on oil mass. However, the long induction period was observed.

However, the main disadvantage of heterogeneous catalyst is mass transfer limitation. Ultrasound wave was introduced to enhance mass transfer rate between immiscible liquid-liquid phases in heterogeneous system. Due to this wave can increase the interfacial area of mixture via cavitation and micro bubble formation. Thus, the rate reaction was increased.

Chen et al. [44] applied ultrasound irradiation for biodiesel production. Biodiesel yield was increased to 70 % for 40 min using ultrasound-assisted reactor while the similar biodiesel yield was obtained at 100 min under magnetically stirring. The highest biodiesel yield (92.7 %) was obtained under the optimum conditions: 8 wt% loading catalyst, methanol to oil molar ratio 9:1, reaction time 60 min and ultrasound power (60 %). From the results, ultrasound assisted reactor can eliminate mass transfer obstacle between oil and methanol phase. Particularly, the ultrasound irradiation improves greatly mixing of reactants which generates the emulsification phase. Then, the biodiesel yield was increased and reaction time was shortened.

Moreover, Poosumas et al. [8] reported the frequency of ultrasound affected on the biodiesel yield in heterogeneous system. The higher biodiesel yield was found using a single high frequency transducer (50 kHz) compared to low frequency transducer (20 kHz) under similar ultrasound power of 400 W. Due to the high frequency transducer can create a smaller bubbles for generating cavitation activity in the liquid mixture resulting to increase the contact area between the reactants and the active sites of calcium oxide. On the other hand, low frequency transducer created the lower distribution of cavitation per unit volume as compared to the high frequency transducer. However, the different ultrasound frequency did not effect for homogeneous system as reported by Choedkiatsakul et al. [7].

Mootabadi et al. [45] studied the effect of ultrasound irradiation in presence of BaO, SrO and CaO as heterogeneous catalysts. Ultrasound processor (20 kHz) with a full power of 200 W (100 %) and magnetically stirred system were used testing. The highest biodiesel yield (95.2 %) was obtained from BaO as catalyst via reaction time 60 min, the methanol to oil molar ratio 9:1, catalyst loading 3 wt% and the optimum ultrasound power was 50 %. When amplitude was increased to 75 and 100 %. There was found similarly behavior and the yield was nearly the same. The highest biodiesel yields of 91.8 and 93.3 % were obtained using 100 and 75 % of amplitude, respectively. For BaO catalyst, biodiesel yield was increased to 95.2 % in 60 min by ultrasound irradiation reactor while using magnetically stirred system reached to yield of 67.3 % at the same time.

Moreover, Gupta et al. [46] reported the effect of ultrasound irradiation power on biodiesel yield. The highest 93.5 % of biodiesel yield was obtained under as molar ratio 9:1, Calcium diglyceroxide (CaDG) as catalyst loading 1.0 wt% of WCO, temperature 60°C, ultrasound irradiation power was 120 W and duty cycle of 50 %. The raise ultrasound irradiation power from 60 to 120 W can increase biodiesel yield from 76.2 to 93.5 %. Ultrasound irradiation power rises the cavitation effect also increases which results in sufficient mixing of two immiscible liquid layers. When the ultrasound irradiation power was increased, the violent collapse of the cavitation bubble was occurred. The violent the collapse of cavitation bubble provides the higher the jet velocity and micro-mixing at the phase boundary between the oil and methanol phases resulting in higher mass transfer coefficient and thus higher biodiesel yield.

In additional, researcher was found co-solvent method that can be improved biodiesel production. Encinar et al. [1] used the several co-solvents to improve transesterification process. Diethyl ether (DEE), tert-butyl methyl ether (tMBE) and tetrahydrofuran (THF) were found to have significantly affected to biodiesel yield. The biodiesel yield can be achieved to 97-98 % under optimum condition 9:1 as methanol to oil molar ratio, 0.7 wt% KOH, 1:1 DEE and THF as co-solvent to methanol molar ratio and at 30°C with mechanically stirrer 700 rpm.

Moreover, amount of co-solvent has effect to biodiesel yield. Singh et al. [34] synthesized biodiesel through transesterification of waste cooking oil (WCO) and methanol as feedstocks. Calcium aluminum oxide ($Ca_2Al_2O_5$) was used as heterogeneous catalyst. The amount of acetone was investigated 0 to 25 wt%. The highest yield (97.98 %) of biodiesel was obtained at 20 wt% of acetone, 6:1 molar ratio (MeOH:oil), 1.2 wt% calcium aluminate at 55 ± 1°C within 25 min of reaction time for mechanical stirrer reactor. Amount acetone was risen that it affects to increase biodiesel yield. When amount acetone increased more than 20 wt% that biodiesel yield was decreased because of the effect of dilution for starting reactants in co-solvent.

Ayegba et al. [47] investigated the effect of co-solvent in transesterification for biodiesel production in a tubular reactor. They found the optimum conditions of transesterification at 40°C, 200 rpm, 0.7 wt% of KOH catalyst concentration of 4:1 methanol-to-oil and molar ratio of 1:1 methanol to THF volume ratio. Biodiesel yield was obtained within 10 min. Thus, using THF as co-solvent can reduce cost of material in terms of catalyst concentration and lower methanol to oil molar ratio. Furthermore, the transesterification to completion at lower mechanically stirrer can be decreased energy consumption.

Using co-solvent has significantly affect to reduction reaction time that a feasibility reason to apply using co-solvent in continues process of biodiesel production. Roschat et al. [2] investigated biodiesel production by using river snail shells-derived heterogeneous catalyst and co-solvent method. Addition of another solvent or co-solvent into methanol can improve the efficiency of biodiesel production by the enhancement of mixing of reagents between methanol and palm. Physicochemical properties particularly polarity and boiling point of THF were appropriated to increase the dissolving between palm oil and methanol. However, the increase polarity of co-solvents might conduct to a decreased biodiesel yield because the high polar co-solvents can dissolve well in methanol but not in palm oil [2] .

Moreover, the effect of polar and non-polar solvents on activity in biodiesel production was reviewed. Pollardo et al. [48] reported the partition coefficient (log P) and relative polarity can affect to biodiesel yield. The log P is nearly zero that the solvent has the intermediate polarity. The intermediate polarity can miscibility in both oil and methanol that generate led to homogeneous phase to increase the solubility between reactants. Accordingly, the mass transfer enhancement from a bipolar property of solvent is led to increase biodiesel yield. Generally, bipolar property of solvent was used acetone [49], THF [50], etc.

Hashemzadeh and Sadrameli [13] investigated the continuous biodiesel production from linseed oil using heterogeneous catalyst in a packed bed reactor in the presence and absence a co-solvent. DEE was used as a co-solvent. Biodiesel yield in the presence of co-solvent was higher than that of absence co-solvent. Due to co-solvent can generate a single phase in the mixture of methanol and oil. Using DEE as a co-solvent increased yield from 75.83 to 98.08 %. The mass transfer between oil and methanol was solved by addition of DEE. Under optimum conditions, molar ratio of methanol and oil was 9.48:1, flow rate was reported of 1.37 mL/min and molar ratio of DEE to methanol was reported at 1.19:1. The optimum residence time was calculated to be 27.9 min at temperature reaction of 30°C. Therefore, an increase in the molar ratio affected to increase biodiesel yield due to the reversible transesterification. Flow rate is relatively with residence time which has significantly to continuous biodiesel production. A flow rate was decreased resulting in a high yield of biodiesel. Because the mixture of methanol and linseed oil have more time to react in the reactor. Therefore, this can be a reason for boosting the FAME yield.

Although co-solvent can be improved biodiesel production. But co-solvent separation step is required to split co-solvent from product. Parida et al. [35] investigated the addition diesel as co-solvent in biodiesel production to decrease mass transfer limitation and eliminate separation co-solvent step. The biodiesel yield was increased when amount of co-solvent was risen due to the miscibility of the insoluble oil and alcohol layers was enhanced. The maximum yield of 92 % was obtained using co-solvent volume 30 % and reaction time 30 min. On further increasing the volume of co-solvent to 40 %, the maximum percentage yield of product was similar. However, at the initial period of the reaction, the yield was reasonably higher than the reaction with 30 % of co-solvent.

Therefore, co-solvent method and ultrasound-assisted can be possible to apply to improve the efficiency of biodiesel production process.

Chapter 3

Methodology

3.1 Materials

Commercial refined palm oil “Morakot” brand was purchased from a local store in Thailand. Methanol analytical reagent grade was purchased from QRëC®. Methyl heptadecanoate (95 %) and heptane (99% grade) used as internal standard and solvent, respectively for GC analysis were purchased from Sigma-Aldrich and Fisher Scientific, respectively. Purity calcium oxide, CaO (96 %) fine powder catalyst was used as a heterogeneous catalyst in this experimental provided by Sigma-Aldrich. Catalyst was prepared by calcining CaO in a muffle furnace with the heating rate 10 °C/min to 900°C for 5 h then kept in a desiccator cabinet before use. Acetone (99%), Tetrahydrofuran (THF 99.5 %) and methyl myristate (99 %) as co-solvent were obtained from Fluka. The methyl myristate was chosen to represent FAME composition as a co-solvent because it was less composition in FAME produced from palm oil.

Bromthymol blue and phenolphthalein used as indicator for hammet titration method were purchased from Ajax fine chemical. 2, 4-Dinitroaniline and 4-Nitroaniline were purchased from Merck. Anhydrous ethanol reagent grade provided by Merck. Benzoic acid was purchased from Ajax fine chemical.

3.2 Experimental design

The experiment was divided into four parts consisting of catalyst characterization, transesterification activity, analysis of biodiesel yield and calculation of yield efficiency.

3.2.1 Catalyst characterization

3.2.1.1 XRD

X-ray powder diffraction (XRD) patterns was performed by a Bruker D8 Advance Diffractometer at 40 kv, 40 mA with Cu-Kα radiation (λ =1.54056 nm). Data were collected over a 2θ range from 20 to 80° with a step size of 0.02 at a scanning speed of 0.5/min.

3.2.1.2 FTIR

Fourier transform infrared (FTIR) spectrum was performed on a Nicolet 6700 FT-IR spectrometer over a scanning range from 400 to 4000 cm^{-1}.

3.2.1.3 Hammet titration method

Basic strength of catalysts was evaluated by a Hammett indicator method. Base strength of the catalyst (pKa) was evaluated by using Hammett indicators. For this evaluation about 300 mg of the sample was shaken with 1 mL of a solution of Hammett indicators diluted in 10 mL methanol and left to equilibrate for 2 h. The basic strengths of base catalyst are reported as being stronger than the weakest indicator, the color will be changed. On the other hand, if it is weaker than the strongest indicator, there was no color change. The basicity (mmol/g) of solid base catalyst was evaluated by the method of Hammett indicator-benzene carboxylic acid (0.02 mol/L anhydrous ethanol solution) titration until the color changes back to its original color [51].

3.2.2 Transesterification activity

There are two types of reactors for catalytic activity of co-solvent addition test via transesterification of palm oil with methanol using ultrasound probe reactor (UP) and ultrasound-assisted reactor (US).

3.2.2.1 Ultrasound probe reactor (UP)

The catalytic activity via transesterification of palm oil with methanol was carried out in UP reactor (Fig. 13). Palm oil and co-solvent were heated at 60°C. Then, methanol was added in this UP reactor. In case using co-solvent, the mixture solution was maintained temperature at 60°C. CaO catalyst was added after methanol, co-solvent and palm oil were mixed together at 60°C. The operating condition was shown in Table 6. Samples were collected on time schedule. Sample was separated methanol, biodiesel product and glycerol by centrifugal machine before analysis of biodiesel yield with a gas chromatography (GC).

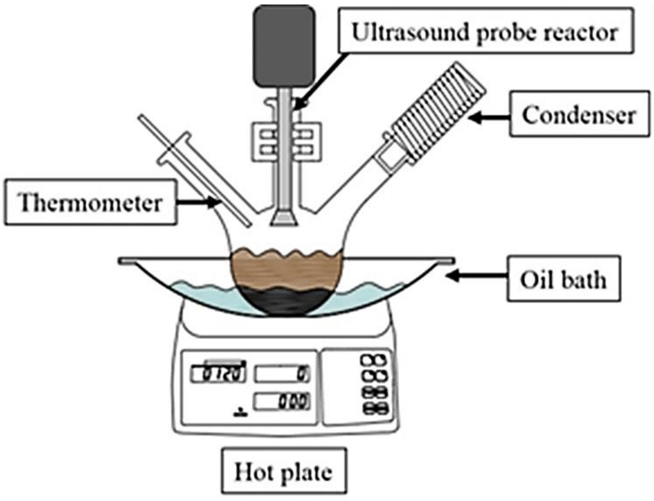


Fig. 13 Transesterification in an ultrasound probe reactor (UP)

The ultrasound probe reactor (UP) as shown in Fig. 13 consisting of (1) generator (2) transducer 20 kHz and (3) fan was applied as a batch reactor.

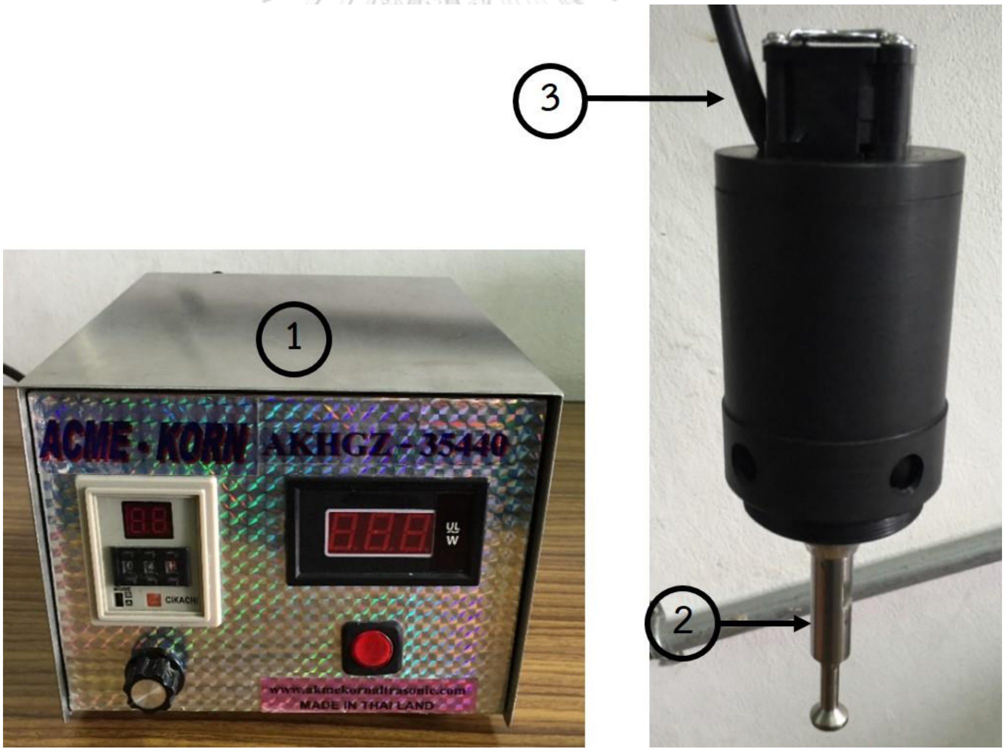


Fig. 14 Apparatus of ultrasound probe reactor (UP)

Table 6 Operating condition for ultrasound probe reactor experiments

Parameter	Condition
Feedstocks	Palm oil
Reaction temperature	60^{o}C
Methanol to oil molar ratio	9:1
Methanol to co-solvent volume ratio	1:0.1,1:0.25, 1:0.5, and 1:1
Catalyst loading	10 wt% based on oil
Catalyst	CaO
Co-solvent	Acetone, THF and methyl myristate

3.2.2.2 Ultrasound-assisted reactor (US).

Ultrasound-assisted reactor (US) was used to test the catalytic activity via transesterification. US reactor was divided to three main equipment; reactant tank, generator and reactor. US reactor schematic diagram was shown in Fig. 14. Volume of reactant tank was 6 L to keep reactant feeding. Reactor was in the rectangular shape (2.5×2.5×30 cm^3) and has a horizontal axial for spin and packed catalyst. Transducers were installed at the wall of outside reactor and two different frequency 20 and 50 kHz. CaO catalyst was packed with three catalyst baskets at a horizontal axial. Sample was collected through a sampling valve. Then, sample was separated methanol, solid catalyst, biodiesel production and glycerol by centrifugal machine. Biodiesel yield was analyzed by a gas chromatography (GC) [7]. The operating condition is shown in Table 7. Methanol to co-solvent molar ratio was chosen from the results obtained from section 3.2.2.1.

