การผลิตไบโอดีเซลจากน้ำมันปาล์มด้วยเครื่องปฏิกรณ์ที่อาศัยคลื่นอัลตร้าโซนิคร่วมด้วย โดยใช้ตัวเร่งปฏิกิริยาแบบวิวิธพันธุ์แคลเซียมออกไซด์

นายจุติพงศ์ ภูสุมาศ

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Ultrasound Assisted Reactor for Biodiesel Production from Purified Palm Oil on Calcium Oxide Heterogeneous Catalyst

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
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Thesis Title	Ultrasound Assisted Reactor for Biodiesel Production from Purified Palm Oil on Calcium Oxide Heterogeneous Catalyst
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จุติพงศ์ ภูสุมาศ : การผลิตไบโอดีเซลจากน้ำมันปาล์มด้วยเครื่องปฏิกรณ์ที่อาศัยคลื่นอัลตร้าโซนิคร่วมด้วย โดยใช้ตัวเร่งปฏิกิริยาแบบวิวิธพันธุ์แคลเซียมออกไซด์ (Ultrasound Assisted Reactor for Biodiesel Production from Purified Palm Oil on Calcium Oxide Heterogeneous Catalyst) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ศ. ดร. สุทธิชัย อัสสะบำรุงรัตน์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ดร. กนกวรรณ ง้าวสุวรรณ, 101 หน้า.

ไบโอดีเซลเป็นหนึ่งในพลังงานทางเลือกที่มีศักยภาพ ซึ่งมีการศึกษาและพัฒนามาอย่างต่อเนื่อง ไบโอดีเซลเป็นสารประกอบแอลคิลเอสเตอร์ของกรดไขมันที่ผลิตขึ้นจากน้ำมันพืชผ่านปฏิกิริยาทรานส์เอสเทอริฟิเคชันกับแอลกอฮอล์โดยใช้ตัวเร่งปฏิกิริยาทั้งแบบเอกพันธุ์และวิวิธพันธุ์ อย่างไรก็ตามปัญหาด้านการถ่ายเทมวลระหว่างสารทั้งสองที่ไม่ละลายด้วยกัน และตัวเร่งปฏิกิริยาแบบวิวิธพันธุ์ยังคงเป็นอุปสรรคต่อผลได้ของไบโอดีเซล เครื่องปฏิกรณ์ที่อาศัยคลื่นอัลตร้าโซนิคเป็นทางออกหนึ่งที่ช่วยเพิ่มระดับการผสมของสารผ่านปรากฏการณ์คาวิเทชันในของเหลว อีกทั้งคาวิเทชันเจ็ทยังช่วยนำสารตั้งต้นไปเกิดปฏิกิริยาที่ผิวของตัวเร่งปฏิกิริยาในสภาวะยิ่งยวด ที่อุณหภูมิประมาณ 5,000 องศาเซลเซียส ความดัน 1,000 เท่าของบรรยากาศ ในงานวิจัยนี้ได้ทำการผลิตไบโอดีเซลจากน้ำมันปาล์มด้วยเครื่องปฏิกรณ์ที่อาศัยคลื่นอัลตร้าโซนิคเปรียบเทียบกับเครื่องปฏิกรณ์ที่อาศัยใบกวนทางกล โดยใช้ปฏิกิริยาทรานส์เอสเทอริฟิเคชันที่อุณหภูมิ 60 องศาเซลเซียส ความดันบรรยากาศ และอัตราส่วนโดยโมลระหว่างเมทานอลและน้ำมันเท่ากับ 9 ต่อ 1 เมื่อใช้ปริมาณตัวเร่งปฏิกิริยาแคลเซียมออกไซด์สูงสุด (ร้อยละ 3 โดยมวล) จะให้อัตราการเกิดปฏิกิริยาที่รวดเร็วที่สุด จากนั้นปริมาณผลได้ของไบโอดีเซลจะเกิดขึ้นอย่างต่อเนื่องจนถึงสมดุลปฏิกิริยาค่าหนึ่ง (ร้อยละ 80 ของผลได้โดยประมาณ) คลื่นอัลตร้าโซนิคที่ความถี่และพลังงานสูงที่สุด (50 กิโลเฮิรตซ์ 800 วัตต์) ช่วยสนับสนุนการเกิดปฏิกิริยาทรานส์เอสเทอริฟิเคชันของตัวเร่งปฏิกิริยาแบบวิวิธพันธุ์จากน้ำมันปาล์ม จากการศึกษาความสามารถในการนำตัวเร่งปฏิกิริยาแคลเซียมออกไซด์มาใช้ซ้ำในการผลิตไบโอดีเซลด้วยเครื่องปฏิกรณ์อัลตร้าโซนิคพบว่าตัวเร่งปฏิกิริยาสามารถนำมาใช้ซ้ำได้ และให้ปริมาณผลได้ของไบโอดีเซลที่สูงตลอดปฏิกิริยาทั้งสามรอบโดยมีอัตราการเกิดปฏิกิริยาต่ำลงในแต่ละรอบเล็กน้อยอันเนื่องมาจากสารประกอบอินทรีย์ที่เกาะบนพื้นผิวของตัวเร่งปฏิกิริยา องค์ความรู้ที่ได้จากการวิจัยครั้งนี้สามารถนำไปต่อยอดเป็นระบบที่มีกำลังการผลิตที่สูงขึ้นในลำดับต่อไป

ภาควิชา	วิศวกรรมเคมี	ลายมือชื่อนิสิต	....
สาขาวิชา	วิศวกรรมเคมี	ลายมือชื่อ อ.ที่ปรึกษาหลัก	....
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JUTIPONG POOSUMAS: Ultrasound Assisted Reactor for Biodiesel Production from Purified Palm Oil on Calcium Oxide Heterogeneous Catalyst. ADVISOR: PROF. DR. SUTTICHAI ASSABUMRUNGRAT, CO-ADVISOR: DR. KANOKWAN NGAOSUWAN, 101 pp.

Biodiesel is one of the promising alternative energy that has been studied and developed in the recent year. It consists of compounds of fatty acid alkyl ester (FAAE) mostly produced from vegetable oil and alcohol using homogeneous or heterogeneous catalyst via transesterification. However, mass transfer between two immiscible reactants and also heterogeneous catalyst are hindrance resulting in the biodiesel yield. Ultrasonic assisted reactor is a practical solution to increase the level of mixing by cavitation phenomena in fluid and carrying reactants to active site of catalyst with cavitation jet. The cavitation phenomena also produce an extremely reaction condition around 5,000°C and 1,000 atm. In this work, a study of biodiesel production from transesterification of palm oil using ultrasonic assisted reactor was investigated and compared to mechanical stirred reactor. Transesterification was operated at 60°C, 1 atm, methanol to oil molar ratio of 9:1. Sodium hydroxide homogeneous catalyst provides higher methyl ester yield and faster rate of reaction than that of calcium oxide heterogeneous catalyst. The fastest rate of reaction was achieved in ultrasonic reactor at highest catalyst loading (3%wt) and methyl ester yield increases steadily until reach the same transesterification equilibrium (about 80%). The higher ultrasonic frequency and power (50 kHz, 800 W) promoted the heterogeneously catalyzed transesterification of refined palm oil. Reusability of calcium oxide catalyzed transesterification using ultrasonic assisted reaction was also studied. It was found that calcium oxide catalyst can be used to produce biodiesel and provide high biodiesel yield for three cycles with slightly decreasing rate of reaction due to organic compounds deposition. The cognitive results from this study can be developed for the further process scale up.

Department:	Chemical Engineering	Student's Signature	....
Field of Study:	Chemical Engineering	Advisor's Signature	....
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Chapter 1
Introduction

1.1 Introduction

Energy is essential to life which is associated with human civilization for several century. Energy usage is originated from human need for heating themselves. The need for energy is continuously increase as well as the increasing of human population. The conventional energy source such as petroleum, natural gas, coal will not be able to reserve for the worldwide energy consumption in the next 40 years.

According to a report available on the United States Energy Information Administration (EIA) website shown that industrial part consume the most energy and oil was held to be the most popular source of energy (Figure 1.1) but opposed to its prices (Figure 1.2)

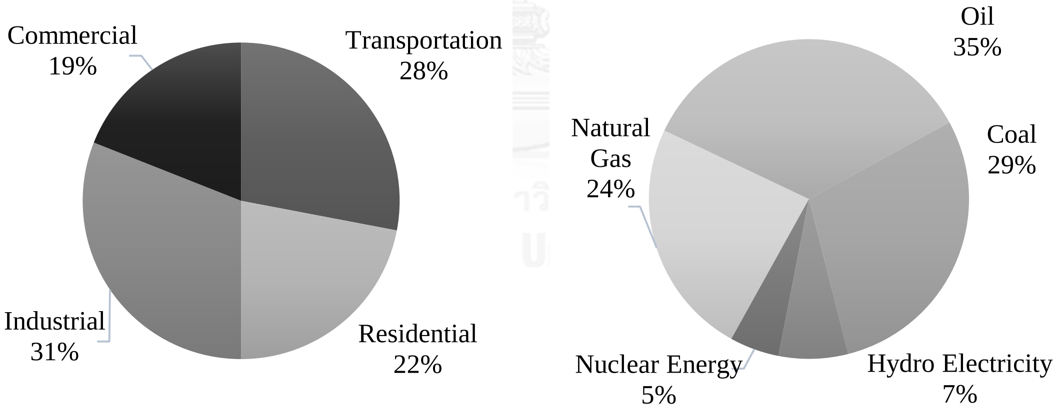


Figure 1.1 Energy consumption and energy sources for the year 2014 [1].

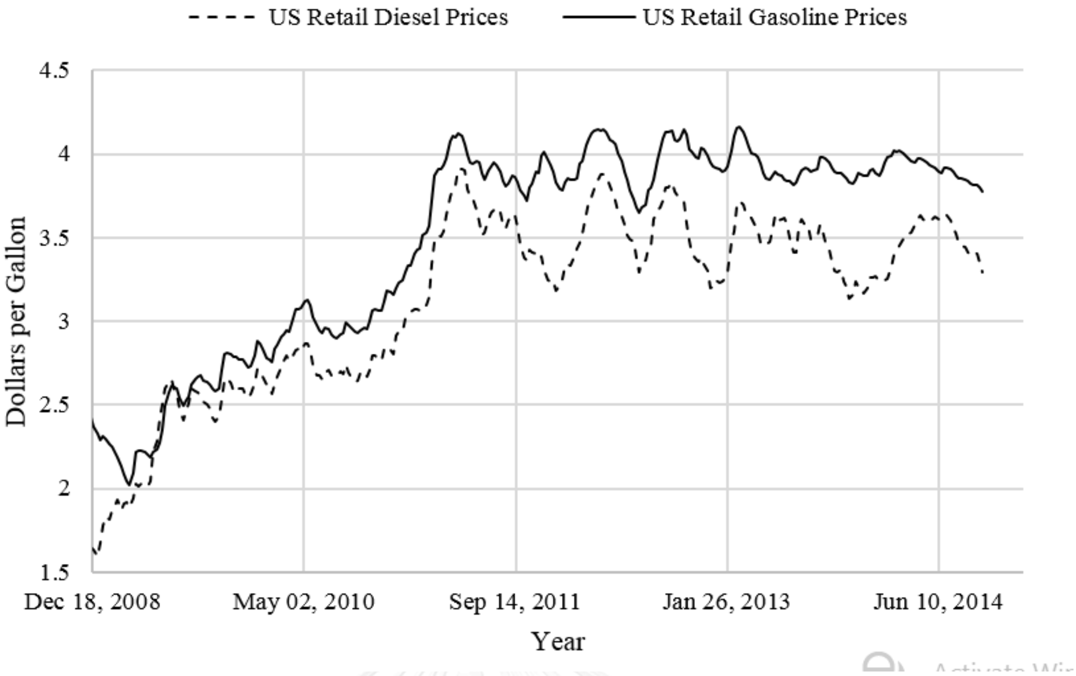


Figure 1.2 US regular conventional retail diesel and gasoline prices [1].

So the alternative energy is to be more important such as solar energy, wind energy, hydro energy or geothermal energy.

Biodiesel is also one of the promising alternative energy that has been studied and developed in the recent year. Biodiesel is not only environmental friendly, but also sustainable supplied due to its renewable energy. It consists of compounds of fatty acid alkyl ester (FAAE) produced from vegetable oils, animal fats and waste cooking oils [2, 3] from several methods: dilution (blending), micro-emulsification, pyrolysis (thermal cracking), esterification or transesterification via catalysts [4, 5].

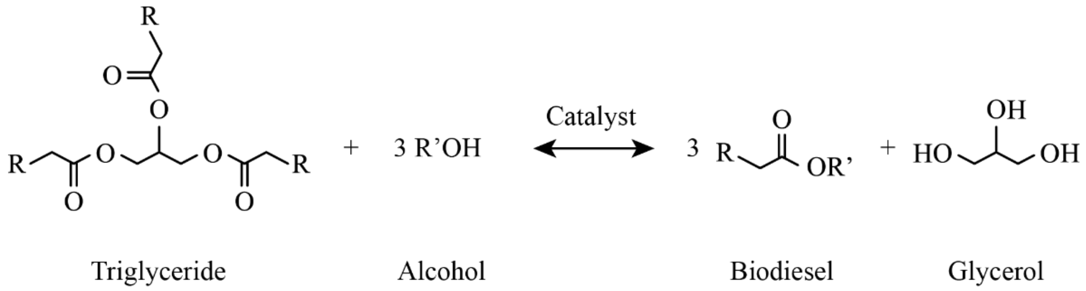


Figure 1.3 Transesterification reaction.

Transesterification (shown on Figure 1.3), also called alcoholysis, has been used for biodiesel production. This is a chemical reaction of oils or fats to form esters and glycerol with or without presence of a catalyst. However, there are two obstacles for transesterification of oil and low molecular alcohol. Firstly, the limitation of biodiesel yield is due to reaction equilibrium which is involved a sequence of three consecutive reversible reactions. Lastly, mass transfer between two immiscible reactants and also catalyst are hindrance due to the solubility of oil and alcohol resulting in low process efficiency [6].

Ultrasonic biodiesel reactor is a practical solution to increase the level of mixing and shift the reaction equilibrium by cavitation phenomena in fluid. This can help by increasing the interfacial of reactants bubble to active site of catalyst with cavitation jet. The cavitation phenomena also produces an extreme reaction condition around 5,000°C and 1,000 atm. Ultrasonic provides the mixing energy for reducing the activation energy of transesterification and increases rate of reactions, efficient alcohol to oil molar ratio and biodiesel yield with less energy consumption as compared to the conventional mechanical stirring reactor [7].

A catalyst is a substance that accelerates chemical reaction rate and also decreases activation energy of reaction. The catalysts used in the transesterification are broadly divided into two type: homogeneous catalysts and heterogeneous catalysts. Common homogenous catalysts are sodium hydroxide, potassium hydroxide, sodium methoxide and potassium methoxide etc. Although the performance of homogeneous catalysts are higher than that of heterogeneous catalysts but the drawback of them is difficult to separate from biodiesel product. It also requires a tremendous amount of water to separation having an impact to the environment. In contrast to the heterogeneous catalysts, because heterogeneous catalysts are different phase from reaction mixture leading to easy to separate and it can be recycled. Common heterogeneous catalyst are calcium oxide, magnesium oxide, strontium oxide, zinc oxide, titanium oxide or even natural-based such as eggshell, mollusk shell, sea sand and bones etc. Therefore, this study focuses on the effect of ultrasound and operating parameters on the catalytic activity of heterogeneous catalyzed transesterification of refined palm oil under batch and continuous process.

1.2 Objective

To study the effect of ultrasound and variable parameters on the catalytic activity and stability of heterogeneous catalyzed transesterification of refined palm oil.

1.3 Scope of work

1.3.1 Study the effect of ultrasound assisted reactor on the catalytic activity of heterogeneous catalyzed transesterification of refined palm oil under batch process

1.3.2 Study effect of variable parameters such as ultrasound irradiation frequency and power, catalyst loading and catalyst calcination temperature on the catalytic activity of heterogeneous catalyzed transesterification of refined palm oil under batch process

1.3.3 Study effect of stability of heterogeneous catalyst catalyzed transesterification of refined palm oil under ultrasound irradiation.

1.4 Expected Outputs

The biodiesel production process which is more efficient and economic operation can be adopted in applications in the industry.

Chapter 2

Theory

2.1 Biodiesel

Biodiesel is an alternative fuel similar to conventional fossil diesel. It consists of compounds of fatty acid alkyl ester (FAAE) such as methyl palmitate, methyl linoleate, methyl oleate, methyl stearate etc. Mostly, it is produced from vegetable oil and short chain alcohol using homogeneous or heterogeneous catalyst via transesterification. Properties of fatty acid alkyl esters are shown in Table 2.1 [8].

Table 2.1 Properties of fatty acid alkyl eaters.

Fatty acid alkyl ester	Formula*	Molecular weight [g/mol]	Higher heating value [MJ/kg]	Oxidation stability [h]	Kinematic viscosities [cSt]
Methyl palmitate	$C_{16:0}$	256.42	39.18	22.13	4.41
Methyl stearate	$C_{18:0}$	284.48	40.21	17.93	5.82
Methyl oleate	$C_{18:1}$	282.46	40.13	6.61	4.55
Methyl linoleate	$C_{18:2}$	280.45	40.06	4.37	3.69
Methyl linolenic	$C_{18:3}$	278.43	39.98	3.87	3.22
Ethyl palmitate	$C_{16:0}$	284.48	40.64	23.76	4.62
Ethyl stearate	$C_{18:0}$	312.53	41.98	21.77	5.92
Ethyl oleate	$C_{18:1}$	310.51	41.63	6.68	4.81
Ethyl linoleate	$C_{18:2}$	308.5	40.86	5.02	4.28
Ethyl linolenic	$C_{18:3}$	306.5	40.69	4.23	3.46

* Note: $C_{a:b}$ describes a fatty acid with a carbon atoms and b double bonds.

However, there is no requirement quantities of each fatty acid alkyl ester in biodiesel, but physical and chemical properties of biodiesel must comply with specification of American Society for Testing and Materials (ASTM) D6751 or The European EN 14214 biodiesel international standard (shown as Table 2.2)

Table 2.2 Specification of ASTM and EN standard.

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 (max)	D-7501	360	-	-
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 2.2 Specification of ASTM and EN standard (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/ ^{o}C	D-1160	90% at 360 ^{o}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 ^{o}C, WSD/ µm	-	-	-	-

Reactants for biodiesel production can be divided into two major sources: vegetable oil (or animal fat) and alcohol. Palm oil, soy bean and sunflower oil are generally used for triglyceride source to produce biodiesel as considered edible feedstocks to be 1st generation biodiesel feedstocks. The non-edible feedstocks such as jatropha oil, mahua oil, jojoba oil, sea mango oil, waste cooking oils are considered to 2nd generation biodiesel feedstocks. The several feedstocks with their benefits and drawbacks for each generation compared to petroleum refinery are show in Table 2.3 [9].

Table 2.3 The difference of feedstocks, benefits and drawbacks between each generation compared to petroleum refinery.

Topic	Petroleum refinery	1st generation	2nd generation
Feedstocks	Crude petroleum	Edible sources such as vegetable oil & corn sugar etc.	Non-edible sources, cheap and abundant waste biomass
Benefits	- Economical technology. - Fit with mostly present diesel engine.	- Environmental friendly. - Economics & social security	- Non competing with food. - Environmental friendly. - Economics & social security
Drawbacks	- Depletion & declining of petroleum reserve - Environmental pollution - Economics and ecological problems	- Limited feedstock (food versus fuel competition) - Blend partly with conventional fuel	- Advance technology still under development to reduce the cost of conversion. - High cost of production. - Hardly to produce in larger scale.

However, the composition of fatty acid in each type of feedstocks (Table 2.4) will relate to alkyl ester composition in biodiesel including of molecular weight and physical properties of produced biodiesel. Alcohol, another reactant for biodiesel production, methanol is common choice for use in the reactions. Due to it is cheaper and higher activity than the other long-chain alcohol. Besides that, methanol has a lower boiling point. Thus, it can recovered by decanting unit or distillation unit from biodiesel product easily than that of the other higher molecular weight alcohol. Currently, methanol is produced using feedstock derived from petroleum-based which cannot be considered truly green reactant. Therefore, researcher have developed a bio-methanol by adding carbon monoxide to react with hydrogen (Equation (2.1)).

$$CO_2 + 2\,H_2 \rightarrow CH_3OH \tag{2.1}$$

Table 2.4 Composition of fatty acid in each type of feedstock [10].

Source	**Structure**	**Molecular weight (MW)**		**Typical composition, wt%**				
		Fatty acid	**Triglyceride**	**Jatropha**	**Palm**	**Canola**	**Soybean**	**Sunflower**
Capric	$C_{10:0}$	172.3	554.8	0.0	0.0	0.6	0.0	0.0
Lauric	$C_{12:0}$	200.3	639.0	0.0	0.0	0.0	0.0	0.0
Myristic	$C_{14:0}$	228.4	723.2	0.0	2.5	0.1	0.0	0.0
Palmitic	$C_{16:0}$	256.4	807.3	15.9	40.8	5.1	11.5	6.5
Palmitoleic	$C_{16:1}$	254.4	801.3	0.9	0.0	0.0	0.0	0.2
Stearic	$C_{18:0}$	284.5	891.5	6.9	3.6	2.1	4.0	5.8
Oleic	$C_{18:1}$	282.5	885.4	41.1	45.2	57.9	24.5	27.0
Linoleic	$C_{18:2}$	280.4	879.4	34.7	7.9	24.7	53.0	60.0
Linolenic	$C_{18:3}$	278.4	873.3	0.3	0.0	7.9	7.0	0.2
Arachidic	$C_{20:0}$	312.5	975.6	0.0	0.0	0.2	0.0	0.3
Eicosenoic	$C_{20:1}$	310.5	969.6	0.2	0.0	1.0	0.0	0.0
Behenic	$C_{22:0}$	340.6	1059.8	0.0	0.0	0.2	0.0	0.0
Erucic	$C_{22:1}$	338.6	1053.8	0.0	0.0	0.2	0.0	0.0
			Estimated MW:	869.7	847.0	876.9	871.9	876.7

The oil feedstock can be used directly in biodiesel production process or it may be improved quality by using process improvement such as cleaning, separating impurities and purifying process (Table 2.5)

Table 2.5 Process improvement for purification of oil feedstock.

Process improvement	**Eliminated contaminations**
Degumming	Phospholipid, Color pigment, Carbohydrate, Protein, Metal
Neutralization	Sulfur, Metal, Insoluble substances in oil, Soluble substance in water
Water washing	Soap
Drying	Water
Bleaching	Color pigment, Product from oxidation, Sulfur, Metal, Soap
Filtration	Solid
Deodorization	Fatty acid, Mono and diglyceride, Product from oxidation and color pigment
Steam refining	Product from oxidation and color pigment
Polishing	Remaining insoluble substances in oil

2.1.1 Biodiesel production method

Biodiesel can be produced from 4 main method:

2.1.1.1 Direct use and blending

Vegetable oil can be directly used as diesel without any changes to engine but it may cause to problem in the long run because of high viscosity such as coking, gelling or carbon deposit in the engine. To prevent high viscosity, the blending method can be applied by mixing vegetable oil and petroleum oil in varies ratio.

Advantages of direct use and blending method are

- Easy to applied
- High heat content
- Renewability
- No need complex process

Disadvantage of this method are

- Engine ignition more difficult
- Thickening
- Carbon deposit on injector, cylinder and jacket
- Engine corrosion

2.1.1.2 Micro-emulsification

Micro-emulsification is defined as colloidal dispersion of fluid microstructure (1-50 nm) in immiscible phase solvent and some additive. The common solvents are methanol and ethanol. Micro-emulsification is the probable solution to reduce viscosity of vegetable oil.

2.1.1.3 Pyrolysis or thermal cracking

Pyrolysis means conversion of one substance to another one by heat. Catalysts can be used to reduce activation energy and speed up the process. Different products can be obtained from the same substance with different path way of reactions and depend on pyrolysis temperature (example shown on Table 2.6). Pyrolysis always give lighter molecular weight substance in each step of reaction (Figure 2.1).

Table 2.6 Example of rape seed thermal cracking selectivity.

