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THE EFFICIENT BIODIESEL PRODUCTION IN THE NON-CONVENTIONAL REACTORS

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วิทยานิพนธ์นี้นำเสนอการผลิตไบโอดีเซลด้วยเทคนิคอื่นๆ ที่ไม่ใช่วิธีผลิตแบบดั้งเดิม ได้แก่การผลิตไบโอดีเซลในเครื่องปฏิกรณ์ที่อาศัยคลื่นอัลตร้าโซนิคและไมโครเวฟร่วมด้วย โดยการทดลองแบ่งออกเป็น 4 ส่วน คือ 1) การศึกษาความเป็นไปได้ในการผลิตไบโอดีเซลด้วยเครื่องปฏิกรณ์อัลตร้าโซนิคในระบบกะ 2) การศึกษาประสิทธิภาพและภาวะที่เหมาะสมของเครื่องปฏิกรณ์ที่อาศัยคลื่นอัลตร้าโซนิคช่วยในการผลิตไบโอดีเซลในระบบต่อเนื่อง 3) การศึกษาระบบการผลิตไบโอดีเซลโดยการประยุกต์ใช้งานเครื่องผสมแบบตัดเฉือนและเครื่องปฏิกรณ์ไมโครเวฟ 4) การศึกษาความเป็นไปได้ในการผลิตไบโอดีเซลในระบบต่อเนื่องด้วยเครื่องปฏิกรณ์ไมโครเวฟ ผลการทดลองส่วนที่หนึ่งพบว่าสามารถผลิตไบโอดีเซลได้ผลผลิตที่สูงภายในระยะเวลาที่สั้นเมื่อเทียบกับระบบการผลิตแบบดั้งเดิม นอกจากนี้พบว่าการใช้งานเครื่องปฏิกรณ์ชนิดนี้ยังสามารถช่วยลดการเสื่อมสภาพของตัวเร่งปฏิกิริยาของแข็งได้อีกด้วย การทดลองในส่วนที่สองพบว่าสามารถผลิตไบโอดีเซลจากเครื่องปฏิกรณ์ที่ทำการออกแบบได้ผลการผลิตที่สูงภายในระยะเวลาเพียง 5 นาที เมื่อเทียบกับการผลิตแบบดั้งเดิมที่ต้องใช้ระยะเวลานานถึง 60 นาที เนื่องจากเครื่องปฏิกรณ์ชนิดนี้ช่วยเพิ่มอัตราการเกิดปฏิกิริยาเริ่มต้น นอกจากนี้พบว่าสมบัติของไบโอดีเซลที่ผลิตได้เป็นไปตามมาตรฐานสากล การทดลองในส่วนที่สามพบว่าการประยุกต์ใช้งานเครื่องปฏิกรณ์ทั้งสองชนิดเข้าด้วยกันทำให้สามารถเพิ่มประสิทธิภาพด้านการถ่ายเทมวลและการถ่ายเทความร้อนไปพร้อมๆ กัน จึงทำให้สามารถผลิตไบโอดีเซลได้สมบูรณ์ภายในระยะเวลาเพียง 5 นาที นอกจากนี้พบว่าระบบนี้ต้องการพลังงานในการผลิตเพียงครึ่งหนึ่งของระบบการผลิตแบบดั้งเดิม การทดลองในส่วนสุดท้ายพบว่าสามารถผลิตไบโอดีเซลได้ค่าผลผลิตที่สูงเป็นไปตามมาตรฐานสากลโดยใช้เวลาเพียง 4 นาที ทั้งนี้มีการคำนวณค่าพลังงานกระตุ้นของปฏิกิริยาพบว่าเครื่องปฏิกรณ์ไมโครเวฟสามารถลดค่าพลังงานกระตุ้นของปฏิกิริยาให้น้อยลงเกือบสิบเท่าของค่าปกติ นอกจากนี้พบว่าพลังงานที่ต้องการในการผลิตมีค่าน้อยกว่าระบบการผลิตแบบดั้งเดิมถึงสิบเท่า

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KEYWORDS: BIODIESLE / ULTRASONIC / MICROWAVE / MASS TRANSFER / HEAT TRANSFER / NON-CONVENTIONAL REACTOR

ISSARA CHOEDKIATSAKUL: THE EFFICIENT BIODIESEL PRODUCTION IN THE NON-CONVENTIONAL REACTORS. ADVISOR: PROF. SUTTICHAI ASSABUMRUNGRAT, Ph.D., CO-ADVISOR: PROF. GIANCARLO CRAVOTTO, M.D., KANOKWAN NGAOSUWAN, D.Eng., 108 pp.

This dissertation proposed the biodiesel production from non-conventional reactors, ultrasonic assisted reactor and microwave reactor which mainly divided into 4 parts i) study of the possibility use of ultrasonic assisted reactor for biodiesel production in a batch mode ii) study efficiency and optimization of ultrasonic assisted reactor for biodiesel production in a continuous mode iii) study system for biodiesel production by high shear mixer integrated with microwave reactor iv) study of the possibility use of microwave reactor for biodiesel production in a continuous mode. For the first part, the results show that ultrasonic assisted reactor provides high biodiesel yield in a relatively short reaction time compared with the conventional reactor. Moreover, this reactor also promotes the heterogeneously catalyzed transesterification by hindering the catalyst deactivation. The experimental results from the second part indicates that the designed reactor can produce high biodiesel yield in only 5 min of reaction time compared with 60 min was required from the conventional reactor. Since this reactor can increase the initial rate of reaction. Moreover, the properties of obtained biodiesel also conform to the ASTM standard. In case of the third part, the results show that the application of high shear mixer integrated with microwave reactor can simultaneously enhance both mass transfer and heat transfer. This provides the complete conversion within only 5 min of reaction time. In addition, this system only requires around half the energy use for the conventional system. The high yield of biodiesel following ASTM and EN standard requirements can be also obtained within only 4 min of reaction time from the last part. The activation energy has been calculated and it was found that microwave heating provides a lower 10 times of activation energy than that of the conventional process. Furthermore, the energy requirement for biodiesel production was also lower 10 times than the conventional process.

Department:	Chemical Engineering	Student's Signature	....
Field of Study:	Chemical Engineering	Advisor's Signature	....
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CHAPTER I

INTRODUCTION

1.1 Rationale

Nowadays, the world energy crisis become more crucial issue due to the much more energy demand compared to the energy supply. Therefore, another alternative energy and fuels have been explored to indemnify the higher demand of natural fuels that requires a long reproduction time. Many types of renewable energy especially, biodiesel has been concerned due to its reliable on the environmental-friendly, sustainability and high heating values as nearly equivalent to diesel fuels. The monthly data of biodiesel production from 2011 to 2013 provided by U.S. Energy Information Administration (EIA) as seen in Fig.1.1 shows that its production has clearly increased [1]

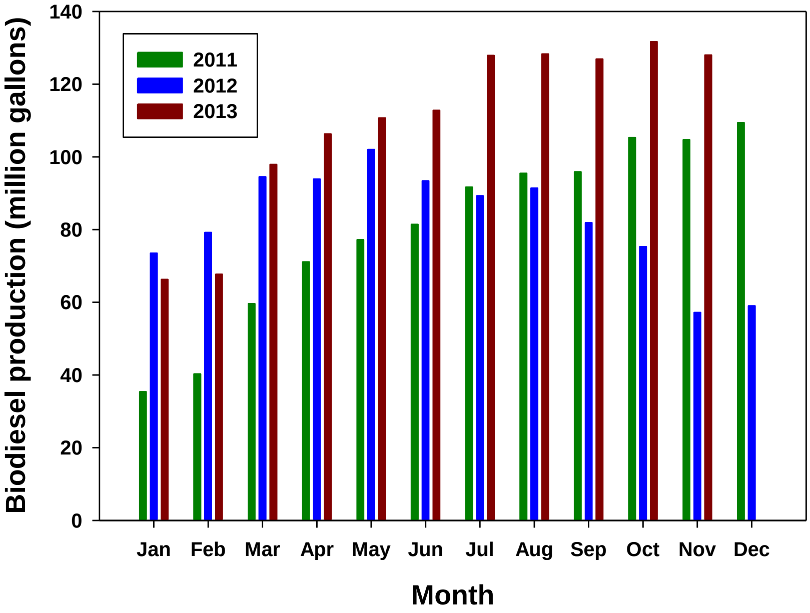

Fig.1.1 U.S monthly biodiesel production from 2011 to 2013 [1]

In general, biodiesel is possibly derived from many types of feedstocks such as edible oils [2-5], non-edible oils [6-10], waste oils [11-13], etc. Fats or oils are reacted with a low molecular weight alcohol to form biodiesel and glycerol with or without the presence of catalyst. However, transesterification of triglycerides (TGs) involves three reversible consecutive steps which limit to biodiesel yield [14]. Moreover, mass transfer between the reactants phase is acknowledged as one of the major problem in the production process. Many types of reactor have been proposed to overcome the reversible reaction by removing the products during the reaction, thus shifting the reaction equilibrium and facilitating increased biodiesel yield [15-19] and to assist the mixing of two reactant by generating a sufficient contact surface area between two immiscible phases [20-22].

The non-conventional reactor, ultrasound assisted reactor (US) and microwave reactor (MW), are interesting technologies for biodiesel production. Ultrasound assisted reactor employs an ultrasound irradiation affecting the variations of pressure in the liquid medium. It induces the generation of microbubbles by cavitation in a reactor to form the emulsion phase. When the microbubbles were collapsed at the reactants boundary, the interfacial area for reaction was largely increased [23, 24]. A recently review summarized that this type of reactor provided a good efficiency for biodiesel production in terms of processing time reduction, sustainable raw materials usage and safer operation [25]. Vichare et al. [26] reported that the mixing time characteristic of sonochemical reactor could be correlated in a way similar to that of the case of jet mixing in tanks. Eventually, this enhanced mass transfer between two phases and accelerated the rate of reaction [27]. By applying this technique, high yield of biodiesel was achieved in a short reaction time. Under this operation, transesterification can be carried out at the lower temperature [4, 28, 29] and less amount of catalyst and methanol are required which are considered as advantages of this reactor [30-32]. However, most of research proposed this application only in a batch reactor but in order to scale-up to the industrial process, the continuous flow reactor is more preferably. This limitation of scale-up process was due to the fact that the local existence of the cavitation phenomena was just near the irradiating surface from ultrasonic transducers [33]. Therefore, the proper design should be optimized to distribute the energy dissipation patterns in this reactor.

Microwave assisted reactor is another interesting non-conventional reactor for biodiesel production. It has been proved to enhance heat transfer for transesterification with the lower energy requirement as compared to conventional heating, especially in the flow system as can be seen in Table 1.1 [34]. Energy is directly transferred through the reactants and accelerated the rate of chemical reactions in a few seconds compared to the longer heating time required for the conventional heating. Microwaves irradiation can interact instantly with a sample matrix via two mechanisms, dipolar rotation and ionic conduction. The dipolar rotation generates heat when the dipoles of the sample aligns themselves after the oscillation of the electric field. For the ionic conduction, heat is generated when the electric field direction is changed via the friction at the molecule levels and the larger ions was slow down. Both mechanisms conduce to the localized superheating of material in a short time period [35, 36].

Table 1.1 Energy consumption for the biodiesel production using conventional and microwave heating

Reaction conditions	Energy consumption (kJ/L)
Conventional heating (continuous)	94.3
Microwave, continuous-flow (7.2 L/min)	26.0
Microwave, continuous-flow (2 L/min)	60.3
Microwave heating, batch reactor (4.6 L)	90.1

Many research proposed the application of biodiesel production in a batch reactor [37-40]. However, the inability to work with mass production of materials and scale up to industrial level are also barrier for this application. Since the penetration depth of microwave radiation into the absorbing materials is normally in a few centimeters. Moreover, the batch processing with a large volume might be not safe if there is any malfunction incident [41]. Therefore, microwave reactor should be operated in a continuous flow to solve this problem.

As mentioned before, the scale up to the industry level as the continuous flow reactor is the necessary issues for economical biodiesel production. Therefore, this research proposed the design of new flow non-conventional reactors employing both of ultrasonic and microwave irradiation for biodiesel production. The systems have been also compared to the conventional mechanical stirred reactor to ensure the overcome of these techniques.

1.2 Objectives

1.2.1 To explore the effect of ultrasound irradiation on the catalytic activity and the catalyst stability of commercial heterogeneous catalysts for transesterification of refined palm oil with methanol and compare to those of the conventional mechanical stirred reactor.

1.2.2 To propose a flow US reactor for biodiesel production using homogeneous sodium hydroxide catalyst. The integration of horizontal mechanical stirrer mixing and ultrasound irradiation has also been investigated.

1.2.3 To investigate and propose the efficient system employing microwave reactor (MicroSynth, Milestone) and high-shear mixing (Magic-Lab, IKA) for sodium hydroxide catalyzed transesterification of refined palm oil and methanol in order to dramatically enhance both of mass and heat transfer for the reaction.

1.2.4 To propose the continuous flow system for biodiesel production by employing microwave reactor (FlowSynth, Milestone). The involved parameters, the energy consumption and kinetics study have also been investigated.

1.3 Scope of Work

1.3.1 The effect of ultrasound irradiation on the catalytic activity and catalytic stability of commercial heterogeneous catalyst, calcium oxide (CaO) and potassium phosphate (K_3PO_4), has been investigated in the batch reactor to gain more understanding about the effect of mixing characteristics on the catalytic activity and catalyst stability. Moreover, the results have been compared with those results from the conventional mechanical reactor. This is the preliminarily study to ensure the advantage of ultrasound irradiation on transesterification before proposed the system in the flow process.

1.3.2 The flow ultrasonic assisted reactor working at two different frequencies, 20 kHz and 50 kHz, has been designed and applied for transesterification. The integration of horizontal mechanical stirrer mixing inside the ultrasonic reactor has also been proposed as a means to improve flow behavior in this reactor. The operating parameters, such as the methanol to oil molar ratio and the amount of catalyst loading have been studied so as to obtain a high biodiesel yield. Moreover, the effects of key flow US reactor operating parameters, such as, frequency, the US transducer location and number of US transducers have also been investigated.

1.3.3 The proposed an efficient combination of two commercial reactors, microwave reactor (MicroSynth, Milestone) and high-shear mixing (Magic-Lab, IKA), has been employed to dramatically enhance both of mass and heat transfer for transesterification of palm oil. The other systems such as high-shear mixing (Magic-Lab, IKA) or the combination of turbo mixer and microwave reactor were also investigated to reveal the effect of mass and heat transfer on biodiesel yield. The energy consumption for biodiesel production and the properties of biodiesel produced from each system have been concerned as the main criteria for consideration.

1.3.4 Biodiesel production in a continuous flow microwave reactor (FlowSynth, Milestone) has been designed and proposed. Many parameters that effect biodiesel yield such as the methanol to oil molar ratio, the operating temperature, amount of catalyst loading, microwave heating power and feed flow rate have been optimized. Moreover, the activation energy of transesterification employing microwave reactor has been calculated. Furthermore, total energy consumption and biodiesel properties analysis have also been considered.

CHAPTER II

THEORY

2.1 Biodiesel

2.1.1 What is Biodiesel?

Biodiesel is a mixture of fatty acid alkyl esters (FAAE) derived from renewable lipid feedstock, such as vegetable oils or animal fats, for use in the compression ignition of diesel engines. Transesterification is the most commonly method used for biodiesel production. The overall reaction is illustrated in Eq.(2.1) which is the reaction between triglycerides (TG) in oil and low molecular weight alcohol (ROH) to produce 3 mol of alkyl esters ($R'CO_2R$) or biodiesel and 1 mol of glycerol (GL). This reaction including three consecutive steps with the intermediate formation of diglycerides (DG) and monoglycerides (MG) as expressed in Eq.(2.2), (2.3) and (2.4).

$$TG + 3ROH \rightleftharpoons 3R'CO_2R + GL \tag{2.1}$$

$$TG + ROH \rightleftharpoons DG + R'CO_2R \tag{2.2}$$

$$DG + ROH \rightleftharpoons MG + R'CO_2R \tag{2.3}$$

$$MG + ROH \rightleftharpoons GL + R'CO_2R \tag{2.4}$$

Commercialized biodiesel can occur on the condition that it must be in accordance with the specifications of ASTM D6751 or EN14214 standards as summarized in Table 2.1 and 2.2, respectively [42].

Table 2.1 Biodiesel standard ASTM D6751.

Property	Limits		Unit
	min	max	
Flash point (closed cup)	130.0	-	°C
Water and sediment	-	0.050	% vol
Kinematic viscosity, 40°C	1.9	6.0	$mm^2\ s^{-1}$
Sulfated ash	-	0.020	% wt
Sulfur	-	0.0015 or 0.05[a]	% wt
Copper strip corrosion	-	No. 3	-
Cetane number	47	-	-
Cloud point	-	Report [b]	°C
Carbon residue (100% sample)	-	0.050	% wt
Acid number	-	0.80	mg KOH g^{-1}
Free glycerol	-	0.020	% wt
Total glycerol	-	0.240	% wt
Phosphorus content	-	0.001	% wt
Distillation temperature, atmospheric equivalent temperature, 90%recovered	-	360	°C

Note: [a] The limits are for Grade S15 and Grade S500 biodiesel, respectively. S15 and S500 refer to maximum sulfur specifications (%wt).

[b] Report: Because the requirements regarding low-temperature properties are vary, the standard ASTM D6751 has a report requirement for its cloud point parameter.

Table 2.2 Biodiesel standard EN14214.

Property	Limits		Unit
	min	**max**	
Ester content	96.5	-	% wt
Density (15°C)	860	900	kg m^{-3}
Viscosity (40°C)	3.5	5.0	mm^2 s^{-1}
Flash point	120		°C
Sulfur content	-	10.0	mg kg^{-1}
Carbon residue (10% dist. residue)	-	0.30	% wt
Cetane number	51	-	-
Sulfated ash	-	0.02	% wt
Water content	-	500	mg kg^{-1}
Total contamination	-	24	mg kg^{-1}
Copper strip corrosion (3 hr, 50°C)	-	1	-
Oxidative stability (110°C)	6.0	-	Hr
Acid value	-	0.50	mg KOH g^{-1}
Iodine value	-	120	g iodine/100 g
Linolenic acid content	-	12	% wt
Content of FAME with ≥4 double bonds	-	1	% wt
Methanol content	-	0.20	-
Monoglyceride content (MG)	-	0.80	% wt
Diglyceride content (DG)	-	0.20	% wt
Triglyceride content (TG)	-	0.20	% wt
Free glycerol	-	0.02	% wt
Total glycerol	-	0.25	% wt
Alkali metals (Na+K)	-	5.0	% wt
Earth alkali metals (Ca+Mg)	-	5.0	mg kg^{-1}
Phosphorus content	-	10.0	mg kg^{-1}

Note: FAME is fatty acid methyl ester.

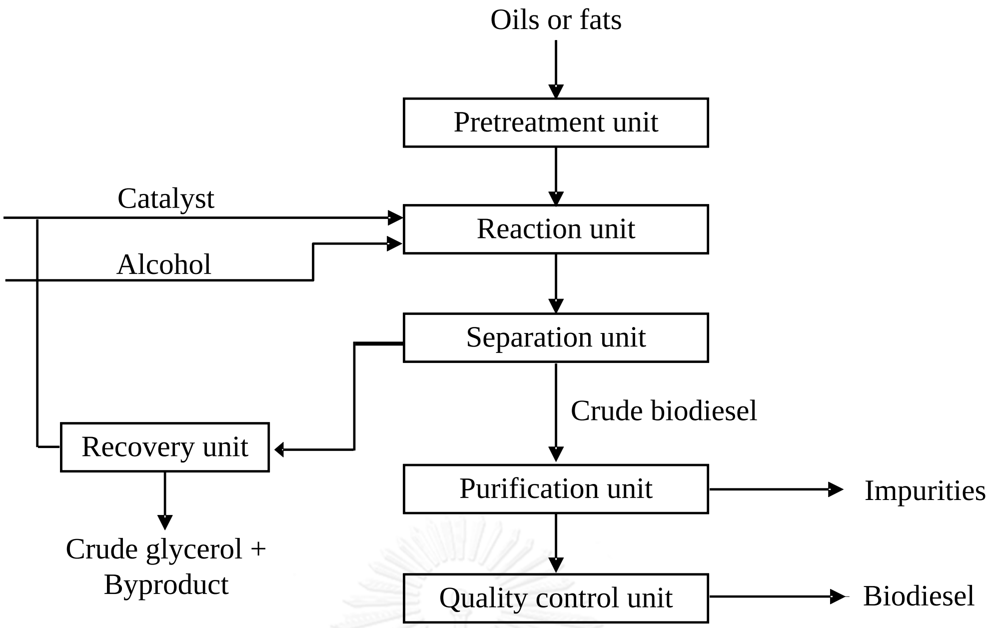

Fig.2.1 The schematic diagram of biodiesel production process.

2.1.2 Biodiesel Production Process

Figure 2.1 shows the commonly biodiesel production process [43]. Any impurities in oils or fats are firstly removed by the pretreatment unit before reacting with alcohol in the presence of catalyst. The generated products including biodiesel, glycerol, unreacted alcohol, trace amounts of water and by-products such as soap, are subsequently separated by a separation unit. The crude biodiesel has to purify and improve the quality in order to obtain biodiesel which meets the specifications of the international standard.

2.1.3 Related Reactions

2.1.3.1 Esterification

Esterification is the reaction between carboxylic acid and alcohols to produce esters product as shown in Eq.(2.5). This reaction is generally occurred in the pretreatment step of biodiesel production from high free fatty acids (FFAs) raw materials. FFAs ($R'CO_2H$) can be reduced by reacting with low molecular weight alcohol in the presence of acid catalyst. The products from this reaction are biodiesel and water.

$$R'CO_2H + ROH \rightleftharpoons R'CO_2R + H_2O \qquad (2.5)$$

2.1.3.2 Hydrolysis

Hydrolysis can occurs when there is a presence of water. As seen in Eq.(2.6), TGs will react with water result in the formation of FFAs and glycerol. FFAs from the reaction can then be converted to biodiesel via esterification reaction.

$$TGs + 3H_2O \rightleftharpoons 3RCO_2H + GL \qquad (2.6)$$

2.1.3.3 Saponification

When high FFAs materials are used to produce biodiesel in a presence of alkali catalyst such as KOH, FFAs can occur a side reaction called "saponification" as shown in Eq.(2.7). There is an undesirable product such as potassium soap (RCO_2K) forms. This soap not only causes the severe product separation problem but also eventually hinders the catalytic activity.

$$RCO_2H + KOH \rightleftharpoons RCO_2K + H_2O \qquad (2.7)$$

2.1.4 Catalytic and Non-catalytic Methods

Biodiesel can produce via both catalytic and non-catalytic methods.

2.1.4.1 Catalytic method

In general, two types of catalysts are applied for the reaction; homogeneous and heterogeneous catalysts. For homogeneous catalyst, biodiesel is typically produced by alkali catalysts such as sodium hydroxide (NaOH) or potassium hydroxide (KOH). The reaction can operate at low temperature and atmospheric pressure with high yields in a short reaction time. However, this catalyst is sensitive to water and FFAs contents since it can cause the side reactions to form soap and water as mentioned above. Therefore, the acid catalysts such as sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) are used because it can react both esterification and transesterification at the same time. However, the rate of reaction is relatively slow.