Table 7 Operating condition for ultrasound-assisted reactor experimental

Parameter	Condition
Feedstocks	Palm oil
Reaction temperature	60°C
Methanol to oil molar ratio	9:1
Catalyst loading	5 wt% based on oil
Catalyst type	CaO
Feed flow rate	35 to 100 mL/min
Frequency	20, 50 and 20&50 kHz
Power	400 and 800 W

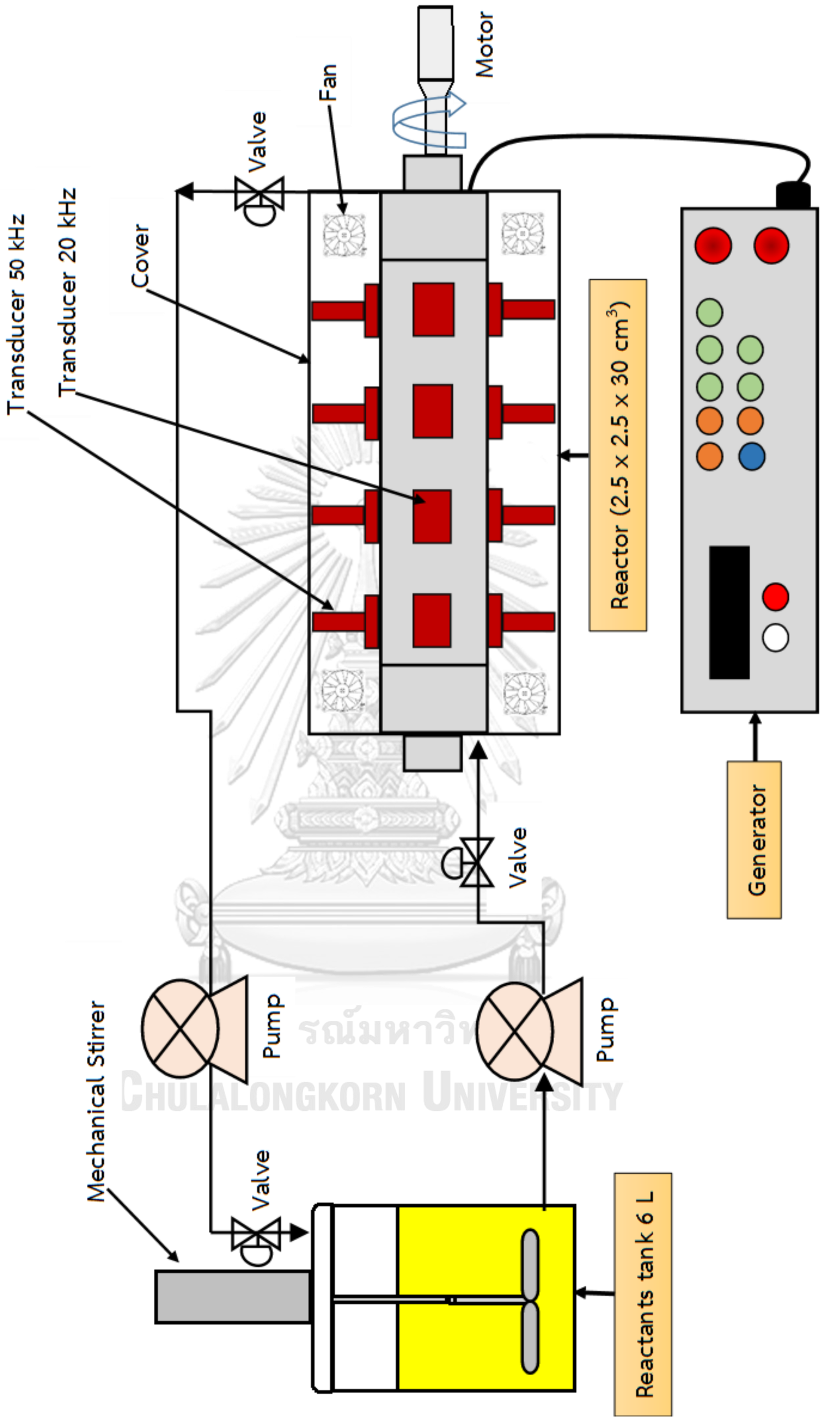


Fig. 15 US reactor schematic diagram.

3.3.3 Analysis of biodiesel yield

The standard used to determine biodiesel yield analysis is EN14103 standard. Methyl heptadecanoate was used an internal standard. Biodiesel yield was determined by Shimadzu GC-2010 Plus with capillary column, DB-WAX (0.25 mm × 30 m) and flame ionization detector (FID). The initial oven temperature was started at 150 ^{o}C for 5 min, heat up to 190 ^{o}C for 5 min and the final temperature in column oven was 220 ^{o}C for 5 min using ramp rate is 10 ^{o}C/min. The injection temperature was 250 ^{o}C. Carrier and make up gas were helium (He) and nitrogen (N_2). Biodiesel yield calculation was followed the equation (1) [7].

$$\text{Biodiesel yield} * \ (\%) \ = \frac{(\sum A)-A_{IS}}{A_{IS}} \times \frac{C_{IS} \times V_{IS}}{m_s} \times 100\% \qquad (1)$$

where

Σ A Total area peak,

A_{IS} Area of methyl heptadecanoate (Internal standard),

C_{IS} Concentration of methyl heptadecanoate (mg/mL),

V_{IS} Volume of methyl heptadecanoate (mL),

M_s Mass of biodiesel sample (mg).

*Remark The methyl myristate peak area was subtracted from total area peak (Σ A) for using methyl myristate as a co-solvent.

3.3.4 Calculation of yield efficiency

The yield efficiency is defined in the equation (2) [52].

$$\text{Yield efficiency} = \frac{\text{Amount of product produced (g)}}{\text{Power supplied} \left(\frac{\text{J}}{\text{s}}\right) \text{x reaction time(s)}} \qquad (2)$$

3.3.5 Calculation of residence time and number of passes in US reactor

Because the flow US reactor was operated in the circulation system, the definition of residence time and number of passes are calculated [69] as follows:

$$\text{Residence time(s)} = \frac{\text{Volume of sonication reactor}}{\text{Flow rate}} \qquad (3)$$

$$\text{Number of passes} = \frac{\text{Flow rate}}{\text{Total processing volume}} \times \text{Time} \qquad (4)$$

Chapter 4

Results and Discussion

4.1 Characterization of the catalysts

CaO catalyst was calcined at 900 °C for 5 h with a heating rate of 10 °C/min before using as a heterogeneous catalyst for transesterification of palm oil. XRD technique was used to confirm the formation of CaO phase and the XRD results are shown in Fig. 16. The XRD pattern of fresh catalyst indicated that CaO was a main composition of catalyst. CaO peaks were demonstrated at 2θ of 32.3°, 37.4°, 53.8°, 64° and 67° according to the standard JCPDS file (JCPDS82-1691) for CaO. A small $CaCO_3$ peaks were observed at 2θ of 34°, 47.2° and 50.8°. CaO and $CaCO_3$ peaks were corresponding to the previous work [53]. Crystallite size of fresh catalyst was found to be 4.3 nm that was corresponding to the other work [54].

Hammett indicators method for determining basicity and basic strength of fresh CaO catalyst was also investigated. It was found that the basicity of CaO catalyst was 0.067 mmol/g and the basic strength was $7.2 \leq pKa \leq 9.3$. This basic strength of this CaO catalyst was less than the previous work using CaO derived from waste egg shell [43]. This is might be due to the different source of CaO resulting in difference in the texture properties.

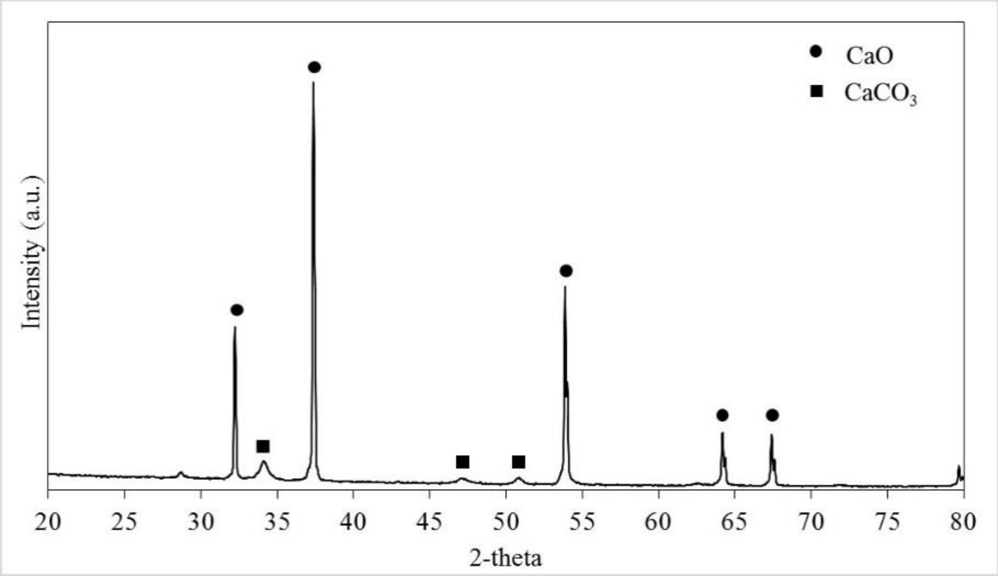


Fig. 16 Powder X-ray diffraction pattern of fresh CaO catalyst.

Table 8 The physical properties of co-solvent.

Co-solvent	Boiling point (°C)	Melting point (°C)	Viscosity 40 °C (mPa.s)	Density 15 °C (kg/m^3)	Relative Polarity to Water	Ref
Palm oil	562.8	27-29	37.92	925	-	[55]
Methanol	64.7	-98	0.449	791.3	0.762	[56]
Acetone (C_3H_6O)	56	-94.3	0.272	706	0.355	[48]
THF (C_4H_8O)	66	-108.4	0.403	845	0.207	[48]
Methyl myristate ($C_{15}H_{30}O_2$)	323	18	2.84	868.2	-	[57]

Table 8 presents the physical properties of co-solvent used in this research. Acetone and THF seem to be appropriate solvent for transesterification of palm oil and methanol because of their polar solvents properties providing the relatively polarity like the methanol [48]. Consequently, the rules “like dissolves like”, the interaction between methanol and co-solvent will be adequate for dissolution of each other [49]. Moreover, acetone and THF have low viscosity which is less likely being an obstacle of mass transfer. However, these two solvents require the separation process to purify biodiesel product. Therefore, the selection of methyl myristate as a co-solvent for transesterification should probably be a good choice regardless of its higher viscosity because this compound is FAME, a component of biodiesel product, which does not require additional separation from biodiesel. The next section will test their catalytic activities of CaO catalyzed transesterification using co-solvents.

4.2 Effect of co-solvent on FAME yield

Transesterification of palm oil was performed using the operation condition as shown in Table 6. Fig. 17 shows FAME yield of transesterification of palm oil using the different co-solvent types.

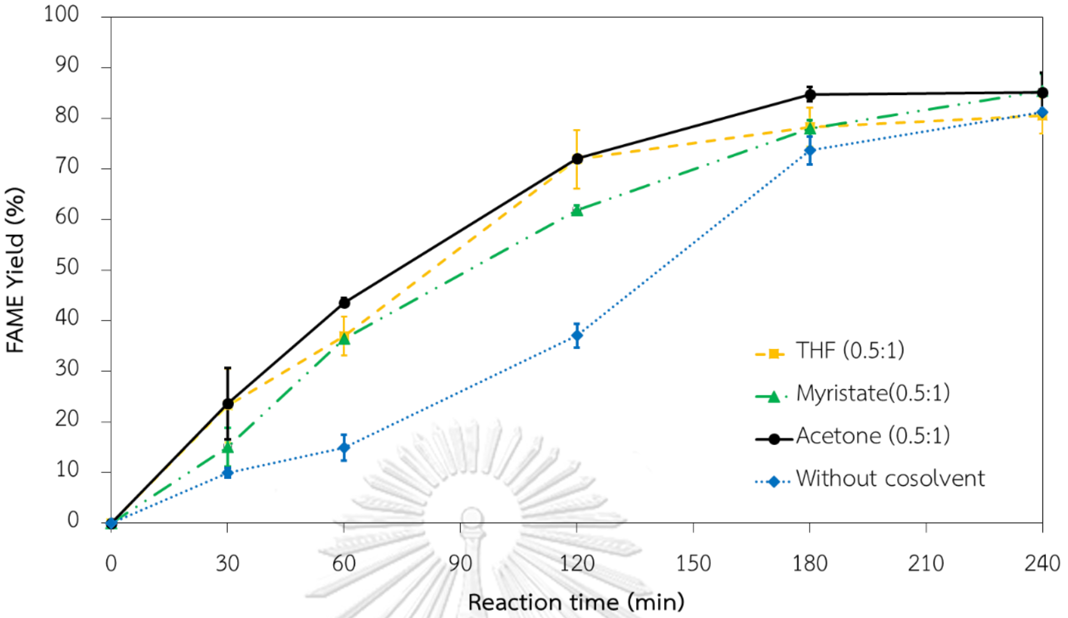


Fig. 17 FAME yield (%) obtained from CaO catalyzed transesterification of palm oil using the different types of co-solvent UP reactor.