Composition	Selectivity (%mole)						
	550 °C	**600 °C**	**650 °C**	**700 °C**	**750 °C**	**800 °C**	**850 °C**
C_1-C_4	10.0	18.6	28.2	38.7	35.1	45.1	66.1
C_5-C_9	36.0	19.6	17.6	13.2	17.5	12.6	3.6
C_{10}-C_{44}	3.0	3.5	3.5	2.7	1.7	1.0	0.3
C_{15}-C_{18}	0.9	0.7	0.3	1.1	1.0	0.2	0.3
Aromatics	5.2	2.0	2.7	3.9	7.2	11.6	8.9
$C_{3:1}$-$C_{8:1}$	8.5	16.6	10.3	7.2	5.9	4.1	0.9
$C_{9:1}$-$C_{16:1}$	2.3	3.2	3.4	2.3	0.9	0.5	0.3
Ester	2.0	1.2	1.6	2.4	3.7	3.1	2.6
CO	0.5	1.2	1.3	2.3	2.7	3.8	5.3
CO_2	0.3	0.6	0.6	1.1	1.5	1.6	2.1
Coke	6.1	3.8	4.2	4.7	2.2	3.1	4.5
Other	25.2	29.0	25.3	20.4	21.3	13.3	5.1

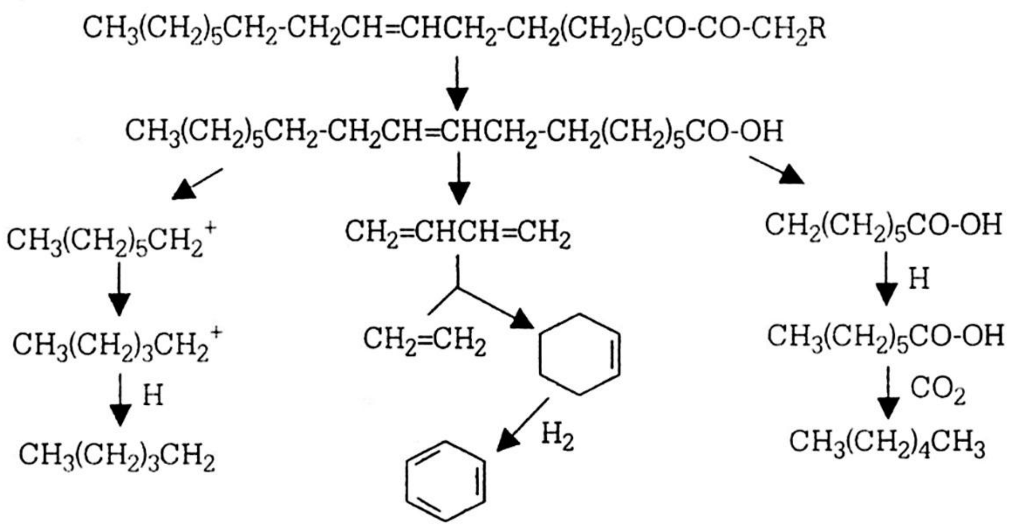


Figure 2.1 Pyrolysis or thermal cracking mechanism.

2.1.1.4 Transesterification and esterification

Transesterification and esterification have been popular for the production of biodiesel because reactions can occur at lower temperature than that of pyrolysis. These reactions give specific product at narrow range and close to petroleum diesel.

Both reactions can be reversible and give glycerol as byproduct for transesterification and water as byproduct for esterification

Conversion of vegetable or animal oil to biodiesel is effected by several parameters including of:

- Time of reaction
- Reaction temperature
- Type of catalyst
- Catalyst loading
- Reactant ratio (molar of alcohol to oil ratio)
- Amount of free fatty acid
- Amount of water or moisture

2.2 Reactions involving for biodiesel production

2.2.1 Transesterification

Transesterification involves three consecutive reversible reactions. Triglycerides (TGs) are converted to diglycerides (DGs) then, diglycerides are converted to monoglycerides (MGs) followed by conversion of monoglycerides to glycerol. A fatty acid alkyl ester (biodiesel) was produced for each step of reactions. For overall reaction, one molecule of triglycerides can produce three molecules of fatty acid alkyl ester [11]. The consecutive reactions are expressed in Equation (2.2) to (2.4) and overall transesterification reaction are shown in Equation (2.5). Molecular structures in the reactions are expressed in Figure (2.2)

Consecutive reactions

$$Triglyceride + R'OH \leftrightarrow Diglyceride + R'COOR \quad (2.2)$$

$$Diglyceride + R'OH \leftrightarrow Monoglyceride + R'COOR \quad (2.3)$$

$$Monoglyceride + R'OH \leftrightarrow Glycerol + R'COOR \quad (2.4)$$

Overall reaction

$$Triglyceride + 3\ R'OH \leftrightarrow 3\ R'COOR + Glycerol \quad (2.5)$$

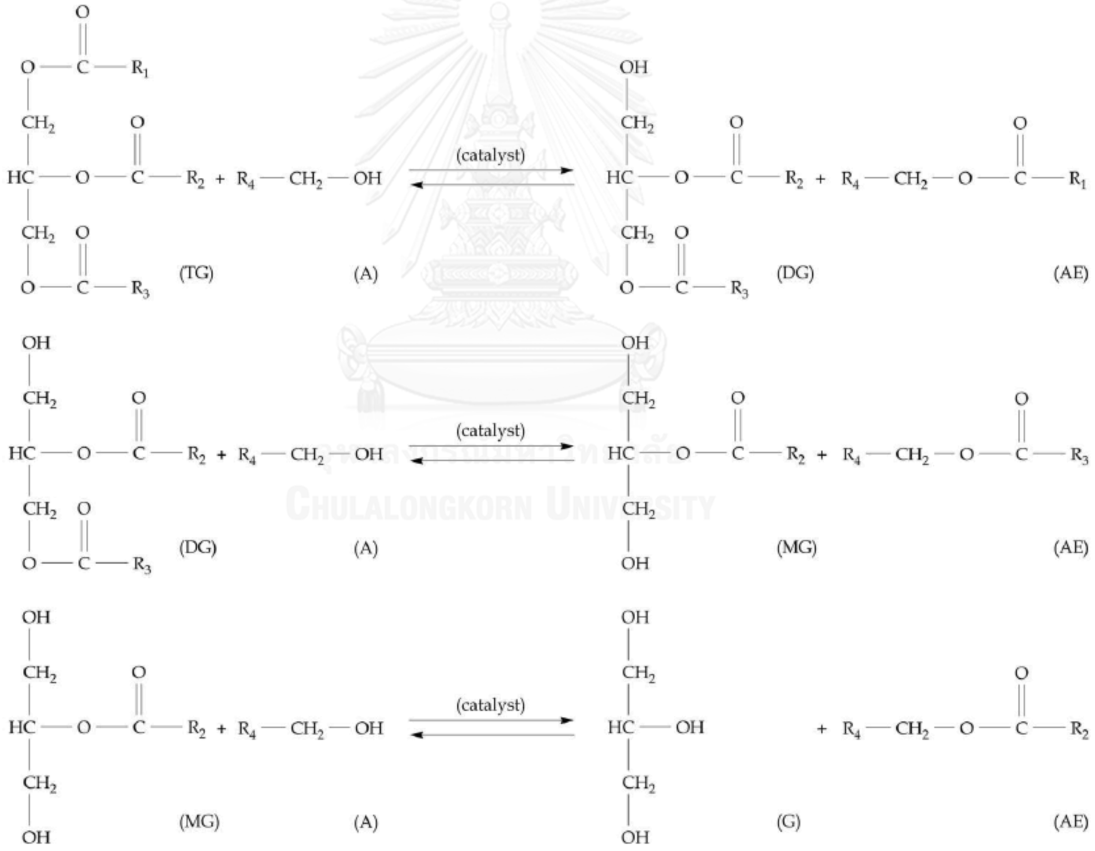


Figure 2.2 Molecular structures in the reactions.
Triglecerides (TG), Diglycerides (DG), MG:Monoglyceride (MG), Alcohol (A), Alkyl esters (AE), Glycerol (G)

2.2.2 Esterification

Esterification is a reaction between carboxylic acids and alcohols to produce esters and water. The reaction is expressed in Equation (2.6). Esterification usually occurs on the substrate with a high amount of free fatty acid (FFAs) such as waste cooking oil reacted with methanol in the presence of acid catalyst. The byproduct as water is probably react with excess alcohol in the next hydrolysis reaction.

$$R'COOH + R'OH \leftrightarrow R'COOR + Water \tag{2.6}$$

2.2.3 Sponification

Sponification is the reaction between carboxylic acids and strong base reactant such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) to produce sodium soap (R'COONa) or potassium soap (R'COOK) respectively (shown in Equation (2.7) and (2.8)). Sponification was considered to be undesirable reaction because the soap product causes the many problems of reaction, such as hinders the catalyst activity, hard to separate from product, make the higher viscosity of product and clog up the process. The byproduct as water may probably be a reactant of the next hydrolysis reaction too.

$$R'COOH + NaOH \rightarrow R'COONa + Water \tag{2.7}$$

$$R'COOH + KOH \rightarrow R'COOK + Water \tag{2.8}$$

2.2.4 Hydrolysis

Hydrolysis is a chemical reaction in which a molecule of water is added to a substance. As shown in Equation (2.9), one mole of triglycerides react with three moles of water and converted to 3 moles of free fatty acids and one mole of glycerol. However, the product as free fatty acids can continued convert to biodiesel via esterification.

$$Triglyceride + 3\ Water \rightarrow 3\ R'COOH + Glycerol \tag{2.9}$$

2.3 Catalyst

A catalyst is a substance that accelerate chemical reaction rate and also decreases an activation energy of reaction. The catalysts used in the transesterification are mainly divided into two type including of homogeneous and heterogeneous catalysts. Common homogenous catalysts for transesterification are sodium hydroxide, potassium hydroxide, sodium methoxide, potassium methoxide. Although the performance of homogeneous catalysts are higher than that of heterogeneous catalysts but its drawback is difficult to separate the catalysts from biodiesel product [12]. It also requires a tremendous amount of water to separation which have an impact to the environment [13]. In contrast, the heterogeneous catalysts are easy to separate, very little amount of water usage and it can be recycled. Common heterogeneous catalyst for biodiesel production are calcium oxide, magnesium oxide, strontium oxide, zinc oxide, titanium oxide or even natural-based such as eggshell [14, 15], mollusk shell [16], sea sand [17], bones [18] etc.

For heterogeneous catalyst, rate of reaction is controlled under catalytic reaction. Each steps of catalytic reaction can be explained as follows [19]:

1. Mass transfer (diffusion) of the reactants from the bulk fluid to the external surface of the catalyst pellet.
2. Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface.
3. Adsorption of reactants onto the catalyst surface.
4. Reaction on the surface of the catalyst.
5. Desorption of the products from the catalyst surface.
6. Diffusion of the products from the interior of the pellet to the pore mouth at the external surface.
7. Mass transfer of the products from the external pellet surface to the bulk fluid.

A schematic diagram of a tubular reactor packed with catalytic pellets is shown in Figure 2.3. The overall process by which heterogeneous catalytic reactions is shown in Figure 2.4.

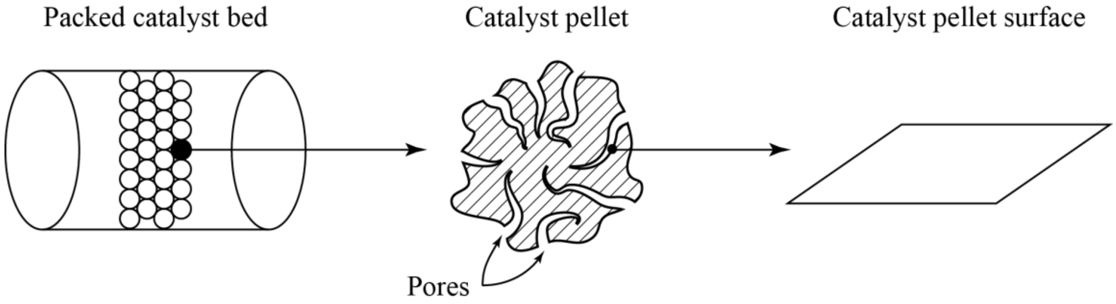


Figure 2.3 A schematic diagram of a tubular reactor packed with catalytic pellets.

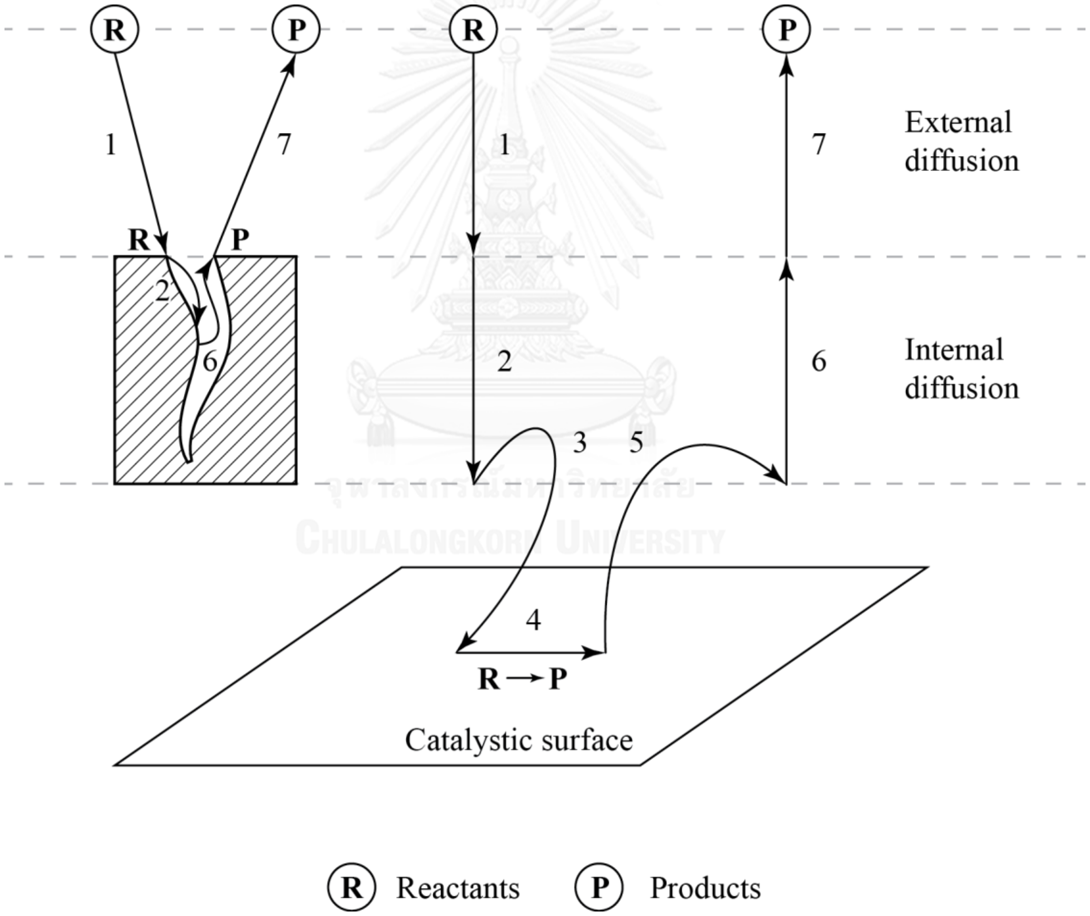


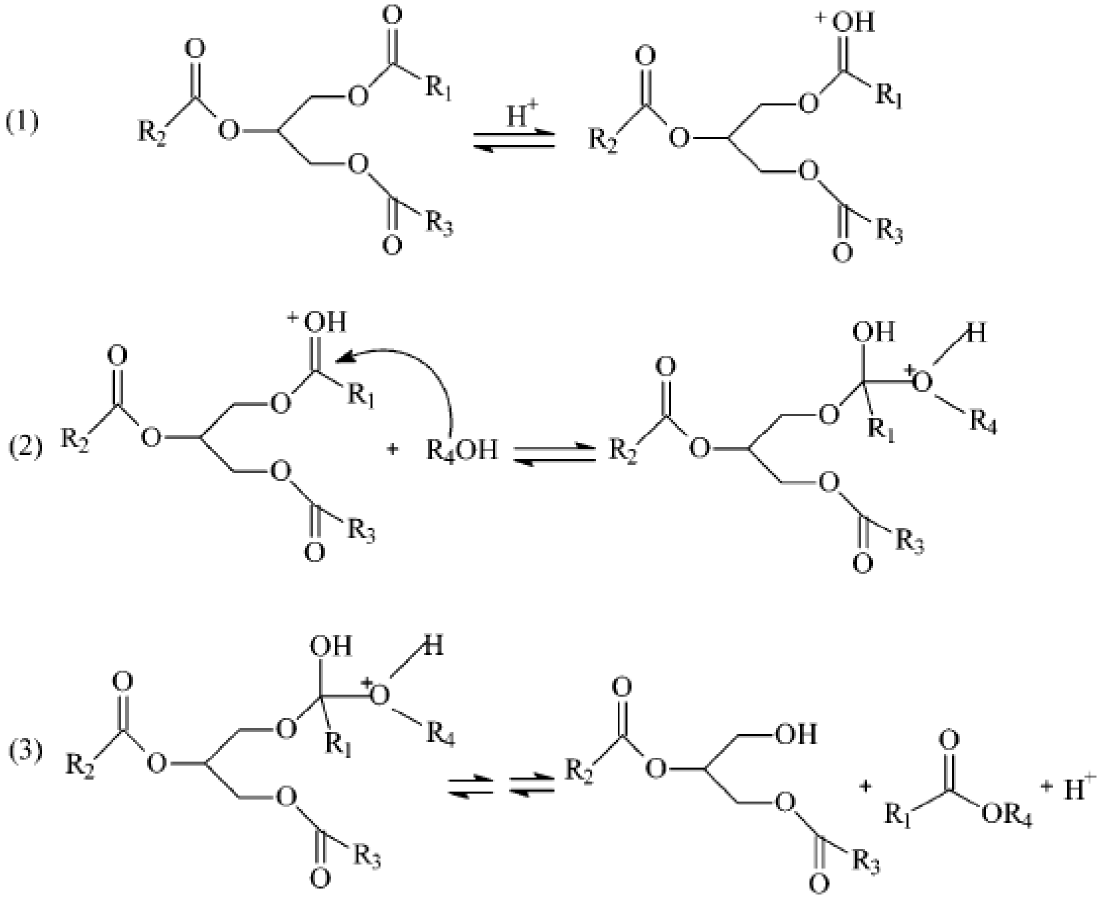
Figure 2.4 Heterogeneous catalytic reaction step.

The overall rate of reaction is equal to the rate of the slowest step in the mechanism. When the diffusion steps (steps 1, 2, 6 and 7) are very fast compared with the reaction steps (steps 3, 4 and 5), the concentrations in the immediate vicinity of the active sites are indistinguishable from those in the bulk fluid.

Type of catalyst is not only sort by phase of the catalyst, but we also sorted catalyst by acid or base catalyzed. Acid catalyzed transestrification gives very high yields in alkyl ester, but the rate of reaction is slow (around 5 to 20 hours to reach equilibrium). Sulfuric acid, phosphoric acid, sulfonic acid are commonly used. Acid catalyzed mechanism consist of three reaction steps to product biodiesel. Each steps of reaction can be explained as follows:

1. The first step: Acid catalyst protonate to carboxylic group of free fatty acid.
2. The second step: Nucleophilic attack of the alcohol, forming a tetrahedral intermediate.
3. The third step: Tetrahedral intermediate is cracked to ester, diglycerides and hydrogen proton. After that, diglycerides are protonate to carboxylic group in the first step over again and produce monoglyceride and glycerol, respectively.

Figure 2.5 shows the mechanism of an acid catalyzed transesterification process.



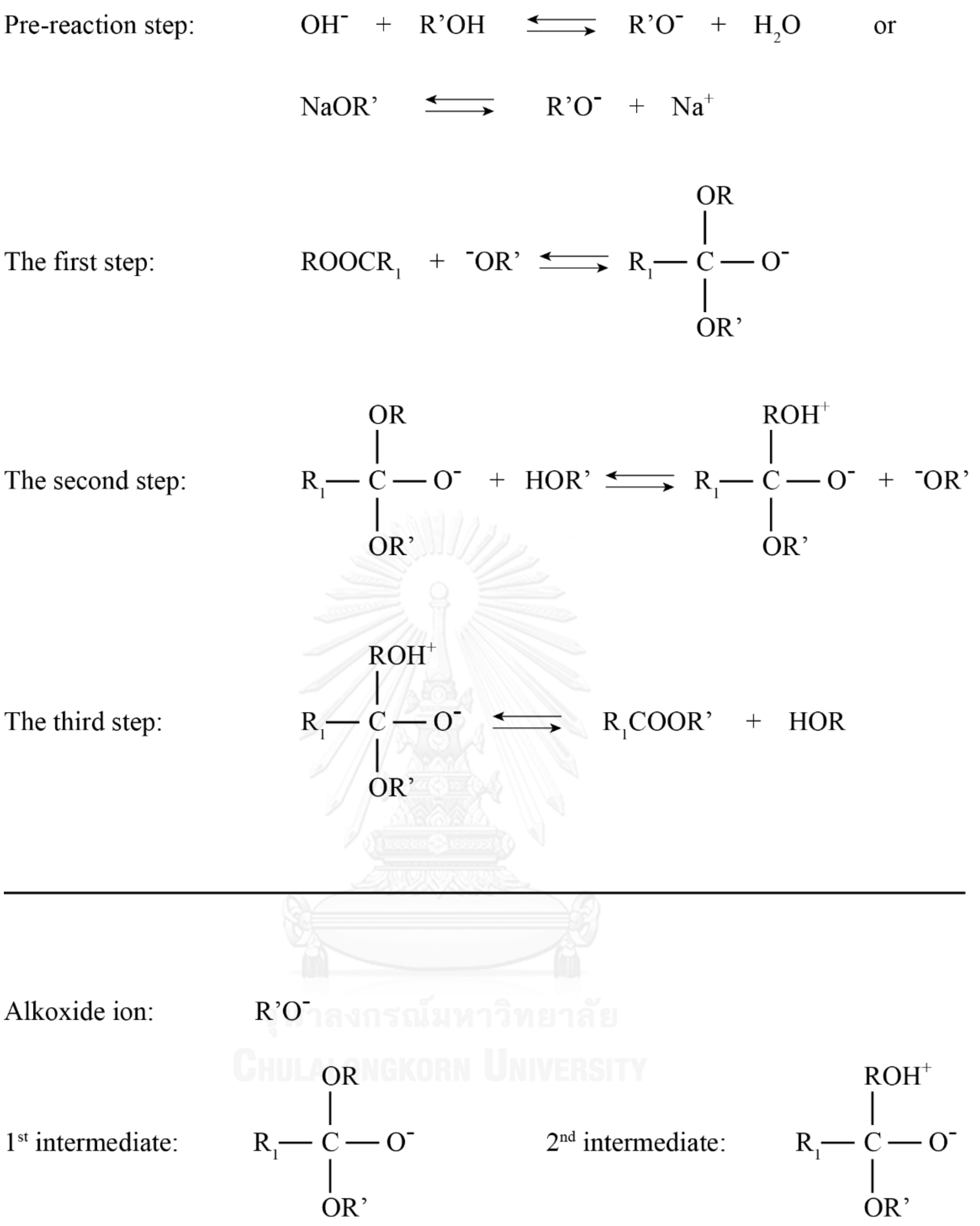
R_1, R_2, R_3: carbon chain of the fatty acids
R_4 : alkyl group of the alcohol

Figure 2.5 Acid catalyzed transesterification mechanism [20].

Base catalyzed transesterification gives faster rate of reaction (around 1 to 8 hours to reach equilibrium) and also less corrosive than acid catalyzed. Popular base catalysts such as sodium hydroxide, sodium methoxide, potassium amide, potassium hydride, calcium oxide, magnesium oxide. Base catalyzed mechanism consist of one pre-reaction step to produce alkoxide ion ($OC_nH_{2n}^-$) and three reaction steps to product biodiesel. Each steps of reaction can be explained as follows:

1. Pre-reaction step: The catalysts such as calcium oxide or sodium hydroxide are reacted with alcohol and produce alkoxide ion.
2. The first step: Alkoxide ion is reacted with triglycerides in oil and produce 1st intermediate agent.
3. The second step: 1st intermediate agent receive hydrogen atom from alcohol and then produce new alkoxide ion and 2nd intermediate agent.
4. The third step: 2nd intermediate agent is cracked to ester and diglycerides. After that, diglycerides are reacted with alkoxide ion in the first step over again and produce monoglyceride and glycerol, respectively.

Overall mechanism of base catalyzed process can be shown in Figure 2.6 and the mapping of catalyst for biodiesel production via transesterifization can be summarized as shown in Figure 2.7.



Pre-reaction step: $OH^- + R'OH \rightleftharpoons R'O^- + H_2O$ or

$NaOR' \rightleftharpoons R'O^- + Na^+$

The first step: $ROOCR_1 + {}^-OR' \rightleftharpoons R_1 - \underset{\displaystyle OR'}{\underset{|}{\overset{\displaystyle OR}{\overset{|}{C}}}} - O^-$

The second step: $R_1 - \underset{\displaystyle OR'}{\underset{|}{\overset{\displaystyle OR}{\overset{|}{C}}}} - O^- + HOR' \rightleftharpoons R_1 - \underset{\displaystyle OR'}{\underset{|}{\overset{\displaystyle ROH^+}{\overset{|}{C}}}} - O^- + {}^-OR'$

The third step: $R_1 - \underset{\displaystyle OR'}{\underset{|}{\overset{\displaystyle ROH^+}{\overset{|}{C}}}} - O^- \rightleftharpoons R_1COOR' + HOR$

Alkoxide ion: $R'O^-$

1st intermediate: $R_1 - \underset{\displaystyle OR'}{\underset{|}{\overset{\displaystyle OR}{\overset{|}{C}}}} - O^-$ 2nd intermediate: $R_1 - \underset{\displaystyle OR'}{\underset{|}{\overset{\displaystyle ROH^+}{\overset{|}{C}}}} - O^-$

Figure 2.6 Base catalyzed transesterification mechanism [21].