Heterogeneous catalyst is employed since large amounts of waste water generated from homogeneous catalyst process. This catalyst earns some advantages such as easy to separate from reaction products and reduce the wastewater problem. Enzyme catalyst is another type of catalyst used. It provides high efficiency for biodiesel production. The side reactions can be suppressed when apply this catalyst. However, high cost of enzyme seem to be the major disadvantage.

2.1.4.2 Non-catalytic method

This method uses the supercritical alcohol to operate at the high temperature and pressure without catalysts. High yield within a few minutes can achieve with supercritical conditions. However, the capital and operating costs of this process is also higher than that from the conventional process.

Table 2.3 represents the advantages and disadvantages of each method used to produce biodiesel [44].

Table 2.3 The advantages and disadvantages of each method used for biodiesel production

Variable	Homogeneous Catalyst		Heterogeneous Catalyst	Enzyme Catalysis	Supercritical Alcohol
	Alkali Catalysis	**Acid Catalysis**			
Reaction temperature (°C)	60–70	55–80	180-220	30–40	239–385
FFAs in raw materials	Saponified products	Biodiesel	Not sensitive	Methyl esters	Biodiesel
Water in raw materials	Interference with reaction	Interference with reaction	Not sensitive	No influence	-
Yield of methyl esters	Normal	Normal	Normal	Highest	Good
Recovery of glycerol	Difficult	Difficult	Easy	Easy	-
Purification of esters	Repeated washing	Repeated washing	Easy	None	-
Cost of catalyst	Cheap	Cheap	Potentially cheaper	expensive	Medium

2.1.5 Advantages and Disadvantages of Biodiesel

Obviously, biodiesel provides various advantages compared to fossil fuels, such as a renewable resource and then creating independence from the commodity petroleum. Although biodiesel is only valid for some applications now, but its attractive advantages make it challenge to overcome. However, there are also some disadvantages impede the development and the commercialization of biodiesel.

2.1.5.1 Advantages

- It is produced from non-petroleum, renewable resources.
- It can perform just as well as the normal diesel fuel and can be used in most diesel engines.
- It causes less pollution and greenhouse gases as compared to standard diesel and no sulphur content.
- It is safer to handle due to it is relatively less inflammable compared to the normal diesel.
- It is biologically degradable and non-toxic.
- It has a very good lubricity properties and higher cetane number than diesel fuel, which improves engine's efficiency and life.
- Its production is simpler and environmental-friendly in design than petrochemical productions.

2.1.5.2 Disadvantages

- It is currently more expensive compared to standard diesel fuel.
- It has significant problems with use in low temperatures.
- It releases more nitrogen oxide which lead to the formation of smog.
- It is more sensitive to moisture which can lead to the corrosion problems.
- It has less energy content compared to standard diesel.
- There are a few petrol stations offer biodiesel-fuel.

2.2 Ultrasound

2.2.1 Ultrasound Principles

Ultrasound is a sound of a frequency beyond human hearing (>18 kHz) as shown in Figure 2.2. This sound is normally in the range of 20 kHz to above 100 MHz [45]. Sound is transmitted through a medium by inducing vibration of the molecules. The vibration energy is transmitted as series of compression waves separated by rarefaction waves as illustrated in Figure 2.3. The pitch (or node) of the sound produced by this series of waves depends upon their frequency.

Ultrasound is divided into three regions depending on the frequency [46] that are power ultrasound (20-100 kHz), high frequency ultrasound (100 kHz – 1 MHz) and diagnostic ultrasound (1-500 MHz). Normally, ultrasound in the range of 20-100 kHz is used for chemical and physical changing systems. The other range of ultrasound is used in another application such as animal navigation and communication, medical scanning and detection of cracks in solid, etc.

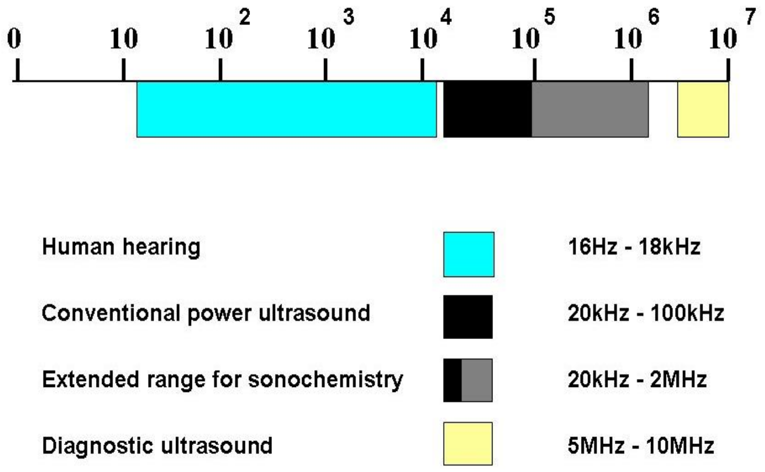

Fig.2.2 The frequency ranges of sound.

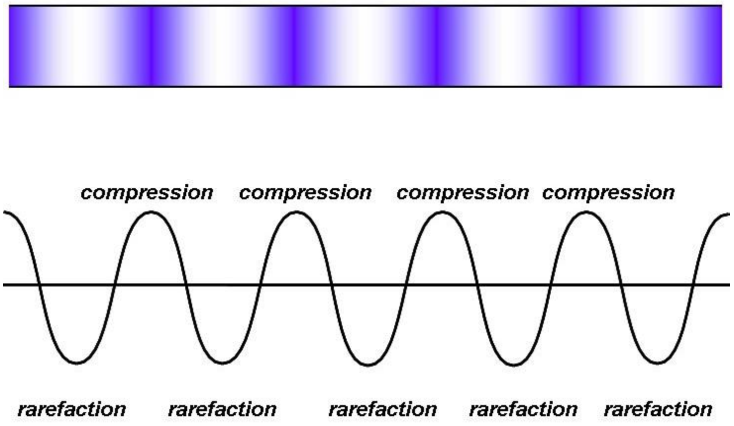

Fig.2.3 Sound transmission in a medium.

2.2.2 Cavitation Phenomenon

Ultrasound enhances the chemical and physical changing in a liquid medium by the formation and destruction of microbubbles. Ultrasound is transmitted via a series of compression and rarefaction waves which induces the molecules of the medium. At sufficiently high power, the rarefaction cycle may exceed the attractive forces of liquid molecules and some microbubbles will form as expressed in Figure 2.4. At this point, small amount of vapor from the medium enter the bubbles during its expansion phase and is not fully discharged during compression. The microbubbles grow over a few cycles to reach an unstable size and then collapse in the successive compression cycles which generates the energy for chemical and mechanical effects. This microbubbles collapse generates shock waves with the temperature of about 5,000°C and the pressures above 1,000 atmospheres.

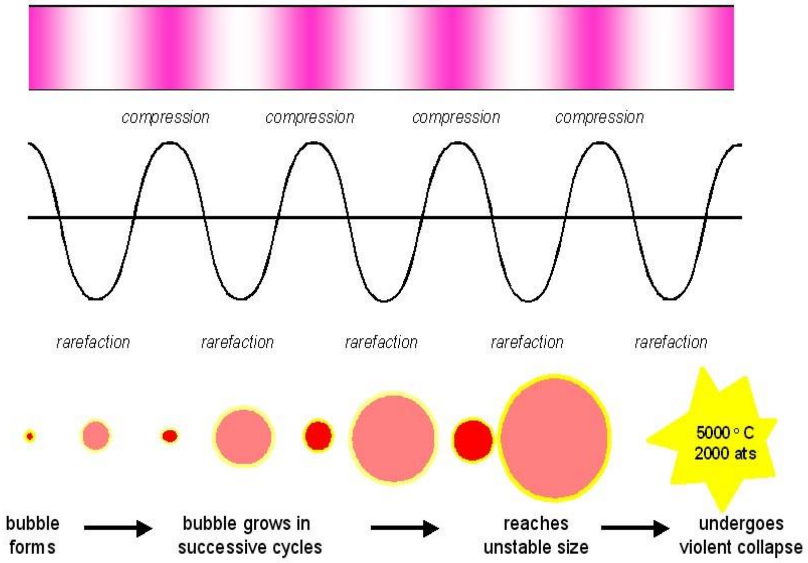

Fig.2.4 Cavitation phenomenon.

2.2.3 Ultrasonic Assisted Reactor

A low frequency ultrasound irradiation could be useful for transesterification. Ultrasound improves the mixing properties of the reactants enhancing the rate of reaction. In addition, ultrasonic-assisted transesterification proviedes more advantages such as less energy required compared to conventional mechanical stirring method i.e.

In general, ultrasound equipment composes of three major components: transducer, booster and horn as represented in Figure 2.5.

2.2.3.1 Transducer

There are two main types of transducer used for ultrasound generation, magnetostrictive and piezoelectric. For magnetostrictive transducer, the electrical energy is converted to mechanical energy by a magnetic coil attached to the vibrating piece. In case of piezoelectric transducer, the electrical energy is converted to high frequency electric energy with the piezoelectric crystals attached to the vibrating piece.

2.2.3.2 Booster

The booster is a device that amplify the mechanical vibrations produced at the tip of the transducer and transfer them to the horn.

2.2.3.3 Horn

Horn is the device that delivers the ultrasonic energy to the liquid medium. The tip of horn should be specifically designed to ensure the maximum energy transfer between the horn and the liquid medium.

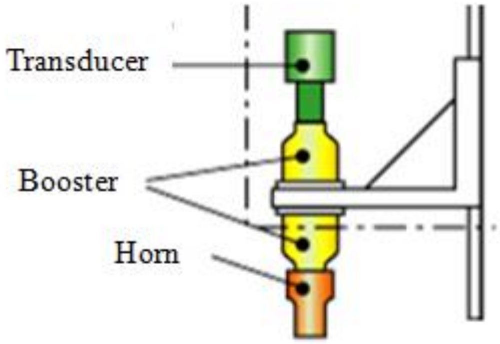

Fig.2.5 Ultrasound equipment

2.3 Microwave

2.3.1 Microwave Principles

In general, the microwave irradiation range is located between the infrared radiation and radio waves. It has 1 mm to 1 m of wavelengths that is corresponding to 0.3 and 300 GHz of frequencies. To avoid the interference from the telecommunication and radar equipment frequencies, the industrial and domestic microwave is regulated to 12.2 cm of wavelength that is corresponding to 2.450 GHz of frequency.

2.3.2 Heat Transfer from Microwave Heating

Microwave heating is called dielectric heating since it employs the dielectric properties of the solvent molecules to transform the electromagnetic energy into heat.

Therefore, the magnitude of heat depends on the dielectric properties of the molecules that unlike to the conventional heating. Since the energy is directly introduced to the reactants, not to the reaction vessel. Then, it generates the uniform heating in the reactor with the short time period. In case of conventional heating, heat transfer occurs by the conduction to the reactor vessel and convection/radiation to the reactants. This requires the long time and results in the non-uniform heating in the reactor. For microwave heating, heat transfer occurs by the dipolar rotation and ionic conduction. These two mechanisms conduce to the localized superheating in a short time period.

2.3.2.1 Dipolar rotation

Fig.2.6 (a) shows the mechanism of dipolar rotation. This mechanism generates heat when sample dipoles try to align themselves after an oscillation in the electric field. The alignment of diploes with the electric field depends on the frequency and the viscosity of the liquid medium. The frequency of irradiation must low enough for the dipole to respond to the electric field and rotate itself. Moreover, it must also not to high for the rotation to precisely follow the field.

2.3.2.2 Ionic conduction

The mechanism of ionic conduction is showed in Fig.2.6 (b). Heat is generated when the electric field direction is changed via the friction at the molecular level and the larger ions slow down. This mechanism is stronger interaction than the dipolar rotation regarding to the heat generating capacity.

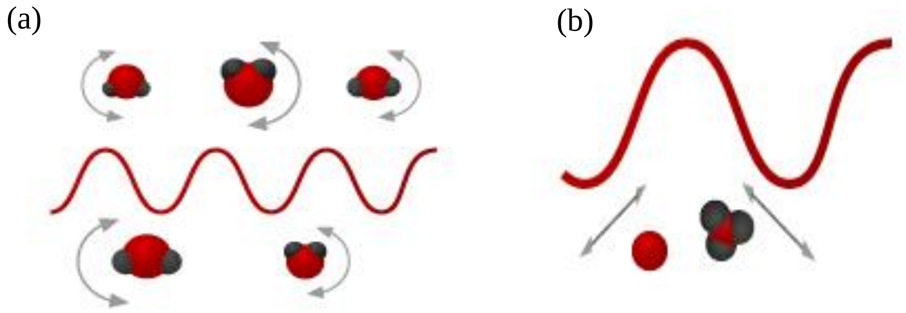

Fig.2.6 (a) Dipolar rotation and (b) Ionic Conduction

CHAPTER III

LITERAURE REVIEW

Biodiesel production has been extensively studied by many researchers. In this chapter, the literature reviews are divided into four main parts. Firstly, the researches on biodiesel production by the conventional process are mentioned. Secondly, the current development of the intensification reactors have been reviewed. Thirdly, the ultrasonic assisted reactor application in both batch and continuous systems are summarized. Finally, the application of biodiesel production by microwave reactor have been provided.

3.1 Conventional Reactors for Biodiesel Production

It is know that the conventional biodiesel technology involves the use of the mechanical stirred reactor. Transesterification is catalyzed by homogeneous alkaline catalyst due to it is able to catalyze at low reaction temperature and ambient pressure with high conversion in acceptable time. The widely used alkaline catalysts are NaOH and KOH. Rashid et al. [47] reported the transesterification of crude sunflower oil using NaOH. The optimum operating conditions were methanol/oil molar ratio of 6, reaction temperature of 60°C and NaOH loading of 1wt% of oil. Biodiesel yield was 97.1% within 2 h and agitation rate of 600 rpm. KOH catalyzed-trasesterification was also studied by Meher et al. [48]. The result revealed that biodiesel yield was more than 85% within 15 min. when the reaction conditions were 1wt% of catalyst, methanol/oil molar ratio of 6:1, reaction temperature of 65°C and agitation rate of 360 rpm. Then the reaction was completed within 2 h with biodiesel yield of 98%. By increasing the molar ratio of methanol/oil to 12, the reaction was completed within 1 h.

The influence of catalyst types, NaOH, KOH and sodium methoxide (CH_3ONa), on biodiesel yield was studied by Leung and Guo [49]. It was found that CH_3ONa was the optimum catalyst. Since upon the mixing of NaOH and KOH with methanol, a small amount of water is produced results in hydrolysis of some esters produced, thus, biodiesel yield is lower. On the other hand, CH_3ONa catalyst only dissociates into CH_3O^- and Na+ without any forming of water. Rashid et al. [50] also investigated the effect of catalysts type on biodiesel production. The results agreed with the previous work, CH_3ONa seem to be the optimum catalyst. 97% of biodiesel yield was achieved when the operating conditions were 6:1 methanol/oil molar ratio, 0.75wt% of CH_3ONa catalyst, 65°C of reaction temperature, 600 rpm of agitation speed and 90 min of reaction time.

However, when applying alkaline catalysts for biodiesel production, high purity feedstock is required because saponification reaction of FFAs with the alkaline catalyst to form soaps could occur. Moreover, the formation of soap also hinders the separation of glycerol from biodiesel [51]. Therefore, acid catalyst has been used to avoid that problem. Zheng et al. [52] studied the acid-catalyzed transesterification of waste frying oil using sulfuric acid (H_2SO_4) as a catalyst. The results indicated that biodiesel yield of 99% can be obtained at the reaction temperature of 70C°, pressure of 169 to 190 kPa, oil/methanol/catalyst molar ratios of 1:245:4 and reaction time of 4 hrs. Goff et al. [53] investigated the acid catalyzed of soybean oil using various types of catalyst : sulfuric, hydrochloric, formic, acetic, and nitric acids, at 100 and 120°C. It was found that only sulfuric acid was effective. At 120°C, 1 wt% H_2SO_4 catalyst and methanol/oil molar ratio of 9, the conversion of oil was 99% when the reaction time was more than 20 h.

Wang et al. [54] proposed the comparison between the acid catalyzed transesterification and the two-step catalyzed process for biodiesel production from waste cooking oil (WCO). For acid catalyzed transesterification, H_2SO_4 was used to catalyze the reaction. For the two-step process, WCO was first catalyzed from ferric sulfate followed by transesterification with potassium hydroxide. It was found that the conversion of FFAs in WCO of the two-step process was 97% at the reaction time of 4 h, molar ratio of methanol to oil of 10:1, while the conversion in the acid process was only 90% within 10 h and molar ratio of methanol to oil of 20:1. This indicates that the two-step process showed more advantages such as higher efficiency with shorter reaction time. In addition, there are many research have studied the two steps process: homogeneous acid followed by alkaline catalyzed transesterification [55, 56].

The feedstock was first treated with acid catalyst to obtain lower level of FFAs and then normally transesterified with alkaline catalyst. Although this process plays a useful way for high FFAs feedstock but the requirement of extra separation in each steps and the slowly process in esterification step are the main significant drawbacks. Heterogeneous catalyst could be an attractive solution to solve about the separation problem of homogeneous catalyst which causes a large amount of waste water. Many types of heterogeneous catalyst are used to produce biodiesel, including both alkaline and acid catalyst. Heterogeneous alkaline catalyst such as zeolites, alkaline earth metal oxides and hydrotalcites were proposed by a numerous of researchers. For example, calcium oxide (CaO) is one of the mostly catalyst used since it provides a high activity and can be operated at the moderate reaction condition. Son et al. [57] studied the transesterification of sunflower oil (SFO) and waste cooking oil (WCO) using CaO as a catalyst. It was pointed out that the maximum biodiesel yield were 92% and 84% for SFO and WCO, respectively. These highest yields achieved at 9 molar ratio of methanol to oil, 3wt% of catalyst, reaction temperature of 80°C and reaction time of 2 h. Since CaO was rapidly hydrated and carbonated in air, then Kouzu et al. [58] proposed solution to prevent that problem by converting CaO to calcium glyceroxide. The results shown that calcium glyceroxide was active in the reaction and was not deactivated by exposing into air. However, biodiesel yield seemed to slightly drop compared to CaO. Moreover, the combination of CaO with other oxide compounds in order to provide the higher catalytic activity and recovery properties has been wildly studied [59-61].

For heterogeneous acid catalyst system, there are a lot of the advantages such as it is not sensitive to FFAs content in feedstock and the esterification and transesterification can occur simultaneously. Nevertheless, this type of catalyst has some significant limitations, slow reaction rate and undesirable side reactions, hence, there is a few research explored its application [62-64]. Supercritical process also requires large amount of energy for the reaction at high temperature and pressure. For example, in supercritical methanol reaction, the temperature and pressure required are higher than 239°C and 8.1 MPa, respectively [65]. Therefore, the modification and improvement of this process to minimize the amount of total energy such as the integration of heat recovery system, is required.

3.2 Intensification Reactors

There are a number of researches proposing some novel reactors for biodiesel production in order to solve the problems occurred when using a conventional reactor. According to the reversible reaction problem that limits the upper conversion of biodiesel, Feng et al. [66] proposed a fixed bed reactor for esterification of FFAs from acidified oil packed with cation-exchange resin. The results indicated that this reactor provides more advantage in term of catalyst damage since there is no mechanical agitation occurring. Consequently, the catalytic property remains nearly constant with long time operation. Moreover, the obtained conversion is higher since it can operate in a continuous mode, hence, water produced from reaction was suddenly removed by the mixture flowing through the reactor. The combination of a fixed-bed and a down-stream plug-flow reactors was setup to produce biodiesel by Lu et al. [67]. An ion-exchange resin was packed in the fixed-bed reactor and used as the pretreatment step for highly FFAs feedstock. After that, a plug-flow reactor acted as the transesterification step. It was found that the residence time was only 19 min at the reaction temperature of 65°C, methanol/oil molar ratio of 6:1 and KOH loading of 1.2 wt% of oil.

A packed bed membrane reactor has been investigated by Baroutian et al. [15]. High quality biodiesel was obtained without the separation and purification steps. Since the membrane selectively removes the products from the reaction mixture and controls the addition of reactants to the reaction mixture simultaneously. The results indicated that the obtained biodiesel also follows the ASTM standard. Kiss et al. [18] proposed the reactive distillation for biodiesel production. Reactive distillation combines the transesterification and product recovery in a single unit. It can shift the reaction equilibrium by continuous removal of byproduct leading to the higher product conversion and yield. However, this reactor requires high energy consumption, hence, Kiss [19] presented the reactive absorption for biodiesel production and compared its performance with that of reactive distillation. This reactor offers significant benefits in term of energy requirement since there are no condenser and reboiler units unlike the reactive distillation. The results indicated that the capital investment and operating costs of this process were 20% and 30% lower than those from the reactive distillation.

As mentioned earlier, the insolubility of oil and alcohol restricts the rate of reaction. Therefore, the development of efficient reactor for vigorous mixing is required. Chen et al. [68] proposed the rotating packed bed reactor to solve the problem mentioned above. The rotary bed was mounted with the motor and powered to rotate in the container. The centrifugal rotation of the rotary bed forced the oil and catalyst passing through the packed bed region and reacting with the reactant gas. Hence, the rate of reaction increased and high conversion was obtained. In addition, Chen et al. [20] also enhanced biodiesel yield in the rotating packed bed reactor by mounting the rigid baffles inside the wall of the container. This carried out the fast and preliminary esters and glycerol phase separation. It was found that the obtained conversion was in the range from 86 to 91% with the rotation speed range of 300 to 1,500 rpm and reaction temperatures of 40 to 58°C.

Rayes et al. [22] investigated the transesterification of soybean and sunflower oil with a dual jet flow stirred reactor. This reactor used the nozzles to generate many small drops of reactants which provide higher mass transfer. Moreover, it was found that 98% of conversion was achieved without requiring any external heat source. Since the frictional effect of the recirculation hoses and nozzles produced self-heating of the inlet fluid to the reactor. In addition, Lafleur et al. [69] also proposed a method for biodiesel production using the atomizers. The atomizers make the reactants and catalyst in a mist form, hence, the maximum mixing in a short time is obtained. Joelianingsih et al. [21] investigated a bubble column for biodiesel production. Methanol solution was heated to be the bubbles and continuously blown into vegetable oil without any catalysts. It was found that highest yield of 95% was obtained at the reaction temperature of 250°C under atmospheric pressure.

3.3 Ultrasonic Assisted Reactor

Ultrasonic assisted reactor is one of the promising technologies used for biodiesel production. This technique employs the cavitation phenomenon to generate a vigorous mixing of the reactants and enhance the mass transfer as cited before. In general, low frequency ultrasound in the range of 20-100 kHz has been used for this application. This type of reactor does not only provide high yield with short reaction time but it also requires less amounts of catalyst and methanol used in the reaction. There are many researches using homogeneous catalyst in an ultrasonic assisted reactor. Some of that research and its optimal operating condition are summarized in Table 3.1. [70-81]

In addition, ultrasonic assisted reactor could be operated at room temperature which plays an excellent benefit in term of operating condition. Hanh et al. [82] investigated the ultrasonic assisted reactor for transesterification of triolein with various alcohols at room temperature. The ultrasound frequency of 40 kHz with a maximum power of 1,200 W was applied. The results indicated that the steric hindering of high carbon atom alcohol would hinder the reaction and obtained the lower conversion rate compared with low carbon atom alcohol. It was found that biodiesel yield over 95% was achieved within 25 min of reaction time when using methanol to oil molar ratio of 6 and KOH loading of 1wt%. Moreover, Fan et al. [29] studied the transesterification of crude cottonseed oil with methanol in the presence of various types of catalyst with ultrasonic irradiation at room temperature. It was pointed out that potassium methoxide (CH_3OK) exhibits the high activity which high yield within 5 min of reaction time. Furthermore, Van Manh et al. [83] also investigated the application of 25 kHz and 270W ultrasonic assisted reactor for biodiesel production from low cost feedstock, Tung oil, at room temperature. It was found that only 30 min. is required for 91% of biodiesel yield with 1wt% of KOH catalyst and alcohol to oil molar ratio of 6.