Using co-solvent did not only accelerate the initial transesterification rate but also increase the FAME yield as compared to the blank test (without co-solvent). From Fig. 17, the blank test showed the lowest FAME yield. It might be because the heterogeneous calcium oxide catalyst has obstacle between active site of catalyst and the reactants indicated by the induction period [35]. The highest FAME yield at 240 min was obtained from the addition of methyl myristate (85.35%) as well as acetone (85.19%) respectively. The induction period of the CaO catalyzed transesterification using co-solvent was reduced because the addition of co-solvent can increase the solubility of immiscible of methanol and palm oil to overcome mass transfer limitation and the new phase of CaO catalyst was also possibly generated during the catalytic process [41]. Acetone and THF are polar solvents which were found to reduce induction period and increase FAME yield as similar to the previous works [2, 49]. It means that using these polar solvents can enhance mass transfer between the reactants with the CaO active sites. Methyl myristate, on the other hand, can dissolve in palm oil which is required more lagging time to react with methanol (Polar chemical) to produce FAME via base catalyzed transesterification pathway. However, the FAME yield profile obtained from polar co-solvents (acetone and THF) tended to reach maximum at about 85% for the longer reaction time. While the FAME yield profile of methyl myristate was more likely to further increase. Roschat et al. [2] found that the increasing polarity of co-solvents might conduct to decrease biodiesel yield because the high polar co-solvents can dissolve well in methanol but not in palm oil. The enhancement of miscibility of polar solvent with the methanol might be leading to dilution of methanol which reduces the biodiesel yield. Chiang et al. [58] found that the relative proton affinity between the acetones and methanol sub-clusters is not a sufficient factor to be a preferred reaction channels as well as protonation of methanol. Therefore, the amount of methanol was consumed during the reaction resulting in lower methanol to oil molar ratio in case for acetone as well as THF compared to non-polar solvent (Methyl myristate). This is leading to obtaining the highest FAME yield at the longer reaction time for the addition of methyl myristate.

XRD, FTIR, basic strength and basicity characterization of fresh and used CaO catalyst after transesterification were also investigated as presented in Figs. 18-19 and Table 9. The used catalyst was washed with methanol until the resulting solution was clear. Then, the settle used CaO catalyst was dried at 110 °C for overnight before using for characterization.

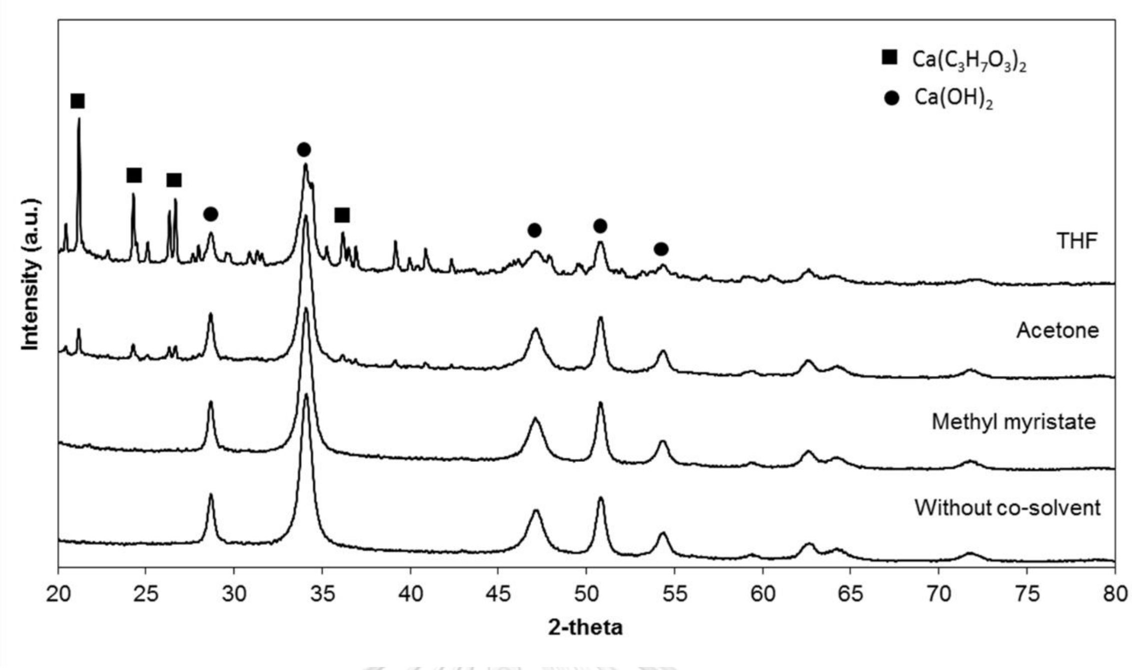


Fig. 18 Powder X-ray diffraction pattern of catalyst after reaction.

Fig. 18 shows the XRD pattern of used CaO catalyst after transesterification of palm oil. All samples of used CaO catalyst showed calcium hydroxide ($Ca(OH)_2$) peaks at 2θ of 28°, 34.1°, 47.1°, 50.8° and 54° following JCPDS (N 01-073-5492) file font [7, 59]. Calcium diglyceroxide ($Ca(C_3H_7O_3)_2$) or CaDG was indicated for the used CaO catalyst derived from the addition of THF and acetone. Intense peaks were found at 2θ of 21.2°, 24.3° and 26.6° [53, 60]. This indicated that CaDG was formed by the bonding of CaO catalyst and by-product (Glycerol). Nevertheless, no CaDG phase and the other peaks were observed from the used CaO catalyst was obtained from the addition of methyl myristate and without co-solvent. However, the FAME yield at 240 min using methyl myristate was highest compared to the other co-solvents. Lukić et al. [61] reported that the CaDG has affected mostly on the initial period of reaction because CaDG acts an emulsifier that enhances solubility of the immiscible liquid to accelerate the methanolysis of sunflower oil rate.

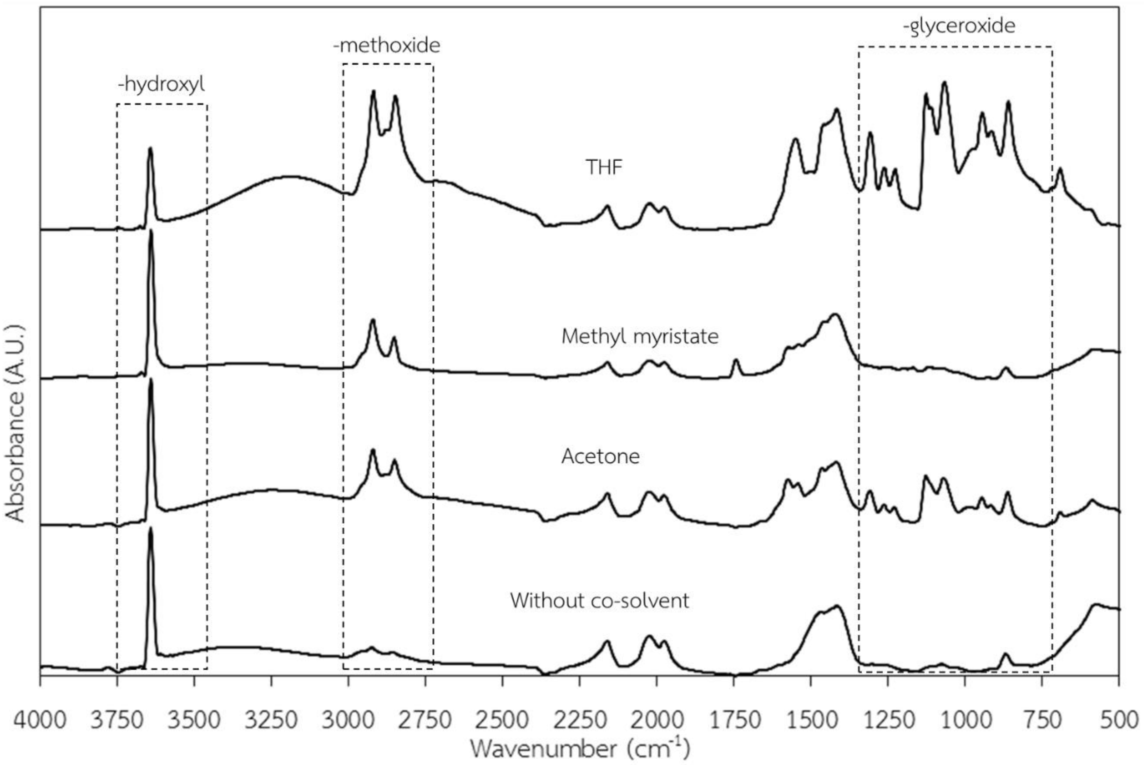


Fig. 19 FTIR spectra of catalyst after reaction.

FTIR spectra of used CaO catalyst for transesterification of palm oil is shown in Fig. 19. FTIR of used catalyst with addition of THF and acetone were observed peaks at 3600, 2800-3000 and 900-1500 cm^{-1} which indicated calcium methoxide and glyceroxide species, respectively. However, there was no glyceroxide peak for the used CaO catalyst in absence of co-solvent and addition of methyl myristate. Puna et al. [62] reported that the main IR peak of CaDG species presented in the range 1200 -1350 cm^{-1}. Kouzu et al. [60] also proposed that the formation of CaDG also likely acted as the solid base catalyst that can accelerate the transesterification rate as corresponding to FAME yield profile (Fig.17). Using acetone and THF as co-solvents can increase the initial transesterification rate than that of methyl myristate. This is because of the synergistic effect that the addition of acetone and THF not only increase the solubility of oil and methanol but also generate the new phase (CaDG) to provide the higher FAME yield in a short reaction time. However, when the methanol was consumed during the reaction, the dilution of methanol with acetone and THF was more pronounced resulting in limited reaction rate as illustrated in the lower equilibrium compared to using methyl myristate as a co-solvent.

Table 9 Basic strength, basicity, BET surface area and crystallite size of fresh CaO catalyst and used CaO catalyst

Co-solvent Type	Basic strength	Basicity (mmol/g)	BET surface area (m^2/g)	Crystallite size (nm)
Fresh catalyst	7.2 ≤ pKa ≤ 9.3	0.067	5.77	4.3
Used catalyst				
Non co-solvent	7.2 ≤ pKa ≤ 9.3	0.02	11.73	10.1
THF	7.2 ≤ pKa ≤ 9.3	0.09	-	11.1
Acetone	7.2 ≤ pKa ≤ 9.3	0.13	7.52	9.6
Methyl myristate	7.2 ≤ pKa ≤ 9.3	0.04	12.53	10.2

Table 9 reports the basic strength, basicity, crystallite size and specific surface area of fresh CaO and used CaO catalysts obtained from the addition of various co-solvents in transesterification of palm oil. It was found that the basicity of used CaO catalyst with THF and acetone were higher than that of fresh CaO catalyst due to the possibility of formation of new active sites as CaDG with corresponding to XRD and FTIR results. The basicity of CaO catalyst using methyl myristate as a co-solvent was lower than that of CaO fresh catalyst and the other co-solvents. This is probably because of the non-polar nature of methyl myristate resulting in increased amount of reaction mixture deposited on the active site (Basic site) [57]. However, the basicity of used CaO catalyst with addition of methyl myristate as a co-solvent was higher than that of used CaO catalyst in absence of co-solvent. This should be because the addition of methyl myristate can be increase the solubility of reaction mixture compared to the reaction mixture without co-solvent [54, 57]. Moreover, the specific surface area and crystallite size of used catalysts were higher than that of fresh catalyst for all reaction condition (with and without co-solvent). This might be because the adsorption of organic matter could generate the other pores resulting in increasing in surface area and crystallite size [63]. Reyero et al. [53] reported that surface area of CaDG is higher than that of CaO which is corresponding to this work.

As already mentioned that the advantage of using methyl myristate as a co-solvent is the similar chemical structure as well as FAME which does not require the co-solvent separation step. The selection constrain of appropriate co-solvent does not only provide high FAME yield but also concern in the separation step. However, using product as a co-solvent can eliminate the separation step of co-solvent. As can be seen from Fig. 17, the addition of methyl myristate provided the highest FAME yield at 240 min. Methyl myristate is one of biodiesel composition and hence there was no requirement of co-solvent separation step. Therefore, methyl myristate was selected to further investigate the effect of amount co-solvent on the FAME yield as illustrated in Fig. 20.

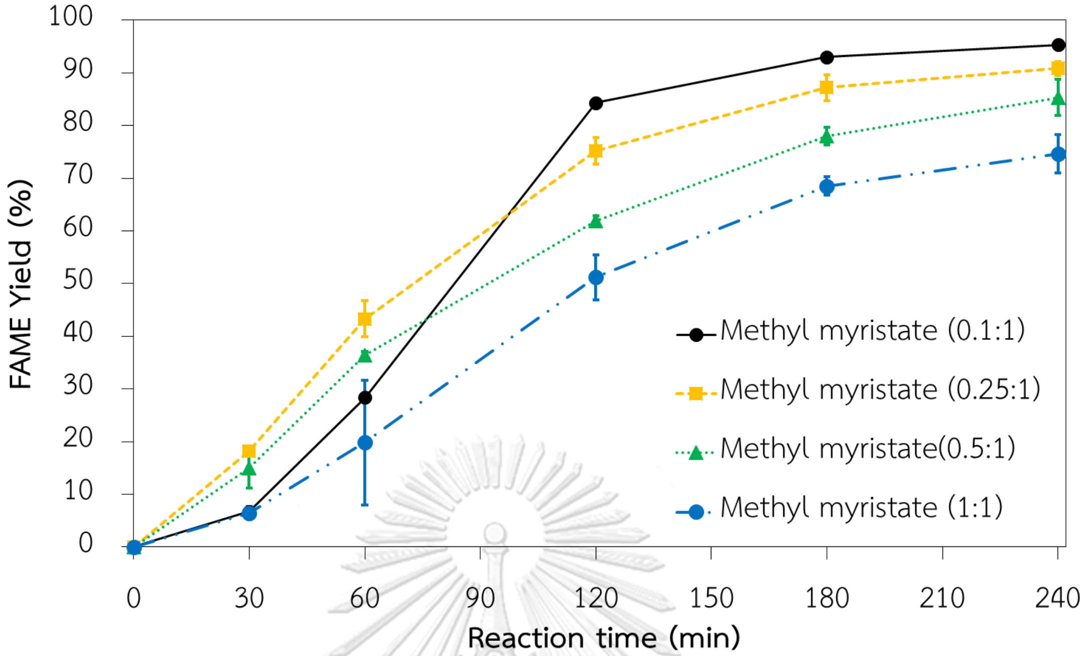


Fig. 20 Effect of methyl myristate to methanol ratio for transesterification of palm oil and methanol in UP reactor.