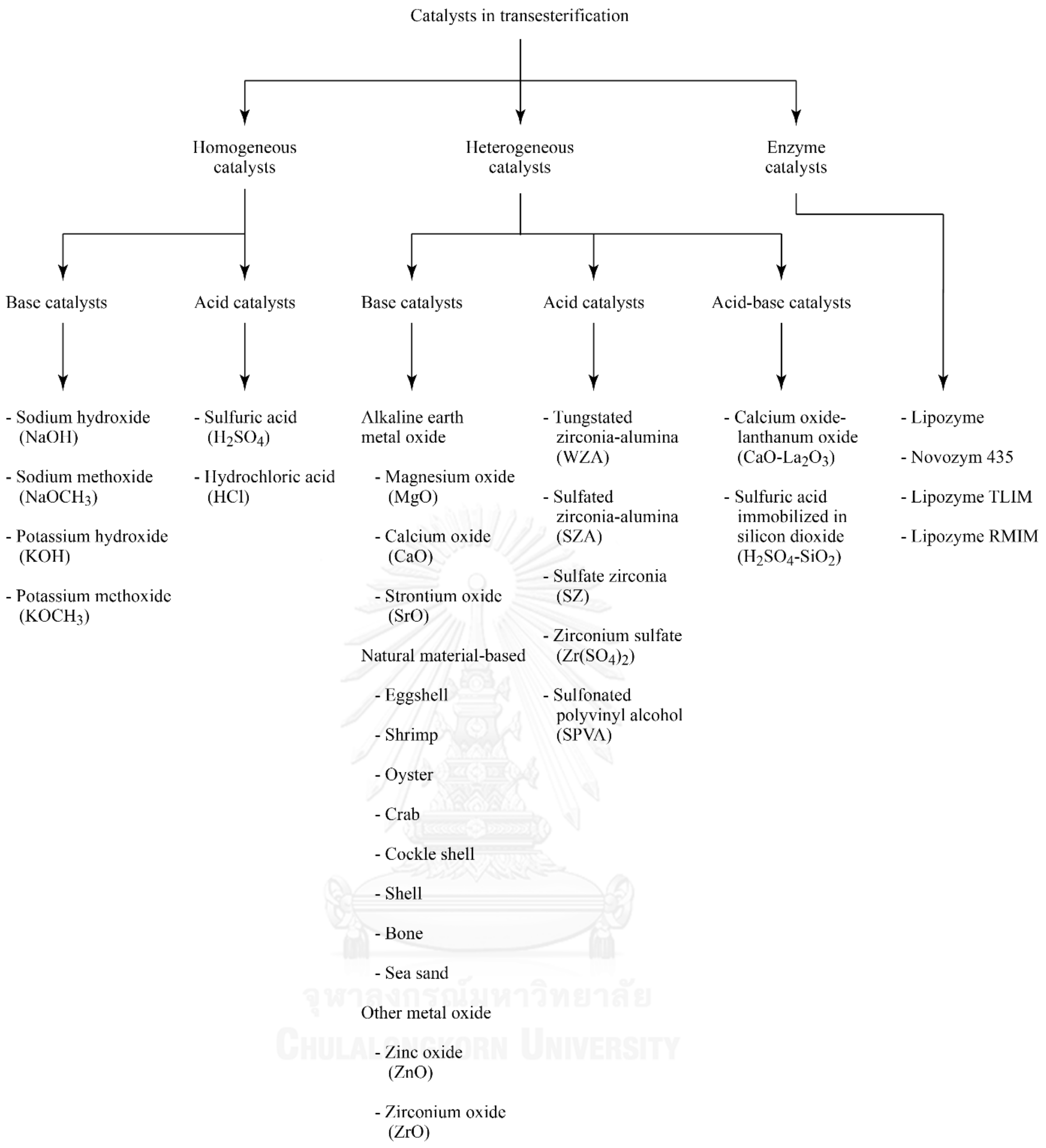


Figure 2.7 Catalysts in biodiesel production via transesterifization.

2.4 Biodiesel production process

There are many step in order to produce biodiesel in the commercialization as described below:

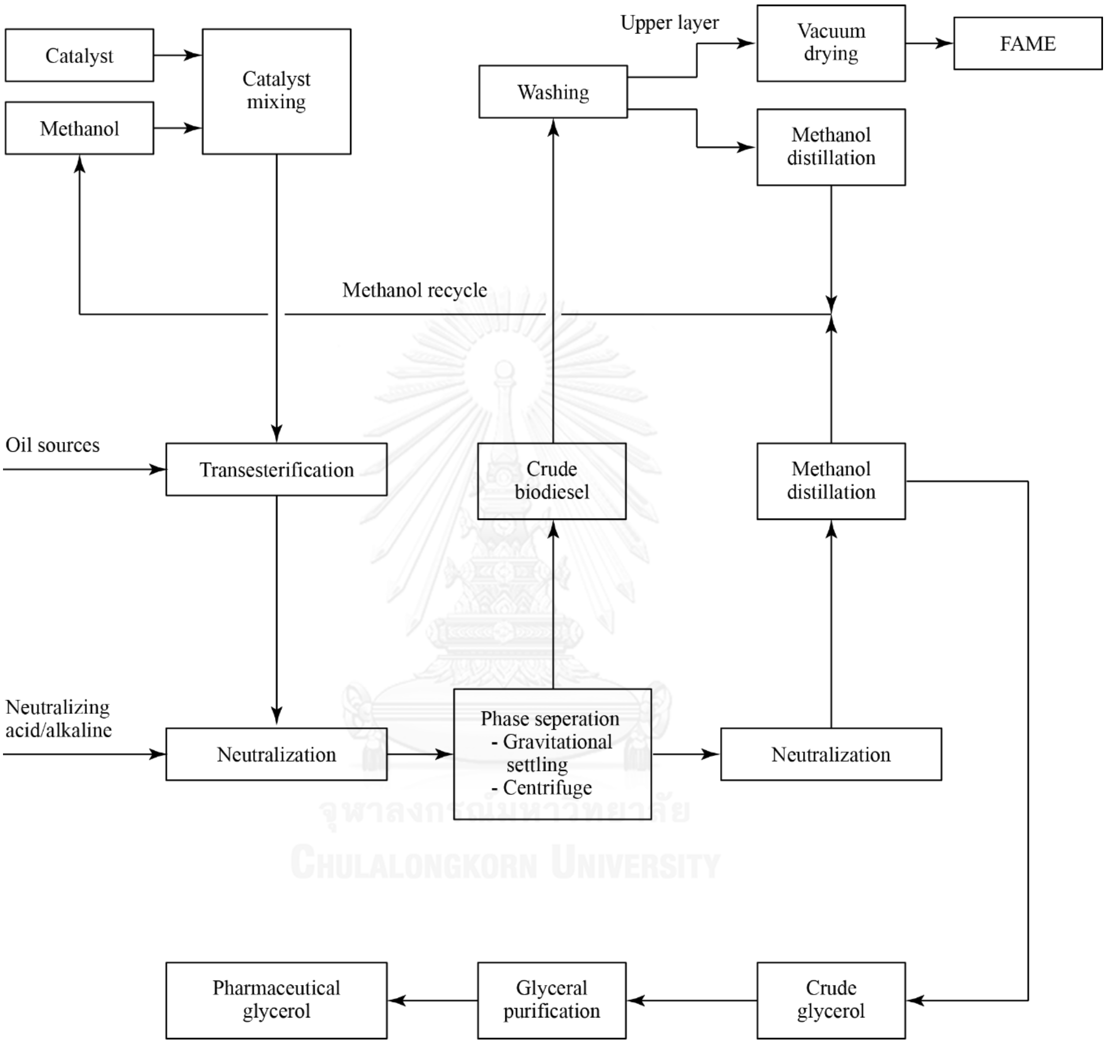


Figure 2.8 Process flow diagram of conventional homogeneous acid/alkaline-catalyzed transesterification reaction [22, 23].

Figure 2.8 shows the process flow diagram of conventional homogeneous acid/alkaline-catalyzed transesterification. The homogeneous catalyst is mixed with methanol before reacted with oil via transesterification. The neutralizing step is used to remove catalyst residue from reaction mixture. Then, it is fed to decanting unit to separate the polar and non-polar phase. The non-polar phase contains crude biodiesel with a few of methanol as impurity. Thus, addition of water is required to flush methanol out of the biodiesel product and dry biodiesel under vacuum before sent to product tank. The polar phase containing of methanol and glycerol has to be neutralized sodium hydroxide where dissolved in the polar phase by adding acid such as sulfuric acid or hydrochloric acid. After that, this mixture is sent to distillation column to separate recycle methanol and glycerol as byproduct. The glycerol will be purified to be valuable subtract for other process.

2.5 Ultrasonic process

2.5.1 Ultrasonic wave

Ultrasound is acoustic (sound) energy in the form of waves having a frequency above the human hearing range. It is approximately 20 kHz or higher as shown on Figure 2.9. It has been proven to be useful equipment for enhancing reaction rates in many reaction. Ultrasonic wave provides the mechanical energy for mixing and stimulates the reaction. One wave cycle consists of two sessions including of compression and rarefaction sessions. The number of switching session times is equivalent to the frequency of the wave.

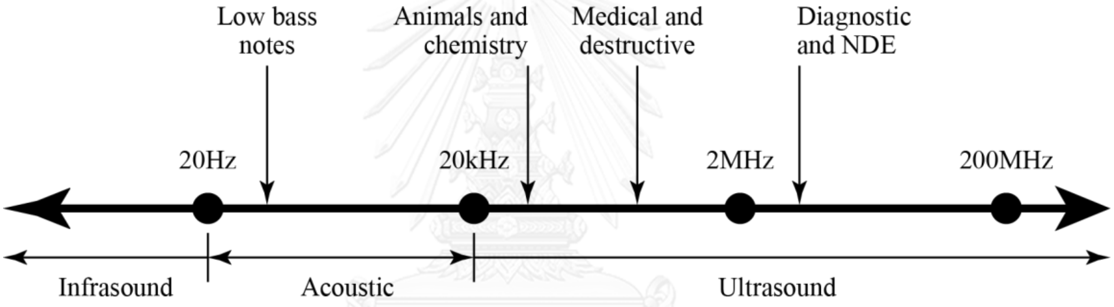


Figure 2.9 Approximate frequency ranges corresponding to ultrasound.

Ultrasound is a spectrum covering a wide frequency range using in a different frequency range for many application such as medical equipment, fishing, geology and engineering industries etc. Ultrasound in the frequency range of 1-20 MHz will be used in the medical field to diagnostic, physiotherapy and treatment of various diseases. In industrial field, ultrasonic has been used to measure the thickness of the pieces which are difficult to access without damaging the subject, such as checking the thickness of tires or metal sheet. For frequency range of 15-400 kHz has been used for plastic welding, cleaning equipment (ultrasonic bath), homogenizing the substances, checking the defect in the solid product and also useful to exploring the marine.

2.5.2 Acoustic cavitation phenomena

Ultrasonic wave enhances the cavitation phenomena by stimulate the formation of bubbles in the liquid phase. Figure 2.10 shows the bubbles are compressed and expanded continuously from the frequency and amplitude of the wave before reach the unstable and collapse. The collapse of bubbles causes shock waves and released energy with the temperature around 5,000°C and pressure around 1,000 atm.

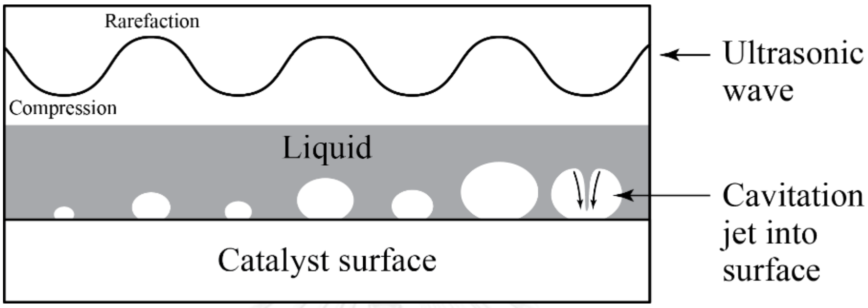


Figure 2.10 The bubble growth [24].

2.5.3 Type of ultrasonic reactor

Ultrasonic reactor is the unit that take advantage of the acoustic wave. It can divided into two types: direct ultrasonic reactor and indirect ultrasonic reactor. Figure 2.11 shows the direct and indirect ultrasonic reactor drawing

2.5.3.1 Direct ultrasonic reactor: The oscillated part of reactor will exposed to the substrate directly. This type has the highest energy transferred to substrate but oscillated part of reactor or horn may damage easily by corrosion or cavitation effect.

2.5.3.2 Indirect ultrasonic reactor: The oscillated part of reactor will not exposed to the substrate directly but the wave will transmitted through a liquid medium, solid phase or any other container before entering to the substance. Some of energy is loss from using this type, but the reactor can operate for longer and the oscillated part is not exposed to the substance. Therefore, it is not necessary to clean the oscillated part.

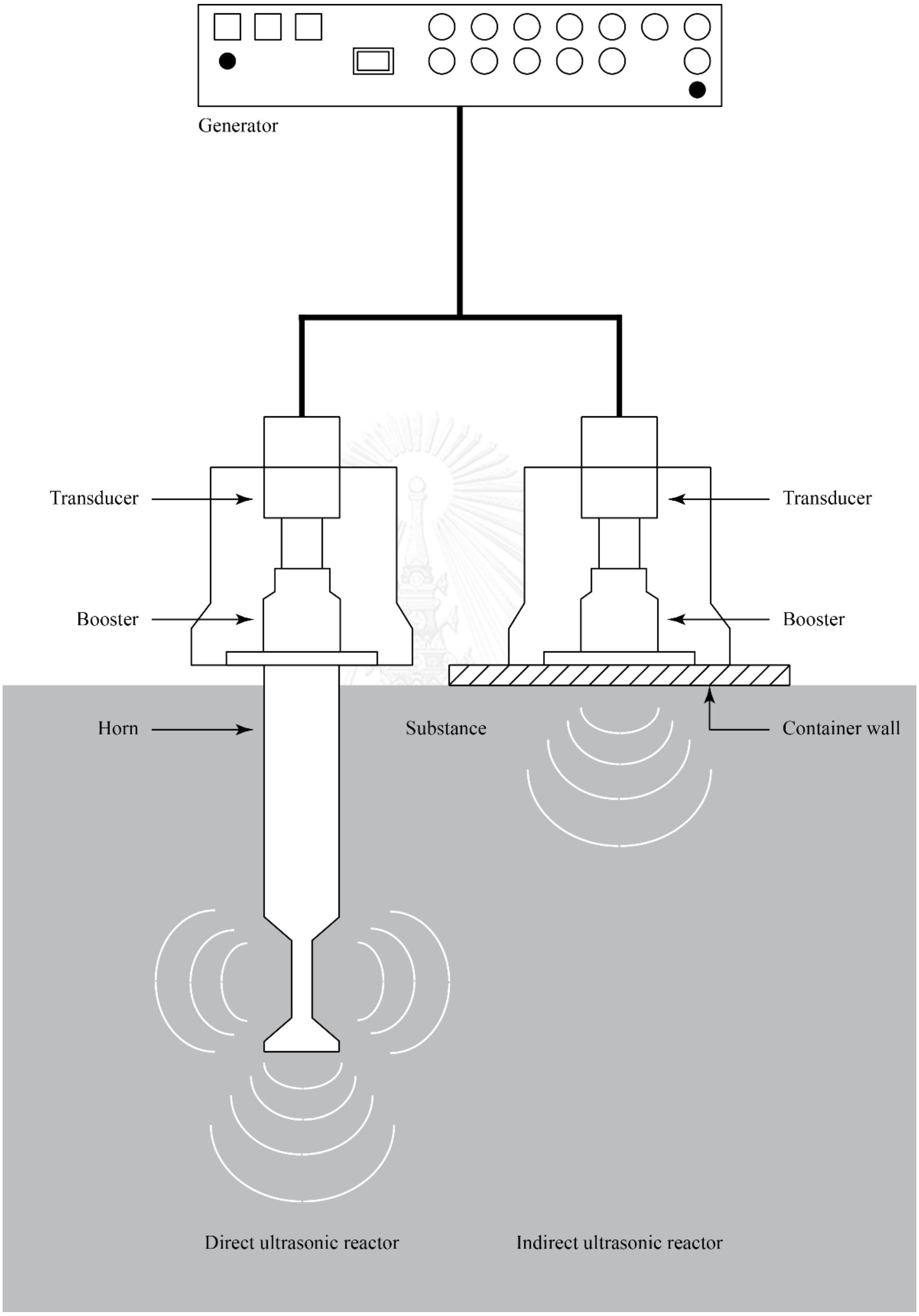


Figure 2.11 Direct and indirect ultrasonic probe drawing.

2.5.4 Ultrasonic reactor equipment

In general, ultrasonic equipment consists of three major equipment: generator, transducer and booster.

2.5.4.1 Generator

An ultrasonic generator transforms the frequency of the electrical energy from the power source into the desired ultrasonic frequency and energizes the transducers to oscillate at the same frequency. The common generator is designed to power a specific number of transducers, specific frequency and amplitude.

2.5.4.2 Transducer

The transducer oscillates at resonant frequency and induces amplified vibrations of the diaphragm when excited by electrical signal from generator. There are two main types of transducer: piezoelectric and magnetostrictive. Both types have the same task for converting the electrical energy to mechanical energy. Piezoelectric transducer uses piezoelectric crystals to stimulate vibration (Figure 2.12) while megnetostrictive transducer uses magnetic coil to stimulate vibration (Figure 2.13).

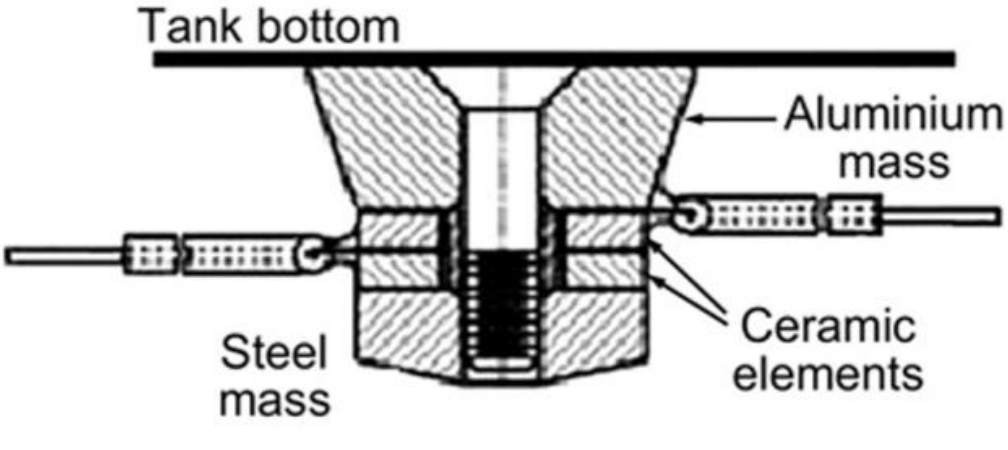


Figure 2.12 Piezoelectric transducer.
(Available online at http://www.blackstone-ney.com/04.TP_mag_vs piezo.php)

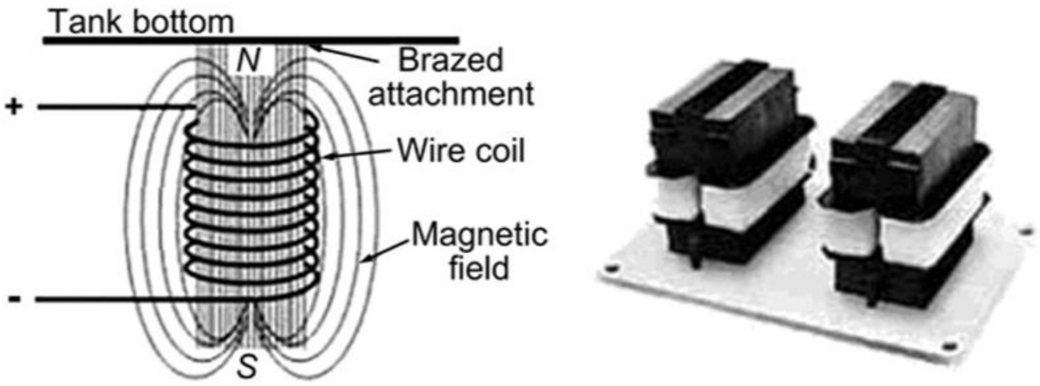


Figure 2.13 Magnetostrictive transducer.
(Available online at http://www.blackstone-ney.com/04.TP_mag_vs piezo.php)

2.5.4.3 Booster

The booster is a part of ultrasonic reactor that amplify the mechanical oscillation before transfer to the horn. This part is attached between the tip of the transducer and surface of container.

2.5.5 Ultrasonic factors

There are many variables involved in the ultrasonic process. All of the main factors to consider in the process affecting the chemical reactions.

2.5.5.1 Frequency: At the same ultrasonic power input, the high frequencies acoustic streaming makes a weaker cavitation effect than that of low frequencies. Figure 2.14 shows a plot of cavitation strength versus frequency. As the frequency of sonication increases rapidly, the cavitation strength decreases.

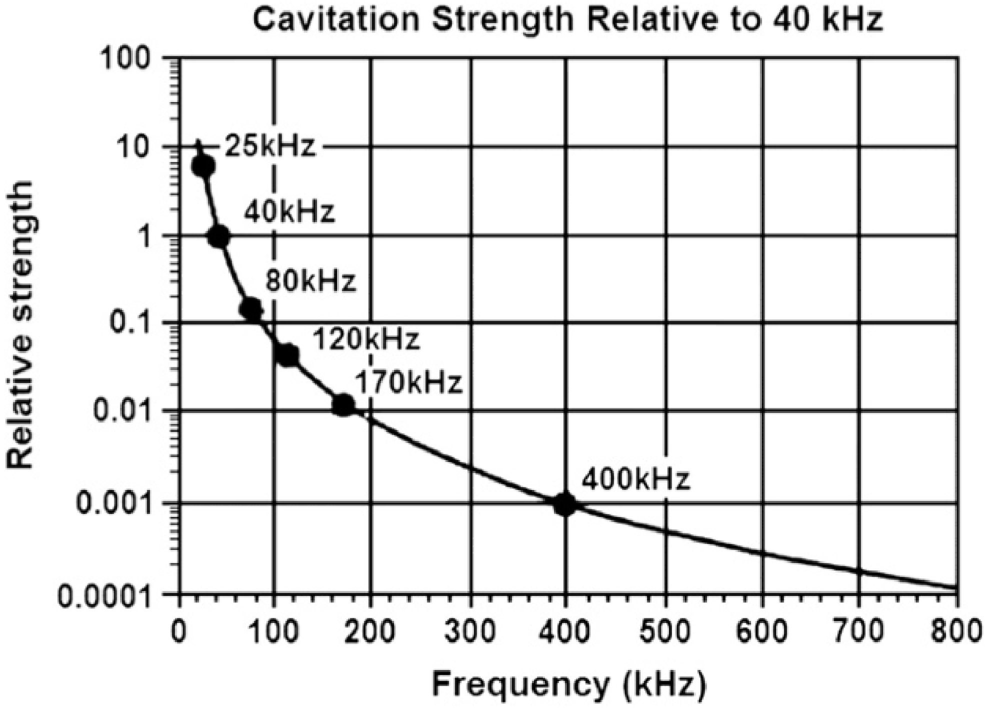


Figure 2.14 Cavitation strength as a function of frequency [25].

2.5.5.2 Intensity: Intensity is an energy transmitted through a cross sectional area per time. When the distance between ultrasonic sources are increased, the intensity will be decreased exponentially.

2.5.5.3 External pressure: External pressure is press the cavity in the liquid medium during the cycle of compression and rarefaction. The cavitation may not reach to unstable point and not collapse.

2.5.5.4 Vapor pressure of liquid medium: The liquid medium with high vapor pressure tends to reduce the violence of implosion because the bubbles are filled with medium vapor and absorb some of cavitation energy. As the higher vapor pressure, the violence of cavitation effect will be lower.

2.5.5.5 Temperature: Higher operating temperature will increase the vapor pressure of liquid medium which reduce the violence of cavitation.

2.5.5.6 Viscosity of liquid medium: As the higher of viscosity, the harder to generate cavitation because viscous medium has higher cohesive force between the molecules.

2.5.5.7 Dissolved gas in liquid medium: Dissolved gas help to nucleate the cavity. Monoatomic gases such as helium, argon with higher heat capacity will provide the greater effect than diatomic gases such as nitrogen, oxygen.

Chapter 3
Literature reviews

3.1 Conventional process and development for biodiesel production

The development of biodiesel production via transesterification was first started in 1853 by two scientists, Patrick and Duffy, using vegetable oil as a substrate. This study aims to produce glycerol for making soap, but the reaction provided biodiesel as byproduct too. Later, biodiesel has been used in diesel engines built by Rudolph Diesel in 1893, but by the property of biodiesel, especially the high viscosity of biodiesel oil, makes them unsuitable for practical implementation. Diesel engines need to use fossil fuels instead. Jimoh et al. [26] was referred Belgian Patent No. 422,877 in 1937 and reported that ethanol is a first type of alcohol for producing biodiesel.

The studies of biodiesel production aims to synthesis fuel with similar properties to petroleum-based diesel fuel. This continued development until being a pilot in South Africa in 1987 by using sunflower oil as subtract.

Because transesterification can be reversible, the primary concept was to drive the reaction forward by increase the amount of alcohol, according to the Le Chatelier’s principle. Consequently, it means that biodiesel production cost will also increased. Catalyst was used for biodiesel process to decrease the reaction time due to the catalyst plays role to accelerate chemical reactions rate and also decreases activation energy of reactions. By using homogeneous acid catalysts such as sulfuric acid [27], hydrochloric acid [28] and sulfonic acid [29] that can reduce the amount of alcohol used in the reaction, significantly. The disadvantage of homogeneous acid catalysts for transesterification of triglycerides are that it take the reaction a long time, high temperature reaction and corrosion of the equipment.

The homogeneous base catalysts such as sodium hydroxide or potassium hydroxide [30] can greatly reduce the reaction time, higher reaction rate, lower temperature and pressure (1% by weight sodium hydroxide at 60°C takes 2 hours to perform the 97.1% of oil conversion).