Table 3.1 The homogeneous ultrasonic assisted reactor for biodiesel production.

Type of oil	**Frequency (kHz) /Power (W)**	**Temperature (°C)**	**Time (min)**	**Alcohol:oil molar ratio**	**Catalyst (wt% of oil)**	**Yield (%)**	**Ref.**
Soybean*	19.7/150	45	30	6:1	1 NaOH	100	[70]
Rapeseed	40	40	25	6:1	0.5KOH	97	[71]
Castro	45/1920	Autogeneous	20	9:1	0.75 KOH	92	[72]
Soybean	24/400	79	5	6:1	1 KOH	98	[73]
Soybean	20/pulse mode	20-30	1.5	3:1	1 NaOH	96	[74]
Coconut	24/200	60	7	6:1	0.75 KOH	98	[75]
Sunflower	40/150	33	60	7.5:1	0.7 KOH	88	[76]
Jatropha							
1st step	-/210	60	60	10:1(vol)	4 H_2SO_4		[77]
2nd step			60	24:1 (vol)	1.4 NaOH	96.4	
Jatropha	59/150	60	150	5.5:1	1KOH	98	[78]
Waste cooking	24/200	60	40	6:1	1.5 NaOH	98	[79]
Waste cooking	20/400z	30	30	6:1	0.75 KOH	90	[80]
Waste cooking	20/200	45	40	6:1	1 KOH	89	[81]

Note: * means ultrasonic as a probe type.

Further works were studied by combining two techniques to heighten the biodiesel production efficiency. Cintas et al. [84] proposed the combination of mechanical stirred reactor with ultrasonic flow reactor to produce biodiesel from soybean oil. The reactants and catalyst were first catalyzed by the stirred tank reactor for 30 min and then was circulated through the ultrasonic reactor for 35 min. This application indicated that it required lower methanol and catalyst loading, energy consumption and reaction time. Riva et al. [85] also studies the mechanical stirred reactor integrated with ultrasonic assisted reactor. This reactor can be operated in both batch and continuous mode with short reaction time and less energy consumption compared to the conventional process. Moreover, biodiesel product also meets the EN 14214 and ASTM D6751 standards. The integration of ultrasonic mixing and closed microwave irradiation reactor was proposed by Hsiao et al. [86]. First, the reaction was preliminary carried out in ultrasonic assisted reactor at 27°C for 1 min. After that it was then catalyzed by the microwave irradiation at 60°C for 2 min. The results shown that highest yield of about 98% was obtained with the NaOH catalyst loading of 1wt% and methanol to oil molar ratio of 6.

Resent researches on ultrasonic assisted reactor have also focused on the use of heterogeneous catalysts. Since it is not only solve the wastewater problem but also easy to handle and separate. Moreover, it is more appropriate for apply in an industrial scale. Salamatinia et al. [87] proposed the application of mathematical models to evaluate and optimize biodiesel production process catalyzed by barium oxide (BaO) and strontium oxide (SrO). The optimal conditions for biodiesel production was first predicted by the mathematical models and validated with the results from the ultrasonic processor. The results shown that the models were able to accurately predict the experiment with less than 5% error. The optimal operating conditions were the catalyst loading of about 3 wt% of oil, the molar ratio of methanol to oil of 9. Highest yield were 94% and 93% for BaO and SrO, respectively within 50 min of reaction time. After that, the catalytic activity of alkali earth metal oxides (CaO, SrO and BaO) from the previous work was investigated by Mootabadi et al. [88] The results indicated that the highest yield of about 95%, 93% and 77% were obtained when using BaO, SrO and CaO catalysts, respectively. Although BaO provided the highest yield but it underwent more severe activity drop in the catalyst reusability test.

The catalysts dissolution was found to be main activity drop of the reused catalysts. Therefore, SrO catalyst seemed to be the most promising catalyst for biodiesel production. Salamatinia et al. [89] also evaluated the quality of biodiesel produced from the previous work and compared with that produced by conventional stirred reactor. It was found that biodiesel produced by ultrasonic assisted reactor exhibited the better quality and satisfied with the ASTM and EN standards than that produced by the conventional method. It had a better clarity, less FFAs and residual amount of catalyst remaining in the product.

Other synthesized catalysts were also investigated by other works [27, 90, 91]. However, for a real application in the industrial scale, commercial catalysts seem to be the suitable catalyst for use.

3.4 Microwave Reactor

Microwave reactor has been widely applied in transesterification due to the efficient heat transfer enhancement. As mentioned before, it provides the fast heating only in a few seconds for the chemical reaction as compared with the longer time required for conventional heating. Some research on biodiesel production in a batch microwave reactor using homogeneous [37-39, 92-99] and heterogeneous catalyst [93, 100-110] are summarized in Table 3.2 and 3.3, respectively.

Table 3.2 The optimal conditions for biodiesel production using homogeneous catalyst in a batch microwave reactor

Type of oil	Power (W)	Temperature (°C)	Time (min)	Alcohol:oil molar ratio	Catalyst (wt% of oil)	Yield (%)	Ref.
Cotton seed	1,200	60	7	6:1	1 KOH	92.4	[37]
Rapeseed	1,200	40 60	5 3	6:1	1 NaOH 1 KOH	92.7 93.7	[92]
Camelina Sativa	800	-	1 1	9:1	0.5 NaOH 1 KOH	96 97	[93]
Crude palm (CPO)							
1st step	70	70	60	24:1	4 H_2SO_4		[94]
2nd step		70	5	4:1	1.5 KOH	80	
Esterified CPO	70	-	5	85.:1	1.5 KOH	85	[95]
Soybean Rice bran	1,600	80	20	5:1	0.15 NaOH	98.64 98.82	[39]
Pongamia pinnata	300	60	5	6:1	0.5 NaOH 1 KOH	96 96	[38]
Palm	750	60 - 65	3	6:1	0.75 CH_3ONa	99.5	[96]
Wasted cooking	300	78	5	6:1	2 KOH	95	[97]
Wasted cooking	750	-	3	6:1	0.75 CH_3ONa	97.9	[98]
Wasted cooking	1000	64	3	9:1	1 NaOH	95.29	[99]

Table 3.3 The optimal conditions for biodiesel production using heterogeneous catalyst in a batch microwave reactor

Type of oil	**Power (W)**	**Temperature (°C)**	**Time (min)**	**Alcohol:oil molar ratio**	**Catalyst (wt% of oil)**	**Yield (%)**	**Ref.**
Castor bean	40	-	5	6:1	1 Al_2O_3/50%KOH	95	[100]
Camelina	800	-	4	9:1	1.5 BaO	94	[93]
					2 SrO	80	
Yellow horn	1,000	60	10	12:1	1 heteropolyacid	96.22	[101]
Oleic acid	40	60	20	20:1	5 Sulfated ziconia	90	[102]
Canola	-	100	5	1:1 (mass)	1 $ZnO/La_2O_2CO_3$	95	[103]
Soybean	900	-	2	6:1	1.84 SrO	96	[104]
Waste cooking	1,100		0.7			99	
Sunflower	-	70	40	4:1	1.5 Nano-MgO	99	[105]
Castor	200	65	60	12:1	5 H_2SO_4/ 55C	94	[106]
Oleic acid	1,400	200	20	10:1	5 Nb_2O_5	68	[107]
					5 S-ZrO_2	68.7	
Soybean	150	75	90	30:1	24 K_2SiO_3/C	96.7	[108]
Soybean	900	65	60	7:1	3 nano-CaO	96.6	[109]
Camelina sativa	800	-	4	9:1	1.5 BaO	94	[110]
					2 SrO	80	

There are a lot of drawbacks for batch operation such as poor adaption to a large scale process and high energy intensive. Therefore, a continuous flow production can be a good choice to provide many significant benefits that include the low production costs and time, the ability to scale up in the large scale process and the higher production capacity. Barnard et al. [34] reported the biodiesel production in a flow microwave reactor with a high flow rate of 7.2 mL/min. The calculated energy consumption showed that this method provided more energy-efficient than using a conventional heated apparatus. The high conversion of 99% can be obtained with the microwave heating power of 1,600W. Terigar et al. [111] proposed the application of microwave-assisted reactor transesterification of soybean and rice bran oil in a continuous mode with the feed flow rate of 100 mL/min. Reactants and catalyst were stirred vigorously for approximately 15 min before apply through the microwave. It was found that the high conversion of 99% can be gained within 10 min of reaction time. The quality of produced biodiesel also conformed to the ASTM standard. Another flow microwave system was presented by Groisman and Gedanken [41]. The canola and sunflower oil was used as the raw material and KOH as a catalyst. The obtained biodiesel yield for canola and sunflower oil were 92% and 89%, respectively. Several batch reactions were tested to compare biodiesel yield with this system. It was found that biodiesel yield of only 64% can be achieved from the batch operation. This emphasizes the inability of large-scale process for batch operation compared with continuous operation.

Lertsathapornsuk et al. [112] proposed biodiesel production by a modified 800W household MW. The configuration applied a coil-shape poly-tetrafluoroethylene tubing (Teflon), with an internal diameter of 0.9 cm and 260 cm length of the reactor. It was found that this system can produce a high biodiesel yield of 97% with a very low residence time of 30 s at 78°C of reaction temperature with ethanol to oil molar ratio of 12:1 in the present of 3.0%wt of NaOH catalyst. Liao and Chung [113] have also studied biodiesel production in a continuous flow household MW. The configuration of this approach is similar to the previous system except for the fact that all reactants were mixed before being fed to the coil reactor. High fatty acid *J. curcas* oil was used as a raw material. Therefore, a two-step process, esterification followed by transesterification, was employed and response surface methodology was used to design the experiment. The results show that a high biodiesel yield of 99.38% can be achieved with a methanol to oil molar ratio of 8 and 1.3%wt of NaOH catalyst loading. However, the system requires high energy consumption of 2.67 kWh/L of biodiesel produced and a feed flowrate was quite low as 3 mL/min. Suppalakpanya et al. [114] also reported the biodiesel production from crude palm oil using a continuous microwave system. The esterification process was first carried out with a ethanol to oil molar ratio of 6, H_2SO_4 loading of 1.25%wt of oil, microwave power of 78 W and reaction time of 90 min to reduce FFAs contents. After that esterified palm oil has been transesterified under the optimal conditions as ethanol to oil molar ratio of 8.5, KOH loading of 2.5%wt of oil, microwave power of 78 W and a reaction time of 7 min. The final yield obtained from this system was 97.4% and ethyl ester product also met with the standard requirement.

Another application of MW for biodiesel production in a flow system was investigated by Encinar et al. [115]. Oil and methanol with dissolved catalyst were fed separately and mixed together before flowing into the Teflon tube reactor placed in the MW oven. It was found that a residence time of 2 min was required to obtain 99% oil conversion using a methanol to oil molar ratio of 12, KOH catalyst loading of 1%wt of oil and an outlet temperature of 70°C.

CHAPTER IV

EXPERIMENT

The experimental set up are divided into 4 parts in accordance with the objectives of this work. The first part is set up for the preliminary work on ultrasonic assisted reactor in order to ensure the efficient biodiesel production from this technique. After that the new flow ultrasonic assisted reactor has been designed and tested biodiesel production in the flow configuration. Furthermore, the application of microwave reactor on biodiesel production has been investigated on the third and fourth parts. For the third part, the system was designed to enhance both mass transfer and heat transfer simultaneously by the integrated of two commercial reactor. However, the system was operated in the semi-continuous mode. Therefore, biodiesel production employing microwave reactor in a flow configuration has been provided in fourth part.

4.1 Biodiesel Production in an Ultrasonic Bath

4.1.1 Chemicals

Refined palm oil as a commercial edible grade was purchased from local department store in Thailand. Methanol employed in the reactions was purchased from Qrëc with 99.5% purity. All experiments were carried out using commercially available catalysts. Sodium hydroxide (NaOH) as purchased from Loba Chemie was ground and dissolved in methanol before use. Sulfuric acid (H_2SO_4, 99.5%) was purchased from Qrëc. Cacium oxide (CaO) was obtained from Riedel-deHaën. The decomposition temperature of uncalcined CaO catalyst was performed to investigate the optimum calcination temperature of CaO catalyst (data not shown). It was found that the weight loss of uncalcined CaO catalyst appeared from 350 to 550°C due to the decomposition of $Ca(OH)_2$. Therefore, this CaO was calcined in a muffle furnace at 550°C for 5 h and kept in a desiccators before transesterification. Moreover, potassium phosphate (K_3PO_4) in a granular form of 2–5 mm was provided from Sigma-Aldrich and used as received. Methyl heptadecanoate and heptane (internal standard and a solvent for GC analysis) was high purity chemicals from Sigma Aldrich and used as obtained.

4.1.2 Catalyst Characterization

Surface area and pore volume of solid catalysts were analyzed by BET method. Catalyst samples were degassed at 300°C and 10^{-3} mmHg for 3 h. Adsorption measurements were carried out using UHP N_2 adsorption at −196°C in a Micromeritics ASAP 2020 automated system. All particle size measurements were performed using a Malvern Zetasizer. The sample was dispersed in the distilled water and placed in the ultrasonic bath for more dispersion before analysis. X-ray powder diffraction (XRD) patterns was measured on a Bruker D8 Advance Diffractometer at 40 kv, 40 mA with Cu-Kα radiation (λ=1.54056 nm). Data were collected over a 2θ range from 20 to 60° with a step size of 0.02 at a scanning speed of 0.5/min. Fourier transform infrared (FTIR) spectrum was performed on a Nicolet 6700 FT-IR spectrometer over a scanning range from 400 to 4000 cm^{-1}. Thermogravimetric analysis (TGA) was conducted with a SDT analyzer Model Q 600 from TA Instrument, under flowing air in the temperature range of 25–900°C. CO_2 temperature program desorption (CO_2-TPD) was carried out to determine the basicity of CaO and K_3PO_4 using a Micromeritics ChemiSorb 2750. For CO_2-TPD, a 0.2 g of catalyst sample was heated to 550°C in 20 mL/min of helium gas for 1 h in order to remove adsorbed impurities. After that, the sample was cooled to room temperature and saturated with 20 mL/min of pure CO_2 for 1 h. Physisorbed CO_2 was eliminated by flushing with a 20 mL/min of helium at room temperature for 1 h, and increase to 100°C with a rate of 10°C/min, then held for 4 h. The temperature was ramped up at a rate of 10 °C/min to 550°C using TPD as a detector.

The methyl esters yield was analyzed according to EN 14103 using a Shimadzu gas chromatography Model GC-14B, equipped with a ZB5-HT capillary column (0.25 mm×30 m). Helium was used as a carrier gas. The oven temperature ramp program was started from 150°C and held for 5 min, 170°C with a rate of 10°C/min and held for 5 min, 220°C with a rate of 3°C/min. Temperatures of the injector and detector were 250°C.

4.1.3 Experimental Set Up

All experiments were performed in a 125 mL 3-neck round bottom flask immersed into an ultrasonic cleaning bath of 40 kHz Crest Ultrasonic Cleaner with a power of 160 W. Since the sound wave propagates through the liquid medium and the attenuation of sound wave increases with the increasing of the distance from transducer [23]. In other words, the ultrasonic activity is more pronounced at the zone nearby the irradiating surface and suddenly decreases as far away from the source both in axial and radial directions [116]. Then, the position of the flask was fixed at the middle of the ultrasonic cleaning bath for all experiments. While using MS reactor, the experiments were performed with the stirrer speed of 800 rpm. The reaction temperature was controlled at 65°C by circulating hot water through the bath for all experiments. Three-neck round bottom flask was equipped with a condenser circulated with cold water from an ice bath, a thermometer and a sampling valve as illustrated in Fig.4.1. Refined palm oil was reacted with methanol in a molar ratio of 1:6. Catalyst loadings were 3, 5, and 1 %wt of oil for solid catalysts, H_2SO_4, and NaOH, respectively. Two millilitres of sample was taken out of the reactor within the intervals of time period and quenched in an ice bath to stop the reaction. The sample was centrifuged to remove the solid catalyst and kept in the refrigerator before analysis by GC.

In the case of catalyst reusability studies, the reaction condition was the same as previously described. Refined palm oil was also reacted with methanol in a molar ratio of 1:6. Solid catalyst loading was 3 %wt of oil without any pre-treatment. The reaction mixture was carefully removed from 3-neck round bottom flask by syringe and the spent catalyst was recovered. Then, fresh refined palm oil and fresh methanol were filled in the reactor. The reaction time for each cycle was set up for 1 h. The catalyst was recovered and used for three times. Then, reaction mixture of each cycle was analyzed.

The fresh and used catalysts were analyzed by TGA, FTIR and Zetasizer to investigate the cause of catalyst deactivation. Moreover, dissolution of catalyst into the reaction mixture was carried out to investigate the possibility of catalyst reusability. First, solid catalyst was mixed with methanol and heated at the reaction temperature for 1 h. After that the catalyst was filtered out and the remaining methanol was then reacted with oil for 2 h at 65°C. Lastly, the product mixture was then analyzed by gas chromatography.

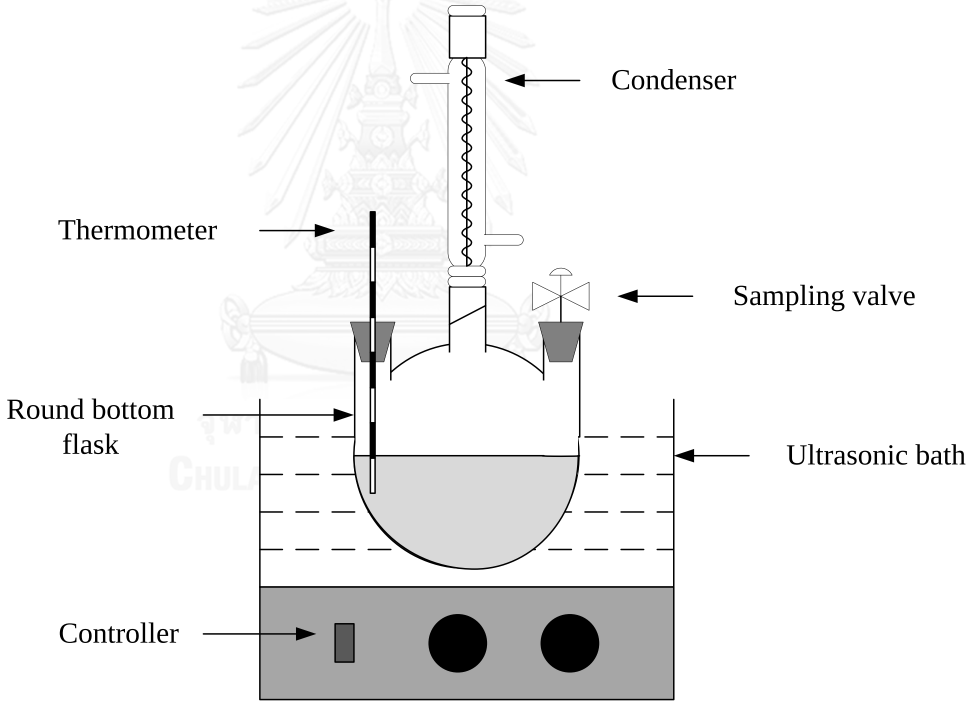

Fig.4.1 Setup of an ultrasonic bath reactor

4.2 Biodiesel Production from the Designed Ultrasonic Flow Reactor

4.2.1 Chemicals

Commercial refined palm oil was purchased from a local department store in Thailand. 99.5% purity methanol, used for transesterification, was purchased from Qrëc. The NaOH catalyst purchased from Loba Chemie was ground and dissolved in methanol before use. Methyl heptadecanoate and heptane (internal standard and solvent for GC analysis, respectively) were high purity chemicals from Sigma–Aldrich and were used as obtained.

4.2.2 Analysis

The methyl ester yield samples were analyzed following the EN 14103 standard method using GC-2010 Plus Shimadzu gas chromatography equipment fitted with a flame ionization detector and a capillary column DB-WAX (0.25 mm x 30 m). Helium and nitrogen were used as carrier gas and makeup gas. The oven temperature ramp program was started at 150°C and held for 5 min, heated up to 190°C with a rate of 3°C/min and held for 5 min, then heated up again to 220°C with a rate of 3°C/min and held for 5 min. Injector and detector temperatures were 250°C. Methyl ester yield was calculated by Eq. (4.1):

$$\%\mathbf{Yield} = \frac{\sum \boldsymbol{A} - \boldsymbol{A_{EI}}}{\boldsymbol{A_{EI}}} \,\mathbf{x}\, \frac{\boldsymbol{C_{EI}} \,\mathbf{x}\, \boldsymbol{V_{EI}}}{\boldsymbol{m}} \,\mathbf{x}\, \mathbf{100}\% \qquad (4.1)$$

where $\sum \boldsymbol{A}$ is total peak area, A_{EI} is the peak area that corresponds to methyl heptadecanoate, C_{EI} is the concentration of the methyl heptadecanoate solution (mg/mL), V_{EI} is the volume of methyl heptadecanoate (mL) and m is the mass of the biodiesel sample (mg).

The biodiesel sample was washed with distilled water at a water; biodiesel ratio of 0.5:1 by volume, 3 times at ambient temperature under a stirrer speed of 200 rpm [117]. The properties of the purified biodiesel were then analyzed according to the ASTM standard.

4.2.3 Experimental Set Up

The schematic diagram of the MS-US flow reactor used in this experiment is shown in Fig.4.2. It can be divided into three main parts, the reactant tank, the generator and the reactor, as can be seen in Fig. 4.3. A 6 L cylindrical reactant tank was used to preheat the raw materials, oil and methanol, before feeding them into the reactor (Fig. 4.3(a)). The preheat temperature and the feed flow rate were fixed at about 45°C and 55 mL/min (corresponding to residence time of 4 min), respectively, and correspond to the best conditions reported by Cintas et al. [84]. Stirrer speed in the preheat tank was about 160 rpm.

The generator (Fig. 4.3(b)) was used to control many operating parameters such as reaction temperature, frequency and location of transducer used along the length of the reactor and the speed of the stirrer inside the reactor. The rectangular shape of reactor as illustrated in Fig. 4.3(c) was applied since it was reported that the rectangular cross-sections provides the excellent distribution of the cavitational activity and it is suitable for the large scale process [118]. Moreover, it has also been reported that a combination of low frequency irradiation (typically 20 kHz) with other frequencies in the range of 50-200 kHz should be applied to gain the maximum benefits from the cavitational activity, hence 20 and 50 kHz of frequencies were employed in this work [23]. A typical range of optimum intensity of irradiation is 5–20W/cm^2 [118].

The NaOH catalyst was fed into the tank after the reactant temperature (palm oil and methanol) was constant. The experiment was carried out by circulating all products and reactants from the US flow reactor outlet into the reactant.