Fig. 20 shows the effect of increasing amount of methyl myristate as a co-solvent for transesterification of palm oil and methanol in the UP reactor. It was found to reduce FAME yield because the increase amount of methyl myristate can decrease the concentration of palm oil as a limiting reactant leading to decreased transesterification rate as well as FAME yield [34]. The highest FAME yield of 95 % was obtained from the addition of methyl myristate to methanol ratio of 0.1:1. Nevertheless, the induction period was also observed for this condition. The objective of using co-solvent is to increase the FAME yield in a short reaction time. Therefore, to eliminate the induction period, the mixture of co-solvent between methyl myristate and acetone was required because using acetone as co-solvent can increase FAME yield at initial period.

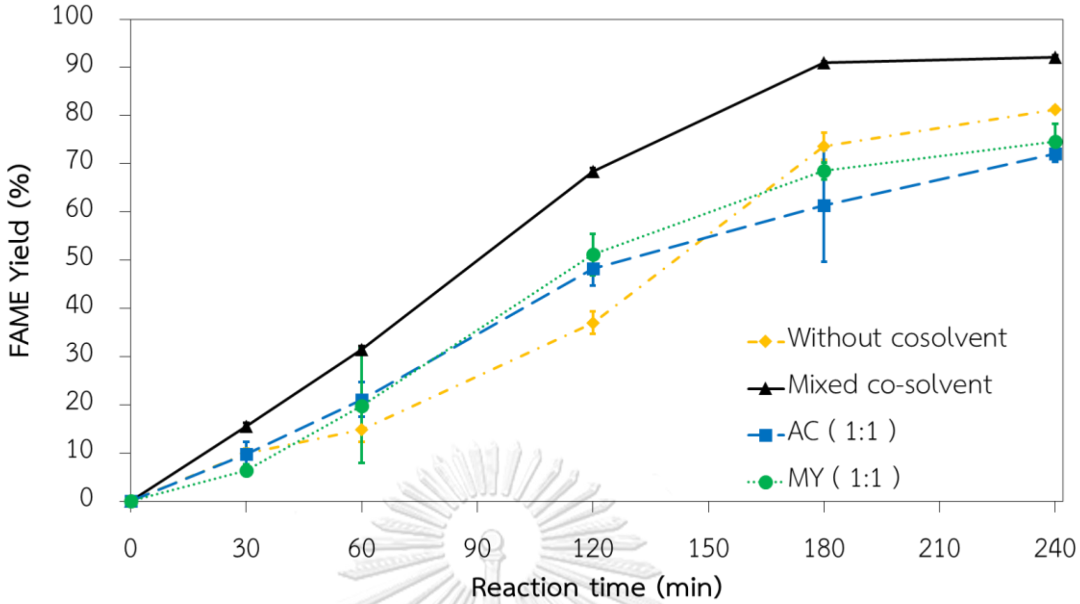


Fig. 21 FAME yield (%) obtained from CaO catalyzed transesterification of palm oil using methyl myristate (MY) acetone (AC) and its mixture in UP reactor.

Fig. 21 shows the comparison of FAME yield obtained from acetone, methyl myristate and the mixture of acetone (AC) and methyl myristate (MY) for transesterification of palm oil and methanol at 65 °C. The ratio of co-solvent addition to methanol was fixed to 1 to 1 by volume ratio.

Using acetone to methyl myristate to methanol volume ratio of 0.25:0.75:1 provided the highest FAME yield of 92.14% at 180 min because the mixture of acetone and methyl myristate gave the synergistic effect for CaO catalyzed transesterification of palm oil in an ultrasound assisted reactor in terms of increasing active site and enhancing the solubility of reaction mixture. Therefore, using the acetone-methyl myristate mixture as a co-solvent was further used to enhance the FAME yield via CaO catalyzed transesterification of palm oil in the flow US reactor. The effect of operating parameter was also investigated for the next section.

4.3 Effect of ultrasound operating parameter on FAME yield

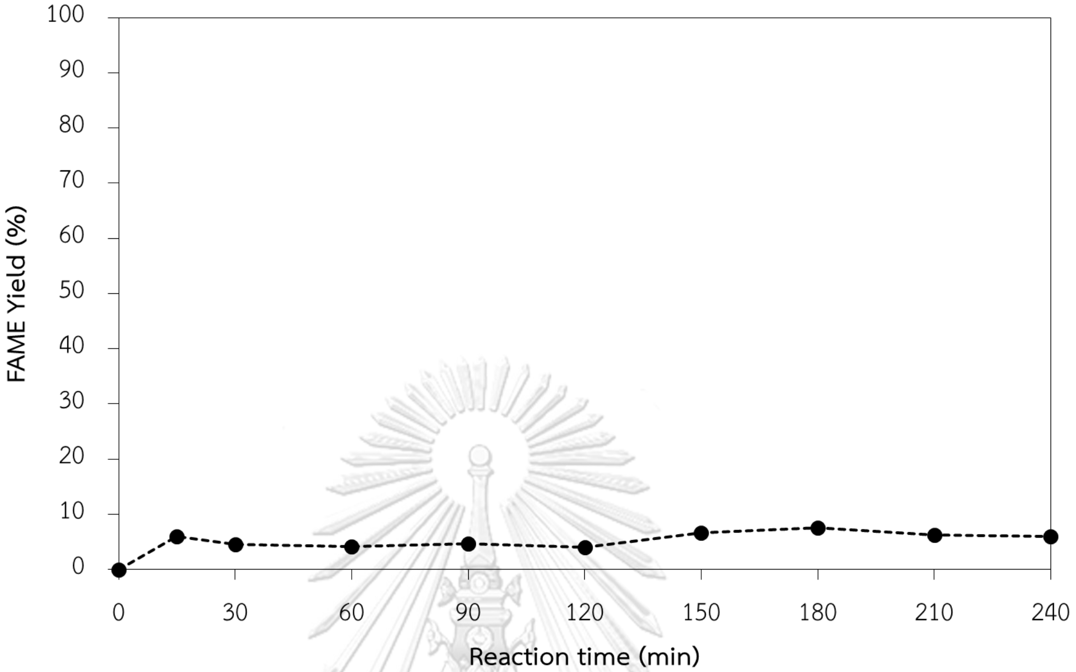


Fig. 22 FAME yield (%) obtained for transesterification of palm oil and methanol using the mixture co-solvents in US with total feed flow rate of 55 mL/min.

Fig. 22 shows FAME yield obtained from transesterification of palm oil and methanol using the mixture co-solvents with total feed flow rate of 55 mL/min in a continuous system in US. FAME yield was very low because heterogeneous catalyst has more mass transfer resistance than that of homogeneous catalyst. The residence time of using CaO catalyzed transesterification with the mixed co-solvent was only 3.4 min which was not enough to activate the reaction. Hashemzadeh and Sadrameli [13] also found that the optimum residence time of 27.9 min for the continuous biodiesel production from linseed oil using CaO in a packed bed reactor in the presence of DEE as a co-solvent. This continuous US system could not be suitably used to produce biodiesel via transesterification using CaO catalyst. Therefore, the circulation system operation was further used to determine the optimum operating condition for CaO catalyzed transesterification of palm oil in presence of the mixed co-solvent in US reactor.

Transesterification of palm oil was performed using the operation condition as shown in Table 7. Only 5 wt% of CaO based on oil was used because of the limit of catalyst basket in US reactor. The different ratio of co-solvent to methanol was applied based on the maximum FAME yield obtained from the previous section. For mixed co-solvent, the ratio of acetone to methyl myristate to methanol ratio was selected to 0.25:0.75:1. While using acetone as a co-solvent, the ratio of acetone to methanol was 0.1:1. The catalytic activity of transesterification was performed using circulated operation in the US reactor.

Fig. 23 illustrates FAME yield (%) of co-solvent (Acetone and mixed co-solvent) and without co-solvent in the circulated US reactor. The mixed co-solvent can accelerate transesterification and eliminate induction period as well as using acetone. Using mixed co-solvent and acetone gave FAME yield 91.75 and 90.16 % at 240 min, respectively while the FAME yield was only 80.75% for non co-solvent system.

It was found that the similar FAME yields at 240 min were obtained for using mixed co-solvent in the circulated US reactor as well as the UP reactor. The induction period was also reduced with the presence of co-solvent.

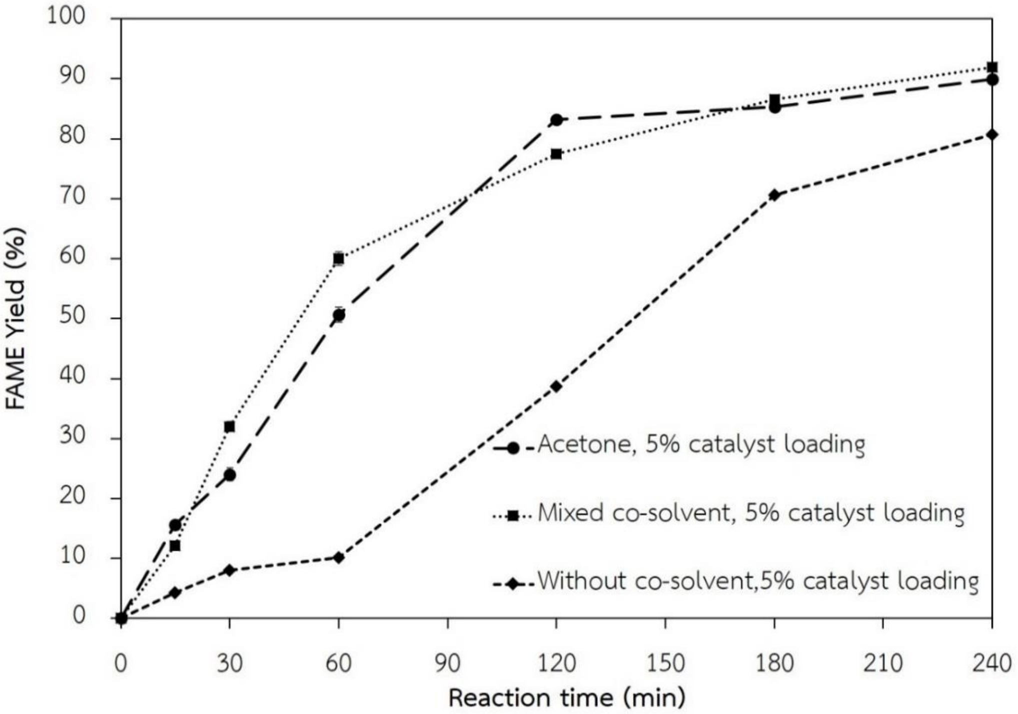


Fig. 23 FAME yield obtained for different of co-solvents and without co-solvent in a circulated US reactor using feed flow rate of 55 mL/min and ultrasound power of 800W.

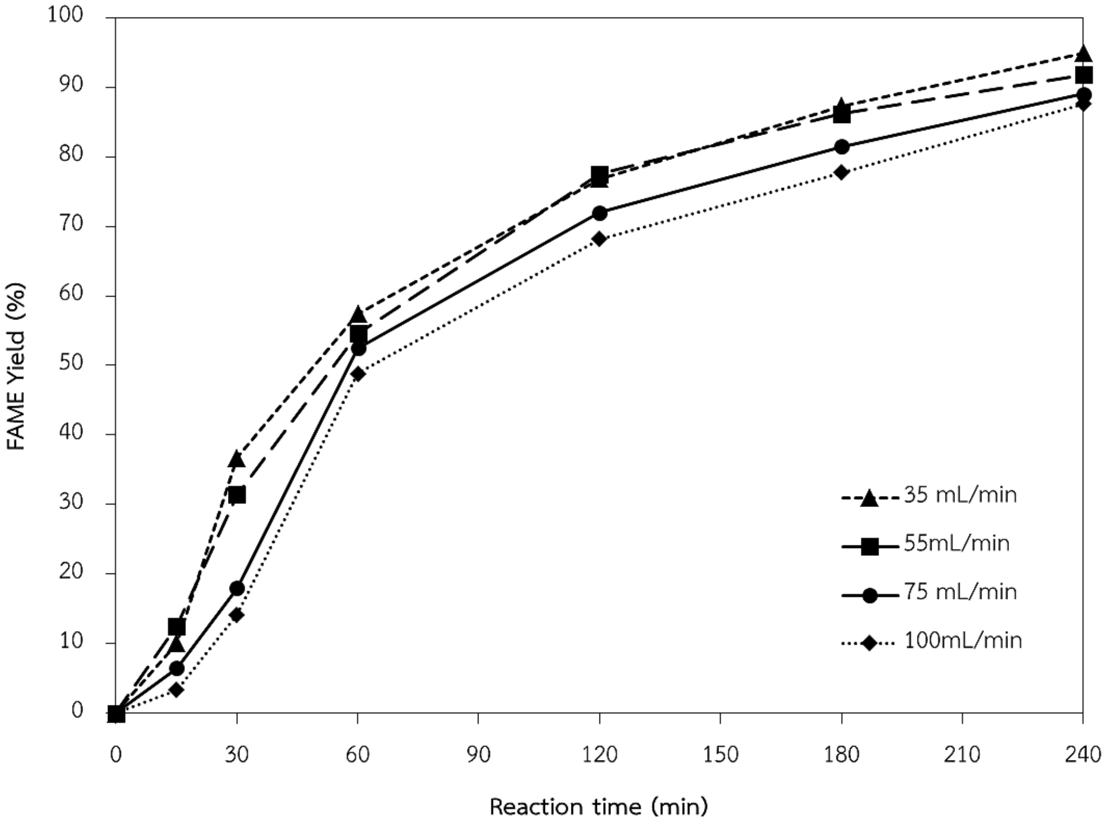


Fig. 24 Effect of flow rate on FAME yield (%) in a circulated US reactor.

Fig. 24 illustrates the effect of flow rate on FAME yield (%) in the circulated US. The flow rates were varied from 35 to 100 mL/min. The results showed that FAME yield decreased from 94.89 to 87.5 % with increasing of flow rates from 35 to 100 mL/min. The highest FAME yield was 94.89 % using total flow rate of 35 mL/min.