The disadvantage of homogeneous base catalysts is quite sensitive to impurities of feedstocks and may interact with the water present in the system to form a soap. A study by Vicente et al. [31] found that the soap affected on the methyl ester product which dissolved in glycerol making the complicated separation in the next step.

Leung et al. [32] compared three types of homogeneous catalysts such as, sodium hydroxide, potassium hydroxide and sodium methoxide. This study found that sodium methoxide is less sensitive to impurities than others, providing the same reaction rate and slightly higher rate than sodium hydroxide (0.75% by weight sodium hydroxide at 65°C takes 90 min to perform the 97% of oil conversion).

However, the drawback of using homogeneous either acid or base catalysts is the need of separation unit to remove the catalyst in the final step by using water and must have a neutralization step by the addition of base or acid. These addition process is making high biodiesel production cost and also causes water pollution and more waste salt Demirbas [33]. Karaosmanoglu et al. [34] have studied the amount of waste water occurred in a separation of catalyst and found to be approximately 10 L of water to produce 1 L of biodiesel. Tai-Shung [35] found that the cost of the separation process represents approximately 60-80% of the total production cost.

A heterogeneous catalyst has been developed to minimize problems of using homogeneous catalyst such as, corrosion of vessel and pipe line, reduce sensitivity of feedstock impurities in the system, catalyst reusability, contamination of catalyst in the final product and amount of waste water to purify them. However, this type of catalyst are also restrictions on the mass transfer limitation due to three phase of reaction including of polar liquid phase, non-polar liquid phase and solid phase of heterogeneous catalyst. The compound such as unreacted triglyceride, biodiesel or glycerol may be stuck on a surface of the catalyst and decrease the active sites of catalyst affecting on the rate of reaction.

A heterogeneous catalyst for biodiesel production can be divided into two groups, acid and base catalyst, such as zeolites, metal oxides, calcium oxide, potassium phosphate and so on. Calcium oxide is one of the catalysts that are suitable for biodiesel production because the reaction rate is relatively high and resistant to the various conditions such as the condition of ultrasonic reactor. Choedkiatsakul et al. [36] found that the 90% yield of biodiesel using calcium oxide loading of 3% by weight of oil to catalyzed transesterification of oil in an ultrasonic assist reactor, at 2 hours of reaction. This catalyst can be reused without any treatment for 3 cycle. Also, Kiss et al. [37] reported that a heterogeneous catalyst can use for biodiesel production while simultaneously separated product from the reaction mixture (reactive separation process) in a catalytic reactive distillation column.

However, calcium oxide has some drawback such as easy to reacts with water and carbon dioxide in the air to form a calcium hydroxide, therefore necessary to prevent this catalyst without air explosion. Calcium oxide is a small powder, resulting in the high pressure drop in a flow reactor. Thus, further studies are needed to develop for continuous process.

In addition, the homogeneous and heterogeneous catalysts as mentioned above, there have one more type of catalyst called biocatalyst. Biocatalyst is natural enzymes to digesting the oil to biodiesel. This biocatalysts are specific to reaction with the high rate of reactions. The experiment of Oda et al. [38] noted that the drawback of this type of catalytic is taking the longer reaction time (24 h to obtain 90% yield), and very specific to the conditions of the reaction. Dizge et al. [39], also stated that the catalyst biological is sensitive to impurities in the system and deteriorate easily

The transesterification can occur without a catalyst under supercritical of alcohol. This condition makes chemically homogeneous of oil and alcohol at high temperature and pressure. According to Tan et al. [40], identified the biodiesel production condition required a temperature over 239°C and pressure more than 8.1 MPa resulting the high amount of energy consumption. The main problems is the reactor design and vapor leaking of alcohol from system causing harmful to the workers respiratory.

3.2 Ultrasonic assisted reactor

The ultrasonic assisted reactor has been promised as one of the suitable technologies for the production of biodiesel. The research of Gogate et al. [41] shown that ultrasonic wave is induced cavity in the fluid with the repeated compression and expansion until reached the unstable state before collapse which generates the energy for mixing and stimulating the reactions. A mixing of immiscible is effective enhancing of mass transfer.

In addition from reducing restrictions on the exchange of material, there are many research results indicate that the use of ultrasonic assisted reactor increases the reaction rate in a shorter reaction time and also reduces the amount of catalyst and alcohol in the system.

The frequency of the ultrasonic wave and input power are usually in the range of 20-50 kHz and 10-1500 W, respectively. Hanh et al. [42] conducted experiments to confirm that the transesterification can occur at room temperature by using the ultrasonic assisted reactor at a frequency of 40 kHz with a power of 1,200 W provided the 95% of oil conversion in the 25 min of reaction time. This experiment showed the effective of biodiesel production, but if considered in terms of energy input to the system through ultrasonic assisted reactor is not economic because, the energy input to the system via ultrasonic irradiation is higher than the energy needed to raise the temperature of the substance directly at the same biodiesel production effective. This is more likely due to some energy for ultrasonic assisted reactor is transformed into other forms of energy such as heat, sound or absorb by a reactor material.

Not only homogeneous catalyst applied, but also heterogeneous catalyst can be applied for biodiesel production in an ultrasonic assisted reactor. Choedkiatsakul et al. [36] performed the experiment using a heterogeneous catalyst and found that the reaction rate is lower than the homogeneous catalyst. However, the catalyst can be reused several times (Biodiesel yield using calcium oxide catalyzed for 1st, 2nd and 3rd cycle without any treatment were 80%, 68% and 45.5%, respectively). Although, under ultrasonic irradiation, the cavitation effect is stimulate a glycerol to adsorb on the calcium oxide surface and generate the glyceroxides species (Ca-glycerol complex) as the alternative active site that promotes the transesterification. The deactivation of this catalyst was mainly from the adsorption of reaction mixture on the catalyst surface. Table 3.1 shows the research studies performance of ultrasonic assisted transesterification reaction for biodiesel production [43].

Table 3.1 Research studies of ultrasonic assisted transesterification reaction for biodiesel production.

Feedstock	**Catalyst (%wt)**	**Temperature (°C)**	**MeOH/Oil molar ratio**	**Time (min)**	**Frequency (kHz)/ Power (W)**	**Yield (%)**	**Reference**
Palm oil	2.8% BrO and SrO	65	9:1	50	20/200	95	[44]
Palm oil	3% CaO	65	15:1	60	20/200	77.3	[45]
Palm oil	3% BaO	65	15:1	60	20/200	95.2	[45]
Palm oil	3% SrO	65	15:1	60	20/200	95.2	[45]
Purified palm oil	3% CaO	65	6:1	60	40/160	80	[36]
Purified palm oil	3% K_3PO_4	65	6:1	60	40/160	70.85	[36]
Purified palm oil	3% Na/SiO_2	25	9:1	15	24/200	98.53	[46]
Purified palm oil	6% Immobilized Novozym 435	40	6:1	240	40/250	96	[47]
Rape seed oil	1% Nanosized Mg/Al oxide	45	4:1	90	-/210	95.2	[48]

Table 3.1 Research studies of ultrasonic assisted transesterification reaction for biodiesel production (continued).

Feedstock	**Catalyst (%wt)**	**Temperature (°C)**	**MeOH/Oil molar ratio**	**Time (min)**	**Frequency (kHz)/ Power (W)**	**Yield (%)**	**Reference**
Soybean oil	1.5% Ca-Mg-Al	60	4:1	30	20/200	94.3	[49]
Soybean oil	3% KF/CaO	65	12:1	60	40/-	99.6	[50]
Soybean oil	2% KF/ γAl_2O_3	65	12:1	60	(53.3 W/dm^3)	95	[50]

Chapter 4
Experimental

4.1 Materials

4.1.1 Reactants

Commercial refine palm oil “Morakot” brand was purchased form a local store in Thailand. Analytical grade (99.8% purity) methanol, the reactant of transesterification reaction, were provided by QRëC.

Mainly triglycerides in refine palm oil consist of tripalmitin, triolein, trilinolein and tristearin. Sort these triglycerides in order of their quantity, from most to least.

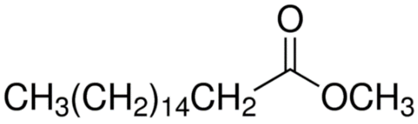
4.1.2 Catalysts

1) Homogeneous catalyst: High purity sodium hydroxide was provided by Loba Chemie and grinded to powder. The sodium hydroxide powder is easier to soluble in alcohol and faster reacted with alcohol to produce alkoxide ion.

2) Heterogeneous catalyst: 96% purity calcium oxide fine powder catalyst provided by Sigma-Aldrich was calcined in a muffle furnace with the heating rate 10°C per minute to 550°C, 700°C or 900°C and hold for 5 hour then kept in desiccator cabinet before use.

4.1.3 Analytical agents

Analytical standard ≥99% purity methyl heptadecanoate (Figure 4.1) and heptane were used as internal standard and solvent respectively for GC analysis are provided by Sigma-Aldrich.



$CH_3(CH_2)_{14}CH_2C(=O)OCH_3$

Figure 4.1 Methyl heptadecanoate molecular structure.
(Molecular weight = 284.48)

4.2 Experimental setup

Figure 4.2 shows overall process block diagram from start to finish. They are consist of three major parts: preparation, reaction and analysis.

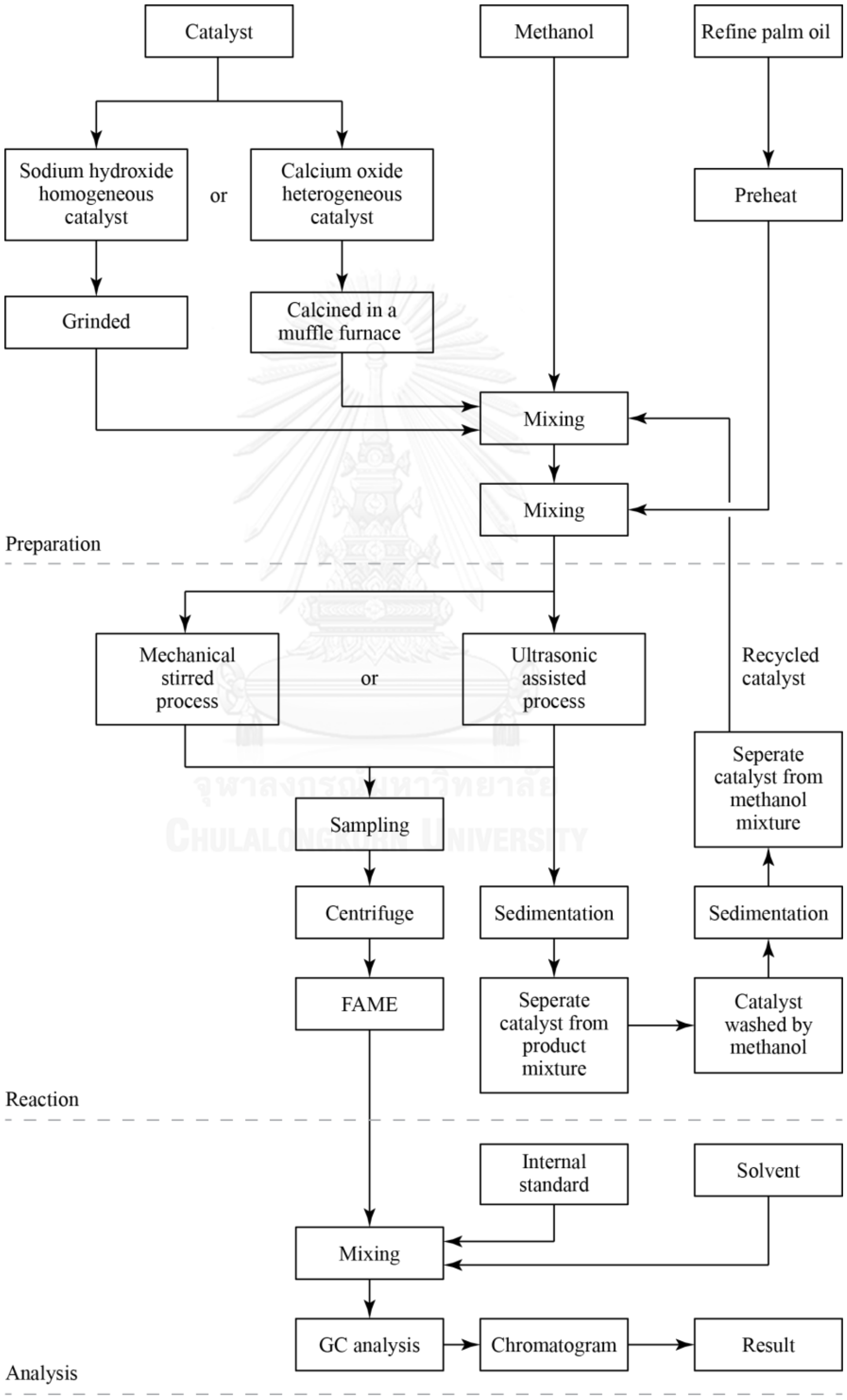


Figure 4.2 Overall process block diagram.

4.2.1 Mechanical stirred process

The schematic diagram of the mechanical stirred process used in this study is shown in Figure 4.3. Sodium hydroxide or calcium hydroxide was mixed with methanol at room temperature before mixed with preheated oil. 125 mL 3-neck round bottom flask immersed into water bath was used to preheat and control temperature of oil and methanol solution at 60°C. The 3-neck round bottom flask was equipped with a condenser circulated with normal temperature water. Magnetic stirrer has been used for mixing with stirrer speed of 800 rpm. The product sample was taken out via sampling valve. Then, it was centrifuged at 3000 rpm for 10 min to sediment solid catalyst, glycerol and biodiesel before analyzed by gas chromatograph (GC).

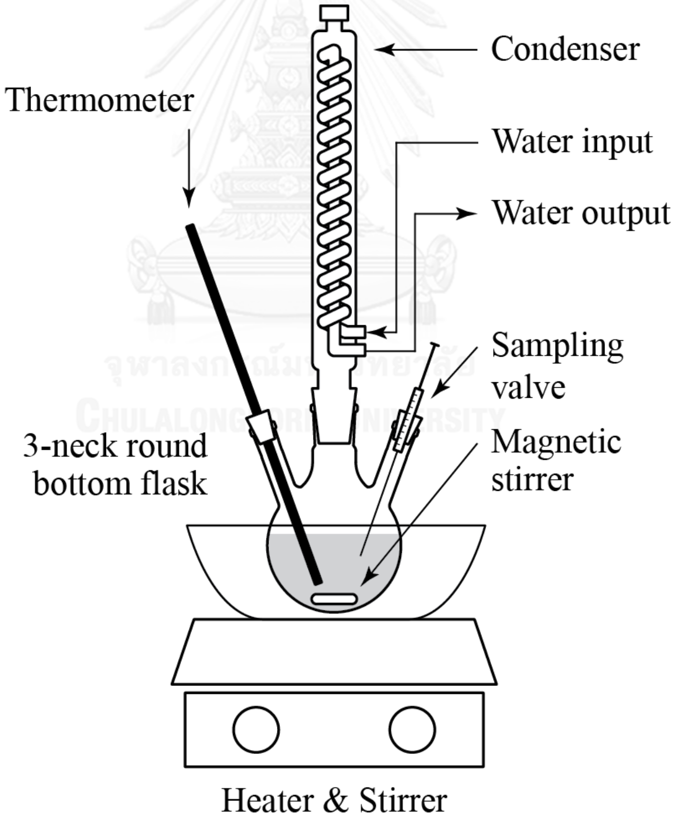


Figure 4.3 The schematic diagram of the mechanical stirred process.

4.2.2 Ultrasonic process

The schematic diagram of the ultrasonic process used in this study is shown in Figure 4.4. 500 mL Erlenmeyer flask was used to preheat and maintain temperature of oil and methanol at 60°C. Magnetic stirrer has been used in the early-stage of mixing (pretreatment tank) before fed to the reactor by peristaltic pump with the optimum feed flow rate of 55 mL/min through 6 mm diameter of silicone tube. The heterogeneous catalyst was packed into the basket placed inside the rectangular shape reactor. Three catalyst baskets were held by a horizontal axial and allow to spin by axial screw along reactor length with speed of 25 rpm. The wall outside of the reactor was attached by 16 transducers (4 each per side, two different frequency 20 kHz and 50 kHz) with total power of 800 W. The substances were introduced from the bottom to the top of reactor before circulated into flask. The sample was taken out via sampling valve. Then, it was centrifuged at 3000 rpm for 10 min to sediment solid catalyst, glycerol and biodiesel before analyzed by gas chromatograph (GC).

The actual equipment photos of the ultrasonic process shown in Figure 4.5. Each tag number can be explained as follows:

1. Ultrasonic generator main power
2. Front and rear temperature monitor
3. Voltage power
4. Frequency selector
5. Pump chamber
6. Pump speed monitor
7. Pump speed
8. Spin direction
9. Inlet port
10. Outlet port
11. Sampling port
12. Axial screw motor
13. Transducers
14. Reactor wall
15. Fan

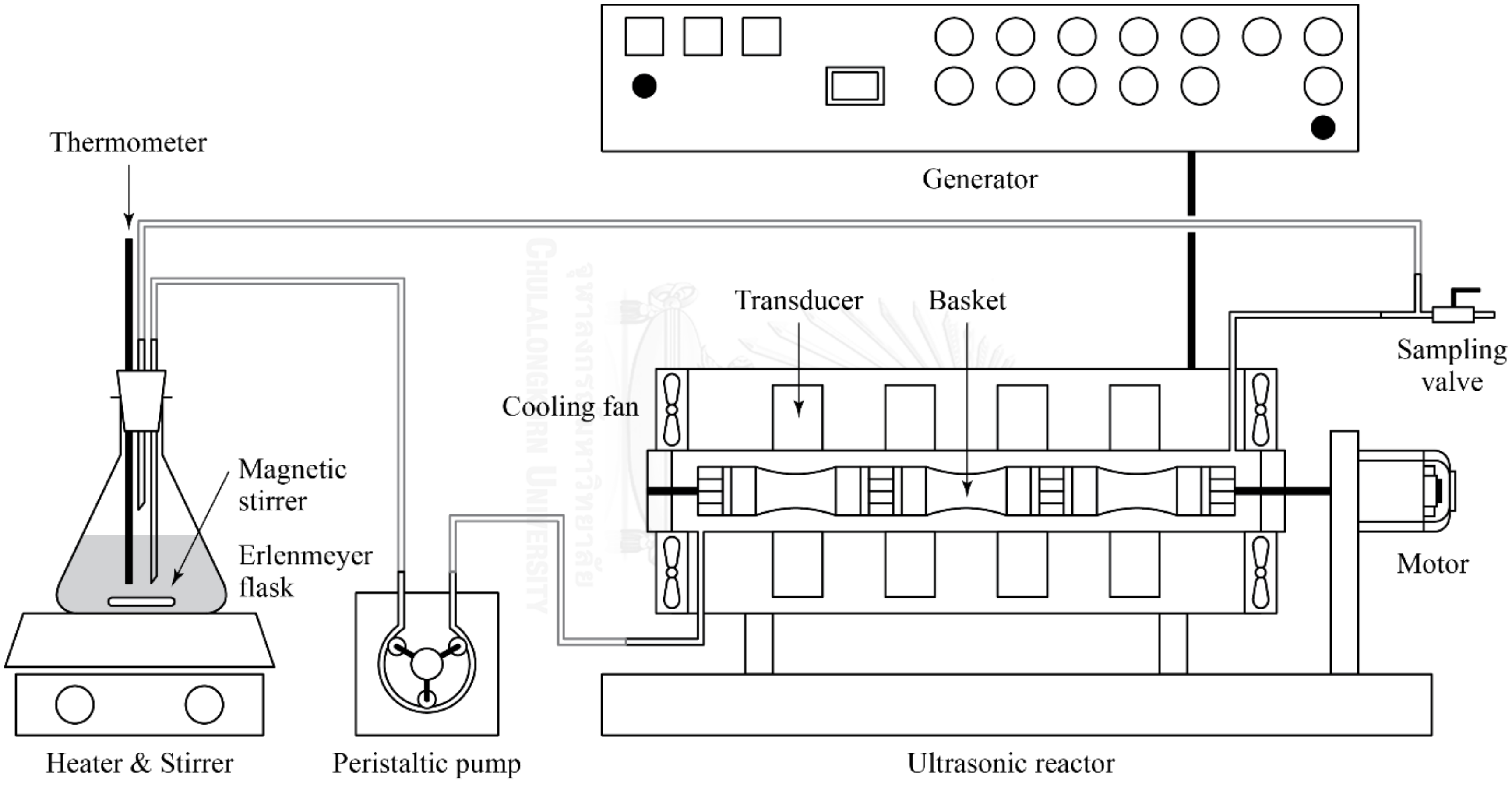


Figure 4.4 The schematic diagram of the ultrasonic process.

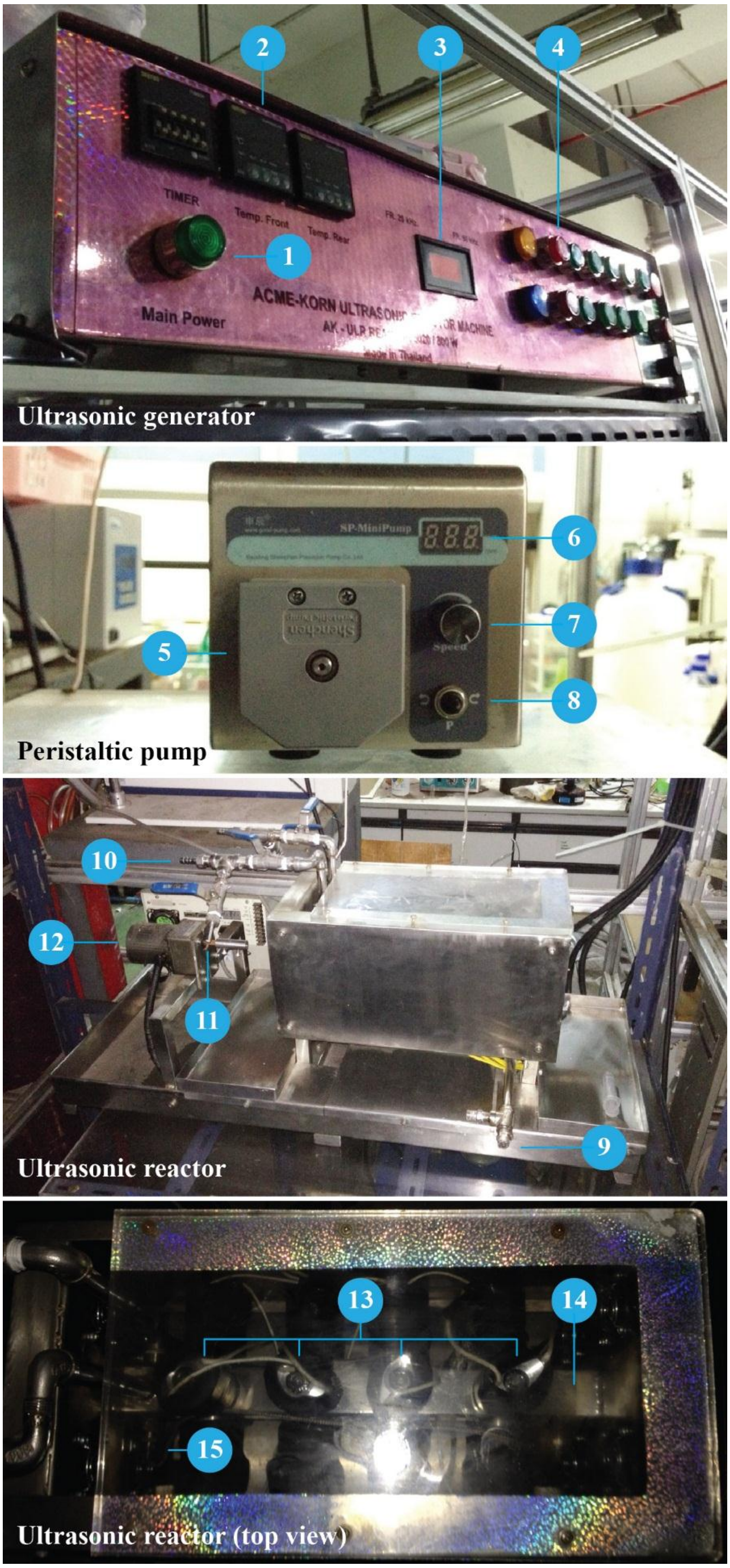


Figure 4.5 Actual equipment photos of the ultrasonic process.

4.2.3 Washing process

Washing process is an additional process for catalyst recycle. Firstly, the resulting mixture was drain out from reactor to Erlenmeyer flask and sealed to prevent a contamination. The resulting mixture was left steadily for sedimentation or centrifuge. A reactor was clean up with methanol before used again.

The resulting mixture was separated to three phase. The first one on top was biodiesel, the second layer was calcium oxide suspended in biodiesel and the bottom layer was glycerol.

Biodiesel and glycerol were sucked out from the container. After that, the remaining calcium oxide catalyst was mixed with fresh methanol and stirred by magnetic bar at room temperature.

Suspended calcium oxide in methanol was separated by centrifuge. Then, methanol was sucked out from the container. Finally, washed calcium oxide catalyst was ready to reuse for the next cycle.