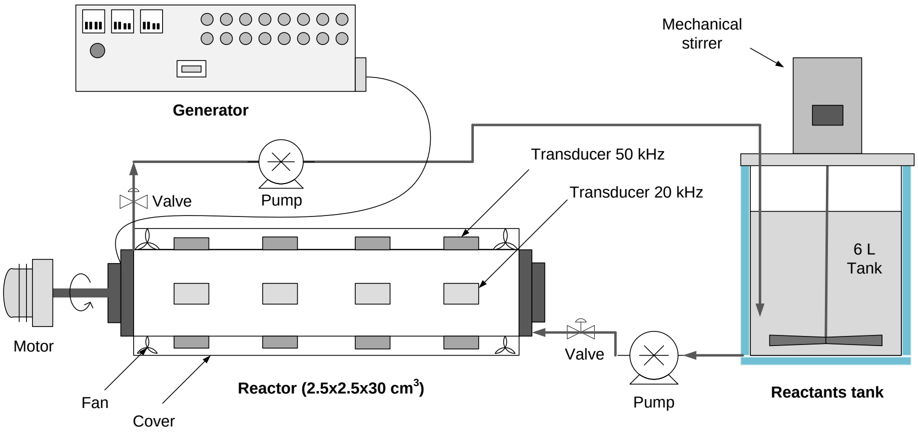

Fig.4.2 Schematic diagram of the MS–US flow reactor system.

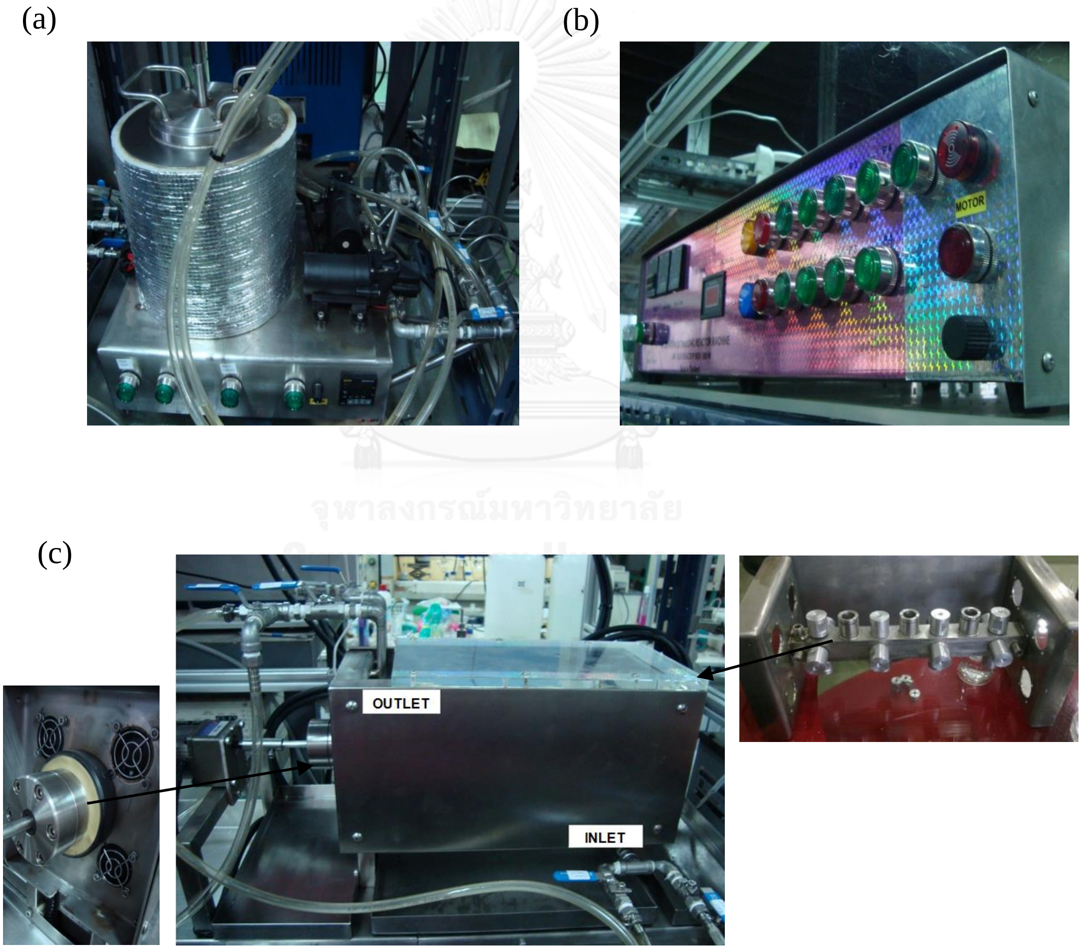

Fig.4.3 Each parts of US flow reactor.

4.3 Biodiesel Production from High Shear Mixer Integrated with Microwave reactor

4.3.1 Chemicals

Commercial refined palm oil was kindly provided by Embouteille Company, Italy. Methanol reactant, of 99.9% purity, and methyl heptadecanoate, used as an internal standard for GC analysis, were purchased from Sigma-Aldrich. The NaOH catalyst, of 97.5% purity, and the heptane solvent, of 99.7% purity, were obtained from Carlo Erba Reagenti.

4.3.2 Analytical Method

Biodiesel yield was analyzed according to the EN 14103 standard method using an Agilent Technologies 7820A GC system. This GC system is equipped with a flame ionization detector and a capillary column MEGA-WAX (0.25µm x 0.25mm x 30m). The method and calculation are the same as mentioned before in part 4.2.2.

4.3.3 Equipment

The HSM (Magic Lab, by IKA Germany) is a new modular laboratory system which is especially designed for mixing, dispersing, wet milling and the incorporation of powders into liquids. It can produce homogeneity and stability in emulsions and suspensions using its three rotors, high-shear dispersing module. The system configuration is illustrated in Fig. 4.4(a). There are three rotors that differ according to orifice shape and slot width, as shown in Fig. 4.4(b), which are used to provide varying dispersal levels. The rotors are arranged in series for optimum performance and functionality and are defined as coarse, medium and fine. The configuration also includes a cooling system which disperses heat, generated by the rotors and the operating unit, and controls the operating parameters such as temperature, rotor speed and rotation time.

MW irradiation was performed in a MicroSynth MW oven (by Milestone, Italy), with a maximum power setting of 800W and equipped with an IR pyrometer.

Fig.4.4 (a) HSM (Magic-Lab, IKA) and (b) Three types of rotor; coarse, medium and fine rotor, respectively.

4.3.4 Experimental Set Up

The experimental set up was divided into 3 systems as follows:

System 1: A combination of the HSM (Magic Lab) and the MW reactor (HSM+MW). This combination is shown in Fig.4.5. The catalyst and all the reactants were firstly fed from the HSM and continually passed through the glass coil reactor, placed in the MW reactor. The outlet products were circulated to the HSM and fed through MW depending on the pre-decided circulation cycles.

System 2: The HSM was used alone. The configuration of the system is illustrated in Fig.4.6.

System 3: A combination of a turbo mixer and MW reactor (TB+MW) was used to enhance mass and heat transfer of the reaction (Fig.4.7). The procedure was the same as system 1. However, TB was used as a conventional means to mix reactants before they were fed into the MW. The aim of this set up is to emphasise the heat transfer effect of the MW.

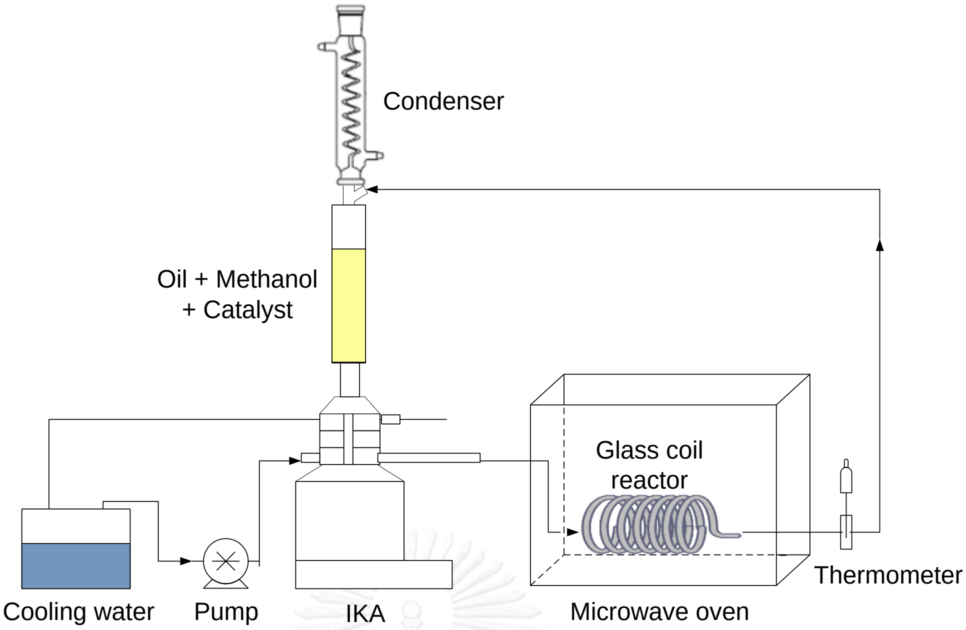

Fig.4.5 System 1: a combination of HSM and MW

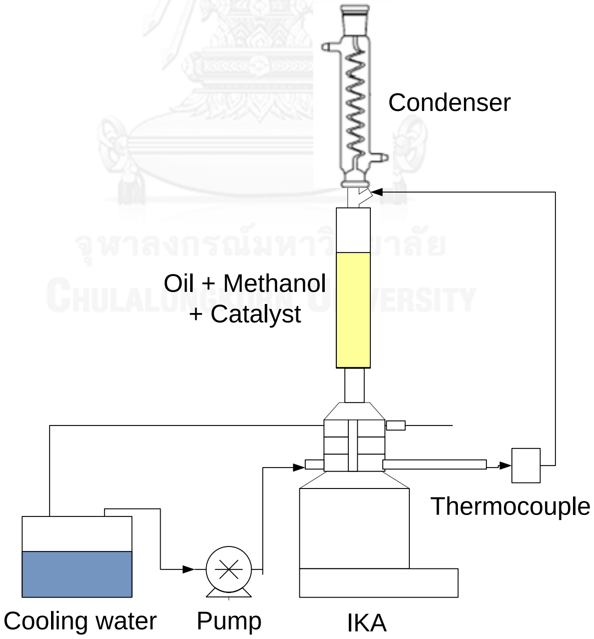

Fig.4.6 System 2: HSM alone

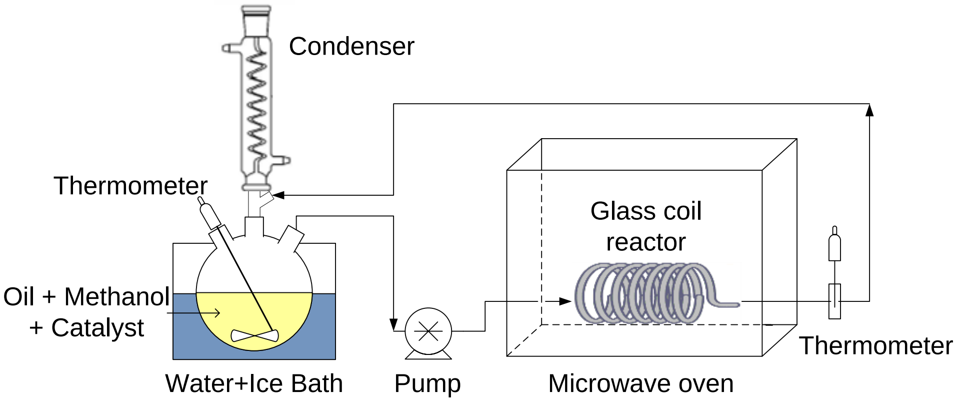

Fig.4.7 System 3: a combination of TB and MW

Feed flow rate was measured by a specific flow meter ASA (model G6-2600/39 for biodiesel, – Sesto S. Giovanni, Italy) and fixed at 250 mL/min for all experiments. All experiment were repeated for 3 times.

4.4 Biodiesel Production from a flow Microwave reactor

4.4.1 Chemicals

Commercial refined palm oil was kindly provided by Embouteille Company, Italy. Methanol reactant, of 99.9% purity, and methyl heptadecanoate as an internal standard for GC analysis were purchased from Sigma-Aldrich. The 97.5% purity of NaOH catalyst and 99.7% purity of heptane solvent were obtained from Carlo Erba Reagenti.

4.4.2 Analytical Method

Biodiesel yield was analyzed according to the EN 14103 standard method using an Agilent Technologies 7820A GC system. This GC system is equipped with a flame ionization detector and a capillary column MEGA-WAX (0.25μm x 0.25mm x 30m). The method and calculation are the same as mentioned before in part 4.2.2.

4.4.3 Equipment

The configuration of biodiesel production from the Milestone FlowSynth microwave illustrates in Fig.4.8. The system consists of a microwave lab station with a maximum power setting of 1,000W equipped with a vertical flow-through Teflon (TFM) reactor. All reactants and catalyst were mixed together in the pre-mixing tank using the 3-blade stirrer with power of 600W before pumped from the bottom of the reactor. Reaction product came out from the top of reactor into a water-cooled heat exchanger. The reaction temperature was monitored continuously by the in-line thermocouple sensors. A unique magnetically driven paddle-stirrer was equipped inside the TFM reactor to ensure the homogeneity of temperature for a whole reactor. A high-performance polymer shield and a back-pressure control valve provide safe conditions in the modified Polytetrafluoroethylene (PTFE-TFM) reactor at all times. An external touch-screen terminal was used to monitor and control all process conditions.

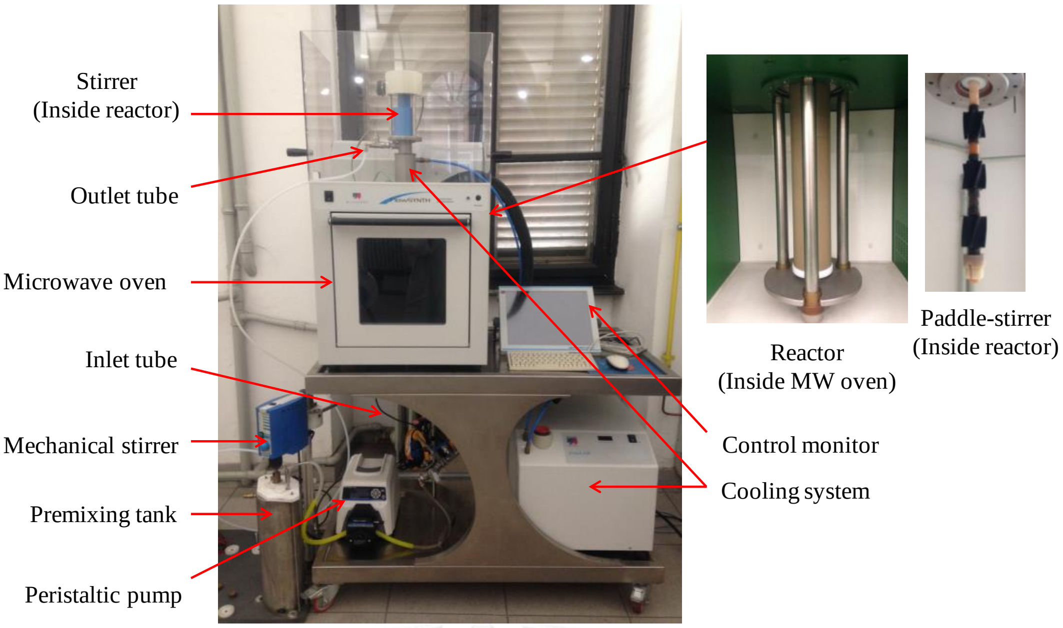

Fig.4.8 The configuration of FlowSynth microwave system

4.4.4 Experimental Set Up

All reactants and catalyst were mixed together in the pre-mixing tank and stirred for 5 min. Then, a portion of this mixture was pumped into the TFM reactor until it was full. The microwave heating power was applied to heat the mixture in the reactor from room temperature to the designed temperature for 2 min. All mixtures were passed through the reactor at a designed feed flowrate for 10 min. The sample was taken every 2 min and analyzed by GC analysis. All experiments were repeated for 3 times.

CHAPTER V
RESULTS & DISCUSSION

In this chapter, the results from each experimental set up as mentioned in the previous chapter have been presented and discussed. The contents have been mainly divided into five sections. Section 5.1 presented the results of biodiesel production in an ultrasonic bath. This section proposed the application of commercial heterogeneous catalysts for biodiesel production hence, the catalyst characterization has been firstly presented. After that the effect of various parameters on biodiesel yield for transesterification has been discussed. Lastly, the reusability and deactivation of catalysts which are one of the important parameter have also been investigated. For section 5.2, an ultrasonic reactor has been designed and tested biodiesel production in a continuous flow configuration. The performance of different reactors i.e. mechanical stirred reactor (MS), ultrasonic reactor (US), combined mechanical stirred and ultrasonic reactor (MS-US), has been explored. Moreover, the effect of MS-US reactor operating parameters, the effect of the operating parameters of MS–US flow reactor and biodiesel chemical composition and physical properties have been studied.

The application of microwave reactor for biodiesel production was presented in section 5.3 and section 5.4. Section 5.3 provides the results of biodiesel production from the high shear mixer integrated with microwave reactor in a circulation system to ensure the simultaneously enhance mass and heat transfer. Therefore, the effects of many parameters such as microwave power, circulation cycle, methanol/oil molar ratio, i.e. on biodiesel yield have been investigated. Furthermore, biodiesel production from different systems i.e. high shear mixer, conventional mixer integrated with microwave reactor, has been tested and the energy consumption required for each system has also been calculated. Lastly, the produced biodiesel was analyzed following ASTM and EN standard. In section 5.4, biodiesel production from microwave reactor in the flow configuration has been proposed. Therefore, the effect of various parameters on biodiesel yield such as methanol/oil molar ratio, microwave power, reaction temperature NaOH catalyst loading and feed flowrate has been studied. Moreover, the activation energy for transesterification assisted by microwave reactor has been determined. Finally, the energy consideration and biodiesel analysis have also been investigated. After that the results from all parts were summarized in section 5.5 for comparison.

5.1 Biodiesel Production in an Ultrasonic Bath

5.1.1 Catalyst Characterization

Table 5.1 shows the properties of fresh solid catalysts used for transesterification of refined palm oil. The BET surface area of CaO was higher than that of K_3PO_4 as well as the pore volume because the particle size of CaO was smaller than that of K_3PO_4. However, K_3PO_4 was found to have a more basic site (348µmole/g) than CaO (only 46 µmole/g). This work was in good agreement with the previous study the BET surface area of CaO was 13 m^2/g [119]. Moreover, the particle size of commercial CaO as reported was more than 100 nm [120] while the pore volume as reported was 0.02 cm^3/g [121].

Table 5.1 Properties of fresh solid catalysts

Catalysts	**Properties**			
	Surface area (m^2/g)	**Pore volume (cm^3/g)**	**Particle size (µm)**	**Basic site (µmole/g)**
CaO	13.66	0.0520	0.150	46
K_3PO_4	1.97	0.0078	3,000	348

XRD patterns of calcined and uncalcined CaO are also shown in Fig. 5.1. For uncalcined CaO, many peaks of calcium hydroxide ($Ca(OH)_2$) were observed at 2θ = 28.8°, 34.1°, 47.1° and 50.8°. However, those peaks disappeared after calcination process. The remaining peaks observed at 2θ = 32.3°, 37.4° and 53.9° were characterized as calcium oxide. Those observed peaks were corresponding with other works [122, 123] It was noted that there was no peak of calcium carbonate ($CaCO_3$) which was not an active phase for transesterification of triglycerides [124].

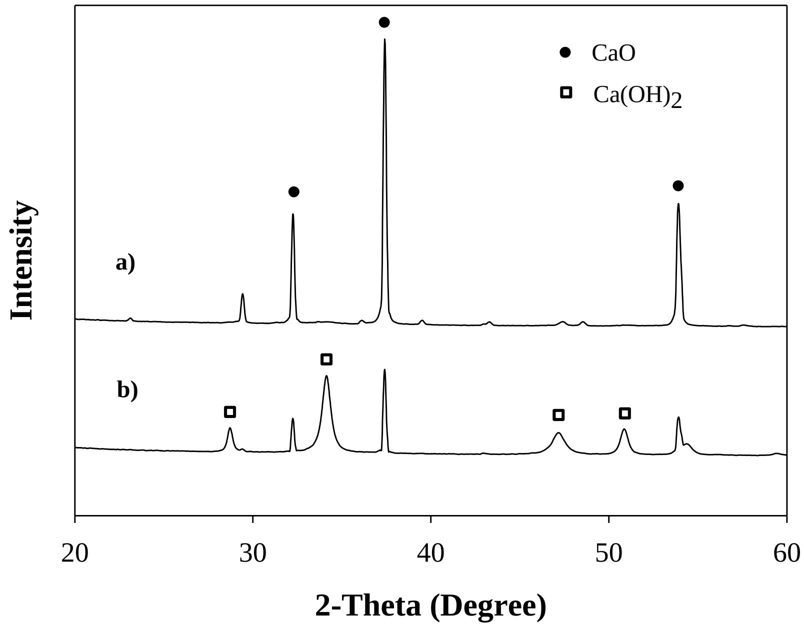

Fig.5.1 XRD patterns of a) calcined and b) uncalcined CaO.

5.1.2 Transesterification of Refined Palm Oil

5.1.2.1 Effect of different catalysts on methyl ester yield

The effect of various homogeneous and heterogeneous catalysts for transesterification of refined palm oil in US reactor on the methyl ester yield is shown in Fig.5.2. Homogeneous base catalyst, NaOH, provided the highest methyl ester yield of nearly 100% within 2 h of reaction time. It was reported earlier by Rashid et al. [47] that the methyl ester yield was 97% at the similar conditions. In case of homogeneous acid catalyst, H_2SO_4, biodiesel yield was rather low (only 15%) because the acid catalyzed transesterification required a high reaction temperature. Goff et al. [53] also proposed that the operation temperature above 100°C can achieve high yield of 99% with H_2SO_4 loading of 0.5 wt.% of oil. Moreover, it also required more reaction time (8 h). The previous work [45] reported that the homogeneous acid catalyzed transesterification is 4000 times slower than that of the homogeneous base catalyst.

For heterogeneous base catalyst, CaO was a good catalyst for transesterification of refined palm oil since a quite high methyl ester yield was obtained under the similar conditions. The methyl ester yield was about 90% within 2 h of reaction time. Although K_3PO_4 has more basic site than that of CaO catalyst, the methyl ester yield was only 80%. This might be due to its less surface area. Viola et al. [125] also reported that the reaction rate was mainly dependent on the active granules surface of K_3PO_4.