The effect of total flow rate is related to residence time and number of circulated US reactor. The residence time for flow rate 35, 55, 75 and 100 mL/min were 5.4, 3.4, 2.5 and 1.9 min, respectively. At the same processing time, the number of circulations were 16, 26, 36 and 48, respectively which was calculated based on the work of Bargole et al. [69]. FAME yield was decreased when the total flow rate was increased because the residence time of the circulated US reactor was decreased. FAME yield obtained from flow rate at 35 and 55 mL/min were similar. While increasing total flow rate to 75 and 100 mL/min, the obtained FAME yields were lower than 90 %. However, this US reactor was operated in the circulation system (not continuous system), the effect of total flow rate and number of circulated might not be dominated. Rahimi et al. [64] investigated the biodiesel production under temperature of 60°C, KOH concentration of 1.2 wt% and molar ratio of methanol to oil of 9 to 1. The results showed that biodiesel yield increased from 82.7 to 97.6% when the residence time was increased from 20 to 180 s. The biodiesel yield was extremely increased with increasing residence time from 20 to 60 s and slightly increased after that because the transesterification of oil was almost complete. Moreover, Bargole et al. [65] synthesized the maximum biodiesel yield of 92% using a novel recirculating flow reactor with oil to alcohol molar ratio of 1:6 and 1% NaOH as catalyst. They found that using the similar processing time, the lower flow rate provided the longer residence time, giving rise in the higher biodiesel yield since the sufficient acoustic energy was transferred to reaction mixture for the completion transesterification resulting in higher biodiesel yield. The selected condition should be used the higher feed flow rate to provide high FAME yield and high production rate. Therefore, at 55 mL/min of total flow rate was used for biodiesel production in this circulated US reactor.

Table 10 Operating frequency patterns and FAME yield at 240 min using a circulated ultrasound-assisted reactor.

Pattern	**The position of 20 kHz transducer**				**The position of 50 kHz transducer**				**FAME yield (%)**
	1	2	3	4	1	2	3	4	
1	-	-	-	-	-	-	-	-	14.1
2	✓	✓	✓	✓	-	-	-	-	59.5
3	-	-	-	-	✓	✓	✓	✓	65.3
4	-	✓	-	✓	✓	-	✓	-	62.7

The effect of ultrasound frequency on FAME yield via CaO catalyzed transesterification in presence with co-solvent was also investigated. The maximum ultrasound power was 800 W using total of 16 transducers. The position of transducer was fixed therefore, the maximum power of US reactor was only 400 W to investigate the ultrasound frequency. The position of operating frequency can be divided 4 pattern; Blank test (Pattern 1), 8 x 50 kHz (Pattern 2), 8 x 20 kHz (Pattern 3) and 4 x 50 kHz combined with 4 x 20 kHz (Pattern 4). The results are shown in Table 10 and Fig. 25.

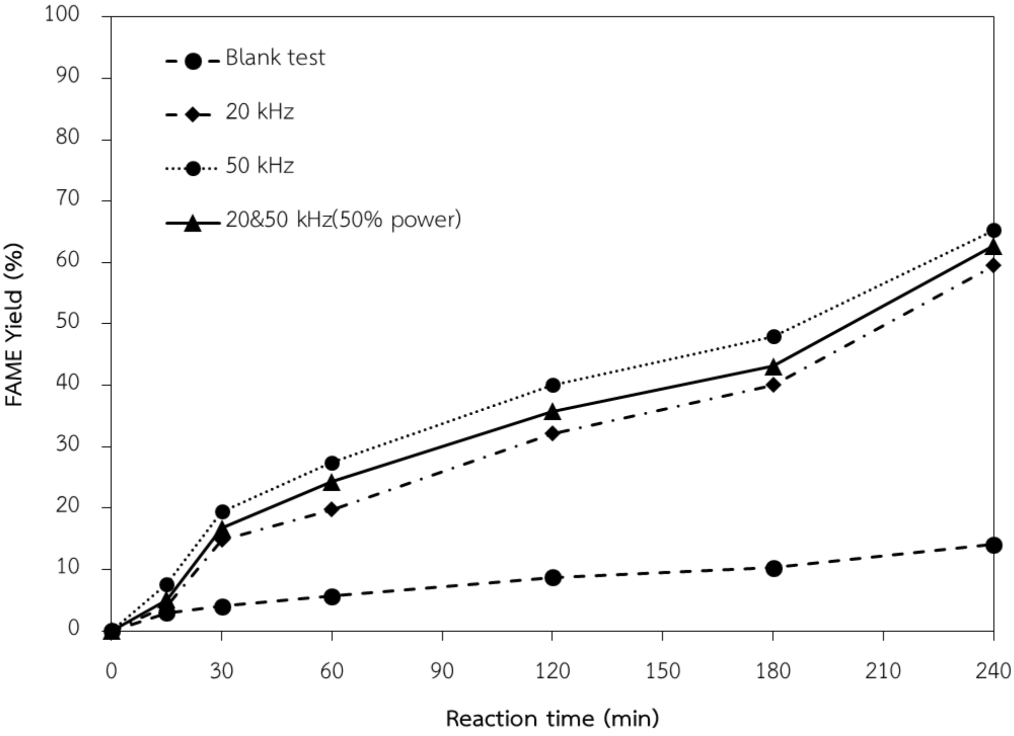


Fig. 25 Effect of ultrasound frequency on FAME yield (%) for CaO catalyzed transesterification using co-solvent in a circulated US reactor.

From first pattern, FAME yield was very low and observed longer induction period because of no ultrasound assisted the reaction. The mass transfer was limited from three phase system (solid catalyst, palm oil and methanol). However, FAME yield was increased for second to fourth pattern because using ultrasound irradiation assisted reactor can improve the mixing rate by cavitation phenomena and elimination mass transfer limitation [7]. The highest FAME yield was obtained from high ultrasound frequency because this condition generates the smaller bubble than that of the lower ultrasound frequency. A small bubble has higher a surface area per volume resulting in increased interfacial contact area of palm oil, methanol and active site of CaO [8]. On the other hand, using the low frequency transducer creates the lower distribution of cavitation per unit volume as compared with high frequency transducer resulting in lower FAME yield. This result was similar to the previous work using CaO catalyzed transesterification of palm oil in a circulated US without co-solvent addition [8].

The effect of ultrasound power was also investigated. The operating power was varied at 0, 50 and 100 % of maximum power. The reactor volume was 187.5 mL and the maximum power was 800 W. The effect of ultrasound power on FAME yield was shown in Fig. 26. There was a blank test for 0% of maximum power (In absence of ultrasound irradiation). It was found that the FAME yield was only 14 % at 240 min. For 50 % of maximum power (400 W) with dual frequency of 20 and 50 kHz, the FAME yield was increased due to the presence of ultrasound irradiation providing the acoustic movement and cavitation phenomena. The acoustic movement provides a mixing of the reaction mixture. However, the cavitation obtained from low power (Amplitude) tends to generate a stable cavitation that does not violent collapse resulting to lower degree of mixing [8]. The induction period was also observed for using 50 % of maximum power. This indicated that the ultrasound irradiation 50 % of maximum power was not enough to enhance the mixing degree of the reaction mixture. The expression of ultrasound power input to system must be evaluated in term of power dissipation per unit volume as shown in equation (5).

$$\text{Power dissipation per unit volume} = \frac{\text{Ultrasound power (W)}}{\text{Reaction mixture volume in the reactor (mL)}} \qquad (5)$$

Power dissipation per unit volume for 0, 50 and 100 % of power were 0, 2.13 and 4.27 W/mL, respectively. It has also been observed that using CaDG as a heterogeneous catalyst under the power dissipation per unit volume obtained from the ultrasound irradiation for biodiesel production from the waste cooking oil was above 3.16 W/mL to provide the significantly greater biodiesel yield [46]. Therefore, the power dissipations derived from 0 and 50 % of maximum power were not enough to provide the well mixing in the system leading to lower FAME yield.

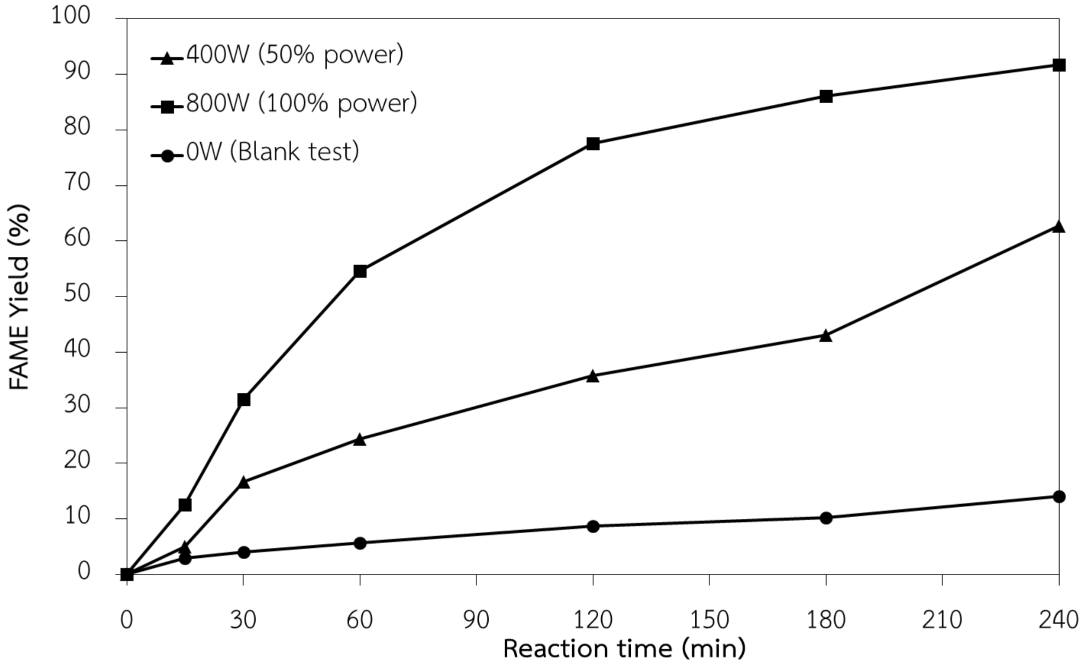


Fig. 26 Effect of ultrasound power on FAME yield (%) in a circulated US reactor.

Using 100 % of maximum power (800 W), FAME yield was significantly increased more than that of 50 % of maximum power because the higher power input related to the amplitude of ultrasound and the maximum power dissipation which can generate the higher number of cavitation with higher degree of bubbles collapse. Moreover, the collapse of the cavitation bubble provides the higher micro-mixing and jet velocity at the boundary phase between the palm oil and methanol phases. This is leading to the formation of finer emulsion which provides a higher mass-transfer coefficient, and thus higher yield [45]. Gupta et al. [46] reported that the effect of ultrasound power for biodiesel production. They observed that the increase of ultrasound power from 60 to 120 W, biodiesel yield was increased from 76.2 to 93.5 %, respectively. Therefore, increasing of ultrasound power can enhance the cavitation effect resulting in the sufficient mixing and finer emulsion of two immiscible reaction mixture.

4.4 FAME yield efficiency calculation

FAME yield efficiency was evaluated to compare the performance of different co-solvent types in UP and a circulated US reactor. The yield efficiency was calculated based on 80% of FAME yield as shown in Fig. 4.27 and Fig. 4.28, respectively.

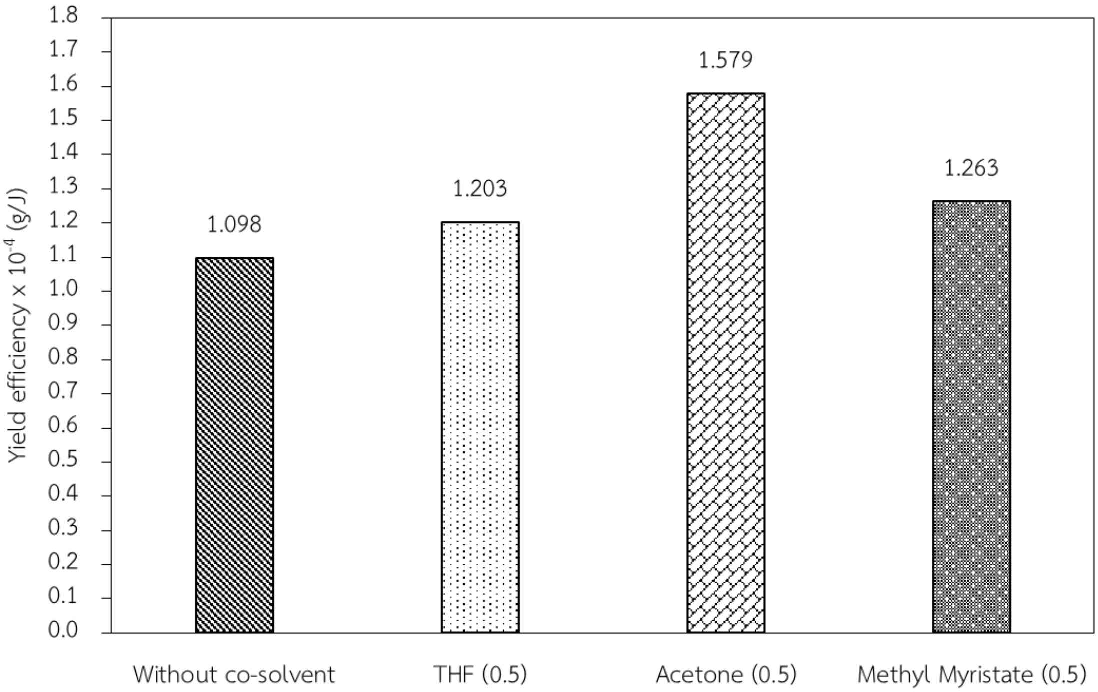


Fig. 27 Effect of different co-solvent in UP reactor on yield efficiency based on 80% of FAME yield.