4.3 Biodiesel analysis

The biodiesel yield were analyzed following EN14103 standard using Shimadzu GC-2010 Plus, with DB-WAX capillary column and detected by flame ionization detector (FID). Helium and nitrogen were used as carrier gas and makeup gas. The gas chromatograph with flame ionization detector machine is shown in Figure 4.6. The oven temperature ramp profile is shown in Figure 4.7 and biodiesel yield was calculated by Equation (4.1)

$$Biodiesel\ yield\ (\%) = \frac{(\sum A) - A_{IS}}{A_{IS}} \times \frac{C_{IS} \times V_{IS}}{m_S} \times 100\% \tag{4.1}$$

where		
	$\sum A$	Total area of 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)

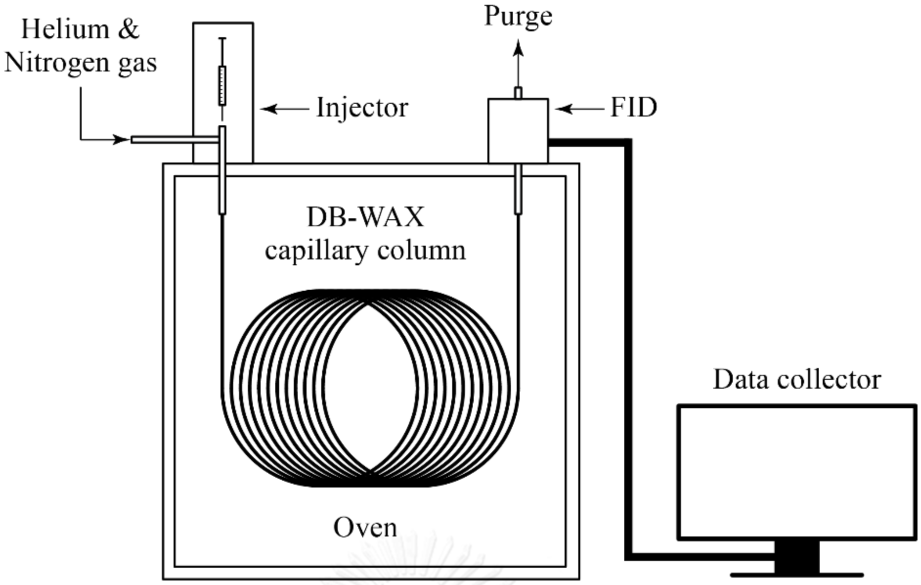


Figure 4.6 Gas chromatograph with flame ionization detector machine.

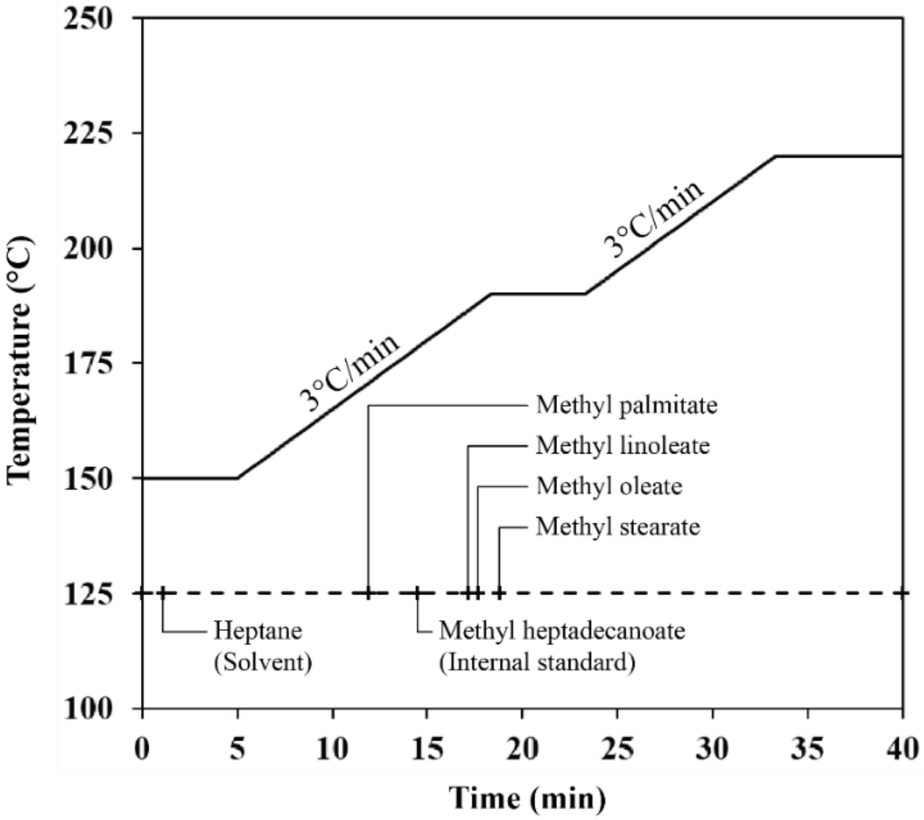


Figure 4.7 Oven temperature ramp profile and substrates peak position.

Chapter 5

Results and discussion

This chapter provides results and discussion of "Ultrasonic reactor for biodiesel production from purified palm oil on calcium oxide heterogeneous catalyst". The variable parameters including of type of catalyst, calcination temperature of catalyst, catalyst loading, mixing type of reactors, ultrasonic frequency and catalyst stability were studied. We had designed the experiments to conduct these parameters. The main experiments in this work can be summarized in Table 5.1. All of experiments were operated at 60°C, 1 atm, methanol to oil molar ratio of 9:1 in an ultrasound assisted reactor and stirred mixing reactor.

Table 5.1 Set-up experiments in this work.

Exp. No.	Catalyst type	Calcine condition (°C)	Catalyst loading (%wt)	Reactor type	US power (Watt)/ frequency (kHz)	Recycle (times)
1	NaOH	-	2%	US	800/20 & 50	-
2	CaO	550	2%	US	800/20 & 50	-
3	CaO	700	2%	US	800/20 & 50	-
4	CaO	900	2%	US	800/20 & 50	-
5	CaO	900	1%	US	800/20 & 50	-
6	CaO	900	3%	US	800/20 & 50	1
7	CaO	900	3%	US	800/20 & 50	2
8	CaO	900	3%	US	800/20 & 50	3
9	CaO	550	2%	MS	-	-
10	CaO	900	2%	US	0/-	-
11	CaO	900	2%	US	400/20	-
12	CaO	900	2%	US	400/50	-
13	CaO	900	2%	US	400/20 & 50	-
14	CaO	900	10%	MS	-	-

The discussion in this chapter can be divided to 9 topics as follows:

5.1 Relation of free fatty acids (FFAs) composition in oil and methyl ester composition in biodiesel
5.2 Effect of catalyst types on biodiesel yield
5.3 Effect of reaction time on biodiesel yield
5.4 Effect of calcination temperature of catalyst on biodiesel yield
5.5 Effect of catalyst loading on biodiesel yield
5.6 Effect of mixing types of reactor on biodiesel yield
5.7 Effect of ultrasonic operating parameters on biodiesel yield
5.8 Catalyst stability

The experiments that related to above topic can be summarized in Table 5.2

Table 5.2 Set-up experiments related to discussion topics.

Topic number	Topic name	Related experiment
5.1	Relation of free fatty acids (FFAs) composition in oil and methyl ester composition in biodiesel	4
5.2	Effect of catalyst types on biodiesel yield	1, 4
5.3	Effect of reaction time on biodiesel yield	1, 2, 4, 9
5.4	Effect of calcination temperature of catalyst on biodiesel yield	2, 3, 4
5.5	Effect of catalyst loading on biodiesel yield	4, 5, 6, 14
5.6	Effect of mixing type of reactor on biodiesel yield	2, 9
5.7	Effect of ultrasonic operating parameters on biodiesel yield	4, 10, 11, 12, 13
5.8	Catalyst stability	6, 7, 8

5.1 Relation of free fatty acids (FFAs) composition in oil and methyl ester composition in biodiesel

The composition of refine palm oil is commonly including of 4 main fatty acids as palmitic, linoleic, oleic, stearic acid that react with a methanol in the presence of a catalyst to produce FAME namely: methyl palmitate, methyl linoleate, methyl oleate and methyl stearate, respectively. Mass fraction based on area under peak from GC analysis of fatty acid methyl esters in this work were corresponding to mass fraction of fatty acids is shown in Table 5.3.

Table 5.3 Composition of fatty acid and FAME from palm oil [10].

Fatty acid	**MW (g/mol)**	**Palm oil composition (%)**
Palmitic acid	256.4	41.85
Linoleic acid	280.4	3.69
Oleic acid	282.5	46.36
Stearic acid	284.5	8.10
Average MW	271.7	
FAME (This work)	**MW (g/mol)**	**Area from GC analysis (%)**
Methyl palmitate	270.5	38.23
Methyl linoleate	294.5	3.97
Methyl oleate	296.5	44.92
Methyl stearate	298.5	12.87
Average MW	286.7	

5.2 Effect of catalyst types on biodiesel yield

The catalysts used in the transesterification are mainly divided into two types including of homogeneous and heterogeneous catalysts. In this work, sodium hydroxide (NaOH) has been used for homogeneous catalyst. Sodium hydroxide was grounded and dissolved in methanol before use. Calcium oxide (CaO) has been used for heterogeneous catalyst. Calcium oxide was calcined at the desired calcination temperature in a muffle furnace before used. There are base catalysts. Transesterification was operated at 60°C, 1 atm, methanol to oil molar ratio of 9:1 and 2%wt of catalyst loading with different catalyst type.

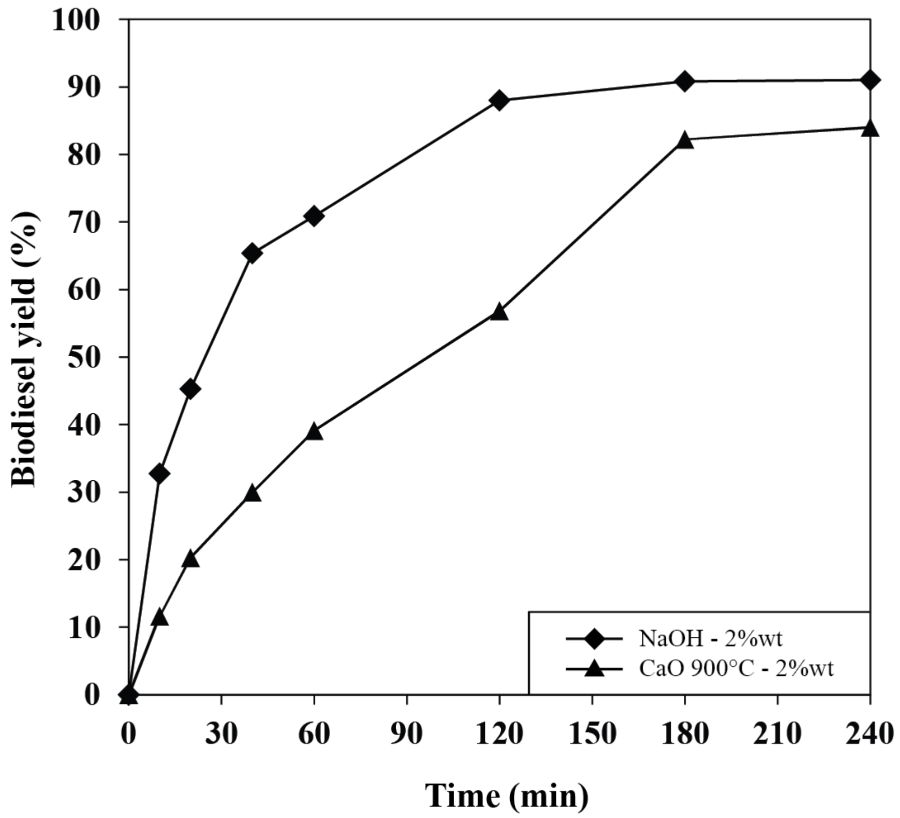


Figure 5.1 Effect of catalyst types on biodiesel yield: Sodium hydroxide homogeneous catalyst and calcium oxide heterogeneous catalyst.

Table 5.4 Related phase and polarity of reaction mixture in this process.

Phase	Polarity	Substrates	Product	Catalyst
Liquid phase	Non-polar	Palm oil	Biodiesel	NaOH
	Polar	Methanol	Glycerol	NaOH
Solid phase	-	-	-	CaO

Figure 5.1 shows that rate of homogeneous sodium hydroxide catalyzed transesterification is greater than that of heterogeneous calcium oxide catalyst because homogeneous catalyst such as sodium hydroxide has none obstacle between active site of catalyst and substrates phase. On the other hand, heterogeneous catalyst such as calcium oxide has a mass transfer limitation due to the existing of three different phases as shown in Table 5.4 and rate of reaction of heterogeneous catalyzed transesterification is controlled under catalytic reaction. Each steps of catalytic reaction can be explained as follows [19]:

1. Mass transfer (diffusion) of the reactants from the bulk fluid to the external surface of the catalyst pellet.
2. Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface.
3. Adsorption of reactants onto the catalyst surface.
4. Reaction on the surface of the catalyst.
5. Desorption of the products from the catalyst surface.
6. Diffusion of the products from the interior of the pellet to the pore mouth at the external surface.
7. Mass transfer of the products from the external pellet surface to the bulk fluid.

Therefore, the rate of mass transfer between reactant or product and catalyst surface is slower than that of surface reaction which indicated by induction period of calcium oxide catalyzed transesterification of palm oil. After that, the biodiesel yield increases steadily until reach the reaction equilibrium. Furthermore, homogeneous catalyst (sodium hydroxide) has more basic sites (all sodium hydroxide species were active sites) than that of calcium oxide. According that, the catalytic activity of calcium oxide catalyzed transesterification of palm oil was lower than that of sodium hydroxide when using similar catalyst loading on weight basis.

Regardless, sodium hydroxide catalyst has higher rate of reactions than calcium oxide, but it also has some drawback as follows:

(1) Heat of reaction dissolution of solid sodium hydroxide in methanol is a highly exothermic reaction in which a large amount of heat is liberated. The molar heat of solution of sodium hydroxide is -44.51 kJ/mol [51]. In this work, the solution of sodium hydroxide and methanol was self-heated from room temperature (30°C) to 85°C. This temperature is over boiling point of methanol, then some of methanol was vaporized off the pre-heat tank. Thus, the heat of reaction may require a cooling system or redesign process that compatibly with heat duty and safely.

(2) At highly sodium hydroxide catalyst loading may produce a lot of water in the system. Water is an undesirable product, which can be contaminate polar substrate such as glycerol. The reaction between sodium hydroxide and methanol is expressed in Equation (5.1). Sodium hydroxide also reacted with triglyceride via sponification reaction and produced soap (Equation 5.2). Soap was defined as impurity and may cause many problem to the equipment and overall process.

$$NaOH + CH_3OH \rightarrow CH_3ONa + H_2O \tag{5.1}$$

$$R'COOH + NaOH \rightarrow R'COONa + H_2O \tag{5.2}$$

(3) Sodium hydroxide is one of the strong base which may be damage the equipment or swelling rubber seal ring. After long term of operation, we found that the polyurethane tube and seal ring were also damage and brittle at operating temperature. To solve this problem, we have changed the higher resistance material as the silicone tube and neoprene seal ring.

(4) To purify product (biodiesel) and byproduct (glycerol), large amount of water was used for washing process and generate a lot of waste water. In this work, double amount of water (by volume) was used to wash biodiesel for 3 times until the biodiesel quality was conform to the ASTM 6751

(5) Sodium hydroxide in methanol solution has a threat to safety through the possibility of splashing. The solution is usually colorless and odorless with slippery feeling upon contact.

All of the above problems are observed during the laboratory scale experiment. Thus, we have to reconsider process and catalyst to prevent these problem for a larger scale as a recommendation in Chapter 6.

5.3 Effect of reaction time on biodiesel yield

In this study, transesterification was operated at 60°C, 1 atm, methanol to oil molar ratio of 9:1 and 2%wt of catalyst loading. Calcium oxide was calcined at 900°C for 5 hours. Biodiesel or fatty acid methyl ester (FAME) yield increases along reaction time as chromatogram shown in Figure 5.2.

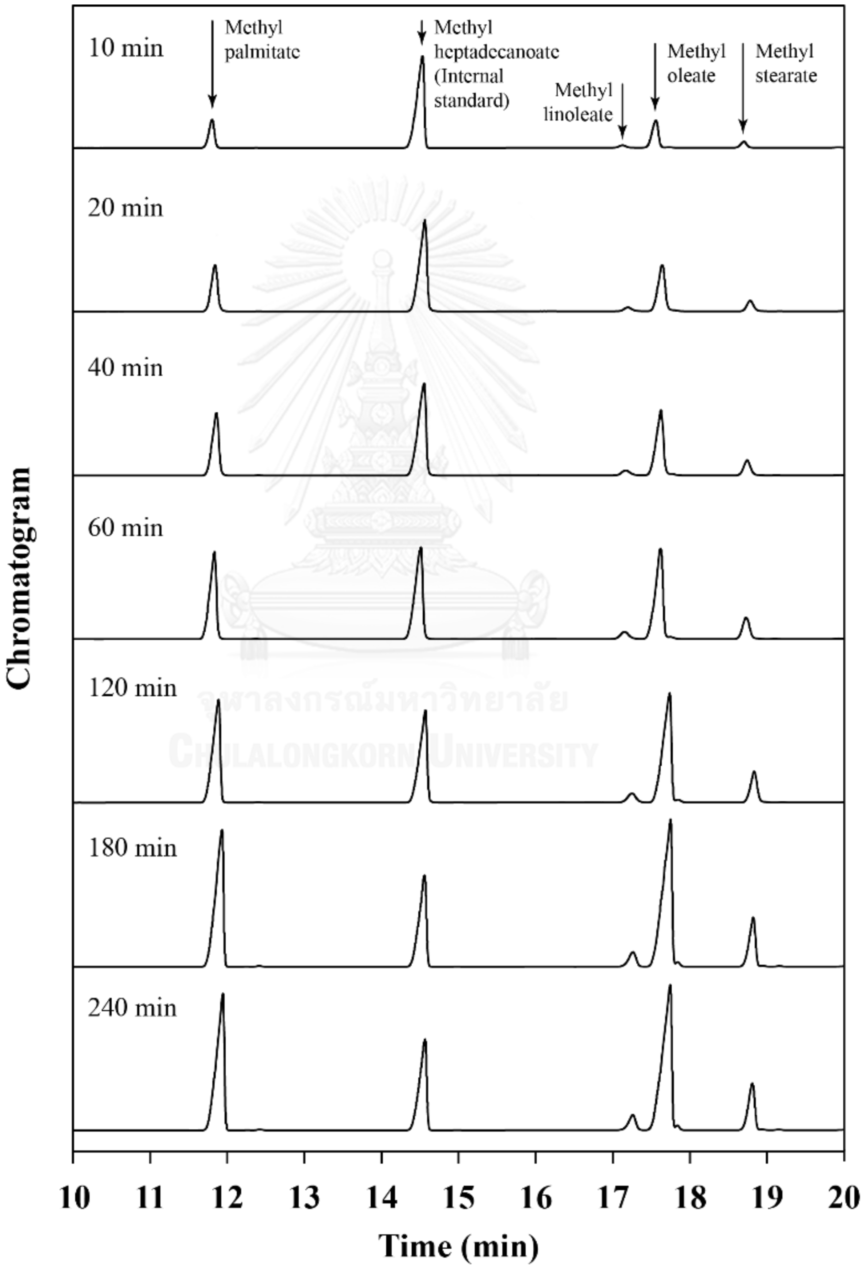


Figure 5.2 Chromatogram and peak position of FAME for calcium oxide calcined at 900°C for 5 hours under ultrasound irradiation.

The longer reaction time is leading to higher biodiesel yield. However, it can be noticed that an induction period was observed for calcium oxide catalyst which is a significant difference due to mixing type of reactors (Figure 5.3). Using mechanical stirred (MS) reactor, the induction period was presented a much longer than that of ultrasonic (US) reactor (180 min and 40 min for calcium oxide calcined at 550°C, respectively) but the induction period did not observed for homogeneous catalyzed transesterification due to no obstacle between the active site of catalyst and liquid phase. In the beginning, the reaction under mechanical stirring is slow due to the mixing and the dispersion of methanol into oil and catalyst opposed to ultrasonic process that increase the mixing rate with increase contact area between methanol and oil.

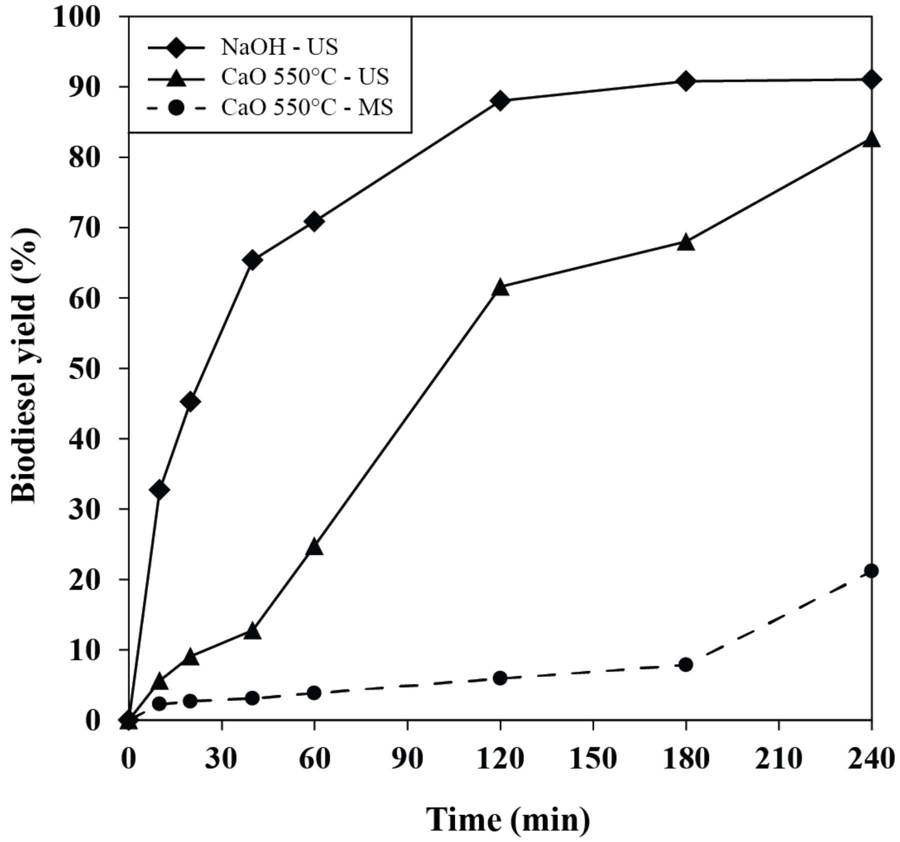


Figure 5.3 Homogeneous and heterogeneous catalyzed transesterification of palm oil using ultrasonic reactor (US) and mechanical stirred (MS) reactor.

The evaluation of biodiesel yield versus reaction can propose the suitable operating time or the time that reaction reach the equilibrium. In this study, the suitable operating time for homogeneous catalyzed transesterification can be summarized in Table 5.5

Table 5.5 Suitable operating time for each experiments.

Experiment number	Suitable operating time	Experiment number	Suitable operating time
1	120 min	8	240 min
2	240 min	9	Data out of range
3	240 min	10	Data out of range
4	180 min	11	Data out of range
5	240 min	12	Data out of range
6	120 min	13	Data out of range
7	180 min	14	120 min

For reversible reaction, the excessive reaction time may cause reaction reversed. Thus, reaction yield may decrease after reach the maximum equilibrium. Sheng-Ho et al. [52] reported that biodiesel produced from refined palm oil and crude palm oil under ultrasonic irradiation have been reach the maximum yield at 84.72% and 73.23% at 30 min and decrease to 75.93% and 64.49% yield for 60 min, respectively.

5.4 Effect of calcination temperature of catalyst on biodiesel yield

In this study, transesterification was operated at 60°C, 1 atm and methanol to oil molar ratio of 9:1, Calcium oxide was calcined at 550°C, 700°C and 900°C for 5 hours before loaded to the reaction for 2% by weight based on oil. The biodiesel yield is shown in Figure 5.4.

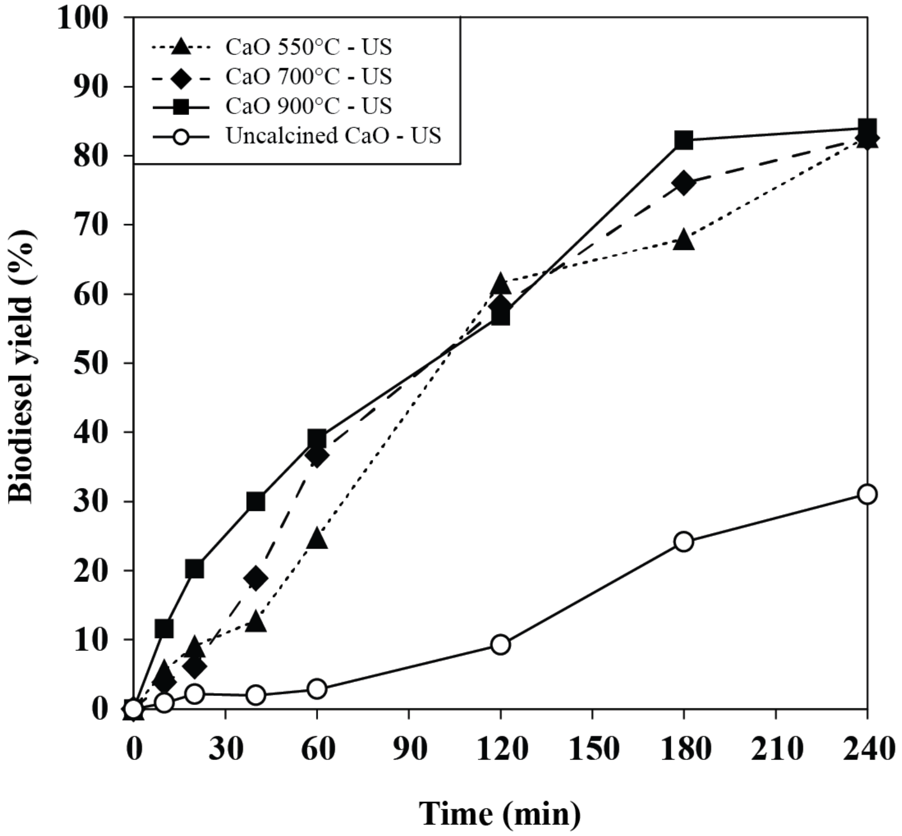


Figure 5.4 Effect of calcination temperature of catalyst on biodiesel yield.