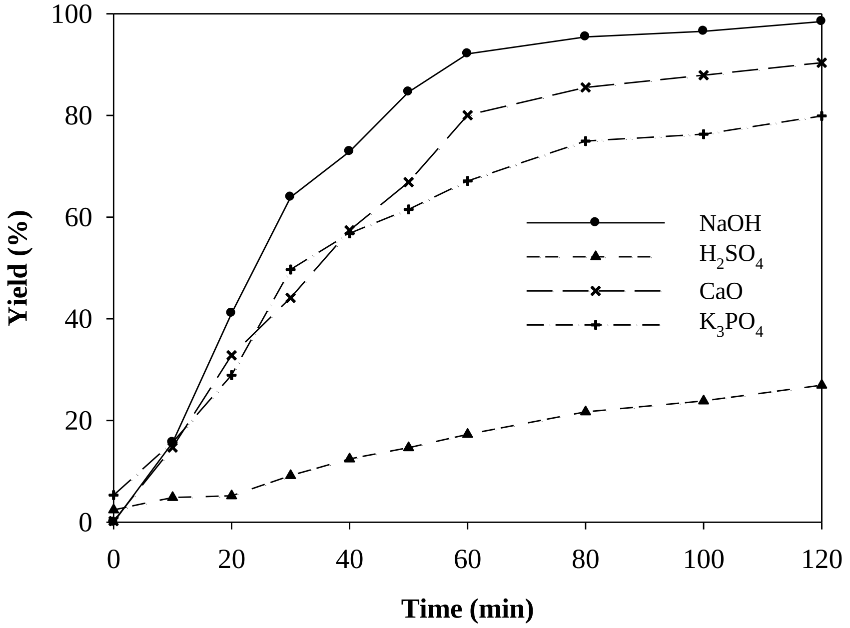

Fig.5.2 Effect of different catalysts on methyl ester yield (US reactor).

5.1.2.2 Effect of mixing types on methyl ester yield

The previous section revealed that CaO and K_3PO_4 could catalyze transesterification of refined palm oil in the US reactor. Therefore, it should be interesting to compare the reaction performance from different mixing types. Fig.5.3 shows the methyl ester yields achieved in MS and US reactors for biodiesel production using heterogeneous catalysts. For CaO catalyst, the yield of methyl ester at 2 h was nearly the same for both types of mixing. However, it can be noticed that at the initial reaction period (0–1 h), the US reactor provided higher methyl ester yield than the MS reactor. It was due to the external mass transfer barrier between oil and methanol phase was eliminated. Since ultrasound irradiation enhances the mixing efficiency in a liquid medium by formation and destruction of microbubbles to form emulsion phase, resulting in the better mixing of the reactants [25].

However, K_3PO_4 catalyst exhibited the remarkably different results. It was found that the MS reactor provided higher methyl ester yield than the US reactor. It might be due to the effect of mixing characteristics on the kinetic mechanism of base catalyzed transesterification of oil which is related to the reactant adsorption step on the catalyst surface [12]. For MS reactor, the methanol phase was more potential to adsorb on the K_3PO_4 surface due to the hydrophilic properties [126]. Therefore, there should be more active sites for the surface reaction, and thus higher yield can be acquired. On the other hand, for US reactor, the production of oil and methanol microbubbles from US irradiation due to the cavitation phenomena was occurred rapidly with less mixing time as proposed by the work [26]. This phenomenon takes place before the adsorption of emulsion phase reactants on the catalyst surface. Thus, the emulsion phase might hinder some K_3PO_4 active sites, resulting in the lower of methyl ester yield. However, the total surface area and the difference in the surface texture properties of CaO and K_3PO_4 catalysts associated to the various catalytic activities. The effect of mixing characteristics on the adsorption of the reactant (from MS) or emulsion phase (from US) as discussed before was less likely significant for CaO catalyst.

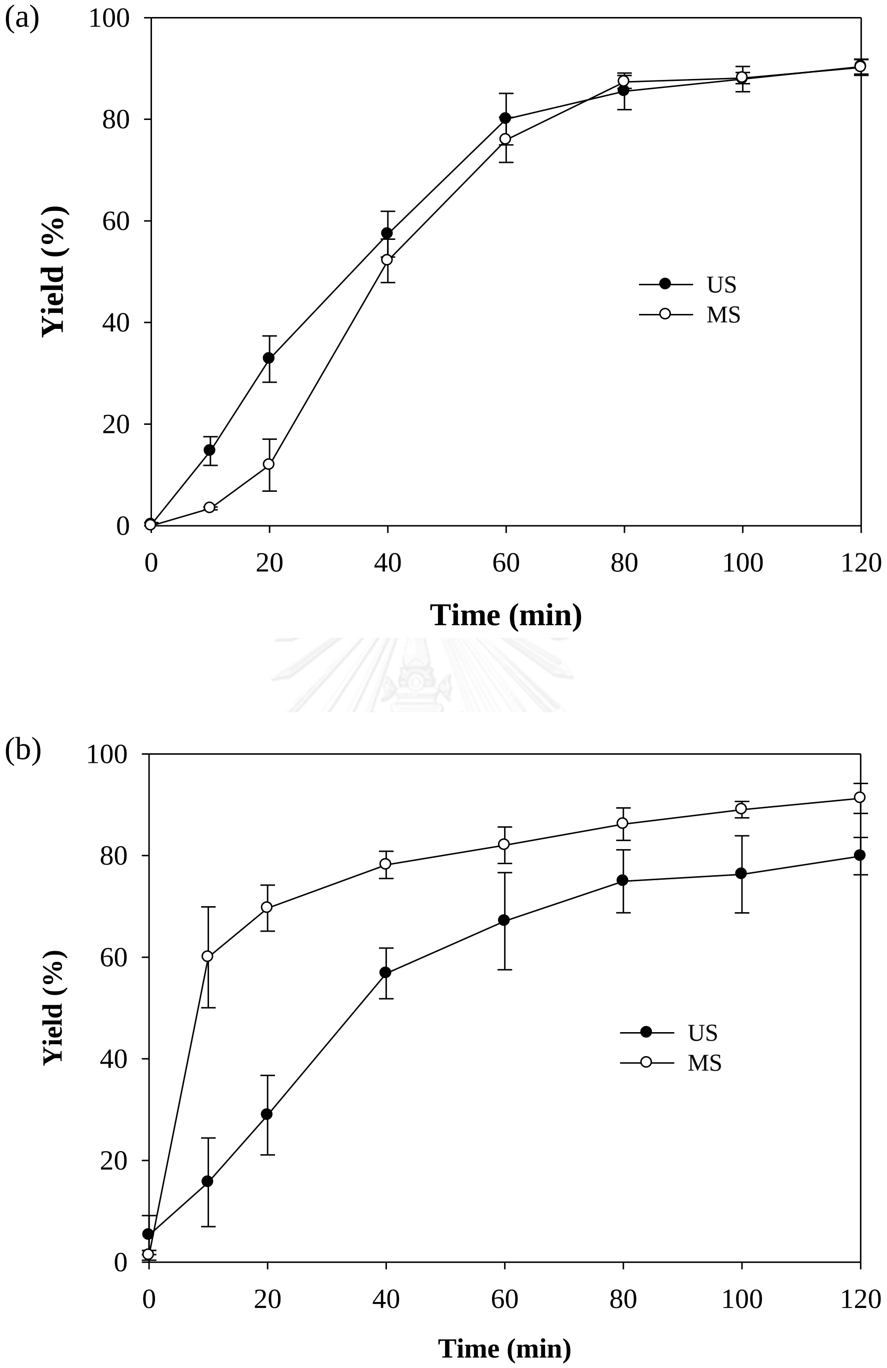

Fig.5.3 Effect of types of mixing on methyl ester yield using solid catalysts: (a) CaO and (b) K_3PO_4

5.1.3 Reusability and Deactivation of Catalysts

5.1.3.1 Reusability of catalyst in US and MS reactors

In this study, the catalyst was instantly reused in three consecutive cycles without any pretreatment step. For CaO catalyst, the methyl ester yield from both the US and MS reactors decreased in the subsequent cycles as shown in Fig.5.4.

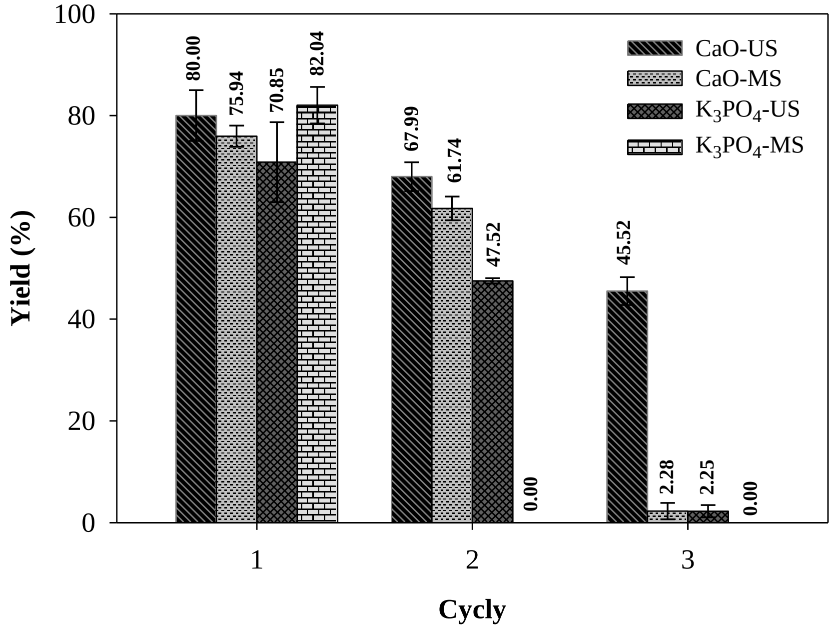

Fig.5.4 Effect of reusability of CaO and K_3PO_4 on methyl ester yield at 1 h

It was significantly found that methyl ester yield from the last cycle using the MS reactor dramatically reduced compared to the US reactor. Under US irradiation, the microbubbles of reaction products especially glycerol have more chance to adsorb on the CaO surface and thus generate the glyceroxides species as the alternative active sites. Kouzu et al. [58, 119] and Granados et al. [127] reported that the glyceroxides species was more active for trasesterification than that of CaO itself. However, the CaO surface did not only adsorb glycerol but also adsorbed the other reaction mixtures, leading to deactivation of CaO catalyst. This phenomenon should be called counter balancing effect with the summation of positive effect (generated glyceroxides species) and negative effect (deactivation of catalyst by adsorption of organics species). On the other hand, using MS reactor provided less chance to form glyceroxides species on the CaO surface. Thus, the deactivation of catalyst from organic adsorption was more pronounced as seen from the results of the last cycle.

As seen in Table 5.2, the size of CaO catalyst used in each cycle was higher in the later cycle. In general, a smaller particle size refers to a larger surface area which provides higher chance of reaction. Therefore, the obtained methyl ester yield decreased in the subsequent cycle which was related to the particle size of CaO catalyst. However, the particle size of CaO in the US reactor used in each reuse cycle was larger than that of MS reactor. This was because of a larger amount of calcium glyceroxides produced in US reactor. Kouzu et al. [128] mentioned that the slight amount of soluble substance from calcium glyceroxides leached into the product mixture. This incident would cause the agglomeration of catalyst since some part of the soluble substance was crystallized under the reacting condition and formed into fine particles functioning as a binder to agglomerate the catalyst. Therefore, the particle size of CaO catalyst in US reactor was larger than that from MS reactor in every cycle. The generation of calcium glyceroxides was also occurred significantly hence, the methyl ester yield in the last cycle can be obtained almost 50% in the US reactor while there was almost no activity in the MS reactor from the full coverage of reaction mixture on the CaO surface. This is because the mixing characteristics affected the size of reaction mixture, resulting in the different catalytic behavior.

Table 5.2 Particle size of calcium oxide used in each cycle of reusability experiment

Reactor	**Particle size (μm)**		
	1st cycle	**2nd cycle**	**3rd cycle**
Ultrasonic assisted	0.150	1.348	2.577
Mechanical stirred	0.150	0.192	1.718

In the case of K_3PO_4 (Fig.5.4), the methyl ester yield decreased in the subsequent cycle of the spent catalyst when using the US reactor. It dramatically decreased to about 2% in the last cycle. However, the deactivation of this catalyst was more likely due to the dissolution of active species into the reaction mixture. Since the amount of catalyst remaining after each reaction cycle noticeably decreased. This result was corresponding with another research [129] reporting that K_3PO_4 showed high sensitivity to water and free fatty acids which caused the dissolution and agglomeration tendency. The soluble K_3PO_4 catalyst was more emphasized in the MS reactor. The catalyst from the first cycle was quite tiny. Then, the catalyst could not be able to reuse in the consecutive cycle. Kouzu et al. [130] reported that the K_3PO_4 catalyst catalyzed transesterification with homogeneous mechanism by partial dissolution of the catalyst. This result also confirmed the effect of mixing characteristics on the catalytic activity as well as those obtained from CaO catalyst. It was concluded that US reactor would diminished this dissolution for K_3PO_4 catalyzed transesterification of refined palm oil. Moreover, the catalyst deactivation has been investigated in the next section.

5.1.3.2 Deactivation of catalysts

As seen in Table 5.2, the size of CaO catalyst used in the subsequent cycles was increased. It might be because of the reaction mixture covering on the catalyst surface and/or the agglomeration of the catalyst. Therefore, the surface of fresh CaO and used CaO catalysts were analyzed by FTIR. It was found that there were many peaks including C=O stretching of ester (1000-1320, 1750 cm^{-1}), C-O and C-H stretching of CaO to calcium methoxide ($Ca(OCH_3)_2$) (1050 and 2800-3000 cm^{-1}), -CH_2 vibration of Ca-glycerol complex (700-1000 and 1200-1350 cm^{-1}) [28, 121] in Fig.5.5. Those products mentioned above did not only hinder the catalyst but also caused the agglomeration of the catalyst as observed by the increased catalyst size in the later cycle [128]. It was noticed that when applying the US reactor, calcium glycerol complex peak was noticeable compared to the MS reactor. This also confirmed that the high amount of calcium glyceroxides was produced from US reactor.

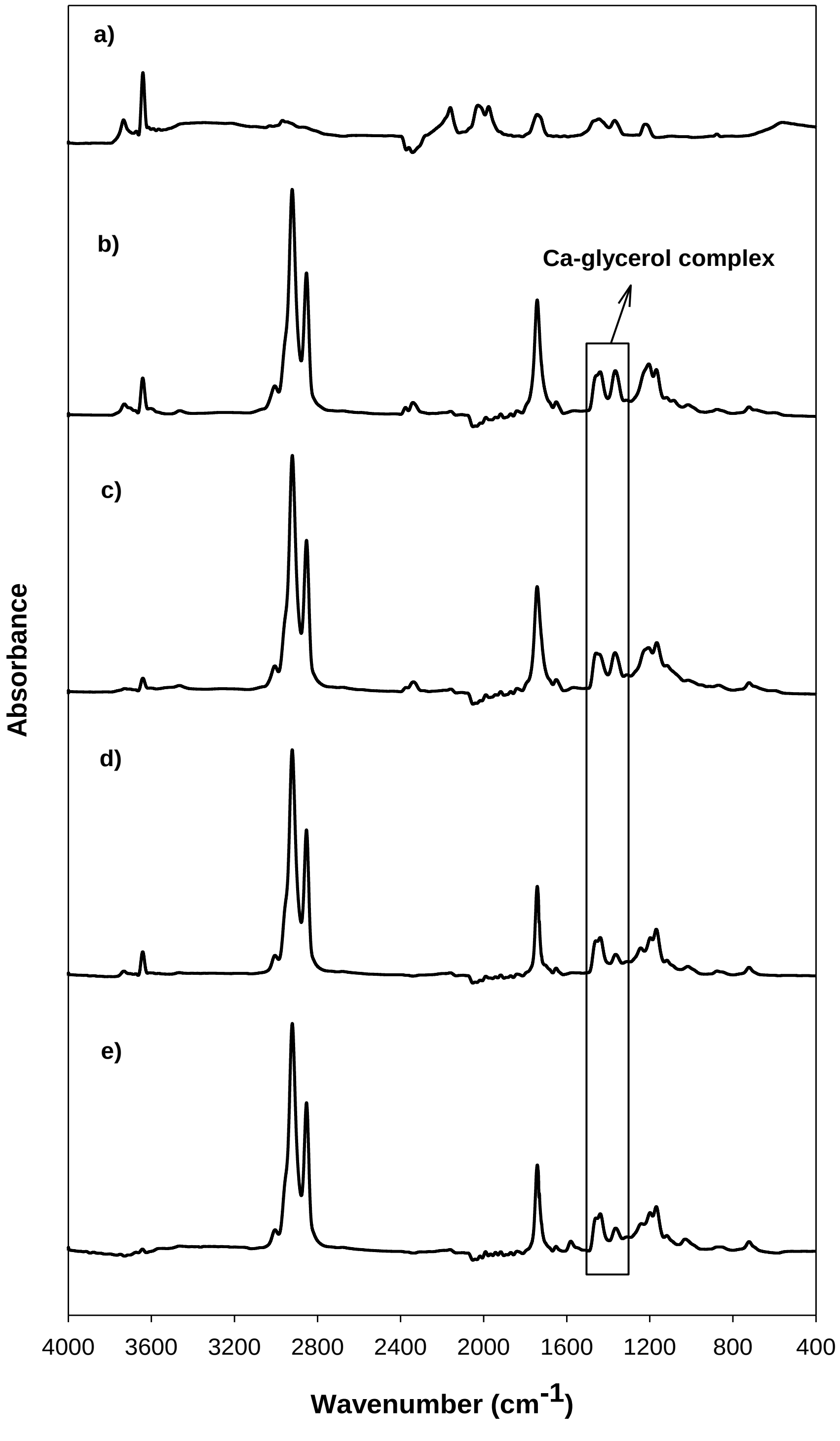

Fig.5.5 FTIR spectra of CaO after the reusability test: a) Fresh catalyst, b) After 1st cycle (US), c) After 2nd cycle (US), d) After 1st cycle (MS) and e) After 2nd cycle (MS).

The covered surface by reaction mixture was also confirmed by TGA results shown in Fig.5.6. The decomposition was divided into 3 periods. The weight loss was present in the first period, as referred to the decomposition of saturated fatty acid methyl esters (100-230°C) [131]. The second period was the decomposition of unsaturated fatty acid methyl esters, glycerol and triglycerides (230-500°C) [132, 133]. Lastly, the weight loss from the third periods which occurred at high temperatures (500-850°C) was referred to the decomposition of carbon residuals [133].

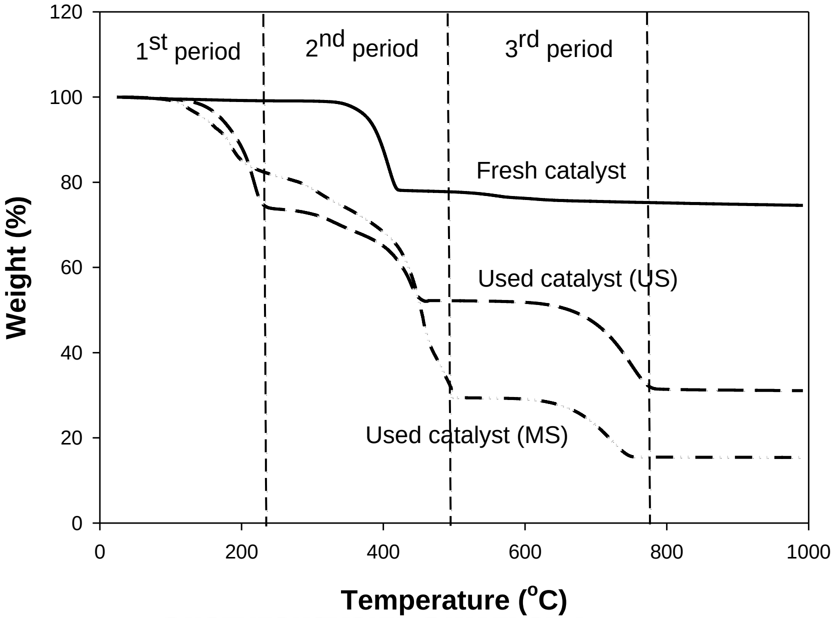

Fig.5.6 TGA profiles of fresh and used CaO.

Furthermore, the spent CaO catalysts also showed a significant loss in mass with temperature when compared to the fresh CaO. It was indicated that there were some organic compound of the reaction mixture deposited on the catalyst surface. The weight loss of the reused catalyst from the US reactor was lower than that from the MS reactor. This indicated that there were fewer organic compounds adsorbed on the catalyst surface since only microbubble of reactants was adsorbed on the CaO for US reactor. Whereas, more amount of organic compounds was adsorbed using MS reactor because of it could not generate the microbubbles of reactants as seen the dramatically decrease in the second period of TGA result (Fig.5.6). This can be concluded that the

US reactor could overcome to diminish the adsorption of organic compounds from the reaction mixture on the catalyst surface [134]. Then, the higher methyl ester yield can be obtained.

For K_3PO_4 catalyst, the methyl ester yield also decreased in the subsequent cycles. This can be explained using the same explanation as that for the CaO catalyst. There was the agglomeration of the catalyst; the active species of catalyst were covered by the reaction mixture as confirmed by particle size (Table 5.2), FTIR spectra (Fig.5.7) and TGA profiles (Fig.5.8). However, the weight loss obtained from the TGA results for the spent K_3PO_4 catalyst in both US and MS reactors were not different. It can be implied that there was the adsorption of organic compounds from reaction mixture on the catalyst surface in both cases. Therefore, the main reason of the K_3PO_4 catalyst deactivation could be the dissolution effect.

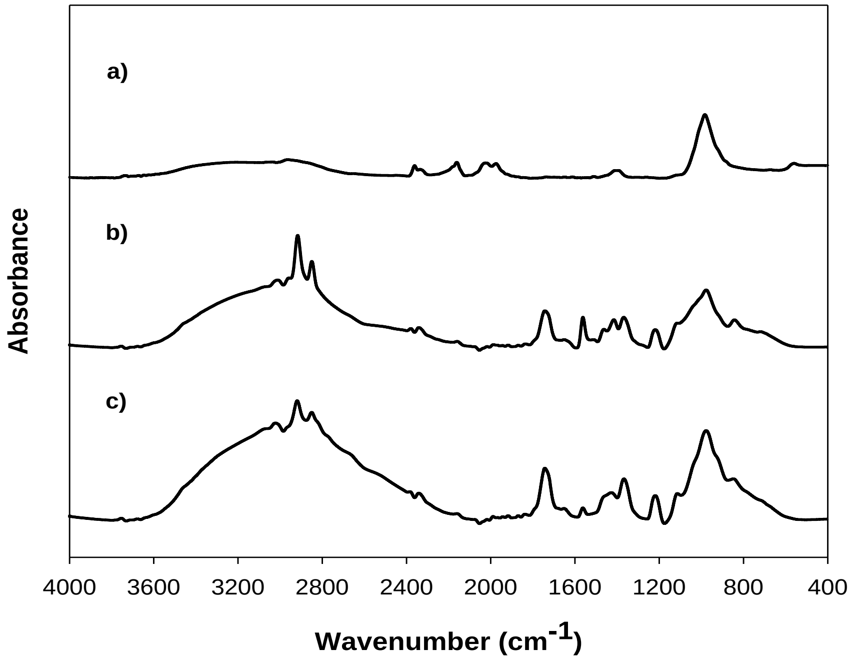

Fig.5.7 FTIR spectra of K_3PO_4 after the reusability test: a) Fresh catalyst, b) After 1st cycle and c) After 2nd cycle (US reactor).