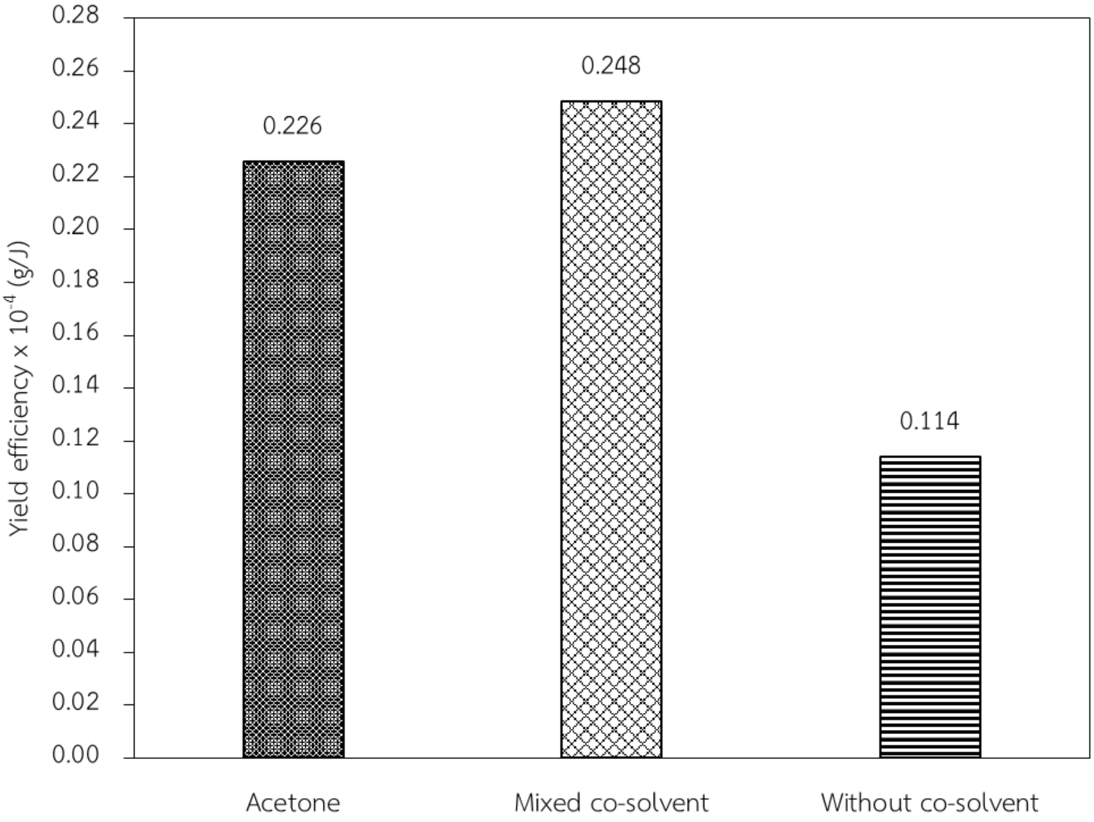


Fig. 28 Effect of different co-solvent in circulation system in a circulated US reactor based on 80 % of FAME yield.

Using co-solvent can increase the yield efficiency compared to that of reaction mixture without co-solvent. Acetone and methyl myristate gave rising in the yield efficiency for 1.579 and 1.263 x10^{-4} g/J, respectively. This can be concluded that both co-solvents of acetone and methyl myristate can enhance the performance for the biodiesel production into ultrasound probe reactor. On the other hand, the lowest of yield efficiency to produce biodiesel was obtained in the absence of co-solvent. Laosuttiwong et al. [66] reported that the maximum yield efficiency for 20 kHz ultrasound probe reactor based on 80 % of biodiesel yield were 1.41 , 2.75 and 4.65 x10^{-4} g/J at 165, 500 and 1,000 mL, respectively. They concluded that using ultrasound probe reactor was slightly more favorable for heterogeneous (CaO) catalyzed transesterification for only the small reaction volume because of its cavitation intensity.

Therefore, the addition of acetone and methyl myristate as co-solvent can be reach 90% of FAME yield in the heterogeneous catalyst system. Moreover, Bargole et al. [65] reported that yield efficiency was 7.66 x 10^{-5}g/J which is obtained from the maximum 95 % yield of biodiesel using the ultrasound probe with frequency of 20 kHz, energy supplied 750 W and reaction time 40 min in batch reactor. Gole et al. [67] also reported that using ultrasound assisted reactor provided the higher yield efficiency than that of the conventional reflux heating. The value of yield efficiency for ultrasound assisted reactor and conventional reflux heating was 1.6 X 10^{-5} and 8 X 10^{-6} g/J respectively. In this work, addition co-solvent in this UP reactor for biodiesel production provided the higher yield efficiency compared to the previous work. This indicated that using co-solvent with ultrasound assisted reactor is an effective method to increase the miscible between methanol and oil interphase to provide a high formation of FAME yield in short time and yield efficiency was also increased.

Fig. 28 shows the effect of different co-solvent in circulation system in a circulated US reactor based on 80 % of FAME yield. The maximum of yield efficiency was 0.248x 10^{-4} g/J for mixed co-solvent into the circulated US reactor. From Fig. 29, the effect of operating parameters of the circulated US reactor on yield efficiency at 240 min including of: (a) Feed flow rate (b) Ultrasound power (c) Ultrasound frequency. The maximum of yield efficiency was 0.223 x10^{-4} g/J for flow rate 35 mL/min because the mixture was in the reactor longer than that of using high flow rate. While the yield efficiency was 0.307 x 10^{-4} g/J for frequency of 50 kHz due to the high frequency of ultrasound generates small bubble in the mixture which results in a larger increase the interfacial area available for mass transfer. Finally, the maximum of yield efficiency at 50% power was 0.295 x 10^{-4} g/J which is higher than using 100 % power because the obtained FAME yield from 50 and 100% were 62.71 and 91.75% while the power using was double resulting to lower yield efficiency for 100% power.

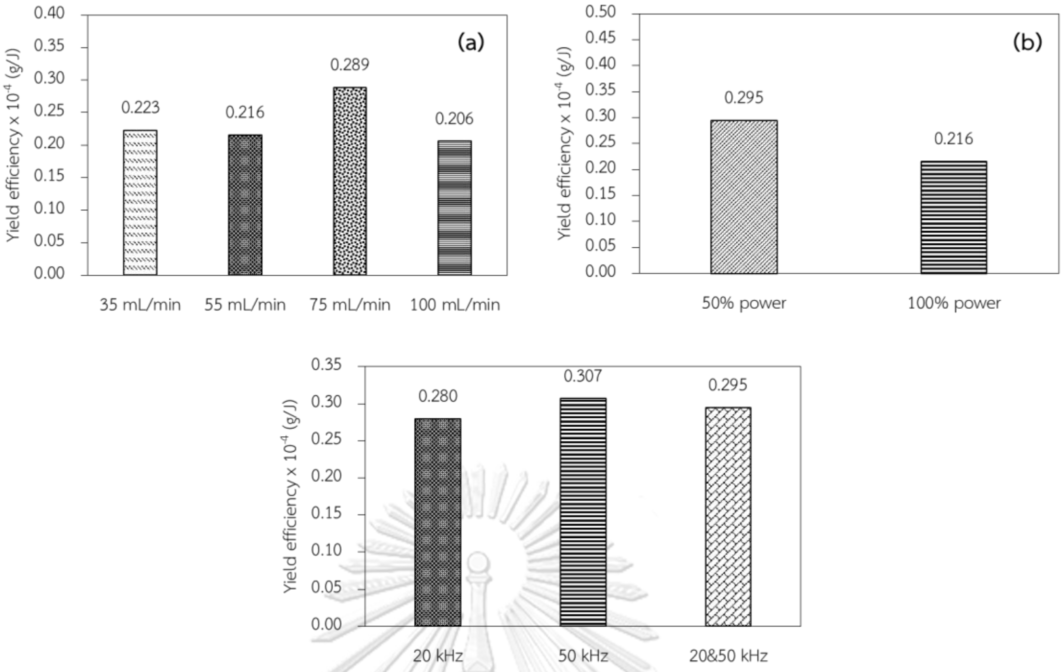


Fig. 29 Effect of parameter of ultrasound assisted reactor based on 80 % of FAME yield (a) Feed flow rate (b) Ultrasound power (c) Ultrasound frequency.

Chapter 5

Conclusions and recommendations

5.1 Conclusions

This work aims to improve the efficiency of biodiesel production from palm oil by addition of co-solvent in the ultrasound-assisted reactor. Transesterification was operated at 60°C, 1 atm, using methanol to oil molar ratio of 9:1. Addition of co-solvent tended to decrease the induction period and enhance the FAME yield via CaO catalyzed transesterification of palm oil because the co-solvent can increase solubility of mixture to overcome the mass transfer limitation. The addition of acetone and THF can generate CaDG from the adsorption of glycerol on CaO catalyst as a new active site as well as an emulsifier to enhance the solubility of mixture to provide the higher FAME yield in a short reaction time. While using the methyl myristate as a co-solvent can diminish the separation process of co-solvent. The highest FAME yield was obtained from the addition of methyl myristate but the small induction period was also observed. Moreover, acetone was selected to mix with methyl myristate as a co-solvent to eliminate the induction period and increase the FAME yield.

The different frequency of ultrasonic irradiation can affect the FAME yield obtained from CaO catalyzed transesterification of palm using co-solvent. High ultrasound frequency generates the smaller bubble than that of the lower ultrasound frequency. A small bubble has higher a surface area per volume resulting in increased interfacial contact area of palm oil, methanol and active site of CaO. Furthermore, ultrasound power has significant effect on biodiesel production. There were blank tests for 0 % of maximum power (In absence of ultrasound irradiation) and 50 % of maximum power (400 W) with dual frequency of 20 and 50 kHz, the induction period was also observed. On the other hand, using 100 % of maximum power can eliminate the induction period. This indicated that using ultrasound irradiation 50 % of maximum power as well as 2.13 W/mL of power dissipation was not enough to enhance the well mixing degree of the reaction mixture.

Therefore, using the higher ultrasound frequency and power tends to produce high FAME yield for heterogeneous catalytic system. This can be concluded that using ultrasound irradiation combined with the mixed co-solvent for CaO catalyzed transesterification can reduce the reaction time and produce high FAME yield as well as yield efficiency due to their advantage as not only elimination of the mass transfer limitation of two immiscible reactants and catalyst but also generation of new active site of CaDG.

5.2 Recommendation

1. Study reusability of catalyst in ultrasound assisted reactor for using co-solvent in transesterification of palm oil.

2. Using the other feedstocks for biodiesel production such as waste cooking oil.

3. Using biodiesel obtained from the esterification of PFAD as a co-solvent instead of methyl myristate to minimization cost of co-solvent

4. Study the feasibility of using co-solvent to improve transesterification efficiency in terms of economic and environmental analysis.

5. Study the effect of co-solvent on the deactivation of catalyst and the solubility in the reaction mixture.

Appendix A
Yield efficiency calculation

Yield efficiency calculation

The biodiesel yield efficiency is defined in Equation below

$$\text{Biodiesel yield efficiency} = \frac{\text{Amount of product produced (g)}}{\text{Power supplied } \left(\frac{\text{j}}{\text{s}}\right) \text{x reaction time (s)}}$$

For example, calculated yield efficiency of ultrasound probe reactor at 175 mL and FAME yield of 80%.

At first step, we might change g of oil to mol of oil. In this section 93.27 g of oil was used.

So, mol of oil = $\frac{93.27\text{ g}}{847\text{ g/mol}}$ = 0.110120 mol

Second step, one mol of oil converted to three mol of methyl ester.

So, mol of methyl ester = 0.110120 x 3 = 0.330361 mol

Third step, mol of methyl ester converted to g of methyl ester.

So, g of methyl ester = 0.330361 mol x 286.7 g/mol = 94.715 g of methyl ester

Fourth step, the selection 80% FAME yield at 240 min was converted to g of actual methyl ester.

So, g of actual methyl ester is equal to $\frac{94.715\text{g x } 80.00\ \%}{100\%} = 75.772\text{ g}$

From the selection of reaction time for 80% of FAME yield was about 230 min.

Thus,

$$\text{Biodiesel yield efficiency} = \frac{75.772\text{ (g)}}{50\ \left(\frac{\text{j}}{\text{s}}\right) \text{x } 230 \text{ x } 60 \text{ (s)}} = 1.098 \times 10^{-4}\text{ g/J}$$

Table A1. The summarization condition and FAME yield using to calculated yield efficiency.

Condition	FAME yield (%)	Reaction time (s)	Energy consumption (J/s)	Yield efficiency×10^{-4} (g/J)
Acetone in a UP reactor	80.0	9600	50	1.579
THF in a UP reactor	80.0	14400	50	1.052
Methyl myristate in a UP reactor	80.0	12000	50	1.263
Without co-solvent in a UP reactor	80.0	13800	50	1.098
Acetone in in a circulated US reactor	80.0	7200	800	0.226
Mixed co-solvent in a circulated US reactor	80.0	6540	800	0.248
Without co-solvent in a circulated US reactor	80.0	14400	800	0.113

Condition	FAME yield (%)	Reaction time (s)	Energy consumption (J/s)	Yield efficiency×10^{-4} (g/J)
Flowrate 35 mL/min in a circulated US reactor	94.89	14400	800	0.223
Flowrate 55 mL/min in a circulated US reactor	91.75	14400	800	0.216
Flowrate 75 mL/min in a circulated US reactor	89.04	14400	800	0.289
Flowrate 100 mL/min in a circulated US reactor	87.59	14400	800	0.255
20 kHz in a circulated US reactor	59.52	14400	400	0.280
50 kHz in a circulated US reactor	65.29	14400	400	0.307

Condition	FAME yield (%)	Reaction time (s)	Energy consumption (J/s)	Yield efficiency×10^{-4} (g/J)
20&50 kHz in a circulated US reactor	62.71	14400	400	0.295
50% of power in a circulated US reactor	62.71	14400	400	0.295
100 % in a circulated US reactor	91.75	14400	800	0.216

Appendix B

Hammet indicator preparation for measurement basic strength and basicity

Table B.1 Indicators and their physical properties

Chemical name	Basic strength (pKa)	Molecule weight (g/mol)
Bromothymol blue	7.2	624.41
phenolphthalein	9.8	318.33
2,4-dinitroaniline	15.0	183.12
4-Nitroaniline	18.4	138.12
Benzene carboxylic acid	-	122.12

B.1 Preparation Bromothymol blue indicator at 0.02 mol/L

Indicator concentration 1 L = Bromothymol blue 624.41 g/mol

Indicator concentration 0.02 L/mol $= \frac{624.41\left(\frac{g}{mol}\right)x\ 0.02\ (\frac{mol}{L})}{1\ (L)}$ = 12.49 g

Solution 1000 mL = 12.49 g

Solution 20 mL $= \frac{\mathbf{12.49\ (g)x\ 20\ (mL)}}{\mathbf{1000\ (mL)}}$

= 0.2498 g

B.2 Preparation Benzene carboxylic acid for Hammet titration method.

Solution 1 L = 122.12 g/mol

Solution 0.02 mol/L $= \frac{\mathbf{122.12\left(\frac{g}{mol}\right)x\ 0.02\ (\frac{mol}{L})}}{\mathbf{1\ (L)}}$ = 2.4424 g

Solution 1000 mL = 2.4424 g

Solution 500 mL $= \frac{\mathbf{2.4424\ (g)x\ 500\ (mL)}}{\mathbf{1000\ (mL)}}$

= 1.2212 g

Appendix C

Basicity calculation

Table C.1 The results of basicity from Hammet titration method.