Uncalcined calcium oxide catalyst in this study have some of calcium hydroxide ($Ca(OH)_2$) contaminated. The calcium hydroxide was defined as an impurities because it was not an active phase for transesterification [53]. The components of catalyst were also confirmed by X-ray diffractometer (XRD) as shown in Figure 5.5 and catalyst components were summarized in Table 5.6. It was noted that there was no peak of calcium carbonate ($CaCO_3$) contaminated for all catalysts.

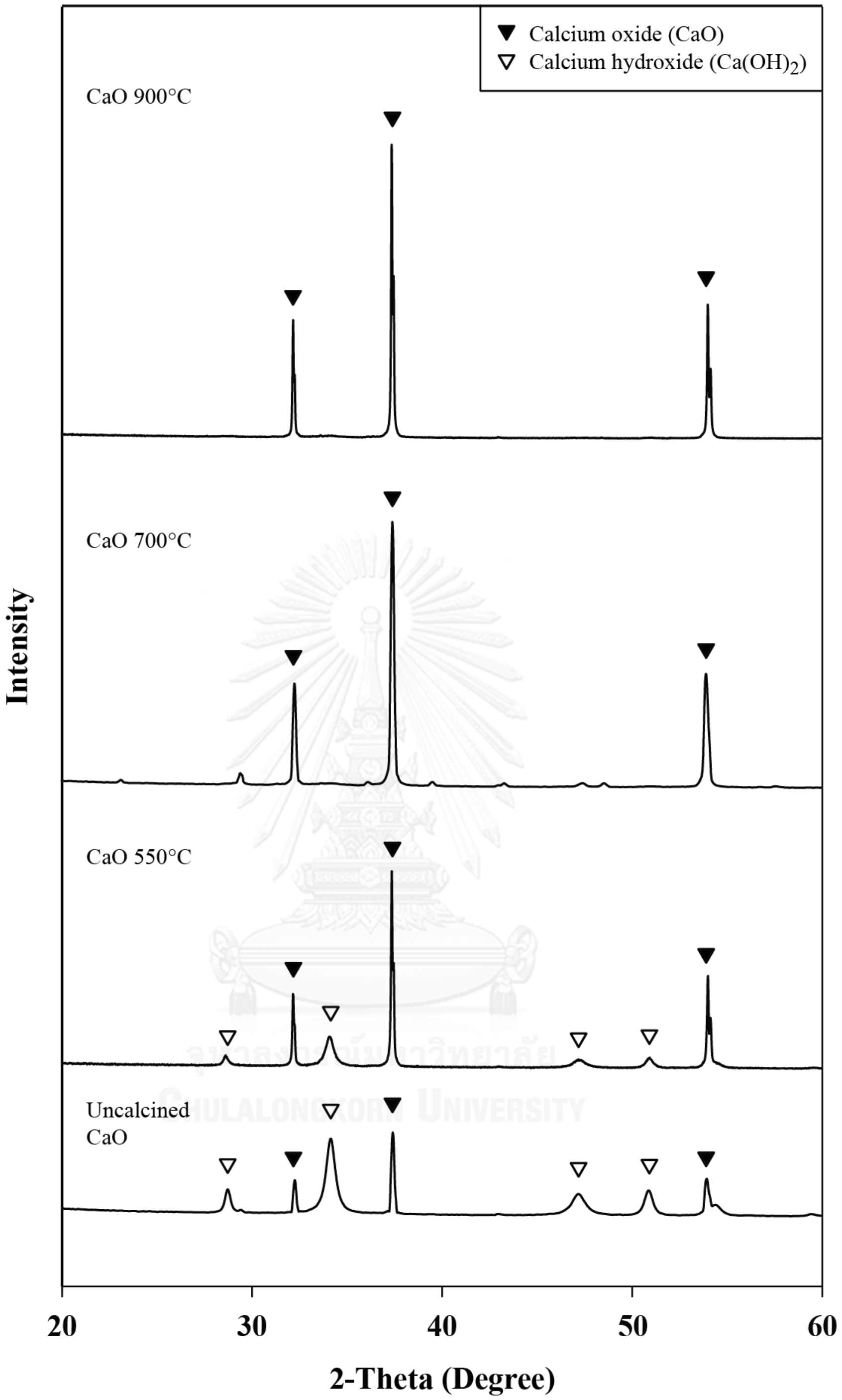


Figure 5.5 X-ray Diffractometer (XRD) patterns of calcium oxide catalyst.

Table 5.6 Components from XRD results [54, 55].

Components	**2-Theta (2θ)**
Calcium hydroxide ($Ca(OH)_2$)	28.8°, 34.1°, 47.1°, 50.8°
Calcium oxide (CaO)	32.3°, 37.4°, 53.9°

Hence, the calcination of catalyst at high temperature can convert calcium hydroxide to calcium oxide. Increase of catalyst calcination temperature will reduce impurities as illustrated in Figure 5.5

5.5 Effect of catalyst loading on biodiesel yield

Catalyst loading is one on the main factors affecting on the biodiesel yield. To investigate this study, transesterification was operated at 60°C, 1 atm and methanol to oil molar ratio of 9:1. Calcium oxide was calcined at 900°C for 5 hours before loaded to the reaction for 1%, 2% and 3% by weight based on oil under ultrasonic irradiation. The biodiesel yield is shown in Figure 5.6.

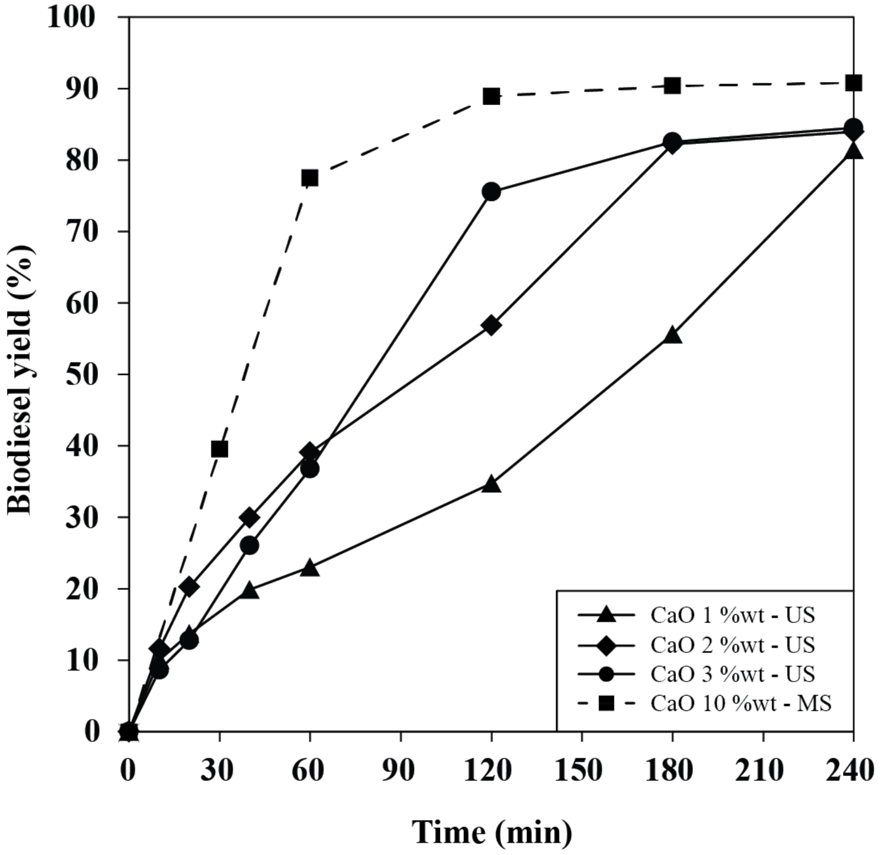


Figure 5.6 Effect of calcium oxide heterogeneous catalyst loading on biodiesel yield.

The higher catalyst loading provides faster rate of reactions since the greater chance of contact between substrates and active sites of catalyst. Then, the rate of reactions will slowdown and finally reach the equilibrium. In this study, the time that reaction reaches the equilibrium for 1%, 2% and 3% loading were 240, 180 and 120 minutes with 81.44%, 83.99% and 84.52% of biodiesel yield, respectively.

However, the increasing of catalyst loading has some drawbacks as follow:

(1) The increasing of catalyst loading requires more amount of calcium oxide catalyst. Therefore, the product and catalyst separation by sedimentation or centrifugal took a longer time.

(2) Calcium oxide heterogeneous catalyst suspended in the solution has a high viscosity and sticky that affected to pressure drop in the flow process. Thus, the system need more pump power to transport substrates through the reactor to maintain the constant flow rate.

(3) A large amount of calcium oxide catalyst may stuck in the peristaltic pump, silicone tube and inlet port of reactor. We operated using 10% catalyst loading in the mechanical stirred reactor as shows in Figure 5.6. After that, we try to use same condition in the ultrasonic reactor but it was unsuccessful because calcium oxide catalyst was stuck in the peristaltic pump and make pump over pressure before leak.

5.6 Effect of mixing types of reactor on biodiesel yield

In this study, transesterification was operated at 60°C, 1 atm and methanol to oil molar ratio of 9:1. Calcium oxide was calcined at 550°C for 5 hours, 2%wt loading using two type of reactor: mechanical stirred reactor and ultrasonic reactor. The biodiesel yield is shown in Figure 5.7.

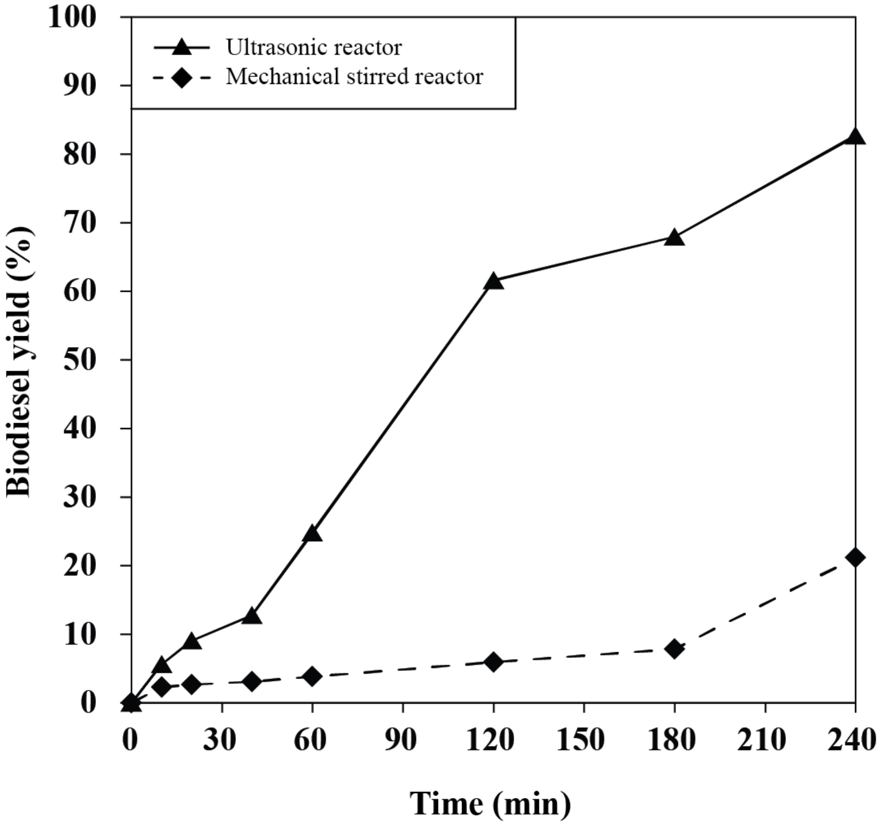


Figure 5.7 Effect of mixing reactor types on biodiesel yield

As shown in Figure 5.7, ultrasonic reactor can accelerate the reaction rate and reduce induction period by increase a level of mixing due to cavitation phenomena in fluid (external convection) and carrying reactants to active site of catalyst (internal convection). Unlike mechanical stirred reactor, it affects only external convection [56]. It has also been observed that the ultrasonic method for biodiesel production from waste cooking oil was more energy efficient (1.083×10^{-4} g/J) as compared with the conventional stirring method (4.89×10^{-5} g/J) [57]. In addition, the use of ultrasonic irradiation can also reduce the settling time of suspended glycerol in biodiesel product, significantly [12, 58].

Under ultrasonic irradiation, glycerol has more chance to adsorb on the surface of calcium oxide catalyst and generate the calcium-glyceroxide specie. This specie can be the one of active sites that promote the rate of reaction. Kouzu et al. [59, 60] and Granados et al. [61] reported that the glyceroxide specie was more active for transesterification than that of calcium oxide active specie. Figure 5.8 shows the FTIR spectra of calcium-glyceroxide specie that occurred under ultrasonic irradiation (this work) but absence in mechanical stirred reactor [36].

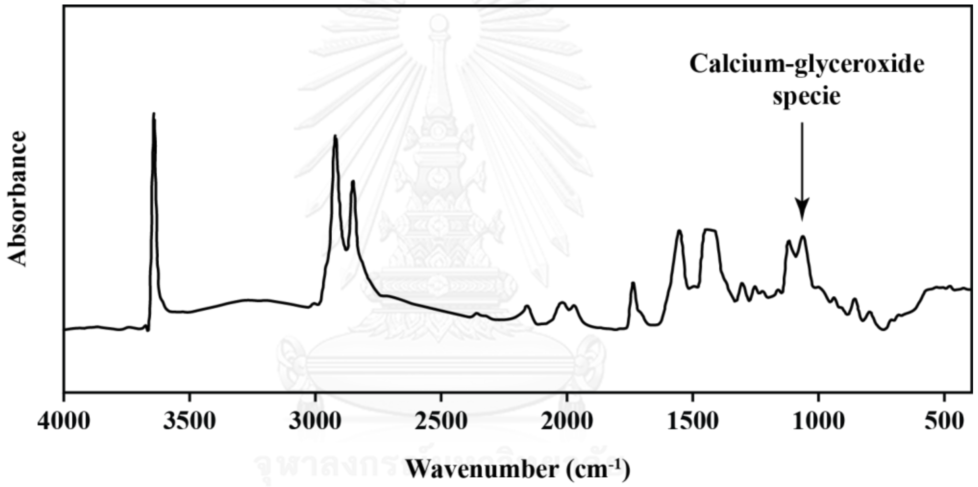


Figure 5.8 FTIR spectra of used calcium oxide catalyst with calcium-glyceroxide specie.

5.7 Effect of ultrasonic operating parameters on biodiesel yield

5.7.1 Effect of ultrasonic frequency

In order to investigate the effect of ultrasonic frequency on biodiesel yield, transesterification was kept constant at 60°C, 1 atm, methanol to oil molar ratio of 9:1 and 2%wt of catalyst loading. Calcium oxide was calcined at 900°C for 5 hours before used and the maximum ultrasonic power was 800 Watt with total of 16 transducers (50 Watt for each transducer). The position of operating frequency can be divided to 4 patterns: none (deactivated transducers), 8×20 kHz, 8×50 kHz and 4×20 kHz combined with 4×50 kHz as summarized in Table 5.6 where employed in four positions along the length of reactor. A drawing of the ultrasonic reactor shows in Figure 5.9 and results are shown in Figure 5.10

Table 5.7 Operating frequency patterns and FAME yield at 240 minutes using ultrasonic 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	-	-	-	-	-	-	-	-	10.16
2	✓	✓	✓	✓	-	-	-	-	43.50
3	-	-	-	-	✓	✓	✓	✓	59.49
4	-	✓	-	✓	✓	-	✓	-	55.61

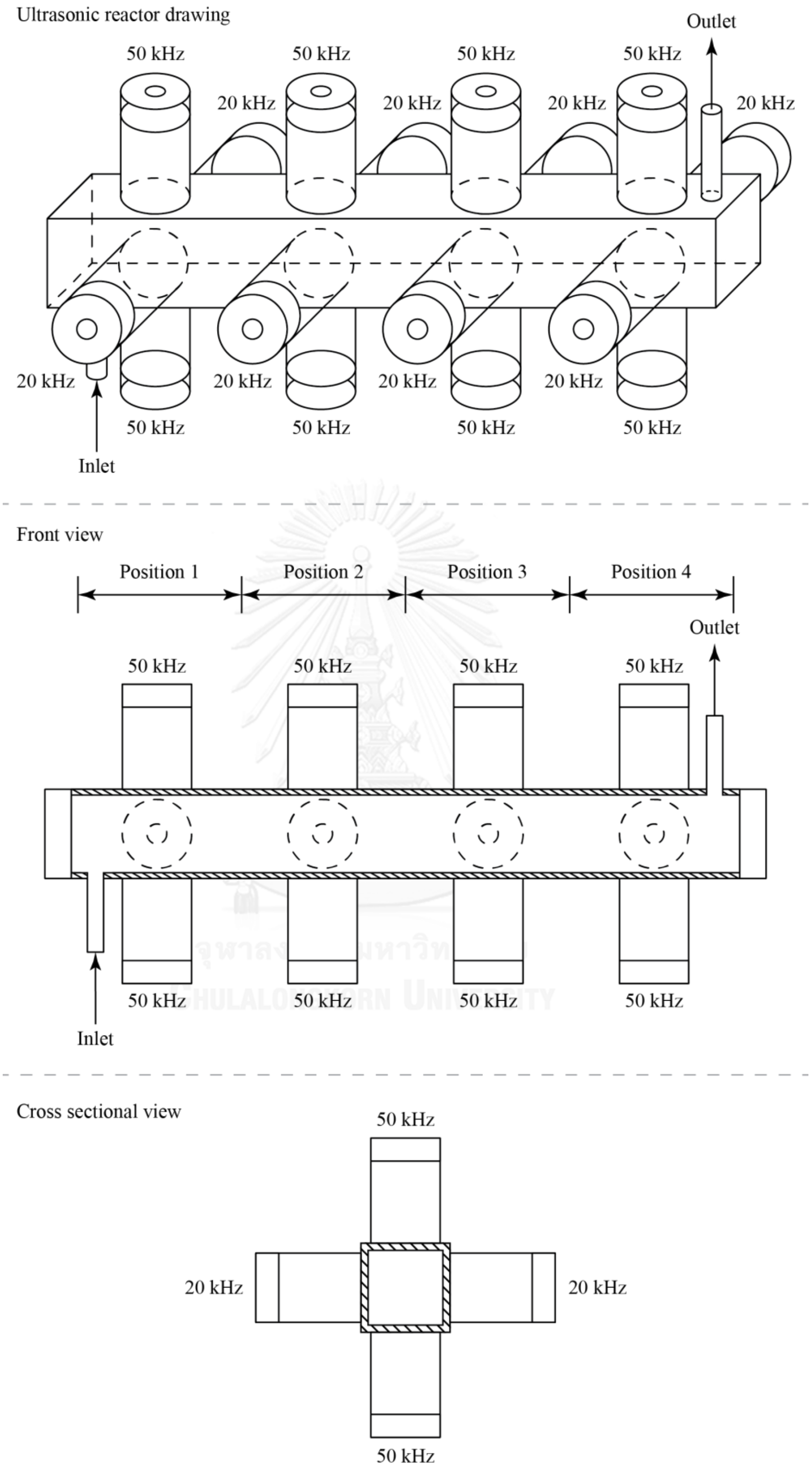


Figure 5.9 A drawing of ultrasonic reactor: 3-dimension drawing, front view and cross sectional view.

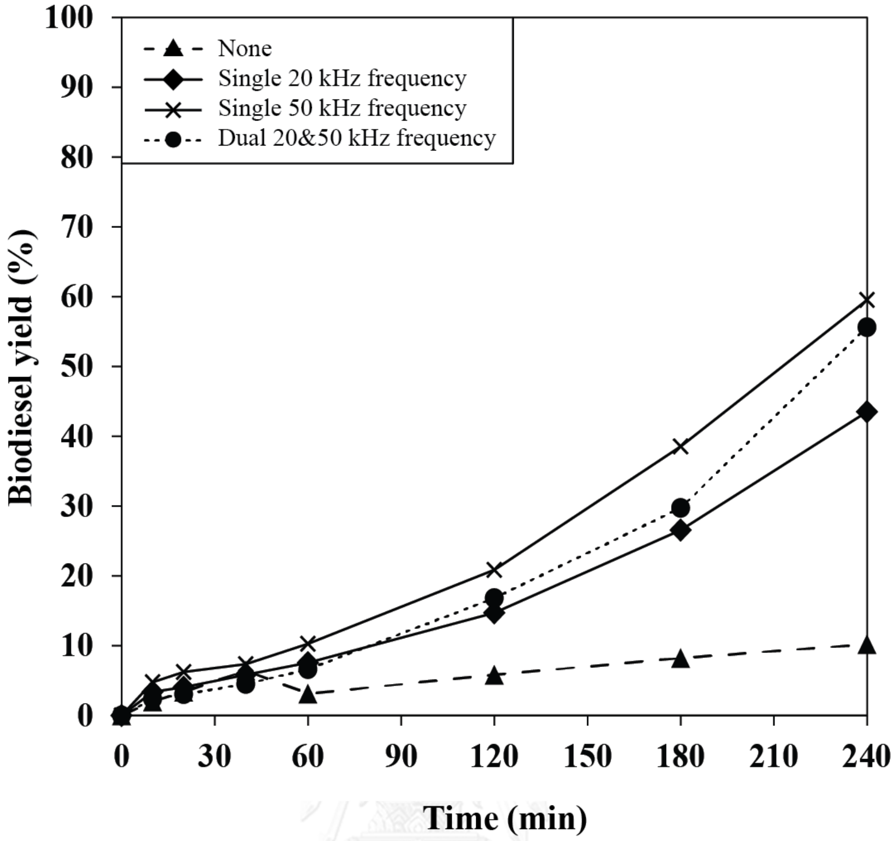


Figure 5.10 Effect of ultrasonic frequency on biodiesel yield.

Methyl ester yield was very low and took a longer induction period in the first pattern due to mass transfer limitation of three phase system (solid phase of catalyst, methanol and oil phase) was dominated. In contrast to, the significant higher methyl ester yield was found in the second to fourth pattern have because ultrasonic irradiation offers more mixing rate by cavitation phenomena. The cavitation phenomena generate emulsification of methanol in oil as increasing the contact area between methanol oil and surface of calcium oxide catalyst resulting in a higher methyl ester yield.

The difference in operating frequency was illustrated in the second and third pattern. It was found that a single transducer frequency at 50 kHz provided a higher methyl ester yield than that of a single transducer frequency at 20 kHz for 1.4 times along the reaction period. Based on ultrasonic power of 400 Watt, 50 kHz frequency provides a smaller bubbles to generate the cavitation in the reaction mixture. Thus, the smaller bubble has higher a surface area per volume ratio. Then, the contact area between the substances and active sites of calcium oxide was higher than that of 20 kHz frequency.

The power of lower frequencies (20 kHz) are greater but not provide a higher biodiesel yield because they concentrate the available power in the localized regions. The higher frequencies (50 kHz) contributes more distribution of available power throughout the reactor volume [25].

The effect of dual transducer frequencies (20 kHz combined with 50 kHz) was also studied in the fourth pattern. It was found that the dual frequencies provided a methyl ester yield between both two single frequency (20 and 50 Hz). To emphasize the effect of frequency on the biodiesel yield related to ultrasonic wave pattern as described below:

The quadratic equations, as shown in Equation (5.1), (5.2), (5.3), were perfectly fitted to each results of biodiesel yield with high coefficient of determination (R-square).

Quadratic equation for a single transducer frequency at 20 kHz

$$yield\ (\%) = 0.0006x^2 + 0.0247x + 3.4476 \tag{5.1}$$

$$R^2 = 0.9994$$

Quadratic equation for a single transducer frequency at 50 kHz

$$yield\ (\%) = 0.0007x^2 + 0.0534x + 4.2969 \tag{5.2}$$

$$R^2 = 0.9996$$

Quadratic equation for dual transducer frequencies
at 20 kHz combined with 50 kHz

$$yield\ (\%) = 0.0009x^2 + 0.0036x + 2.9078 \tag{5.3}$$

$$R^2 = 0.9966$$

where x Reaction time (10 to 240 min)

Ultrasonic irradiation wave sign in the liquid phase of reaction can be expressed by general wave equation (Equation (5.4) and (5.5)) [62].

$$y = A\sin(kx - \omega t) \tag{5.4}$$

$$y = A\sin(\frac{2\pi}{\lambda}x - 2\pi f t) \tag{5.5}$$

where	A	Amplitude of the wave (m or mm)
	k	Angular wavenumber of the wave, which $k = \frac{2\pi}{\lambda}$
	ω	Angular frequency of the wave, which $\omega = 2\pi f$
	t	Time period (s)
	λ	Wave length (m or mm)
	f	Wave frequency (Hz)

The wave equations of second (8×20 kHz, 400 Watt), third (8×50 kHz, 400 Watt) and forth (4×20 kHz, 200 Watt combined with 4×50 kHz, 200 Watt) pattern for 1 second period can be expressed by Equation (5.6), (5.7) and (5.8), respectively. The constant parameters found in Equation (5.6), (5.7) and (5.8) were derived as shown in Appendix B.

$$y_2 = 0.442\sin(\frac{2\pi}{66.712}x - 2\pi \times 20000 \times 1) \tag{5.6}$$

$$y_3 = 0.177\sin(\frac{2\pi}{26.685}x - 2\pi \times 50000 \times 1) \tag{5.7}$$

$$\begin{aligned} y_4 = {} & 0.312\sin(\frac{2\pi}{66.712}x - 2\pi \times 20000 \times 1) \\ & + 0.125\sin(\frac{2\pi}{26.685}x - 2\pi \times 50000 \times 1) \end{aligned} \tag{5.8}$$

Figure 5.11 shows the relation between distance from ultrasonic source and amplitude of the ultrasonic wave derived from above equations.