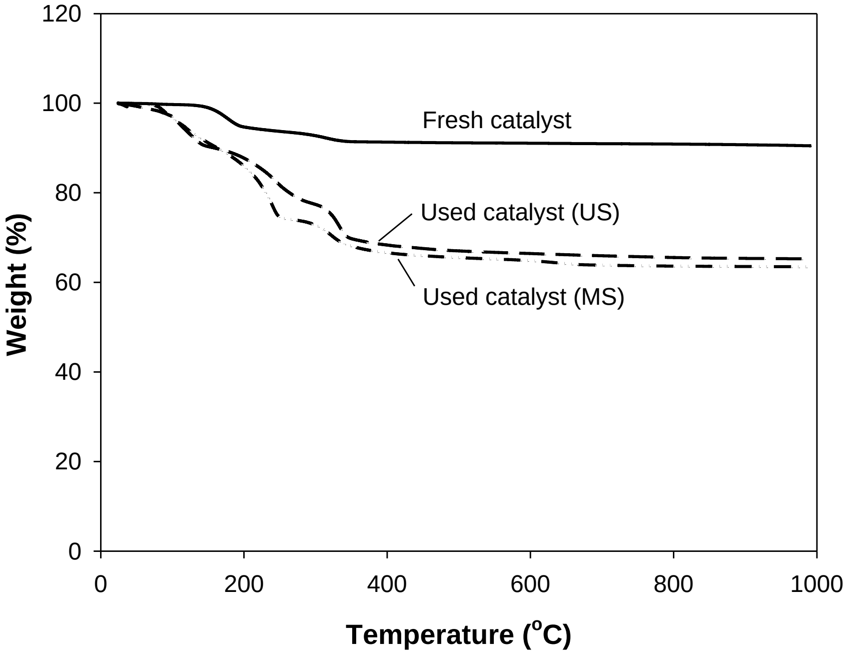

Fig.5.8 TGA profiles of fresh and used K_3PO_4.

As discussed before, the catalyst dissolution seems to be a serious problem when using K_3PO_4 catalyzed transesterification in both reactors. Therefore, the catalyst dissolution experiments were investigated for both catalysts. Based on the dissolution results, it was found that there was no dissolution from CaO catalyst into the reaction mixture in both US and MS reactors. This was corresponding with the results from Mootabadi et al. [88] which reported that only 0.04% weight loss of CaO was leached into biodiesel products for the stability testing in the US reactor. On the other hand, K_3PO_4 catalyst dissolution was occurred apparently. Since K_3PO_4 catalyst is a polar chemical, it could be better dissolved in methanol phase than oil phase. However, Guan et al. [126] reported that K_3PO_4 was relatively insoluble in methanol but rapidly dissolved in water.

Furthermore, it was noticed that K_3PO_4 was more significantly dissolved in the MS reactor (83.9%) than in the US reactor (23.8%). This also supported the hypothesis of the effect of mixing characteristics on the adsorption step of kinetic mechanism. The active species of K_3PO_4 catalyst obtained from the MS reactor should show the greater dissolution and dissolving in methanol because of the mixing characteristics as described in the previous section. Another possibility could be explained that the mixing characteristics were controlled by the stirrer speed for the MS reactor. However, the mechanical stress also promoted the negative effect on the granules of catalyst, then, the catalyst could break into the smaller pieces [125]. It could be attributed to the higher contact between the active sites and reaction mixture, especially methanol and easily to dissolve in the reaction mixture. On the other hand, ultrasound irradiation employed only the bubble collapse between the methanol and the oil phase to form emulsion phase as mentioned before. The catalyst seems not to be affected from the mechanical stress as found in the MS reactor. In this case, dissolution of active species was then lower in the US reactor. From the results, it was noted that US reactor has overcome to scale-up in the industrial process for the heterogeneous catalyzed transesterification of oil.

5.2 Biodiesel Production from the Designed Ultrasonic Flow Reactor

5.2.1 Performance Comparison of Different Reactors

The transesterification of palm oil operated at a methanol to oil ratio of 6:1 and NaOH loading of 0.l5% wt of oil was used to compare the reaction performance of the different reactors (MS, US and MS-US). The mechanical stirrer operated at a speed of 25 rpm while all 16 transducers (dual frequencies of 20 and 50 kHz) were used to provide ultrasonic waves. From Fig.5.9, it can be seen that a high yield value at the outlet (about 76%) can be rapidly achieved in about 5 min with the MS-US flow reactor. The value is about 60% when using the US reactor. On the other hand, it took a much longer time (1 h) to obtain the same methyl ester yield under the similar conditions when using the MS reactor. It should be noted that in the case of US and MS–US reactors, after 5 min the good yields reach a plateau that even with longer reaction times could only slightly increase. The fast transesterification took place in continuous flow using a combined MS-US loop reactor where the liquid mixture was pumped through the system. The circulation rate was kept constant at 55 mL/min, corresponding to a residence time of 4 min The reported yield refers to samples collected at the reactor outlet and values are calculated on the base of the initial reactant concentration in the feed tank. On the other hand, in the MS reactor, used in continuous flow, yields were much more time dependent with a steady increase (Fig.5.9).

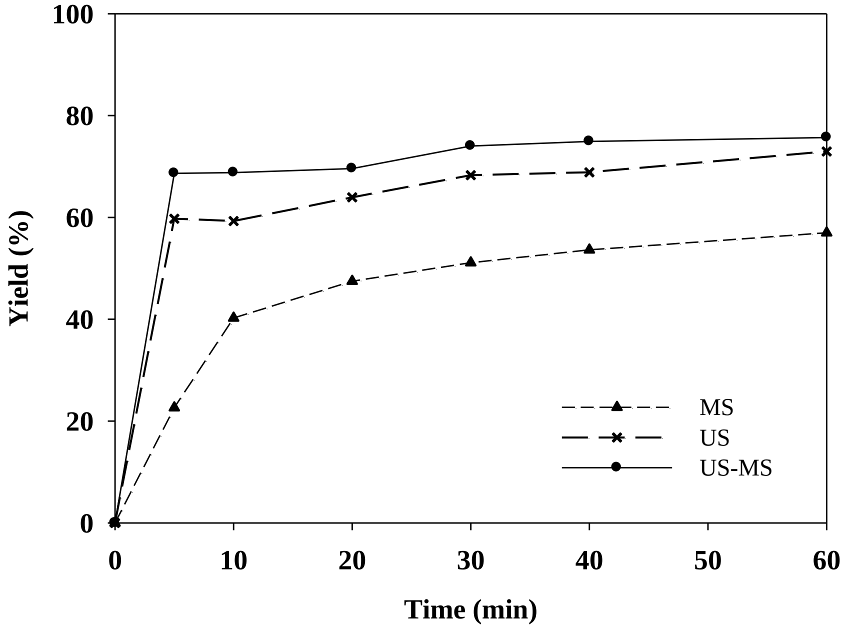

Fig.5.9 Effect of different types of mixing on methyl ester yield at reactor exit at various times (Methanol/oil molar ratio = 6:1, NaOH = 0.15%wt oil, feed flowrate = 55 mL/min).

The initial rate of reaction was also reported to express the speed of this reaction. The initial rate was calculated from the difference between the concentrations of triglyceride at the initial point and at outlet after 5 min of reaction, divided by residence time in the reactor. It was found that the initial rate of reaction in the US reactor (142.9 mmol/L min) was noticeably higher than that in MS reactor (54.1 mmol/L min). This was because the US reactor can provide the rapid emulsion of the reactants, as mentioned previously. Therefore, it enhances the mass transfer process and a high methyl ester yield can be achieved in a relatively short reaction time. This result corresponds to the result from Chand et al. [74], which states that the reaction time to reach a high methyl ester yield can be reduced from 60 min to only 1.5 min when using a probe US reactor rather than a MS reactor. The results also indicated the advantage of the combination of two different frequencies in biodiesel production. Under the same conditions, Yin et al. [32] found that using both a MS reactor and a single-frequency US reactor for biodiesel production required more catalyst loading than 0.5% wt of oil. The result showed that it provided about 60%

biodiesel yield in the MS reactor and only 50% biodiesel yield in the US reactor at 50 min of reaction time. It can be concluded that the dual-frequency ultrasound irradiation for flow reactors exhibited better mixing performance than conventional mechanical mixing.

The combination of horizontal stirrer and dual frequency ultrasound irradiation in the flow reactor (MS-US reactor) gave the highest methyl ester yield. It was found that the methyl ester yield was nearly 70% in 5 min of reaction time and it reached equilibrium in the short reaction time of 30 min when using the same conditions. Moreover, the initial rate of reaction was 164.2 mmol/L min which was higher than US and MS reactor values. Gogate et al. [118] have revealed that maximum energy is dissipated near the irradiating surface in a cone like structure in low frequency operation. This contributed to the maximum cavitational activity very near the irradiating surface and the wide variation in energy dissipation rates in the remaining reaction mixture bulk. The introduction of the horizontal mechanical stirrer may improve distribution of cavitational activity in this reactor. However, it should be noted that the higher stirrer speed possibly also gave a negative effect due to the fact that agitation strongly interferes with the passage of incident ultrasound irradiation. The effect of the MS–US reactor corresponds with the results published by Yin et al. [32]. It was noticed that the combination of US and MS in the reactor gave the high methyl ester conversion of 80%, while the US and MS reactors at catalyst loading of 0.5% wt of oil achieved only 50% and 60%, respectively. The next section will discuss the influence that MS–US flow reactor operating parameters, which are related to the energy consumption for biodiesel production, had on the reaction.

5.2.2 Effect of MS-US Reactor Operating Parameters

5.2.2.1 Effect of methanol to oil molar ratio on methyl ester yield

In general, the theoretical methanol to oil molar ratio, as taken from stoichiometric transesterification, is three. As previously mentioned, this reaction is reversible. The higher concentration of methanol can shift the reaction equilibrium to obtain higher product yields [32]. Furthermore, as the amount of methanol increases, more cavitational bubbles are obtained because ultrasound activity is easier in methanol than in oil. However, some methanol can dissolve into the glycerol by-product phase during the reaction and only the remaining methanol can be reacted with oil in the transesterification [30]. It was found that methanol can completely dissolved in the glycerol phase [135]. Therefore, the effect of the methanol to oil molar ratio on the methyl ester yield should be optimized.

The previous section confirmed that the application of the MS–US reactor gave more advantages than the use of MS and US reactors separately. The effects of the methanol to oil molar ratios of 3, 6, 9, and 12 on methyl ester yield were studied along the reaction period. The results are presented in Fig.5.10. When using a methanol to oil molar ratio of 3, the methyl ester yield increases more than for ratios of 9 and 12 in the first 20 min of reaction time. The initial reaction rate also shows a similar trend; a higher initial reaction rate of 127.5 mmol/L min was obtained when using a methanol to oil molar ratio of 3, whereas only 58.3 and 22.4 mmol/L min were obtained from methanol to oil molar ratios of 9 and 12, respectively. However, the methyl ester yield obtained after 1 h of reaction time was lower. When using a methanol to oil molar ratio of 6, not only was the highest initial reaction rate, of 142.9 mmol/L min, achieved but also the highest methyl ester yield of 75%. This was due to the fact that some methanol is able to dissolve in the glycerol product, as previously described, when using a methanol to oil molar ratio of 3. Therefore, only the remaining methanol can react giving a low yield.

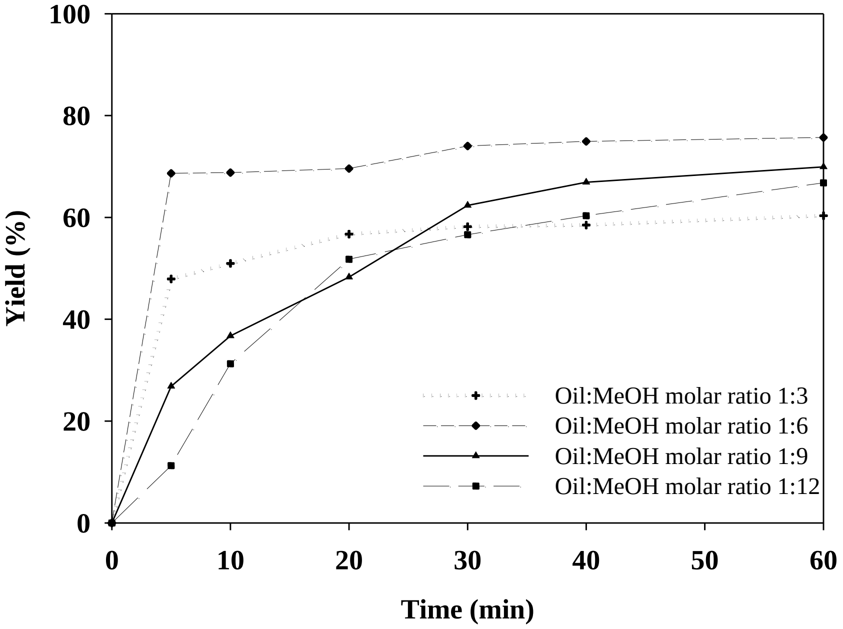

Fig.5.10 Effect of methanol/oil molar ratio on methyl ester yield at reactor exit at various times using the MS-US reactor (NaOH = 0.15%wt oil, feed flowrate = 55 mL/min).

Under US irradiation, the excess methanol was more likely to contribute to the cavitational activity resulting in a higher emulsion quality (smaller drop sizes) and hence increased yield. However, methyl ester yield also decreased when using a molar ratio of methanol to oil over 6. This was because only a limited portion of the methanol is able to act in the transesterification [30]. Moreover, the large amount of methanol that persists after the reaction also leads to a complicated product separation step, since methanol can work as an emulsifier that creates an emulsion between glycerol and biodiesel [49]. Therefore, increasing the molar ratio of methanol to oil beyond 6 was not only detrimental to biodiesel yield, but also caused difficulties in the product separation step. The optimal methanol to oil molar ratio was 6.

5.2.2.2 Effect of catalyst loading on methyl ester yield

This parameter is more significant, especially when a feedstock is composed of high amount of free fatty acids (FFAs). Since FFAs can easily react with a base catalyst and undergo saponification when using a large amount of the catalyst. This resulted in a lower methyl ester yield and complications in product separation and purification [136]. The effect of catalyst loading on methyl ester yield is exhibited in Fig.5.11 as a function of reaction time. The amount of NaOH was varied and 5 concentrations were used; 0.15%, 0.30%, 0.50%, 0.70% and 1% wt oil.

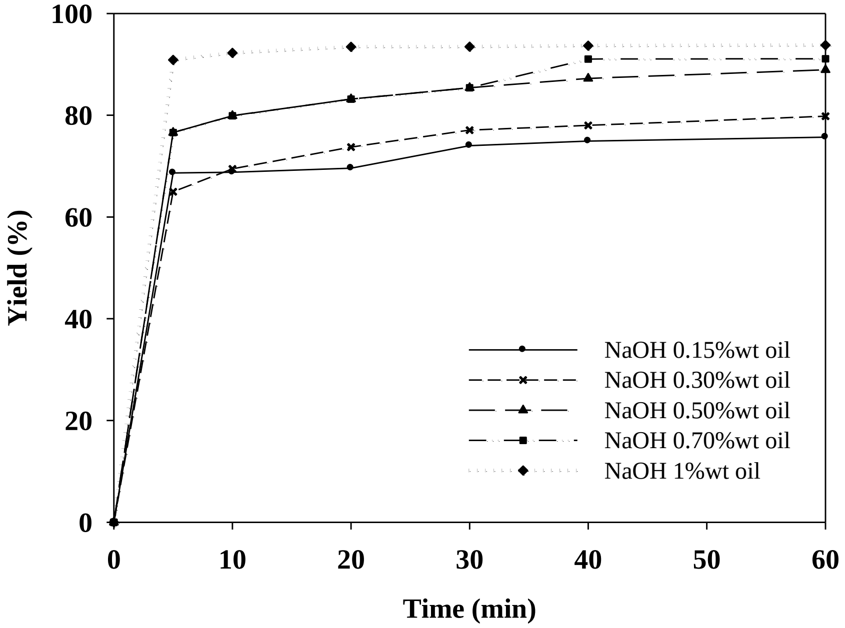

Fig.5.11 Effect of catalyst loading on methyl ester yield at reactor exit at various times using the MS-US reactor (Methanol/oil molar ratio = 6:1, feed flow rate = 55 mL/min).

It was found that methyl ester yield increased with increasing catalyst loading. However, it increased only 4% when the amount of catalyst increased from 0.15% to 0.30% wt oil. The methyl ester yield also increased only 2% when the amount of catalyst was increased from 0.50% to 0.70% wt oil. This result corresponds with the initial rate of reaction. It can be seen in Table 5.3 that the value of the initial reaction rate at a catalyst loading level of 0.15% wt is similar to the rate at 0.3% wt, and that the value of the initial reaction rate at a catalyst loading level of 0.5 was the same as at 0.7% wt. The highest methyl ester yield of 94% and the highest initial rate of reaction, of 217.3 mmol/L min, were both obtained at a catalyst loading level of 1% wt of oil. On the other hand, a catalyst loading of 0.15% wt of oil provided the highest initial TOF (2.90 min^{-1}) which was calculated by dividing the initial rate per gram of catalyst by the basic site concentration of the catalyst per gram. This was because of the lower amount of catalyst used for the reaction, hence lower basic site concentration. This reaction, therefore, reached a lower methyl ester yield compared to the others.

Table 5.3 Methyl ester yield at reactor exit, initial reaction rate and initial TOF as obtained from the MS-US reactor at different catalyst loading amounts (Methanol to oil molar ratio = 1:6, frequency = 20+50 kHz and reaction time = 1 h).

NaOH loading (% wt of oil)	Yield (%)	Initial rate of reaction (mmol/L min)	Initial TOF (min^{-1})
0.15	75.68	164.20	2.8987
0.3	79.81	155.35	0.6908
0.5	88.91	183.11	0.2931
0.7	91.10	183.22	0.1496
1	93.78	217.27	0.0869

It can be seen from the results that the importance of the catalyst loading variable was more pronounced in this process than the methanol to oil molar ratio. This conclusion corresponds with the results published by Choudhury et al. [137]. The influence of these two parameters was studied experimentally and in a simulation model where it was clearly indicated that the amount of catalyst loading had more effect on the methyl ester yield than the methanol to oil molar ratio. Therefore, the optimal operating conditions for biodiesel production in this study are a methanol to oil molar ratio of 6 and catalyst loading of 1% wt of oil. The effect of the application of dual frequency ultrasound irradiation in any location along the length of reactor is investigated in the next section.

5.2.3 Effect of the Operating Parameters of MS–US Flow Reactor

A dual frequency MS–US reactor showed the best biodiesel efficiency as demonstrated in Section 5.2.1. However, it also required the highest energy consumption to supply the transducers and horizontal stirrer. Therefore, this section investigates the effect of location, frequency, and the number of transducers, which are related to power consumption, on the methyl ester yield in the transesterification process. Differences in frequency and transducer location are the significant operating parameters in this reactor. The effect of the sound wave is more intense in the areas closest to the irradiating surface and rapidly decreases further away from the source [23]. Moreover, the combination of two frequencies might enhance the reaction rate by providing better cavitational phenomena from the resonance effect, as compared to a single frequency [138-140]. The reactor was divided into 4 positions according to the location of the transducer attached to the reactor wall, as shown in Fig.5.12.

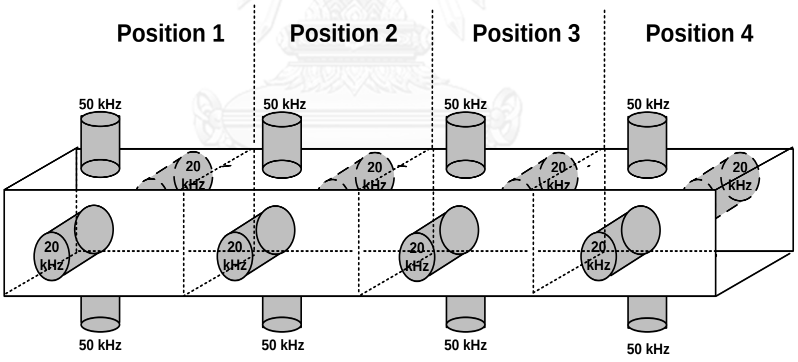

Fig.5.12 The position on the reactor wall of the two transducer frequencies

As mentioned previously, the frequency of the transducers on the opposite side of the wall was the same and the opposite transducer pairs with the same location and frequency were operated together. There were six experiments where the locations and the frequencies of the transducers used for the transesterification of palm oil were varied, and results are shown in Table 5.4. The total number of transducers and operating power for four experiments (1–4) were 8 and 400 W, respectively (50W for each transducer). The first four experiments were compared to the best operating conditions (integrated US reactor with maximum power, fifth experiment) and the conventional mechanical stirrer (MS reactor, sixth experiment).

Table 5.4 Methyl ester yield at reactor exit obtained from the use of two frequencies in each location.

Experiment	**The position of 20 kHz transducer**				**The position of 50 kHz transducer**				**Yield (%)**
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**	
1	●	●	●	●	-	-	-	-	62.23
2	-	-	-	-	●	●	●	●	62.78
3	●	-	●	-	-	●	-	●	62.80
4	-	●	-	●	●	-	●	-	61.68
5	●	●	●	●	●	●	●	●	75.68
6	-	-	-	-	-	-	-	-	57.31

In order to investigate the effect of MS-US flow reactor operating parameters on the reaction, the methanol to oil molar ratio and NaOH loading was kept constant at 6:1 and 0.15% wt oil, respectively for all experiments in this section. The first and the second experiments were carried out using a single transducer frequency, 20 and 50 kHz, respectively. It was found that both experiments provided similar results. The acquired methyl ester yield after 1 h was about 62%. However, the higher frequency (50 kHz) reached the final methyl ester yield more quickly than the lower frequency (20 kHz). This result corresponds to results published by Stavarache et al. [28] and Encinar et al. [72]. For the third and the fourth experiments, different transducer frequencies were used. The experiment was done by switching the location of the two frequencies. In the third experiment, the first and the third 20 kHz transducer locations and the second and the fourth location of the 50 kHz transducers were activated. The opposite 20 and 50 kHz transducer locations were used in the fourth experiment. The results showed a similar methyl ester yield value, of about 62%, as the first and the second experiment. The location of the transducer had no significant effect on methyl ester yield in this study as the identical distance of each transducer from the irradiating surface for both experiments would give uniform cavitational intensity (US power per irradiation area) and resulted in the same effect at the different locations [33].

The use of dual frequencies (20 and 50 Hz) for all transducers was studied in the fifth experiment which saw a total operating power of 800 W. It gave the highest methyl ester yield of about 76% while the MS reactor gave only 57%. It seems that the number of transducers plays a more important role than differences in transducer frequency and location on methyl ester yield. The higher number of transducers was directly related to the intensity of the cavitational activity. More transducers give increased cavitational intensity resulting in a higher oil–methanol interfacial area. Bubble collapse generates high jet velocity and micro-mixing at the boundary layer between the two phases. Finally, it forms a fine emulsion and gives higher mass transfer and hence, higher biodiesel formation [72, 141]. However, the influence of frequency in this study is different to what has been published in other reports [72, 141]. This might be because the transducers generate uniform cavitational intensity in this reactor at both, low frequency range, frequencies, as previously mentioned.

It should be noted that the experimental results obtained from this study indicate that the combined MS–US reactor is a promising technology for biodiesel production. It offers higher biodiesel yield than the US reactor and the MS reactor. However, further investigation will probably optimize the reaction condition by varying the liquid feed rate and other parameters with the aim to achieve full conversion even with shorter residence time and low energy consumption. The reactor design plays an important role. The initial rates of the MS, US and MS–US reactors were 54.1, 142.9, and 164.2 mmol/L min, respectively. The initial rate of the MS–US reactor was found to be less than the additive effects of MS and US individual reactors (197 mmol/L min). Therefore, more in depth energy analysis should be taken into account in the design of the MS–US reactor.