Sample Name	**Bromothymol blue**		**Phenolphthalein**		**Basicity**
	No.1	No.2	No.1	No.2	(mmol/g cat.)
Fresh catalyst	0.35	0.35	0.65	0.65	0.0667
Used catalyst					
Non co-solvent	0.2	0.2	0.05	0.05	0.0167
THF	0.4	0.4	0.9	0.9	0.0867
Acetone	0.6	0.6	1.3	1.3	0.1267
Methyl myristate	0.2	0.2	0.4	0.4	0.0400

C.1 Basicity calculation from Hammet titration method

From $C_1V_1 = C_2V_2$

When C_1 = Concentration of benzoic acid (mol/L)

V_1 = Titration volume of benzoic acid (mL)

C_2 = Concentration of sample (mol/L)

V_2 = Total volume in flask (mL)

Remark: Catalyst sample weight = 0.300 g

Appendix D
Principles of X-ray diffraction techniques

D.1 Principles of X-ray diffraction techniques (XRD) [68]

The principle of the methods is based on the diffraction of X-rays by periodic atomic planes and the angle or energy-resolved detection of the diffracted signal. The geometrical interpretation of the XRD phenomenon that Fig. D-1 shows the details about the geometrical condition for diffraction and the determination of Bragg’s law. Bragg’s law is given in Eq. (D-1).

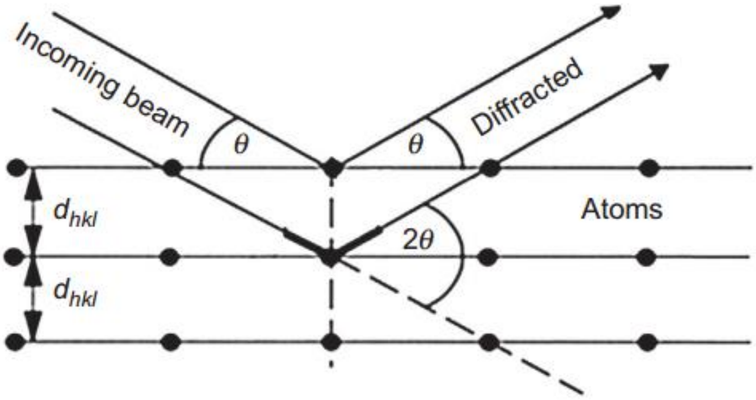


Fig. D-1 The geometrical interpretation of the XRD phenomenon [68]

Bragg’s law for constructive interference,

$$n\lambda=2d\times\sin\theta \qquad \text{(D-1)}$$

where

n is a positive integer,

λ is the wavelength of x-ray

d is the spacing between atomic planes with equal electron density

θ is the incidence and reflection angle

D.2 Crystallite size calculation [69]

Crystallite size can be calculated from the well-known Scherrer formula the average crystallite size, L, is

$$L = \frac{\kappa\lambda}{\beta cos\theta} \qquad \text{(D-2)}$$

where

λ is the X-ray wavelength in nanometer (nm),

β is the peak width of the diffraction peak profile at half maximum height resulting from small crystallite size in radians. The value of β in 2θ axis of diffraction profile must be in radians. The θ can be in degrees or radians, since the cosθ corresponds to the same number.

K is a constant related to crystallite shape, normally taken as 0.9.

Appendix E

The result for N_2 adsorption and desorption of CaO catalyst

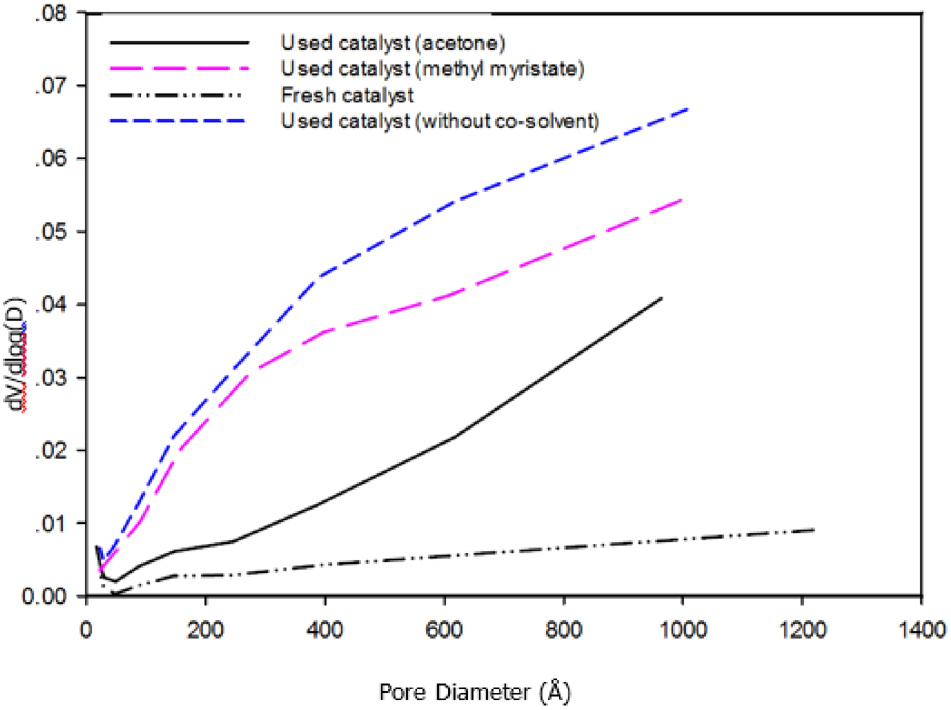


Fig. E-1 Pore size distribution of catalyst

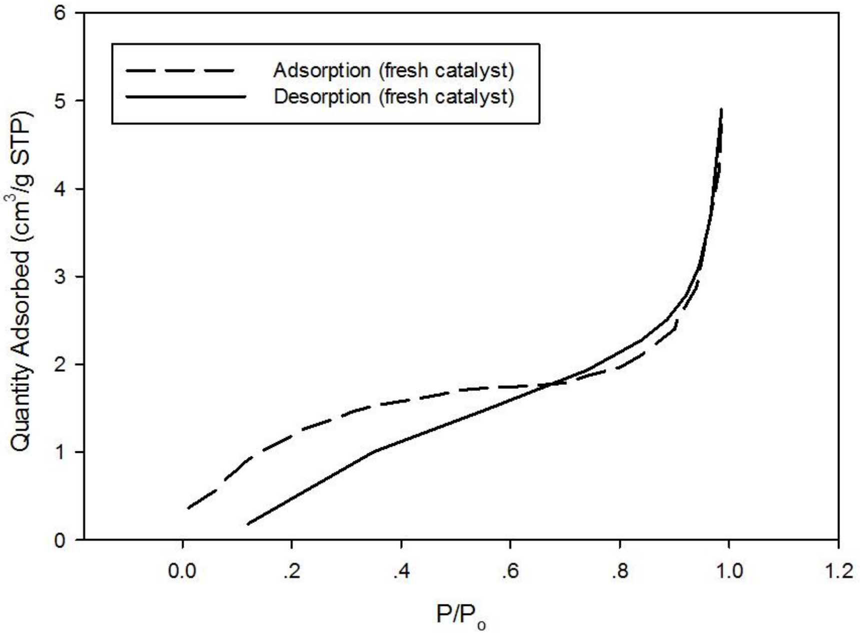


Fig. E-2 Isotherm of fresh CaO catalyst

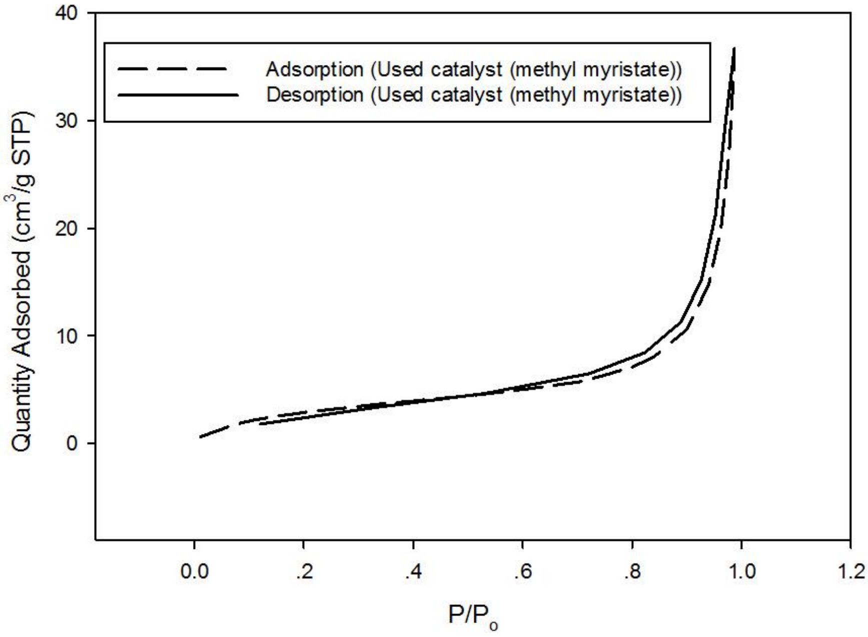


Fig. E-3 Isotherm of used CaO catalyst in addition of methyl myristate

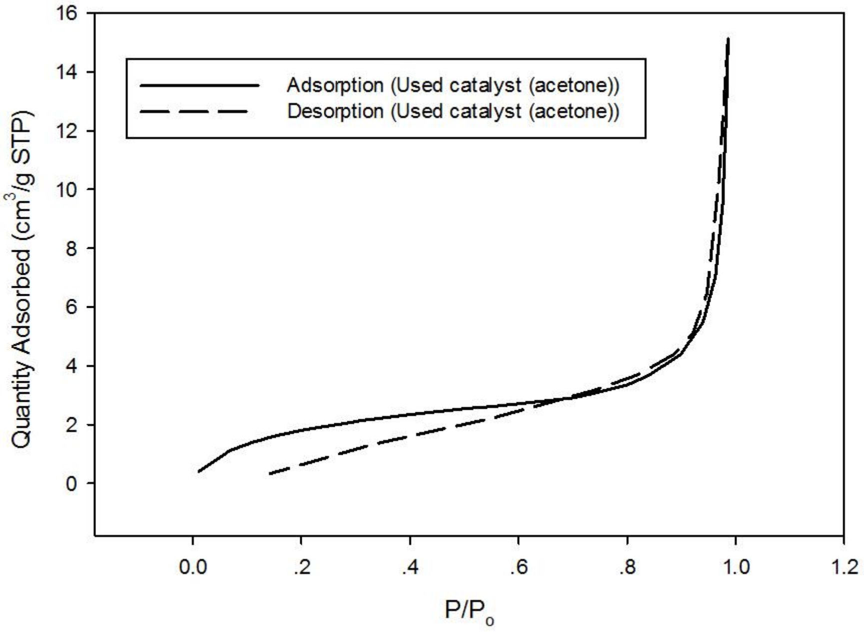


Fig. E-4 Isotherm of CaO catalyst in addition of acetone

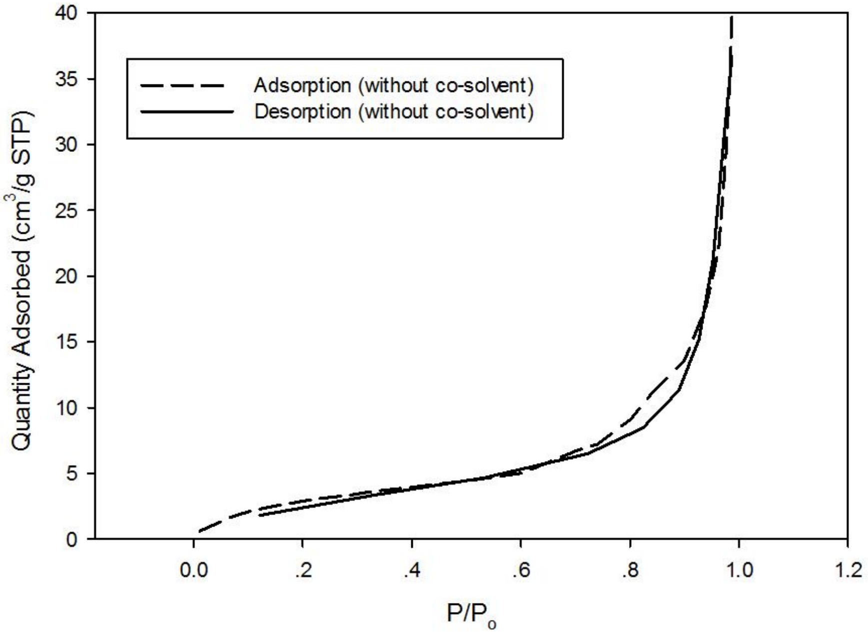


Fig. E-5 Isoterm of used CaO catalyst without co-solvent.

REFERENCES

1. Encinar, J.M., A. Pardal, and N. Sánchez, *An improvement to the transesterification process by the use of co-solvents to produce biodiesel.* Fuel, 2016. **166**: p. 51-58.
2. Roschat, W., T. Siritanon, T. Kaewpuang, B. Yoosuk, and V. Promarak, *Economical and green biodiesel production process using river snail shells-derived heterogeneous catalyst and co-solvent method.* Bioresour Technol, 2016. **209**: p. 343-50.
3. Aransiola, E.F., *Production of biodiesel from crude neem oil feedstock and its emissions from internal combustion engines.* African Journal of Biotechnology, 2012. **11**(22).
4. Ruangpornvisuti, V., *Catalysis Surface and Petrochemical.* 2015.
5. Teng, G., L. Gao, G. Xiao, and H. Liu, *Transesterification of Soybean Oil to Biodiesel over Heterogeneous Solid Base Catalyst.* Energy & Fuels, 2009. **23**(9): p. 4630-4634.
6. Gude, V.G. and G.E. Grant, *Biodiesel from waste cooking oils via direct sonication.* Applied Energy, 2013. **109**: p. 135-144.
7. Choedkiatsakul, I., K. Ngaosuwan, and S. Assabumrungrat, *Application of heterogeneous catalysts for transesterification of refined palm oil in ultrasound-assisted reactor.* Fuel Processing Technology, 2013. **111**: p. 22-28.
8. Poosumas, J., K. Ngaosuwan, A.T. Quitain, and S. Assabumrungrat, *Role of ultrasonic irradiation on transesterification of palm oil using calcium oxide as a solid base catalyst.* Energy Conversion and Management, 2016. **120**: p. 62-70.
9. Alhassan, Y., N. Kumar, I.M. Bugaje, H.S. Pali, and P. Kathkar, *Co-solvents transesterification of cotton seed oil into biodiesel: Effects of reaction conditions on quality of fatty acids methyl esters.* Energy Conversion and Management, 2014. **84**: p. 640-648.

10. Sakthivel, S., S. Halder, and P.D. Gupta, *Influence of Co-Solvent on the Production of Biodiesel in Batch and Continuous Process.* International Journal of Green Energy, 2013. **10**(8): p. 876-884.

11. Edgar Lotero, Yijun Liu, Dora E. Lopez, Kaewta Suwannakarn, David A. Bruce, and J. James G. Goodwin, *Synthesis of Biodiesel via Acid Catalysis.* Ind. Eng. Chem. Res., 2005. **44**: p. 5353-5363.