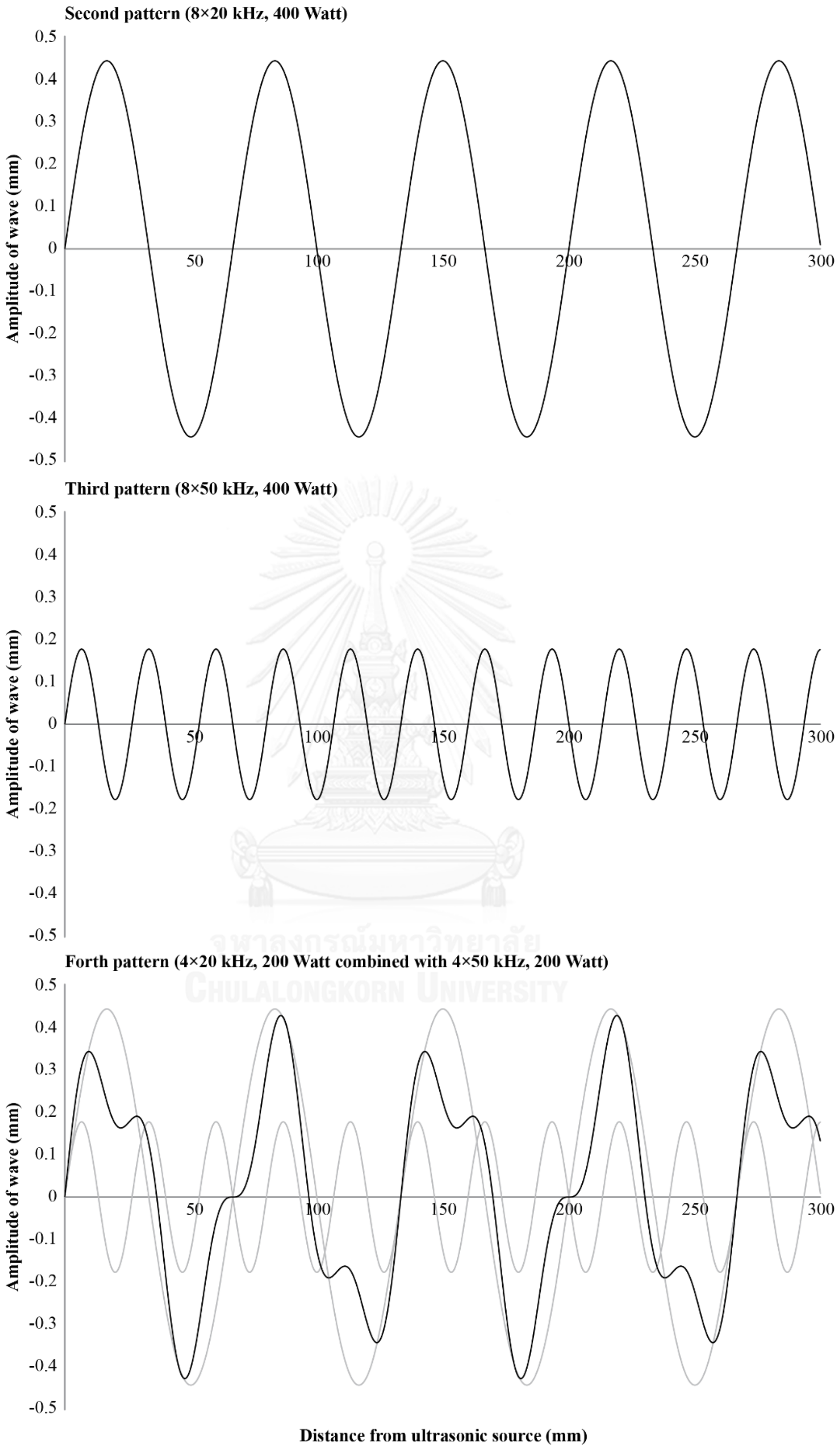


Figure 5.11 Ultrasonic wave sign with difference frequency.

The fourth pattern wave sign (dual frequency) does not show the resonance effect due to periodic frequency (T or 1/frequency) of 20 kHz and 50 kHz might not be corresponding with each other at the same reaction period. Therefore, the maximum amplitude from 20 kHz combined with 50 kHz was lower than that of the single transducer frequency at 20 kHz. On the other hand, if the periodic frequencies corresponding with each other and resonance effect would be obtained, the maximum amplitude can shift and probably cause the higher biodiesel yield [63, 64].

The wave sign of fourth pattern combined with dual frequencies also shows that, the frequency of 20 kHz was more likely dominated than that of the frequency of 50 kHz. Therefore, not only the major frequency of fourth pattern close to second pattern or 20 kHz but FAME yield obtained from fourth pattern also become close to FAME yield obtained from second pattern than that of the third pattern.

In the previous report, the use of ultrasonic for cleaning such as ultrasonic bath for microelectronic devices usually generates a smaller bubble from higher frequency transducers to clean up the sensitive and difficult to access parts [25]. The relative cavitation strength versus frequency was shown in Figure 2.12. Using the same ultrasonic power, the cavitation strength decreases when the frequency of sonication increases. For the same reason, the released energy from a smaller emulsion cavitation using 50 kHz transducers allowing the reactants more change to access onto the active surface of calcium oxide heterogeneous catalyst by internal convection [56] This is leading to a higher efficiency and softer implosion than that of the cavitation using 20 kHz transducers. The cavitation imposes that not only carry the reactants onto the active surface of catalyst but also, take products away from the active surface by dynamic pressure waves. That makes active surface of catalyst is readily catalyze the next reaction with higher turnover rate.

5.7.2 Effect of ultrasonic power

Ultrasonic power is one of the main factor that affecting to biodiesel yield. The expression of ultrasonic power input to process must be evaluated in terms of intensity (ultrasonic power per liquid volume in the reactor as shown in Equation (5.4)). To investigate the effect of ultrasonic power on the biodiesel yield, transesterification was operated and kept constant at 60°C, 1 atm, methanol to oil molar ratio of 9:1 and 2%wt of catalyst loading. Calcium oxide was calcined at 900°C for 5 hours before used and set up ultrasonic dual frequencies at 20 kHz combined with 50 kHz. The operating power will be divided to three levels: 0%, 50% and 100% of maximum power. The liquid volume in reactor was 300 mL and the maximum power of ultrasonic was 800 Watt. Thus, the ultrasonic intensity for each case were 0, 1.33 and 2.66 Watt/mL, respectively. The effect of ultrasonic power on biodiesel yield are shown in Figure 5.12.

$$Ultrasonic\ intensity\ (Watt/mL) = \frac{Ultrasonic\ power\ (Watt)}{Reaction\ mixture\ volume\ in\ the\ reactor\ (mL)} \quad (5.4)$$

There were no ultrasonic irradiation for 0% of maximum power. Therefore, the mixing was only provided in the pre-heat tank (Erlenmeyer flask), inline mixing (in the silicone tube and peristaltic pump) and horizontal stirrer in the reactor. It was found that the biodiesel yield was only 10% at 240 min of reaction period.

For 50% of maximum power (400 Watt or 1.33 Watt/mL), the biodiesel yield was increased due to ultrasonic irradiation promotes the acoustic movement and cavitation phenomena. The acoustic movement provides a mixing in the medium but cavitation of low power tends to form a stable cavitation that does not collapse [65]. However, the induction period was also observed for using 50% of maximum power. This indicated that the ultrasonic irradiation of 1.33 Watt/mL was not enough for minimizing of mass transfer limitation. Gupta et al. [57] was found that the ultrasonic intensity above 1.58 Watt/mL provided the significantly greater biodiesel yield.

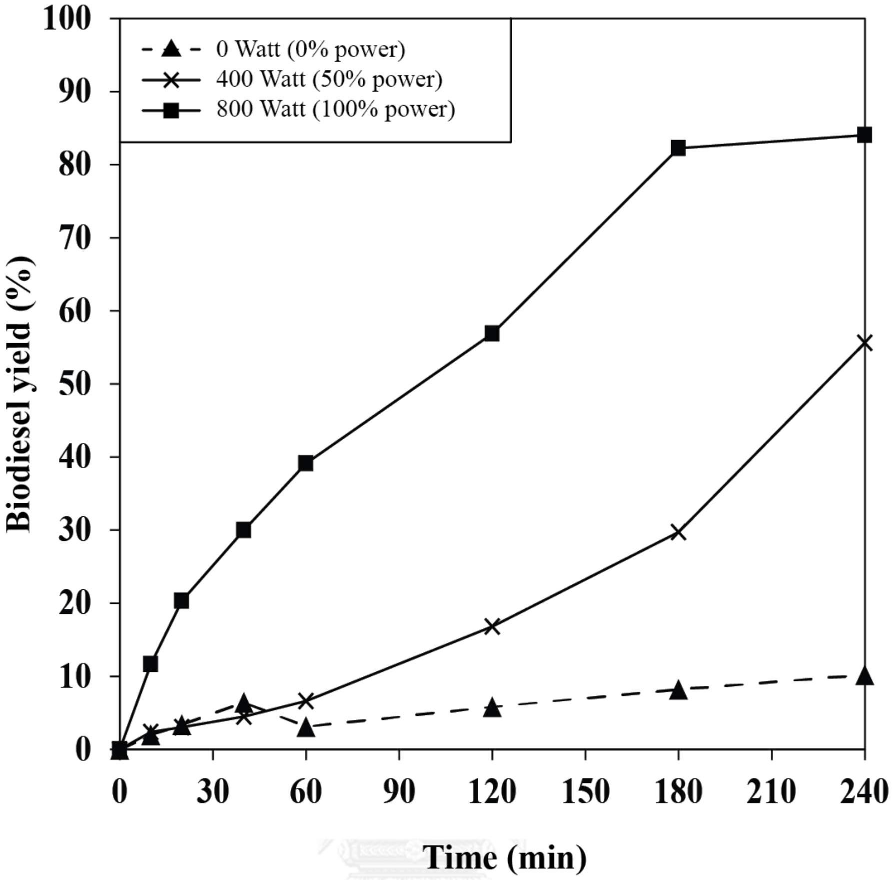


Figure 5.12 Effect of ultrasonic power on biodiesel yield.

For 100% of maximum power (800 Watt or 2.66 Watt/mL), the rate of reaction was significantly faster than using 50% of maximum power because ultrasonic irradiation promotes the acoustic movement and cavitation phenomena. In this case, cavitation was formed under a high power, the cavitation was not stable and collapse with releasing of energy (called transient cavitation). Moreover, the collapse of the cavitation bubble leads to the higher micro-mixing and jet velocity at the phase boundary between the oil and methanol phases. This is leading to the formation of finer emulsion which provide a higher mass-transfer coefficient, and thus higher yield [66]. The transesterification tends to reach the equilibrium after 180 minutes. The minimum amount of energy required to produce ultrasonic cavities must be above the cavitation threshold. In other words, the ultrasonic waves must have enough pressure amplitude to overcome the natural molecular bonding forces and the natural elasticity of the liquid medium in order to grow the cavities [25].

To insight the effect of ultrasonic power on the biodiesel yield. The correlation between ultrasonic power input and amplitude of the wave in this study can be expressed by kinetic energy equation (Equation (5.9) [67].

$$\begin{aligned} E = Pt &= \frac{1}{2}mv_{max}^2 = \frac{1}{2}m(A\omega)^2 \\ &= \frac{1}{2}\rho V(A\omega)^2 = \frac{1}{2}\rho VA^2(2\pi f)^2 \end{aligned} \tag{5.9}$$

where		
	E	Wave energy (J)
	P	Ultrasonic power (Watt)
	t	Time period (s)
	m	Mass of medium (g)
	v_{max}	Maximum kinetic velocity (m/s)
	A	Amplitude of the wave (m or mm)
	ω	Angular frequency of the wave, which $\omega = 2\pi f$
	ρ	Density of medium (kg/m^3)
	V	Volume of medium (m^3)
	f	Wave frequency (Hz)

The correlation between power and amplitude for single 20 kHz and 50 kHz transducer was expressed in Equation (5.10) and (5.11), respectively and Figure 5.13 illustrates based on the above equations.

$$A_{20\ kHz} = 0.0221\ P^{0.5} \tag{5.10}$$

$$A_{50\ kHz} = 0.0088\ P^{0.5} \tag{5.11}$$

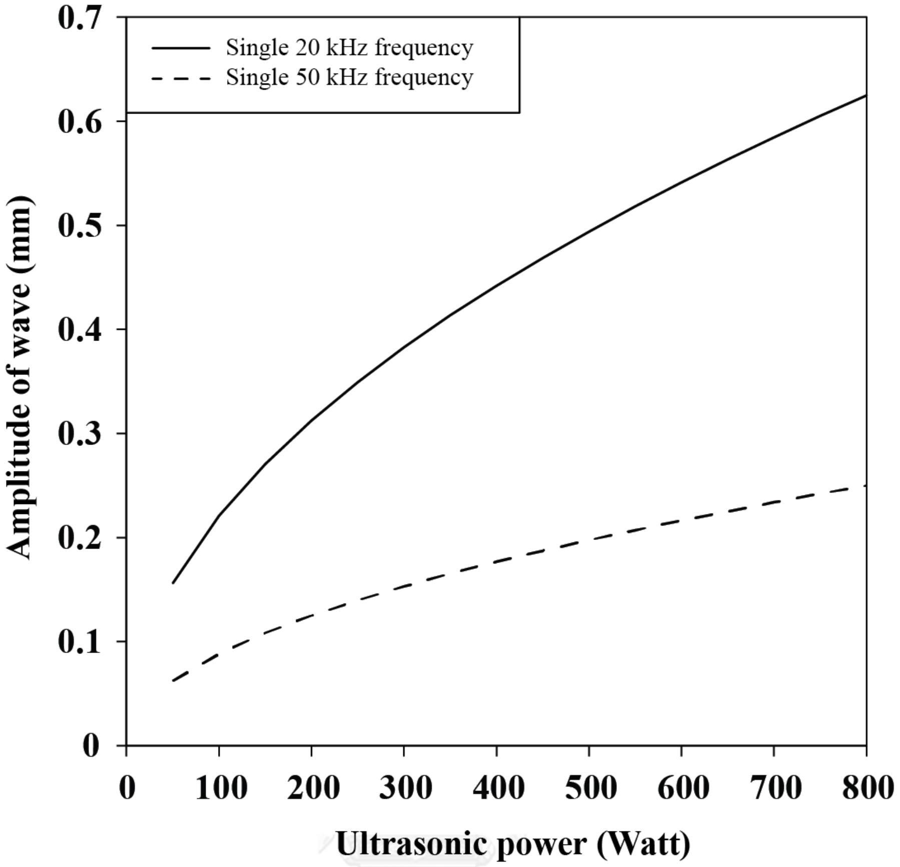


Figure 5.13 Correlation between ultrasonic power input and amplitude of the wave in this study

The general wave sign for every patterns of frequency (20 kHz, 50 kHz and 20 kHz combined with 50 kHz) were shown in Figure 5.14.

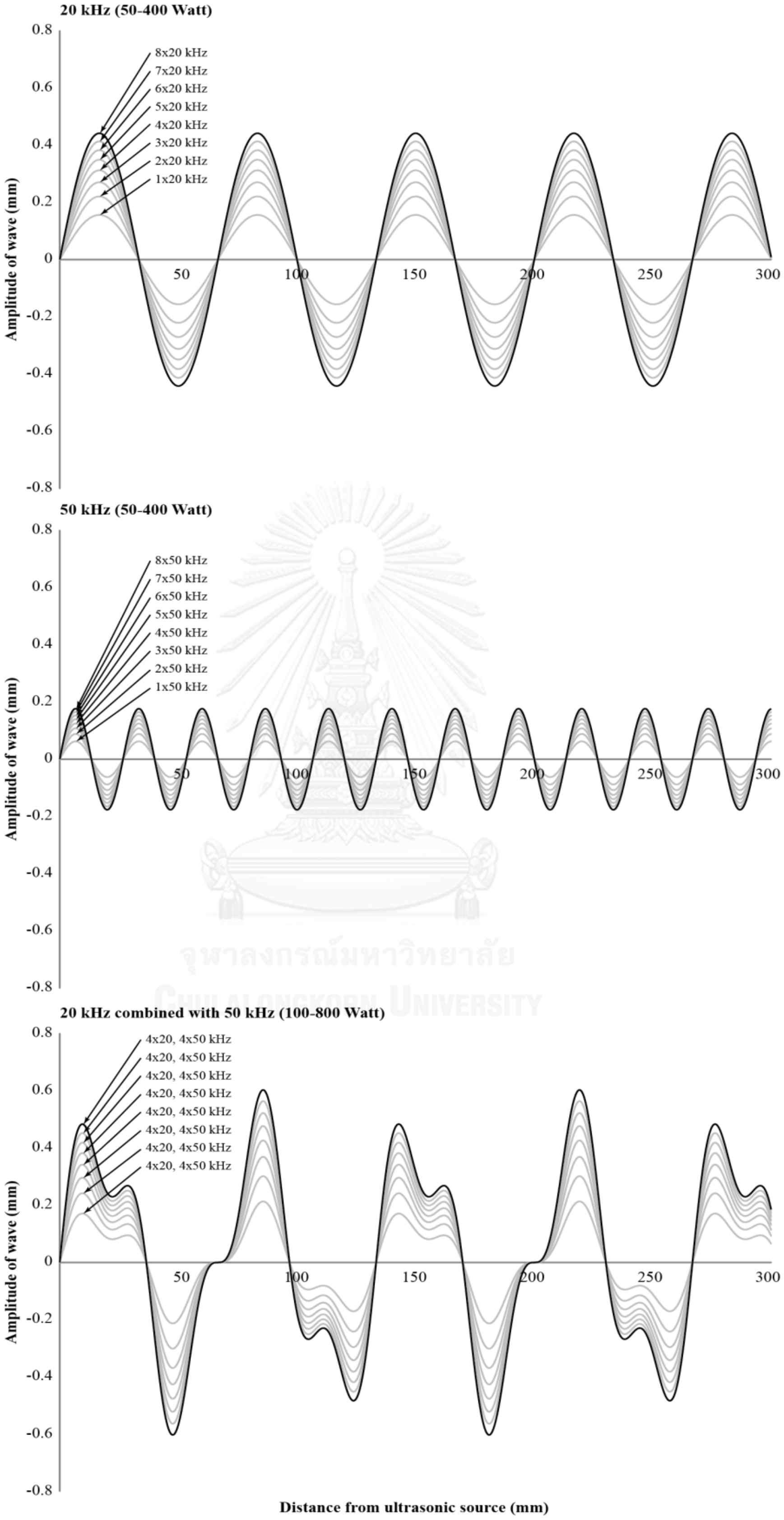


Figure 5.14 Ultrasonic wave sign with difference power and frequency.

Gupta et al. [57] determined the percentage efficiency of the ultrasonic probe by calorimetric method for ultrasonic power 60, 80, 100 and 120 Watt (ultrasonic intensity is 1.58, 2.11, 2.63 and 3.16 Watt/mL, respectively). The percentage efficiencies were found to be 7.46%, 9.88%, 9.94% and 11.07%, respectively. Therefore, the correlation between ultrasonic power and percentage efficiency was expressed in Equation (5.12).

$$efficiency\ (\%) = -0.0008P^2 + 0.1996P - 1.4405 \qquad (5.12)$$

$$R^2 = 0.9152$$

The quadratic Equation (5.12) shows that using the higher ultrasonic power is more likely make more energy absorption of biodiesel mixture as corresponding to the amplitude profiles shown in Equation (5.10) and (5.11).

The higher ultrasonic power provides higher amplitude of wave resulting to the higher FAME yield. This is corresponding to the transesterification using barium oxide (BaO) and strontium oxide (SrO) heterogeneous catalysts as reported by Salamatinia et al. [44].

However, the power or energy input does not perfectly transfer to medium because some of energy was absorbed by the material of reactor in the form of heat or vibration. The material of reactor in this study was 316 stainless steel which absorbed the ultrasonic energy around 10.6%, reflected the energy was back to medium around 88% and loss to the environment around 1.4% [68]. Therefore, the liquid medium in reactor absorbed the ultrasonic energy around 352 Watt (1.17 Watt/mL) and 704 Watt (2.35 Watt/mL) for 50% and 100% of maximum power, respectively.

The material of reactor selection is one of the major part that affect the ultrasonic transfer efficiency. Softer material such as plastic absorbs more ultrasonic energy than that of the harder material. Hard and brittle material such as glass absorbs a few of energy but if excessive energy is greater than the breaking point of material, material would vibrate until cracking. Therefore, hard and tough material such as stainless steel is the best choice for ultrasonic energy transfer [25].

5.8 Catalyst stability

Catalyst stability is one of the important key that make calcium oxide heterogeneous more promising than sodium hydroxide homogeneous catalyst since sodium hydroxide is not easy to reuse by general technique and need a lot of water to dilute sodium hydroxide from biodiesel product. Unlike calcium oxide that can be separated by mechanical separation (sedimentation or filtration).

To investigate this study, transesterification was operated at 60°C, 1 atm and methanol to oil molar ratio of 9:1 using 3% by weight of oil under ultrasonic irradiation at maximum power with dual frequency of 20 kHz and 50 kHz. Biodiesel yield for three consecutive cycles are shown in Figure 5.15.

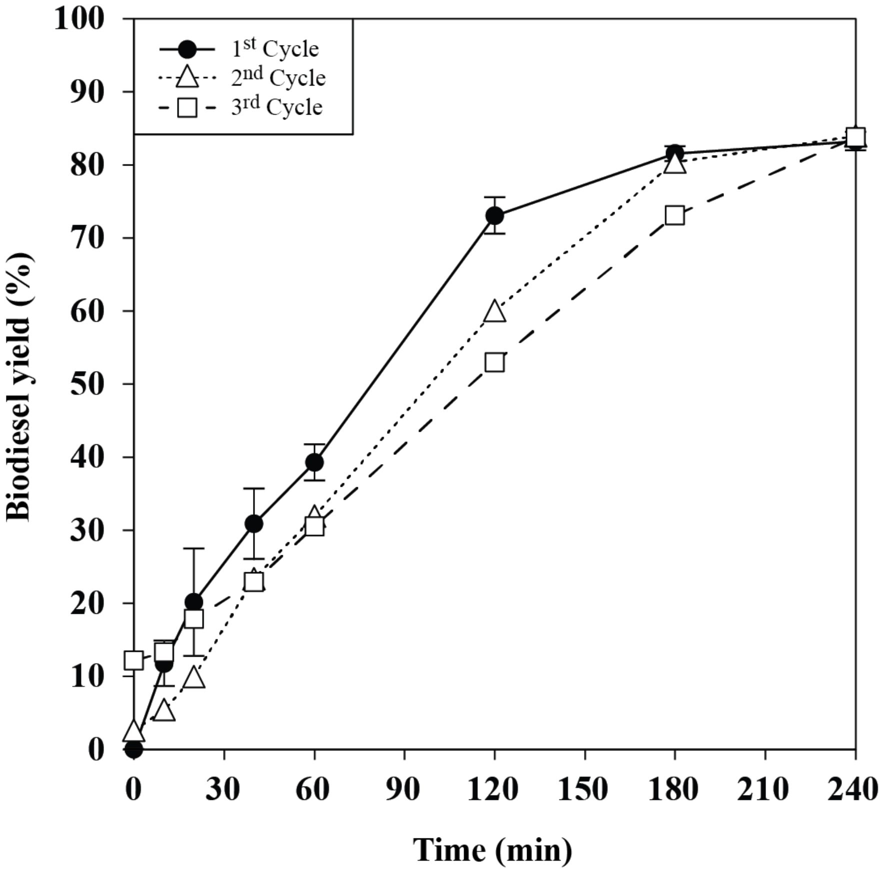


Figure 5.15 Reusability of calcium oxide for transesterification of palm oil.

Calcium oxide catalyst can be used to produce biodiesel and provide high biodiesel yield (more than 80% yield) for three cycles with slightly decreasing rate of reaction. It was found that calcium oxide catalyst separated by sedimentation was change the color from white to gray and more darken for every cycle due to reaction mixture deposition and catalyst layer in reaction mixture was widened because catalyst suspended more in mixture.