5.2.4 Biodiesel Chemical Composition and Physical Properties

The properties of palm oil derived biodiesel were evaluated according to the ASTM standard. The density, viscosity, flash point, pour point, and heating value of biodiesel were all estimated from ASTM D4052, ASTM D445, ASTM D93, ASTM

D6749/D97, and ASTM D240, respectively. The standard values and the values of biodiesel produced in this work are presented in Table 5.5. It was found that the heating value was slightly lower than the standard value. However, the other properties of the biodiesel produced in this work (density, viscosity, flash point, and pour point) met the ASTM standard. Therefore, this MS–US reactor is a promising reactor that can produce biodiesel in accordance with the ASTM standard.

Table 5.5 Biodiesel properties in comparison with ASTM standard (ASTM 6751).

Properties	**Value**		**Unit**
	Biodiesel ASTM 6751	**Biodiesel (This work)**	
Density @15°C	0.86 - 0.89	0.8755	g/cm^3
Viscosity @40°C	1.9 - 6.0	4.46	mm^2/s
Flash point	≥130	254	°C
Pour point	-10 - 12	10	°C
Heating value	9,940	9,527.1	cal/g

5.3 Biodiesel Production from High Shear Mixer Integrated with Microwave reactor

5.3.1 Effect of MW Power on Biodiesel Yield at Various Circulation Cycle

Table 5.6 illustrates the obtained biodiesel yields at various MW power settings and circulation cycles when the methanol/oil molar ratio was fixed at 6. At a MW power of 300W, the obtained biodiesel yield was only 96.37% even when a high circulation cycle rate of 30 cycles was applied (~40 min of total reaction period). This value was not in accordance with the ASTM standard (96.5%). Therefore, the highest MW power setting was employed. The results indicated that the minimum biodiesel yield requirement can be archived at MW power settings of 400, 500 and 600W and at circulation cycles of 30, 10 and 10, respectively. A high biodiesel yield was obtained in a short reaction time (related to the circulation cycles) at high MW power. This was because the rapid dipole moment reorientation of methanol occurred at the high MW power setting. This phenomenon destroys the boundary layer between methanol and oil and reduces the dielectric constant and the polarity of methanol and thus resulted in the homogenization of methanol and oil. Therefore, a high biodiesel yield can be achieved [142].

In addition, MW irradiation can also enhance reaction rate. The reaction rate can be described by the Arrhenius equation, which is shown below.

$$K = A\, e^{-E_a/RT} \tag{5.1}$$

where K is the rate constant, A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant and T is the temperature. MW irradiation can increase the pre-exponential factor (A) by increasing molecular vibration from the mutual orientation of the polar molecule involved in the reaction [143-145]. A high reaction rate can therefore be obtained and full conversion achieved. It can be seen that temperature increased at high power and this also provided the positive influence on reaction rate and yields [146]. Encinar et al. [115] also proposed 65 to 90°C as the optimal temperature range under MW. The evaporated methanol fraction was finely dispersed in the oil causing high conversion in a relatively short reaction time. Moreover, the MW superheating of boiling methanol may also drive the kinetics of the transesterification.

Table 5.6 Biodiesel yield in system 1 at various MW power settings and circulation cycles (methanol to oil molar ratio of 6).

Power (W)	Cycles	$T_{out\ of\ MW}$ (°C)	Yield (%)
300	15	53.5	95.33
	30	63.8	96.37
400	10	66.3	94.51
	15	68.0	96.16
	30	66.7	98.01
500	5	75.0	95.56
	10	76.7	96.84
	15	77.0	98.37
600	5	80.1	95.94
	10	80.8	96.90

5.3.2 Effect of Methanol/Oil Molar Ratio on Biodiesel Yield

The effect of the methanol/oil molar ratio may be a key parameter due to the high MW-absorption of methanol. The effect of the methanol/oil molar ratio on biodiesel yield is shown in Table 5.7 (System 1). It was found that the optimal methanol/oil molar ratio was 9. This was because transesterification is the reversible reaction and hence requires a higher amount of methanol to shift the reaction [93, 96, 146-148]. However, an excessive amount of methanol will also hinder the reaction rate because it would increase the solubility of the by-product glycerol, for the reverse reaction [149, 150]. The methanol/oil molar ratio does not significantly affect the final temperature, perhaps because of the boiling of methanol. At a high molar ratio, the amount of methanol is greater and more energy is needed to turn methanol into vapour and thus the temperature increase is lower [115].

Table 5.7 Biodiesel yield at various methanol to oil molar ratios (MW power of 400W, circulation cycles of 15).

Methanol/Oil Molar Ratio	$T_{out\ of\ MW}$ (°C)	Yield (%)
6	68.0	96.16
9	70.0	97.44
12	69.3	97.18

5.3.3 Effect of MW Power on Biodiesel Yield at the Optimal Circulation Cycle

Biodiesel yield and required circulation cycles, at the optimal methanol/oil molar ratio of 9 and at any MW power setting, are summarized in Table 5.8. It was found that high biodiesel yield can be obtained with a lower number of cycles at this ratio than at a methanol/oil molar ratio of 6. This confirms the effect of the optimal methanol/oil molar ratio for transesterification used in this work. It can be seen that the biodiesel yield for system 1, at MW power settings of 400, 500 and 600 W, were 96.90, 96.87 and 99.80% at circulation cycle numbers of only 10, 7 and 5 cycles, respectively. These results were obtained at a residence time of 30 seconds in MW reactor for each cycle.

Table 5.8 Biodiesel yield at various MW power settings and circulation cycles (methanol to oil molar ratio of 9).

Power (W)	Cycles	$T_{out\ of\ MW}$ (°C)	Yield [a], (%)
400	10	69.30	96.90
500	7	76.40	96.87
600	5	79.20	99.80

[a] The standard deviation (S.D.) is less than 0.24

5.3.4 Effect of Different Systems for Biodiesel Production

The results of all systems are summarized in Table 5.9. The best results were achieved with system 1 (HSM+MW), however, system 3 (TB+MW) can also reach the minimum ASTM standard yield requirement (96.50%). Moreover, high biodiesel yield can be obtained in only 5 circulation cycles (~5 min of total reaction period and

30 sec. of residence time in MW reactor) at a MW power setting of 600W. This clearly emphasizes the efficient mass transfer enhancement caused by applying HSM over conventional TB.

Table 5.9 Biodiesel yield at various MW power settings and circulation cycles from each system (methanol to oil molar ratio of 9).

Cycles	**Yield (%)**		
	System 1[a] (MW Power)	**System 2[b]**	**System 3[c] (MW Power)**
10	96.90 (400W)	93.44	96.55 (400W)
7	96.87 (500W)	92.06	96.50 (500W)
5	99.80 (600W)	91.57	96.40 (600W)

[a] The standard deviation (S.D.) is less than 0.24

[b] The standard deviation (S.D.) is less than 0.41

[c] The standard deviation (S.D.) is less than 0.43

To emphasise the effect of heat and mass transfer in this experimental set up, it was found that the biodiesel yield of system 2 was under the standard limit (<96.5%). This indicated that mass transfer enhancement alone could not shift the reaction equilibrium. It was more likely involved in the first stage of reaction (diffusion stage) [86], while MW irradiation probably dominated the second stage of reaction (kinetic stage). Indeed, it facilitated the reduction in activation energy and raised the pre-exponential factor [143-145]. Therefore, the integration of HSM and MW reactor is the booster process for the continuous transesterification process.

5.3.5 The Energy Consumption for Biodiesel Production from Each System

As mentioned above, energy consumption is another crucial aspect in this study, as illustrated in Table 5.10. Overall energy consumption was measured using a plug-in power meter and is therefore a measure of total actual energy. This is made up of the energy use of the MW reactor, HSM and cooling pump for system 1, the energy use of the HSM and cooling system for system 2 and of the MW reactor, TB and cooling pump for system 3. The results show that system 1 not only gave the highest biodiesel yield, in accordance with the ASTM standard, but it also only used around half of energy for system 3. This is because conventional TB operates (system 3) for the whole reaction mixture at the same time, while HSM (system 1) operates for the specific amount of reaction mixture that is required for the specific space to obtain the high shear rate [151]. This result obviously confirms the advantages of using HSM to enhance mass transfer and the MW reactor to increase the heat transfer for transesterification. Moreover, the theoretical energy consumption for the MW reactor has also been calculated. It was found that the theoretical energy consumption was 0.109 kWh/L of biodiesel. This value corresponds with the result from Lertsathapornsuk et al. [112] that mentioned an energy consumption value for biodiesel production in a continuous flow through MW reactor of 0.0748 kWh/L of biodiesel.

Table 5.10 Energy consumption for biodiesel production by system (MW power = 600W, circulation cycles = 5 and methanol to oil molar ratio = 9).

Type of reactor	**Energy consumption (kJ/L of biodiesel)**	**Yield (%)**
System 1	0.333	99.80
System 2	0.0073	91.57
System 3	0.589	96.40

5.3.6 Biodiesel Analysis

To ensure the quality of the biodiesel, its properties were compared to those of the ASTM standard. Table 5.11 highlights that all the main physical properties of the biodiesel obtained with systems 1 and 3 fully address ASTM standard requirements [36, 144, 152]. Density is one of the most important properties as it is related to other fuel properties such as viscosity, calorific value and cetane number. This parameter also effects fuel storage and transportation [153].

Table 5.11 Biodiesel physico-chemical properties (System 1).

Properties	**Values**		**Units**
	EN 14105/ASTM 6751	**This work**	
Monoglyceride	≤ 0.80	0.28	% m/m
Diglyceride	≤ 0.20	0.07	% m/m
Triglyceride	≤ 0.20	0.07	% m/m
Free Glycerol	≤ 0.02	0.002	% m/m
Total Glycerol	≤ 0.25	0.091	% m/m
Flash point	≥ 130	175	°C
Pour point	-10 - 12	-2	°C
Viscosity 40°C	1.9 - 6.0	4.61	mm^2/s
Density 20°C	0.86 - 0.89	0.87	g/cm^3

5.4 Biodiesel Production from a flow Microwave reactor

5.4.1 Effect of Methanol/Oil Molar Ratio on Biodiesel Yield

The effect of methanol to oil molar ratio on biodiesel yield is showed in Fig.5.13. It is acknowledged that transesterification is a reversible reaction hence, the high amount of reactant is required to shift the reaction equilibrium. The results also indicated that at high methanol to oil molar ratio, biodiesel yield reached steady state rapidly than at the low methanol to oil molar ratio.

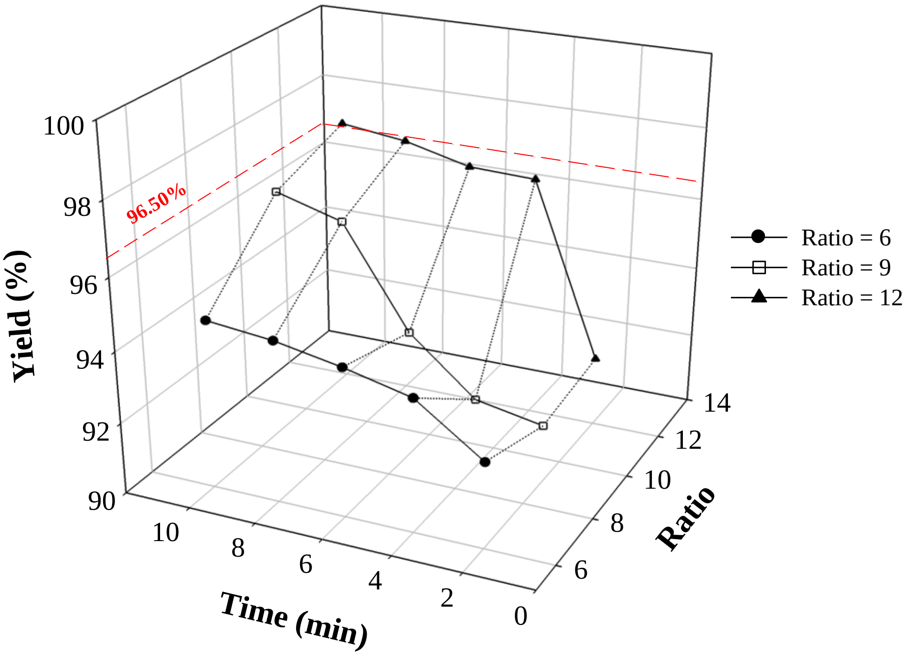

Fig.5.13 Effect of methanol/oil molar ratio on biodiesel yield (MW heating power of 400W, catalyst loading 1%wt of oil, reaction temperature of 70°C and feed flowrate of 100 mL/min)

As can be seen that when using methanol to oil molar ratio of 12, a steady state appeared in 4 min for total reaction time and obtained high biodiesel yield of 96.80% compared to 10 min of reaction time required for the molar ratio of 9. Besides, using methanol to oil molar ratio of 6 cannot provide the minimum biodiesel yield following the requirement of ASTM standard (96.50%). Since the magnitude of heat transfer by microwave irradiation depends on the dielectric properties of the solvent. A large amount of methanol provided more heating media to accelerate the transesterification rate. It was also noticed that the slightly increase in the biodiesel yield from steady state condition was probably due to the reaction was occurred in the pre-mixing tank.

5.4.2 Effect of MW Heating Power on Biodiesel Yield

Fig.5.14 presents the effect of microwave heating power on biodiesel yield. The microwave heating power of 200, 400, 600 and 800W were applied in this work. It can be seen when microwave heating power of 200W was utilized, a long total reaction time of 10 min was required to produce high biodiesel yield at least 96.50%. While, microwave heating power of 400 and 800W can provide high biodiesel yield in accordance with ASTM standard at the same time (4 min). On the other hand, 8 min of reaction time was required for microwave heating power of 600W. In general, high microwave heating power causes the rapid dipole moment reorientation of methanol which destroys the boundary layer between methanol and oil, hence reduces the dielectric constant and the polarity of methanol. This phenomena results in the homogeneity of methanol and oil [142]. Therefore, it not surprised that a high biodiesel yield can be obtained at high microwave heating power.

However, the reaction temperature and microwave heating power were fixed at 70°C for this experiment. It means that when the temperature was higher than the set point temperature, microwave irradiation was stopped. This caused the non-continuous heating from microwave irradiation. This might be the reason that longer reaction time was required for 600W compared with 400W of microwave heating power. Interestingly, using microwave heating power can achieve the steady state condition in 2 min reaction time. However, this condition (800W) employed 2 times of microwave heating power to produce the similar amount of biodiesel compared to that of 400W. Saifuddin and Chua [154] have reported that the irradiation power must be controlled to avoid the overheating that can destroy some organic molecules. This might be the reason that slightly increasing of biodiesel yield can be observed at high microwave heating power of 800W. Therefore, the optimal microwave heating power was 400W.

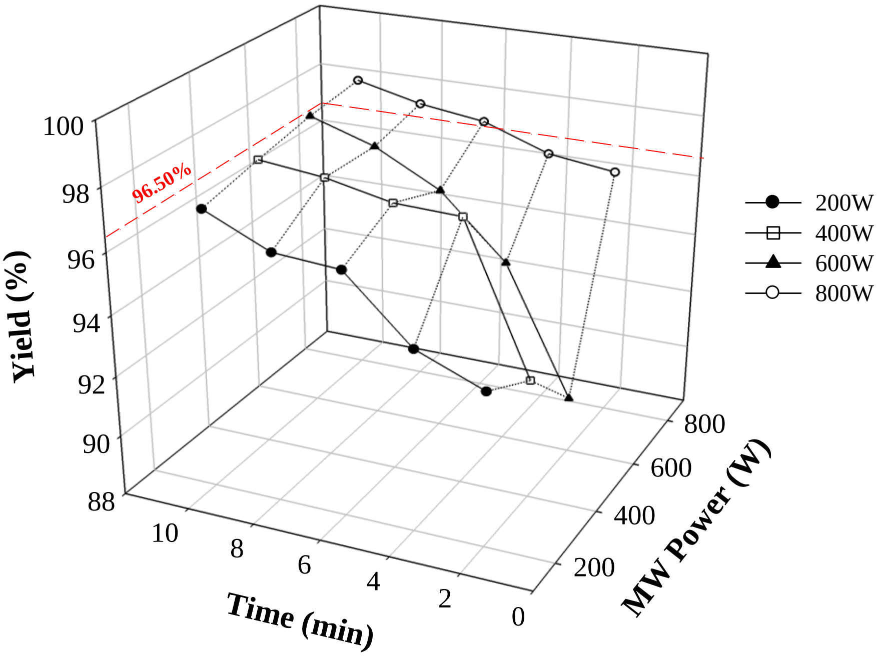

Fig.5.14 Effect of microwave power heating on biodiesel yield (methanol/oil molar ratio of 12, catalyst loading 1%wt of oil, reaction temperature of 70°C and feed flowrate of 100 mL/min)

5.4.3 Effect of Reaction Temperature on Biodiesel Yield

The effect of reaction temperature on biodiesel yield is showed in Fig.5.15. The results show that low biodiesel yield (<96.5%) was obtained when operated at 50 and 60°C even when a long total reaction time of 10 min were employed. This was corresponding with the report by Encinar et al. [115] that high biodiesel yield can be achieved when the reaction temperature was higher than 65°C. Since the contact between alcohol and oil is sufficiently intimate through the reactor for high conversion at relatively short time when methanol is vaporized. Moreover, thermal gradients caused by boiling methanol could encourage the kinetic of the transesterification process [115]. It was found that 96.80% of biodiesel yield can be reached in only 4 min. of total reaction time when operated at 70°C. However, it took about 10 min. to reach 96.50% of yield when operated at 80°C. This result might be due to all methanol was in the vapor phase while oil was still in the liquid resulting in the worse contact between methanol and oil.

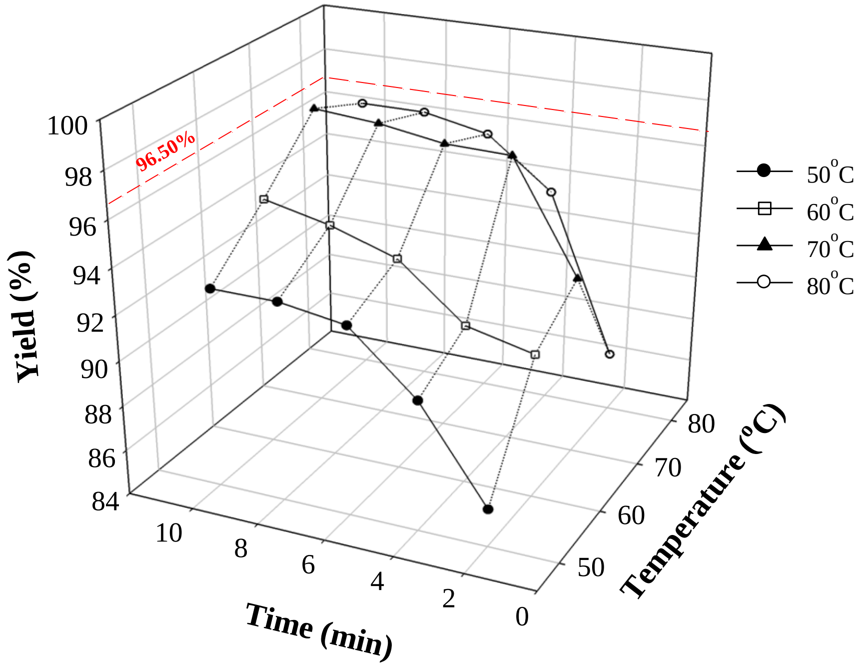

Fig.5.15 Effect of reaction temperature on biodiesel yield (methanol/oil molar ratio of 12, catalyst loading 1%wt of oil, MW heating power of 400W and feed flowrate of 100 mL/min)

5.4.4 Effect of NaOH Catalyst Loading on Biodiesel Yield

Three amount of catalyst loading, 0.5, 1 and 1.5%wt of oil, were investigated. It was found in Fig.5.16 that biodiesel yield clearly increased with increasing of catalyst loading from 0.5 to 1 %wt of oil. This was because low amount of catalyst loading implies low active site leading to low transferification rate. The results also showed that there was no significant increasing of biodiesel yield when increased the catalyst loading from 1 to 1.5%wt of oil. Therefore, the optimal value should be 1%wt of oil. Since high amount of catalyst loading not only causes the high cost of purification but it also gives rise in a formation of an emulsion that increases the viscosity of the mixture resulting in a gel formation and difficult for products separation [96, 146]

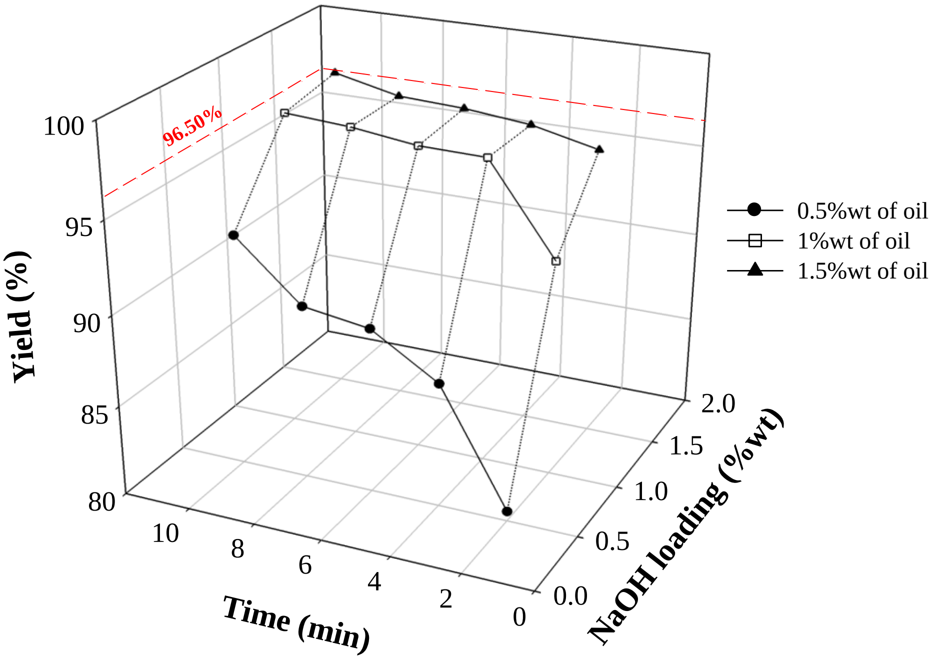

Fig.5.16 Effect of the amount of catalyst loading on biodiesel yield (methanol/oil molar ratio of 12, reaction temperature of 70°C, MW heating power of 400W and feed flowrate of 100 mL/min.)