12. Wu, L., K. Huang, T. Wei, Z. Lin, Y. Zou, and Z. Tong, *Process intensification of NaOH-catalyzed transesterification for biodiesel production by the use of bentonite and co-solvent (diethyl ether).* Fuel, 2016. **186**: p. 597-604.

13. Hashemzadeh Gargari, M. and S.M. Sadrameli, *Investigating continuous biodiesel production from linseed oil in the presence of a Co-solvent and a heterogeneous based catalyst in a packed bed reactor.* Energy, 2018. **148**: p. 888-895.

14. C. ADAMS, J.F.P., M.C. RAND, B.J. SCHROER and M.C. ZIEMKE, Johnson, , *Investigation of soybean oil as a diesel fuel extender. Endurance Tests.* JAOCS, 1983. **60**(8): p. 1574-1579.

15. Arpornpong, N., C. Attaphong, A. Charoensaeng, D.A. Sabatini, and S. Khaodhiar, *Ethanol-in-palm oil/diesel microemulsion-based biofuel: Phase behavior, viscosity, and droplet size.* Fuel, 2014. **132**: p. 101-106.

16. Akkarawatkhoosith, N., A. Kaewchada, and A. Jaree, *Production of Biodiesel from Palm Oil under Supercritical Ethanol in the Presence of Ethyl Acetate.* Energy & Fuels, 2019. **33**(6): p. 5322-5331.

17. Thammachai, P., *Transesterification of palm oil under enthanol using impregnated CaO as solid base catalysts. .* Master's Thesis, Department of Chemical Engineering, Faculty of Chemical Engineering, Chulalongkorn University, 2011.

18. Atadashi, I.M., M.K. Aroua, A.R. Abdul Aziz, and N.M.N. Sulaiman, *The effects of water on biodiesel production and refining technologies: A review.* Renewable and Sustainable Energy Reviews, 2012. **16**(5): p. 3456-3470.

19. Agarwal, M., G. Chauhan, S.P. Chaurasia, and K. Singh, *Study of catalytic behavior of KOH as homogeneous and heterogeneous catalyst for biodiesel*

production. Journal of the Taiwan Institute of Chemical Engineers, 2012. **43**(1): p. 89-94.

20. Krishnamurthy, K.N., S.N. Sridhara, and C.S. Ananda Kumar, *Optimization and kinetic study of biodiesel production from Hydnocarpus wightiana oil and dairy waste scum using snail shell CaO nano catalyst.* Renewable Energy, 2020. **146**: p. 280-296.
21. Jitputti, J., B. Kitiyanan, P. Rangsunvigit, K. Bunyakiat, L. Attanatho, and P. Jenvanitpanjakul, *Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts.* Chemical Engineering Journal, 2006. **116**(1): p. 61-66.
22. Buasri, A., K. Rochanakit, W. Wongvitvichot, U. Masa-ard, and V. Loryuenyong, *The Application of Calcium Oxide and Magnesium Oxide from Natural Dolomitic Rock for Biodiesel Synthesis.* Energy Procedia, 2015. **79**: p. 562-566.
23. Kouzu, M., T. Kasuno, M. Tajika, Y. Sugimoto, S. Yamanaka, and J. Hidaka, *Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production.* Fuel, 2008. **87**(12): p. 2798-2806.
24. Tan, K.T., K.T. Lee, and A.R. Mohamed, *Production of FAME by palm oil transesterification via supercritical methanol technology.* Biomass and Bioenergy, 2009. **33**(8): p. 1096-1099.
25. Tan, K.T., K.T. Lee, and A.R. Mohamed, *Potential of waste palm cooking oil for catalyst-free biodiesel production.* Energy, 2011. **36**(4): p. 2085-2088.
26. Sawangkeaw, R., S. Teeravitud, K. Bunyakiat, and S. Ngamprasertsith, *Biofuel production from palm oil with supercritical alcohols: effects of the alcohol to oil molar ratios on the biofuel chemical composition and properties.* Bioresour Technol, 2011. **102**(22): p. 10704-10.
27. Joshi, S., P.R. Gogate, P.F. Moreira, Jr., and R. Giudici, *Intensification of biodiesel production from soybean oil and waste cooking oil in the presence of heterogeneous catalyst using high speed homogenizer.* Ultrason Sonochem, 2017. **39**: p. 645-653.

28. Rizal Alamsyah, Armansyah H. Tambunan, Y. Aris Purwant, and D. Kusdiana, *Comparison of static-mixer and blade agitator reactor in*

biodiesel production. CIGR Journal, 2010. **12**(1): p. 99-106.

29. Juan Sun, L.J. Jingxi Ju, Lixiong Zhang, and N. Xu, *Synthesis of Biodiesel in Capillary Microreactors.* Ind. Eng. Chem. Res. , 2008. **47**(5): p. 1398-1403.

30. Manickam, S., V.N.D. Arigela, and P.R. Gogate, *Intensification of synthesis of biodiesel from palm oil using multiple frequency ultrasonic flow cell.* Fuel Processing Technology, 2014. **128**: p. 388-393.

31. Dube, M.A., A.Y. Tremblay, and J. Liu, *Biodiesel production using a membrane reactor.* Bioresour Technol, 2007. **98**(3): p. 639-47.

32. Prasertsit, K., C. Mueanmas, and C. Tongurai, *Transesterification of palm oil with methanol in a reactive distillation column.* Chemical Engineering and Processing: Process Intensification, 2013. **70**: p. 21-26.

33. Dianursanti, P. Religia, and A. Wijanarko, *Utilization of n-Hexane as Co-solvent to Increase Biodiesel Yield on Direct Transesterification Reaction from Marine Microalgae.* Procedia Environmental Sciences, 2015. **23**: p. 412-420.

34. Singh, V., M. Yadav, and Y.C. Sharma, *Effect of co-solvent on biodiesel production using calcium aluminium oxide as a reusable catalyst and waste vegetable oil.* Fuel, 2017. **203**: p. 360-369.

35. Parida, S., D.K. Sahu, and P.K. Misra, *Optimization of transesterification process by the application of ultrasound energy coupled with diesel as cosolvent.* Journal of the Energy Institute, 2017. **90**(4): p. 556-562.

36. Ehimen, E.A., Z. Sun, and G.C. Carrington, *Use of Ultrasound and Co-Solvents to Improve the In-Situ Transesterification of Microalgae Biomass.* Procedia Environmental Sciences, 2012. **15**: p. 47-55.

37. J.A.Gallego-Juárez and K.F.Graff, *Introduction to power ultrasonics.* Applications of High-Intensity Ultrasound, 2015.

38. J.Virkutyte, *The use of power ultrasound in biofuel production, bioremediation, and other applications.* Applications of High-Intensity Ultrasound, 2015.

39. Lam, M.K. and K.T. Lee, *Accelerating transesterification reaction with biodiesel as co-solvent: A case study for solid acid sulfated tin oxide catalyst.* Fuel, 2010. **89**(12): p. 3866-3870.

40. Vicente, G., M. Martinez, and J. Aracil, *Integrated biodiesel production: a comparison of different homogeneous catalysts systems.* Bioresour Technol, 2004. **92**(3): p. 297-305.

41. Rashid, U., F. Anwar, B.R. Moser, and S. Ashraf, *Production of sunflower oil methyl esters by optimized alkali-catalyzed methanolysis.* Biomass and Bioenergy, 2008. **32**(12): p. 1202-1205.

42. Kawashima, A., K. Matsubara, and K. Honda, *Development of heterogeneous base catalysts for biodiesel production.* Bioresour Technol, 2008. **99**(9): p. 3439-43.

43. Esipovich, A., S. Danov, A. Belousov, and A. Rogozhin, *Improving methods of CaO transesterification activity.* Journal of Molecular Catalysis A: Chemical, 2014. **395**: p. 225-233.

44. Chen, G., R. Shan, J. Shi, and B. Yan, *Ultrasonic-assisted production of biodiesel from transesterification of palm oil over ostrich eggshell-derived CaO catalysts.* Bioresour Technol, 2014. **171**: p. 428-32.

45. Mootabadi, H., B. Salamatinia, S. Bhatia, and A.Z. Abdullah, *Ultrasonic-assisted biodiesel production process from palm oil using alkaline earth metal oxides as the heterogeneous catalysts.* Fuel, 2010. **89**(8): p. 1818-1825.

46. Gupta, A.R., S.V. Yadav, and V.K. Rathod, *Enhancement in biodiesel production using waste cooking oil and calcium diglyceroxide as a heterogeneous catalyst in presence of ultrasound.* Fuel, 2015. **158**: p. 800-806.

47. Ayegba, C.O., B.O. Aderemi, and I.A. Mohammed-Dabo, *Transesterification of cotton seed oil using cosolvent in a tubular reactor.* Biofuels, 2016. **7**(3): p. 245-251.

48. Pollardo, A.A., H.-s. Lee, D. Lee, S. Kim, and J. Kim, *Solvent effect on the enzymatic production of biodiesel from waste animal fat.* Journal of Cleaner Production, 2018. **185**: p. 382-388.

49. Thanh, L.T., K. Okitsu, Y. Sadanaga, N. Takenaka, Y. Maeda, and H. Bandow, *A new co-solvent method for the green production of biodiesel fuel – Optimization and practical application.* Fuel, 2013. **103**: p. 742-748.
50. Cleber Calgaroto, Selma Calgaroto, Marcio A Mazutti, Debora de Oliveira, Sibele Pergher, and J.V.d. Oliveira, *Production of biodiesel from soybean and Jatropha Curcas oils with KSF and amberlyst 15 catalysts in the presence of co-solvents.* Sustainable Chemical Processes, 2013. **1**(17): p. 1-6.
51. Boz, N. and M. Kara, *Solid Base Catalyzed Transesterification of Canola Oil.* Chemical Engineering Communications, 2008. **196**(1-2): p. 80-92.
52. Chuah, L.F., S. Yusup, A.R. Abd Aziz, A. Bokhari, J.J. Klemeš, and M.Z. Abdullah, *Intensification of biodiesel synthesis from waste cooking oil (Palm Olein) in a Hydrodynamic Cavitation Reactor: Effect of operating parameters on methyl ester conversion.* Chemical Engineering and Processing: Process Intensification, 2015. **95**: p. 235-240.
53. Reyero, I., G. Arzamendi, and L.M. Gandía, *Heterogenization of the biodiesel synthesis catalysis: CaO and novel calcium compounds as transesterification catalysts.* Chemical Engineering Research and Design, 2014. **92**(8): p. 1519-1530.
54. Ljupkovic, R., R. Micic, M. Tomic, N. Radulovic, A. Bojic, and A. Zarubica, *Significance of the structural properties of CaO catalyst in the production of biodiesel: An effect on the reduction of greenhouse gases emission.* Hemijska industrija, 2014. **68**(4): p. 399-412.
55. El-Araby, R., A. Amin, A.K. El Morsi, N.N. El-Ibiari, and G.I. El-Diwani, *Study on the characteristics of palm oil–biodiesel–diesel fuel blend.* Egyptian Journal of Petroleum, 2018. **27**(2): p. 187-194.
56. Robert H. Perry and D.W. Green, *Perry's Chemical Engineers' Handbook.* Eighth edition, 2007.
57. Lapuerta, M., J. Sánchez-Valdepeñas, D. Bolonio, and E. Sukjit, *Effect of fatty acid composition of methyl and ethyl esters on the lubricity at different humidities.* Fuel, 2016. **184**: p. 202-210.

58. Chiang, C.-T., M. Freindorf, T.R. Furlani, R.L. DeLeon, and J.F. Garvey, *Structure, bonding and reactions within protonated acetone–methanol cluster ions.* Chemical Physics Letters, 2011. **509**(4-6): p. 102-107.

59. Sánchez-Cantú, M., L.M. Pérez-Díaz, I. Pala-Rosas, E. Cadena-Torres, L. Juárez-Amador, E. Rubio-Rosas, . . . J.S. Valente, *Hydrated lime as an effective heterogeneous catalyst for the transesterification of castor oil and methanol.* Fuel, 2013. **110**: p. 54-62.

60. Kouzu, M., T. Kasuno, M. Tajika, S. Yamanaka, and J. Hidaka, *Active phase of calcium oxide used as solid base catalyst for transesterification of soybean oil with refluxing methanol.* Applied Catalysis A: General, 2008. **334**(1-2): p. 357-365.

61. Lukić, I., Ž. Kesić, M. Zdujić, and D. Skala, *Calcium diglyceroxide synthesized by mechanochemical treatment, its characterization and application as catalyst for fatty acid methyl esters production.* Fuel, 2016. **165**: p. 159-165.

62. Puna, J.F., J.F. Gomes, J.C. Bordado, M.J.N. Correia, and A.P.S. Dias, *Biodiesel production over lithium modified lime catalysts: Activity and deactivation.* Applied Catalysis A: General, 2014. **470**: p. 451-457.

63. Kouzu, M., J.-s. Hidaka, K. Wakabayashi, and M. Tsunomori, *Solid base catalysis of calcium glyceroxide for a reaction to convert vegetable oil into its methyl esters.* Applied Catalysis A: General, 2010. **390**(1-2): p. 11-18.

64. Rahimi, M., B. Aghel, M. Alitabar, A. Sepahvand, and H.R. Ghasempour, *Optimization of biodiesel production from soybean oil in a microreactor.* Energy Conversion and Management, 2014. **79**: p. 599-605.

65. Bargole, S., J. Carpenter, S. George, and V.K. Saharan, *Process intensification of synthesis of biodiesel using a novel recirculating flow ultrasonication reactor.* Chemical Engineering and Processing: Process Intensification, 2017. **122**: p. 21-30.

66. Laosuttiwong, T., K. Ngaosuwan, W. Kiatkittipong, D. Wongsawaeng, P. Kim-Lohsoontorn, and S. Assabumrungrat, *Performance comparison of different cavitation reactors for biodiesel production via transesterification of palm oil.* Journal of Cleaner Production, 2018. **205**: p. 1094-1101.

67. Gole, V.L., K.R. Naveen, and P.R. Gogate, *Hydrodynamic cavitation as an efficient approach for intensification of synthesis of methyl esters from sustainable feedstock.* Chemical Engineering and Processing: Process Intensification, 2013. **71**: p. 70-76.
68. Epp, J., *X-ray diffraction (XRD) techniques for materials characterization*, in *Materials Characterization Using Nondestructive Evaluation (NDE) Methods*. 2016. p. 81-124.
69. Monshi, A., M.R. Foroughi, and M.R. Monshi, *Modified Scherrer Equation to Estimate More Accurately Nano-Crystallite Size Using XRD.* World Journal of Nano Science and Engineering, 2012. **02**(03): p. 154-160.

VITA

NAME	Panidaporn Ritprasert
DATE OF BIRTH	30 July 1991
PLACE OF BIRTH	Ranong
HOME ADDRESS	54/129 Village No.5, Bangrin Sub-district, Muang District,Ranong, 85000.