The surface coverage by organic compound of reaction mixture was also confirmed by thermogravimetric analysis (TGA) as shown in Figure 5.16

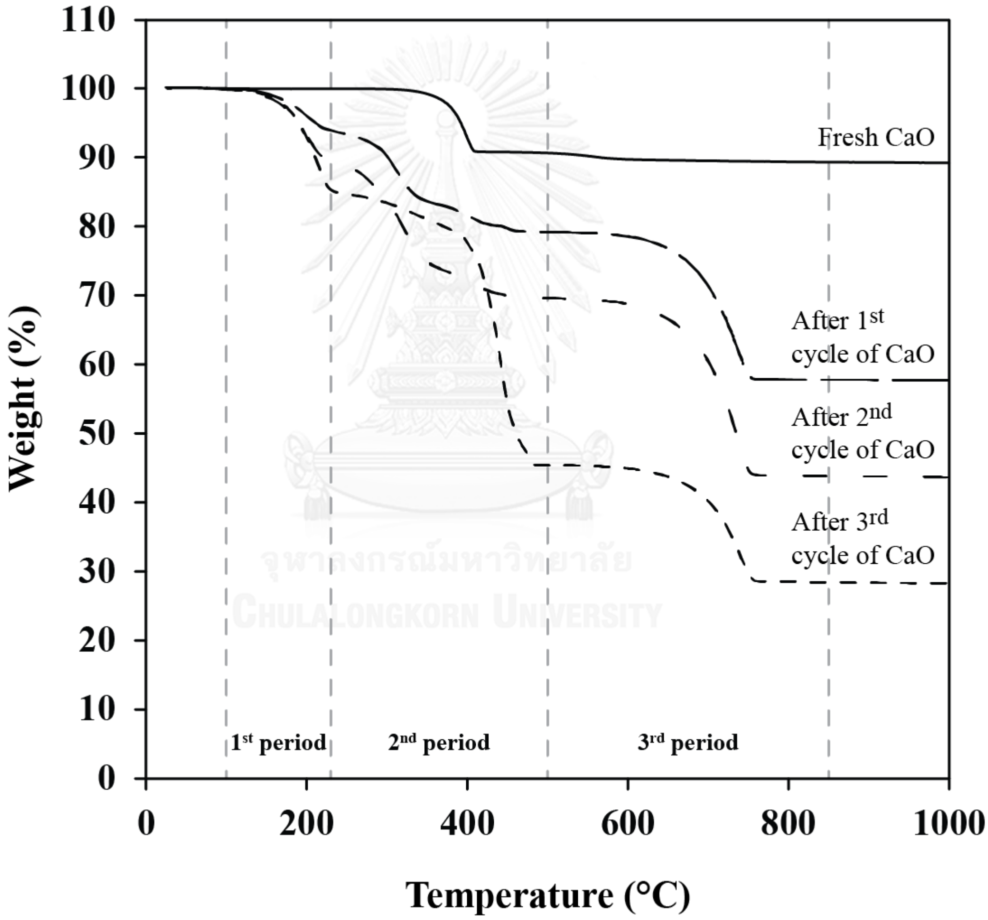


Figure 5.16 TGA profiles of fresh, after 1st cycle, after 2nd cycle and after 3rd cycle of calcium oxide catalyst calcined at 900°C.

The fresh, after 1st cycle, after 2nd cycle and after 3rd cycle of calcium oxide catalyst decomposition was divided into 3 temperature periods which are described as Table 5.8

Table 5.8 TGA temperature range and organic compounds decomposition for each period.

Period no.	**Temperature range (ºC)**	**Organic compounds decomposition**	**Reference**
1st period	100-230	Saturated fatty acid methyl esters	[69]
2nd period	230-500	Unsaturated fatty acid methyl esters, Glycerol, Triglycerides	[70, 71]
3rd period	500-850	Carbon residuals	[71]

The after 1st cycle, after 2nd cycle and after 3rd cycle of calcium oxide catalyst also showed a significant loss in mass along the temperature compared to the fresh calcium oxide catalyst. It was indicated that there were some organic compound of the reaction mixture deposited on the catalyst surface that might affect to rate of reaction for each cycle.

The rate of reaction was deceased in every cycle due to the catalyst deactivate. The organic compound of the reaction mixture was deposited and adsorbed on the catalyst surface that cause the calcium oxide catalyst deactivated. However, the biodiesel yields obtained from used calcium oxide catalysts (2nd and 3rd cycles) were also similar to that of using fresh calcium oxide catalyst in 4 hours of reaction period under ultrasonic irradiation. Therefore, it should be another positive effect making biodiesel yield reach the same equilibrium as seen in Figure 5.15. Choedkiatsakul et al. [36] also reported that the new active site species of used calcium oxide catalyst as calcium glyceroxide was present under ultrasonic irradiation.

To support the calcium glycerol complex statement, the surface of fresh, after 1st cycle, after 2nd cycle and after 3rd cycle of calcium oxide catalysts were analyzed by Fourier transform infrared spectrometer (FTIR) as seen in Figure 5.17. Peak at wavenumber 1050, 2800-3000 cm^{-1} (C – H stretching of calcium oxide to calcium methoxide) and peak at wavenumber 1000-1320, 1750 cm^{-1} (C = O stretching of ester) were observed for all used calcium oxide catalysts. This means that the surface of used calcium oxide catalyst was shielded with the reaction mixture causing catalyst deactivation. On the other hand, peak at wavenumber of 700-1000 and 1200-1350 cm^{-1} was dominated for calcium oxide catalyst after 1st cycle indicated the present of – CH_2 vibration of calcium-glycerol complex [72, 73]. Moreover, using ultrasonic irradiation for heterogeneous catalytic system can provide the higher turnover rate on the surface reaction to achieve its original biodiesel yield at 4 hours [36].

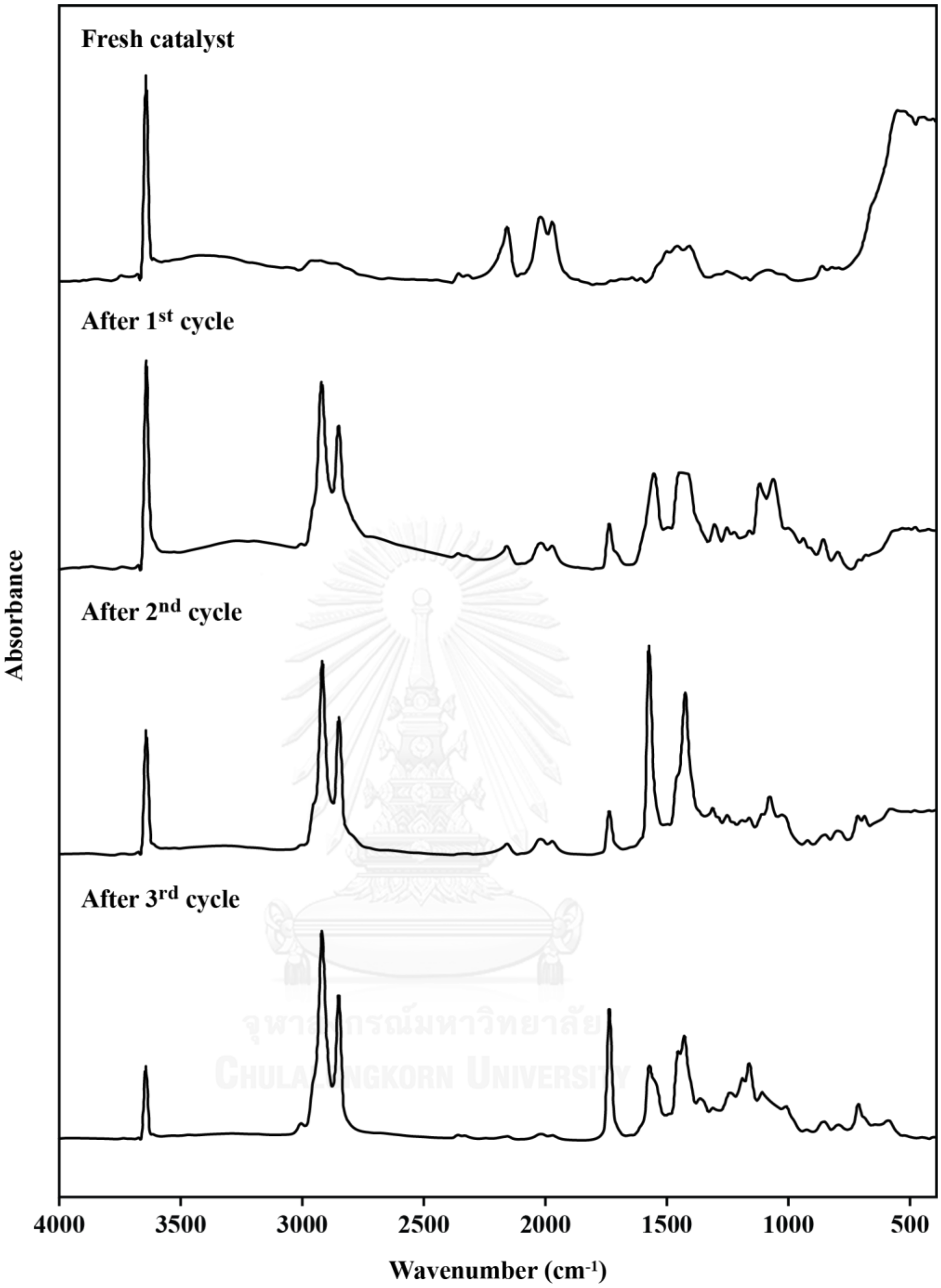


Figure 5.17 FTIR spectra of fresh, after 1st cycle, after 2nd cycle and after 3rd cycle of calcium oxide catalysts

Catalyst washing is one of the parameter that affects to initial yield of FAME (at 0 min). In this study, methanol was used to wash the calcium oxide under magnetic stirred at ambient temperature and pressure for three times before reloaded to the system. The result of initial yield for washed catalyst compare to unwashed catalyst as shown in Figure 5.18

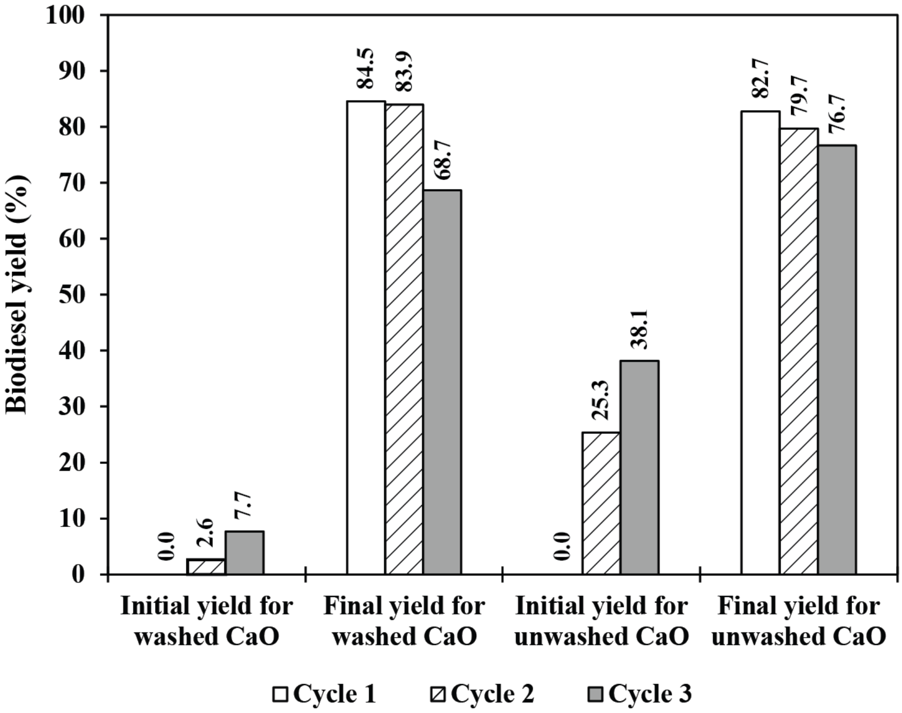


Figure 5.18 The initial and final yield for washed and unwashed calcium oxide catalyst.

However, the final yield of FAME (at 240 min) for unwashed catalyst still high. Thus, the unwashed calcium oxide catalyst can be used instantly in the larger scale. This can be conclude that using ultrasonic irradiation for calcium oxide catalyze transesterification is more promising process due to their advantage as minimize the mass transfer limitation of two immiscible reactants and catalyst, provide high turnover rate on the catalyst surface and generate more active species as calcium glyceroxide.

Chapter 6
Conclusions and recommendation

6.1 Conclusions

In this work, a study of biodiesel production from palm oil by using ultrasonic reactor was investigated and compared to mechanical stirred reactor. Transesterification was operated at 60°C, 1 atm, methanol to oil molar ratio of 9:1. The sodium hydroxide homogeneous catalyst provides higher methyl ester yield and faster rate of reaction than that of calcium oxide heterogeneous catalyst. However, the major drawback of using homogeneous is the need of separation unit to remove the catalyst in the final step while calcium oxide heterogeneous catalyst required the calcination to eliminate calcium hydroxide as an impurity. The fastest rate of reaction was achieved in ultrasonic reactor at highest catalyst loading (3 %wt) and methyl ester yield increases steadily until reach the same transesterification equilibrium (about 80%). The higher ultrasonic frequency and power (50 kHz, 800 W) promoted the heterogeneously catalyzed transesterification of refined palm oil can be separated by sedimentation. Reusability of calcium oxide catalyzed transesterification using ultrasonic assisted reaction was also studied. It was found that calcium oxide catalyst can be used to produce biodiesel and provide high biodiesel yield for three cycles with slightly decreasing rate of reaction. This can be conclude that using ultrasonic irradiation for calcium oxide catalyze transesterification is more promising process due to their advantage as minimize the mass transfer limitation of two immiscible reactants and catalyst, provide high turnover rate on the catalyst surface and generate more active species as calcium glyceroxide.

6.2 Recommendations

The problems observed during the laboratory scale experiment was reconsidered for a larger scale and can be summarized as follows:

(1) The continuous flow process system is a better choice for larger scale than batch process. For support this system, calcium oxide catalyst should be packed in the reactor and no need for a catalyst separate unit. However, catalyst packed in the reactor may reduce the mixing efficiency.

(2) The heat of solution of sodium hydroxide (NaOH) can be used to preheat the oil by heat integration methods.

(3) To prevent the risk from heat of solution or soap formation by using sodium hydroxide, sodium methoxide (CH_3ONa) is one of the attractive options for future work.

(4) Horizontal ultrasonic reactor alignment may cause the air gap inside the reactor. This air gap is one of the barrier film that obstacle the ultrasonic irradiation from transducers to liquid medium. After that, the ultrasonic energy was absorbed by the material of reactor and transducers in the form of heat or vibration before overheat or leak. If the temperature of transducer or reactor wall was raised with usually acceleration, it would have an air gap inside the reactor.

(5) For heterogeneous catalyzed transesterification, indirect ultrasonic transducer is better than direct transducer because viscous solid catalyst can be stacked on the transducer surface which is not only decrease the irradiation efficiency, but also difficult to clean up the reactor and the direct transducer can be erosion by cavitation phenomena.

(6) For heterogeneous catalyzed transesterification, the higher ultrasonic power and frequency provides the greater biodiesel yield due to it enhances mass transfer in reaction mixture and catalyst. It was observed that ultrasound frequency could enhance mass transfer as 611 kHz resulted in the significantly improved mass transfer coefficient (89%) as compared to 20 kHz (48%) [74]

(7) High shear reaction is another way to eliminate mass transfer limitation on biodiesel yield by using heterogeneous catalyzed transesterification. Therefore, transesterification should be studied under high sheer reactor with equally mixing level. If the biodiesel yield under high sheer reactor is same as ultrasonic reactor, it shows that cavitation phenomena is a minor or non-effect to biodiesel yield. On the other hand, if the biodiesel yield under high sheer reactor is lower than ultrasonic reactor, it shows that cavitation phenomena is one of the main parameter which effect to biodiesel yield.

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APPENDIX

Appendix A

Biodiesel produced from ultrasonic reactor

Figure A.1 shows the actual photo of product after sediment overnight. Product can be separated to 3 layers as following:

1st layer: Biodiesel with sodium hydroxide dissolved

2nd layer: Glycerol with sodium hydroxide and water dissolved

3rd layer: Soap with biodiesel, glycerol, sodium hydroxide and water dissolved

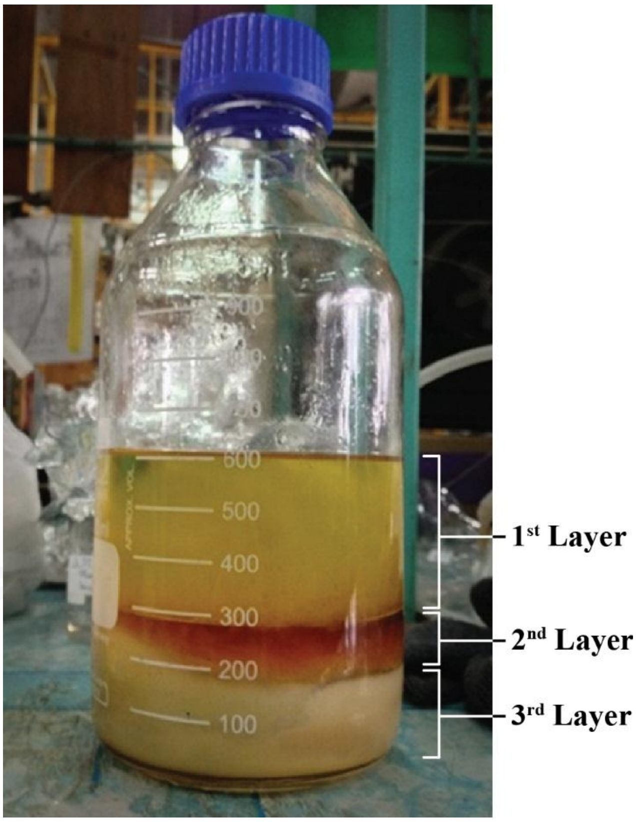

Figure A.1 3 layers of biodiesel product via sodium hydroxide homogeneous catalyst under ultrasonic irradiation.

Soap is not only make high viscosity product mixture, but also stuck and accumulate in the equipment and system such as silicone tube, valve, peristaltic pump (Figure A.2). Clogged soap made the system over pressure and difficult to clean up. Moreover, soap was coated inside the reactor wall, which attach in the same position of transducers which is obstacle of ultrasonic irradiation.

Figure A.2 Clogged soap stuck in the silicone tube after product was drained.

Not only soap formed via sponification, but glycerol and heterogeneous catalyst also stuck and accumulate in the equipment and system. Figure A.3 shows the actual photo of glycerol and heterogeneous catalyst in the stainless inlet port. To prevent this problem, straight and large tube should be used.

Figure A.4 shows the actual photo of the fresh, 1st cycle, 2nd cycle and 3rd cycle of calcium oxide catalyst (from left to right, respectively) after washed and dried to remove methanol. The calcium oxide catalyst was change the color from white to gray, which was darken for every next cycle due to reaction mixture deposition.

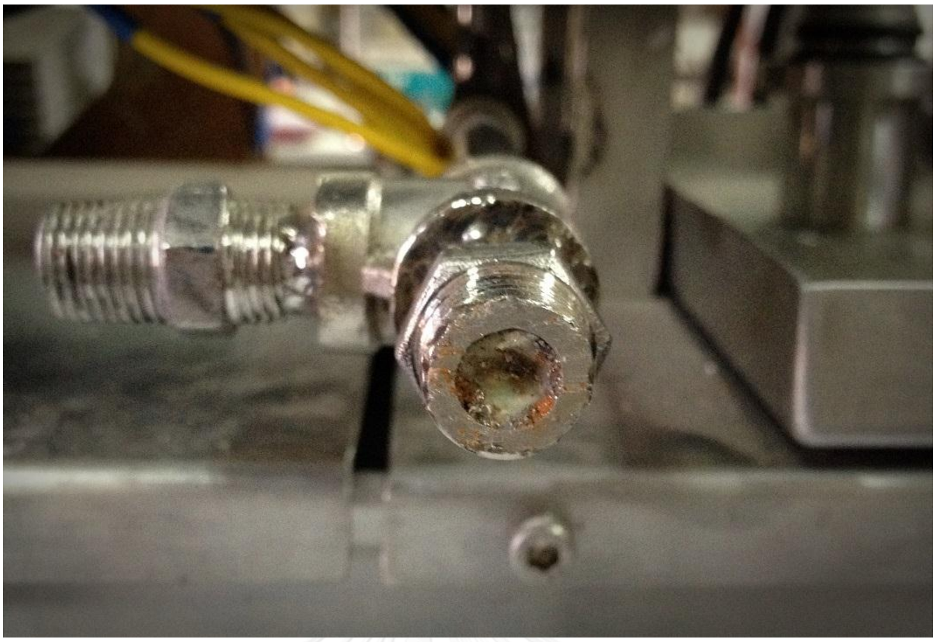

Figure A.3 Clogged glycerol and calcium oxide catalyst stuck in the stainless inlet port.

Figure A.4 The fresh, 1st cycle, 2nd cycle and 3rd cycle of calcium oxide catalyst (from left to right, respectively) after washed and dried to remove methanol.

Appendix B

Ultrasonic wave energy and wave sign calculation

The ultrasonic wave energy comes from the simple harmonic motion of its particles. The total energy will equal the maximum kinetic energy.

$$\begin{aligned} E = Pt &= \frac{1}{2}mv_{max}^2 = \frac{1}{2}m(A\omega)^2 \\ &= \frac{1}{2}\rho V(A\omega)^2 = \frac{1}{2}\rho VA^2(2\pi f)^2 \end{aligned} \tag{5.9}$$

where	E	Wave energy (J)
	P	Ultrasonic power (Watt)
	t	Time period (s)
	m	Mass of medium (g)
	v_{max}	Maximum kinetic velocity (m/s)
	A	Amplitude of the wave (m or mm)
	ω	Angular frequency of the wave, which $\omega = 2\pi f$
	ρ	Density of medium (kg/m^3)
	V	Volume of medium (m^3)
	f	Wave frequency (Hz)

We assume that, the ultrasonic energy does not absorbed by the reactor material. Thus, the ultrasonic energy was transmitted to medium at 100% efficiency.

The ultrasonic energy in a second period can be calculated by Equation (B1.1)

$$E = Pt \tag{B1.1}$$

Thus, at 50% and 100% of maximum ultrasonic power, the ultrasonic energy is 400 J and 800 J, respectively.

The medium in reactor consists of oil and methanol. The density of palm oil and methanol are 890 kg/m^3 and 792 kg/m^3, respectively. Then, the average density of medium can be calculated by Equation (B1.2)

$$\rho_{average} = x(\rho_{palm\ oil}) + (1-x)(\rho_{methanol}) \tag{B1.2}$$

$$= (0.746)(890) + (1-0.746)(792)$$

$$= 865\ kg/m^3$$

where x Mass fraction

From Equation (5.9), we also calculate the amplitude of wave in different patterns as follow:

1. At 50% of maximum power (400 Watt), 20 kHz frequency

$$E = \frac{1}{2}\rho V A^2 (2\pi f)^2$$

$$P \times 1 = \frac{1}{2}(865)(3000 \times 10^{-6})A_{20\ kHz}^2(2 \times \pi \times 20000)^2$$

$$A_{20\ kHz} = 0.0221\ P^{0.5}$$

$$A_{20\ kHz} = 4.418 \times 10^{-4}\ m = 0.442\ mm$$

2. At 50% of maximum power (400 Watt), 50 kHz frequency

$$E = \frac{1}{2}\rho V A^2 (2\pi f)^2$$

$$P \times 1 = \frac{1}{2}(865)(3000 \times 10^{-6})A_{50\ kHz}^2(2 \times \pi \times 50000)^2$$

$$A_{50\ kHz} = 0.0088\ P^{0.5}$$

$$A_{50\ kHz} = 1.767 \times 10^{-4}\ m = 0.177\ mm$$

The sound velocity in palm oil and methanol are 1414 m/s [75] and 1100 m/s [76], respectively. Then, the average sound velocity in medium can be calculated by Equation (B1.3)

$$v_{average} = x\left(v_{palm\ oil}\right) + (1 - x)(v_{methanol}) \tag{B1.3}$$

$$= (0.746)(1414) + (1 - 0.746)(1100)$$

$$= 1334.250\ m/s$$

where x Mass fraction

The wave length of each frequencies can be calculated by Equation (B1.4)

$$\lambda = v/f \tag{B1.4}$$

At 20 kHz frequency:

$$\lambda_{20\ kHz} = 1334.250/20000$$

$$= 0.0667\ m = 66.712\ mm$$

At 50 kHz frequency:

$$\lambda_{50\ kHz} = 1334.250/50000$$

$$= 0.0267\ m = 26.685\ mm$$

Ultrasonic irradiation wave sign in liquid phase of reaction can be expressed by general wave equation (Equation (5.4) and (5.5)).

$$y = A \sin(kx - \omega t) \tag{5.4}$$

$$y = A \sin(\frac{2\pi}{\lambda} x - 2\pi f t) \tag{5.5}$$

where		
	A	Amplitude of the wave (m or mm)
	k	Angular wavenumber of the wave, which $k = \frac{2\pi}{\lambda}$
	ω	Angular frequency of the wave, which $\omega = 2\pi f$
	t	Time period (s)
	λ	Wave length (m or mm)
	f	Wave frequency (Hz)

The wave equations for second (8×20 kHz, 400 Watt), third (8×20 kHz, 400 Watt) and forth (4×20 kHz, 200 Watt combined with 4×50 kHz, 200 Watt) pattern at 1 second period can be expressed by Equation (5.6), (5.7) and (5.8), respectively.

$$y_2 = 0.442\sin(\frac{2\pi}{66.712}x - 2\pi \times 20000 \times 1) \qquad (5.6)$$

$$y_3 = 0.177\sin(\frac{2\pi}{26.685}x - 2\pi \times 50000 \times 1) \qquad (5.7)$$

$$y_4 = 0.312\sin(\frac{2\pi}{66.712}x - 2\pi \times 20000 \times 1) + 0.125\sin(\frac{2\pi}{26.685}x - 2\pi \times 50000 \times 1) \qquad (5.8)$$

VITA

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