5.4.5 Effect of Feed Flowrate on Biodiesel Yield

The effect of feed flowrate is illustrated in Fig.5.17. Three feed flowrate of 100, 150 and 200 mL/min as corresponding to the residence time of 1.75, 1.17 and 0.875 min., respectively have been investigated in this section. The results indicated that the reaction time that required to approach the steady state condition of biodiesel yield depends only on the feed flow rate. As can be seen that long reaction time of 8 min. was required for the feed flow rate of 200 mL/min while only 4 min needed for 100 mL/min of feed flow rate. The results indicated that high biodiesel yield fulfil with ASTM and EN standard can be obtained at only 1.75 min of residence time. This result was corresponding with 2 min of residence time required from other work [115]

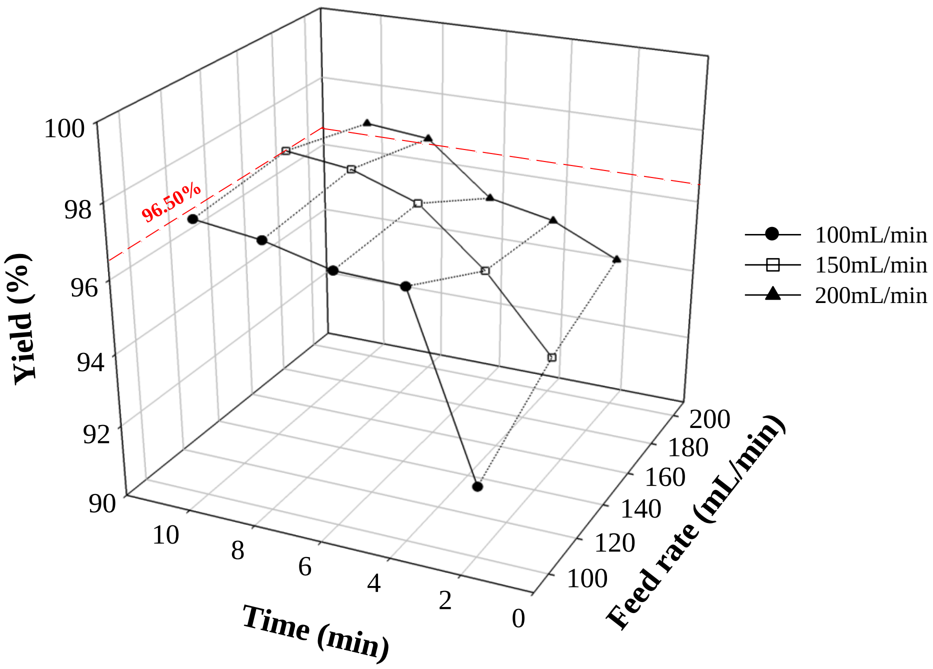

Fig.5.17 Effect of feed flow rate on biodiesel yield (methanol/oil molar ratio of 12, reaction temperature of 70°C, MW heating power of 400W and catalyst loading of 1%wt of oil)

5.4.6 Determination of Activation Energy

In this part, the activation energy of transesterification assisted by microwave reactor has been calculated. Since a lot of research expected that MW irradiation accelerate the reaction rate by decrease the activation energy which is affecting the free energy of activation ΔG as expressed in the following equation:

$$\Delta G = \Delta H - T\Delta S \tag{5.2}$$

where ΔG is the Gibbs free energy, ΔH is the enthalpy, ΔS is the entropy and T is the temperature. When apply microwave irradiation, the magnitude of $T\Delta S$ term would increase because of the higher quick and random dipolar movement of molecular level compared with apply conventional heating [144, 145]. Therefore, the activation energy decrease. In general, the activation energy was calculated from the following equation

$$k = A\, e^{-Ea/RT} \tag{5.3}$$

where k is the rate constant, A is the pre-exponential factor, Ea is the activation energy, R is the universal gas constant and T is the temperature. Temperature change has insignificant effect on the reactant concentration due to transesterification is a liquid phase reaction. Therefore, the Arrhenius plot was determined based on the reaction rate and absolute temperature as shown in Fig.5.18.

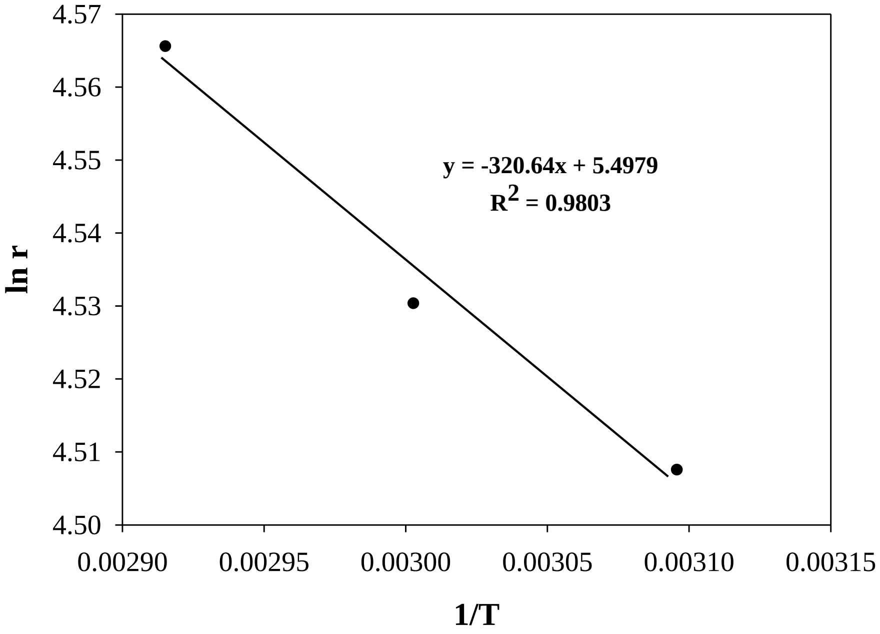

Fig.5.18 Arrhenius plot for transesterification of palm oil in a microwave assisted reactor.

It can be calculated that the activation energy for transesterification assisted by microwave reactor in this work was 2.66 kJ/mol in the temperature range of 50-70°C. There are some reports presented that the activation energy of palm oil transesterification in a conventional heating was about 26.8-61.5 kJ/mol [14, 155, 156]. This clearly indicated that microwave heating can reduce the activation energy of transesterification and accelerate the rate of reaction. Moreover, the activation energy obtained from this work was similar to Terigar et al.'s study [111]. It was founded that the activation energy from soybean and rice bran oil transesterification assisted by microwave reactor in a continuous flow were in the range of 6.3 to 11.1kJ/mol. This can be summarized that the advantage of a microwave assisted reactor can produce biodiesel in the shorter reaction time since microwave irradiation can reduce the activation energy.

5.4.7 Energy Consideration

Overall energy consumption in this work is the actual energy as measured by plug-in power meter. Energy was measured for all equipment used in the experiment including the premixing tank, peristaltic pump, microwave system and cooling system. It was revealed that the total actual energy consumption required to produce biodiesel was 0.1167 kWh/L of biodiesel with related to the theoretical energy consumption based on only microwave reactor of 0.023 kWh/L of biodiesel. This theoretical value was corresponding with 0.0748 kWh/L of biodiesel required for biodiesel production in a continuous flow microwave reactor from other work [112]. It has been reported that the energy consumption of the conventional process was about 0.222 kWh/ L of biodiesel. This clearly emphasizes the efficient heat transfer from microwave heating over conventional heating. Moreover, Patil et al. [93] also reported that the energy consumption for biodiesel production using conventional method was 18 times greater than that of the microwave method.

5.4.8 Biodiesel Analysis

The properties of produced biodiesel i.e., the amount of monoglyceride, diglyceride, triglyceride, free glycerol, total glycerol, flash point, pour point, kinematic viscosity at 40°C and density at 15°C, were determined following the EN 14015 and ASTM D6751 standard method. All properties analysis are summarized in Table 5.12. It can be seen that the high ester content of 99.4% was obtained. Moreover, all measured values are in the range of the standard limit.

Table 5.12 The properties of obtained biodiesel from this work

Properties	**Values**		**Units**
	EN 14105/ASTM 6751	**This work**	
Ester content	≥ 96.50	99.40	%m/m
Monoglyceride	≤ 0.80	0.34	% m/m
Diglyceride	≤ 0.20	0.08	% m/m
Triglyceride	≤ 0.20	0.075	% m/m
Free Glycerol	≤ 0.02	<0.001	% m/m
Total Glycerol	≤ 0.25	0.097	% m/m
Flash point	≥ 130	179	°C
Pour point	-10 - 12	-2	°C
Viscosity 40°C	1.90 - 6.00	4.62	mm^2/s
Density 20°C	0.86 - 0.89	0.86	g/cm^3

5.5 Comparison of Biodiesel Production from Each System

Table 5.13 summarizes the optimal operating conditions and the energy consumption required for each system proposed to produce biodiesel from the previous sections. It can be seen that biodiesel production in a US batch system with heterogeneous catalyst required the highest reaction time and energy consumption. However, US batch system with homogeneous catalyst can also provide the high yield of nearly 100% but this system required a large amount of energy consumption. In case of biodiesel production in the circulation system with both US and HSM integrated with MW reactor, it clearly required less reaction time and energy consumption than for the US batch system. Moreover, biodiesel production from MW reactor in a flow system required the lowest energy consumption. This clearly showed the efficient biodiesel production in a flow process. Therefore, the application in a flow process should be a better method in term of both energy consumption and scaling up process. Moreover, the heterogeneous catalyst plays the possibility apply in the flow system since it is easier to separate from the product mixtures and it can also eliminate the purification step.

Table 5.13 Overall results from each system for biodiesel production.

Parameters	**Batch system**		**Circulation system**		**Flow system**
	US		**US**	**HSM+MW**	**MW**
Catalyst (%wt of oil)	NaOH (1)	CaO (5)	NaOH (1)	NaOH (1)	NaOH (1)
Methanol /oil ratio	6	6	6	9	12
Temperature (°C)	65	65	Autogeneous	Autogeneous	70
Time (min)	120	120	5	5	4
Yield (%)	99	90	90	~100	~99
Energy consumption (kWh/L biodiesel)	5.131	5.634	0.0431	0.1098	0.023

CHAPTER VI

CONCLUSION

6.1 Conclusions

In this work, a study of biodiesel production from the non-conventional techniques, ultrasound assisted reactor and microwave assisted reactor, were investigated. The configuration of each system was different affected on the biodiesel yield. Therefore, the results from each system could be summarized into four sections as below:

6.1.1 Biodiesel Production in an Ultrasonic Bath

The possible use of commercial heterogeneous catalysts, CaO and K_3PO_4, for biodiesel production in the US reactor was investigated. All results were compared with those from the MS reactor. The highest methyl ester yield of 90% from CaO catalyst was achieved in the US reactor at a methanol to oil molar ratio of 6 under the reaction temperature of 65°C using catalyst loading of 3%wt of oil within 2 h of reaction time. CaO catalyst gained higher yield in the short reaction time in the US reactor as compared to the MS reactor. On the other hand, K_3PO_4 catalyst provided the higher yield in the MS reactor. For catalyst reusability test, using CaO catalyst, the methyl ester yield from the last cycle using US reactor was higher than that from MS reactor. Conversely, K_3PO_4 catalyst was observed a severe dissolution to the reaction mixture in MS reactor. It can be concluded that the activation and deactivation of solid catalyst were related to the different mixing characteristics. Moreover, US reactor promoted the heterogeneously catalyzed transesterification of refined palm oil by hindering the catalyst deactivation from adsorption of reaction mixtures.

6.1.2 Biodiesel Production from the Designed Ultrasonic Flow Reactor

A dual frequency US reactor integrated with a horizontal mechanical stirrer has been designed to produce biodiesel from palm oil and methanol in the presence of NaOH as a catalyst. Two transducer frequencies, 20 and 50 kHz, were employed in four possible locations along the length of the reactor. The results showed that this reactor provided high methyl ester yield in only 5 min reaction time, whereas the MS reactor required 60 min. The optimal operating conditions were; a methanol to oil molar ratio of 6 and a NaOH catalyst loading value of 1%wt of oil as operated in the circulation of reaction mixture with feed flow rate 55 mL/min. The influence of transducer number on methyl ester yield was more important than differences in transducer frequency and location along the length of the reactor. The identical distance of each transducer along the length of the reactor was able to provide uniform cavitational intensity and resulted in the same effect at the different locations. Moreover, the properties of biodiesel produced from this reactor conform to the ASTM standard. The combined MS-US reactor enhanced the biodiesel production with better performance than the MS and US reactors alone.

6.1.3 Biodiesel Production from High Shear Mixer Integrated with Microwave reactor

This work proposes a new flow system which is made up of a combination of commercial HSM and MW, to simultaneously enhance both mass and heat transfer in transesterification. Commercial HSM provided excellent mixing (in the diffusion stage) with clearly required less energy than conventional TB. The heat transfer from MW irradiation (in the kinetic stage) has been proved to effectively enhance transesterification in a relatively short time. It was found that a high biodiesel yield of 99.8%, of ASTM standard fulfilling high quality, was obtained in 5 circulation cycles (related to 5 min of reaction time). Moreover, the total energy consumption required for this proposed system was noticeably lower than in the conventional system. The combination of these two reactors provides a valuable guideline for further application in industry in terms of scale up and energy aspects.

6.1.4 Biodiesel Production from a Flow Microwave reactor

In order to approach the sustainable biodiesel production, the large scale process is one of the most significant limitation point for all research study. Therefore, this work proposed a new flow biodiesel production in a commercial microwave reactor due to its reliable, safe and readily to use without the equipment modification. The results indicated that high ester content of 99.4% was archived in only 1.75 min. of residence time. The optimal conditions were the methanol to oil molar ratio of 12, microwave heating power of 400W, reaction temperature of 70°C and NaOH catalyst loading of 1%wt of oil. Microwave heating provides a lower activation energy (2.66 kJ/mol) of transesterification leading to the shorter reaction time for biodiesel production. Energy consumption of biodiesel from this process is 0.023 kWh/L which is lower 10 times of the energy required from the conventional process. This is confirmed that the overcome of using microwave heating for biodiesel production. Moreover, all properties of obtained biodiesel were in accordance with EN/ASTM standard.

6.2 Recommendations for Future Works

The application of non-conventional technologies in flow reactors for biodiesel production is extremely advantageous, both in term of reaction efficiency and energy consumption. Clearly, a scaling up to pilot plant looking for industrial application requires additional data and calculations. The design of high throughput reactor for flow processes is a challenging task. It involves a plethora of relevant parameters such as the attenuation waves of ultrasound, the penetration depth of microwaves, residence time and safety issues. A rule-based multidisciplinary engineering approach should open the door to the ambitious goal of large-scale applications.

REFERENCES

[1] U.S. Energy Information Administration (2012): 1-48.

[2] Satyanarayana, M. and Muraleedharan, C. A comparative study of vegetable oil methyl esters (biodiesels). Energy 36(4) (2011): 2129-2137.

[3] Satyanarayana, M. and Muraleedharan, C. Comparative studies of biodiesel production from rubber seed oil, coconut oil, and palm oil including thermogravimetric analysis. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects 33(10) (2011): 925-937.

[4] Thanh, L.T., Okitsu, K., Sadanaga, Y., Takenaka, N., Maeda, Y., and Bandow, H. Ultrasound-assisted production of biodiesel fuel from vegetable oils in a small scale circulation process. Bioresource Technology 101(2) (2010): 639-645.

[5] Yee, K.F., Kansedo, J., and Lee, K.T. biodiesel production from palm oil via heterogeneous transesterification: optimization study. Chemical Engineering Communications 197(12) (2010): 1597-1611.

[6] Jain, S. and Sharma, M.P. Kinetics of acid base catalyzed transesterification of Jatropha curcas oil. Bioresource Technology 101(20) (2010): 7701-7706.

[7] Jain, S. and Sharma, M.P. Biodiesel production from Jatropha curcas oil. Renewable and Sustainable Energy Reviews 14(9) (2010): 3140-3147.

[8] Kafuku, G., Lam, M.K., Kansedo, J., Lee, K.T., and Mbarawa, M. Croton megalocarpus oil: A feasible non-edible oil source for biodiesel production. Bioresource Technology 101(18) (2010): 7000-7004.

[9] Sahu, G., Das, L.M., Sharma, B.K., and Naik, S.N. Pilot plant study on biodiesel production from Karanja and Jatropha oils. Asia-Pacific Journal of Chemical Engineering 6(1) (2011): 38-43.

[10] Taufiq-Yap, Y.H., Lee, H.V., Yunus, R., and Juan, J.C. Transesterification of non-edible Jatropha curcas oil to biodiesel using binary Ca–Mg mixed oxide catalyst: Effect of stoichiometric composition. Chemical Engineering Journal 178(0) (2011): 342-347.

[11] Cheng, W.-b., Su, F.-y., Wu, G.-y., and Yao, Y.-p. Analysis on the clean production technology of processing waste edible oils to biodiesel. in

Materials for Renewable Energy & Environment (ICMREE), 2011 International Conference on, pp. 449-455, 2011.

[12] Wan Omar, W.N.N. and Amin, N.A.S. Biodiesel production from waste cooking oil over alkaline modified zirconia catalyst. Fuel Processing Technology 92(12) (2011): 2397-2405.

[13] Xu, J., Xiao, G., Zhou, Y., and Jiang, J. Production of biofuels from high-acid-value waste oils. Energy & Fuels 25(10) (2011): 4638-4642.

[14] Darnoko, D. and Cheryan, M. Kinetics of palm oil transesterification in a batch reactor. Journal of the American Oil Chemists' Society 77(12) (2000): 1263-1267.

[15] Baroutian, S., Aroua, M.K., Raman, A.A.A., and Sulaiman, N.M.N. A packed bed membrane reactor for production of biodiesel using activated carbon supported catalyst. Bioresource Technology 102(2) (2011): 1095-1102.

[16] Falahati, H. and Tremblay, A.Y. The effect of flux and residence time in the production of biodiesel from various feedstocks using a membrane reactor. Fuel 91(1) (2012): 126-133.

[17] Dubé, M.A., Tremblay, A.Y., and Liu, J. Biodiesel production using a membrane reactor. Bioresource Technology 98(3) (2007): 639-647.

[18] Kiss, A.A., Dimian, A.C., and Rothenberg, G. Biodiesel by catalytic reactive distillation powered by metal oxides. Energy & Fuels 22(1) (2007): 598-604.

[19] Kiss, A.A. Novel process for biodiesel by reactive absorption. Separation and Purification Technology 69(3) (2009): 280-287.

[20] Chen, Y.-H., Huang, Y.-H., Lin, R.-H., and Shang, N.-C. A continuous-flow biodiesel production process using a rotating packed bed. Bioresource Technology 101(2) (2010): 668-673.

[21] Joelianingsih, et al. Biodiesel fuels from palm oil via the non-catalytic transesterification in a bubble column reactor at atmospheric pressure: A kinetic study. Renewable Energy 33(7) (2008): 1629-1636.

[22] Reyes, J.F., Malverde, P.E., Melin, P.S., and De Bruijn, J.P. Biodiesel production in a jet flow stirred reactor. Fuel 89(10) (2010): 3093-3098.

[23] Sutkar, V.S. and Gogate, P.R. Design aspects of sonochemical reactors: Techniques for understanding cavitational activity distribution and effect of operating parameters. Chemical Engineering Journal 155(1-2) (2009): 26-36.

[24] Gogate, P.R., Tayal, R.K., and Pandit, A.B. Cavitation: A technology on the horizon. Current Science 91(1) (2006): 35-46.

[25] Gole, V.L. and Gogate, P.R. A review on intensification of synthesis of biodiesel from sustainable feed stock using sonochemical reactors. Chemical Engineering and Processing: Process Intensification 53(0) (2012): 1-9.

[26] Vichare, N.P., Gogate, P.R., Dindore, V.Y., and Pandit, A.B. Mixing time analysis of a sonochemical reactor. Ultrasonics Sonochemistry 8(1) (2001): 23-33.

[27] Kumar, D., Kumar, G., Poonam, and Singh, C.P. Ultrasonic-assisted transesterification of Jatropha curcus oil using solid catalyst, Na/SiO2. Ultrasonics Sonochemistry 17(5) (2010): 839-844.

[28] Stavarache, C., Vinatoru, M., Nishimura, R., and Maeda, Y. Fatty acids methyl esters from vegetable oil by means of ultrasonic energy. Ultrasonics Sonochemistry 12(5) (2005): 367-372.

[29] Fan, X., Wang, X., and Chen, F. Ultrasonically assisted production of biodiesel from crude cottonseed oil. International Journal of Green Energy 7(2) (2010): 117-127.

[30] Le Tu, T., Okitsu, K., Sadanaga, Y., Takenaka, N., Maeda, Y., and Bandow, H. A two-step continuous ultrasound assisted production of biodiesel fuel from waste cooking oils: A practical and economical approach to produce high quality biodiesel fuel. Bioresource Technology 101(14) (2010): 5394-5401.

[31] Kumar, G., Kumar, D., Poonam, Johari, R., and Singh, C.P. Enzymatic transesterification of Jatropha curcas oil assisted by ultrasonication. Ultrasonics Sonochemistry 18(5) (2011): 923-927.

[32] Yin, X., Ma, H., You, Q., Wang, Z., and Chang, J. Comparison of four different enhancing methods for preparing biodiesel through transesterification of sunflower oil. Applied Energy 91(1) (2012): 320-325.

[33] Gogate, P.R. Cavitational reactors for process intensification of chemical processing applications: A critical review. Chemical Engineering and Processing 47(4) (2008): 515-527.

[34] Barnard, T.M., Leadbeater, N.E., Boucher, M.B., Stencel, L.M., and Wilhite, B.A. Continuous-flow preparation of biodiesel using microwave heating. Energy & Fuels 21(3) (2007): 1777-1781.

[35] Maddikeri, G.L., Pandit, A.B., and Gogate, P.R. Intensification approaches for biodiesel synthesis from waste cooking oil: A review. Industrial & Engineering Chemistry Research 51(45) (2012): 14610-14628.

[36] Mazubert, A., Poux, M., and Aubin, J. Intensified processes for FAME production from waste cooking oil: A technological review. Chemical Engineering Journal 233 (2013): 201-223.

[37] Anan, N. and Danisman, A. Alkali catalyzed transesterification of cottonseed oil by microwave irradiation. Fuel 86(17-18) (2007): 2639-2644.

[38] Kumar, R., Kumar, G.R., and Chandrashekar, N. Microwave assisted alkali-catalyzed transesterification of Pongamia pinnata seed oil for biodiesel production. Bioresource Technology 102(11) (2011): 6617-6620.

[39] Kanitkar, A., Balasubramanian, S., Lima, M., and Boldor, D. A critical comparison of methyl and ethyl esters production from soybean and rice bran oil in the presence of microwaves. Bioresource Technology 102(17) (2011): 7896-7902.

[40] Jaliliannosrati, H., Amin, N.A.S., Talebian-Kiakalaieh, A., and Noshadi, I. Microwave assisted biodiesel production from Jatropha curcas L. seed by two-step in situ process: Optimization using response surface methodology. Bioresource Technology 136 (2013): 565-573.

[41] Groisman, Y. and Gedanken, A. Continuous flow, circulating microwave system and its application in nanoparticle fabrication and biodiesel synthesis. Journal of Physical Chemistry C 112(24) (2008): 8802-8808.

[42] Knothe, G., Van Gerpen, J.H., Krahl, J. . The biodiesel handbook. : AOCS Press, 2005.

[43] Choedkiatsakul, I., Ngaosuwan, K., Kiatkittipong, W., Laosiripojana, N., and Assabumrungrat, S. Patent review on "biodiesel production process". Recent Patents on Chemical Engineering 4(3) (2011): 265-279.

[44] Helwani, Z., Othman, M.R., Aziz, N., Fernando, W.J.N., and Kim, J. Technologies for production of biodiesel focusing on green catalytic techniques: A review. Fuel Processing Technology 90(12) (2009): 1502-1514.

[45] Vyas, A.P., Verma, J.L., and Subrahmanyam, N. A review on FAME production processes. Fuel 89(1) (2010): 1-9.

[46] Pilli, S., Bhunia, P., Yan, S., LeBlanc, R.J., Tyagi, R.D., and Surampalli, R.Y. Ultrasonic pretreatment of sludge: A review. Ultrasonics Sonochemistry 18(1) (2011): 1-18.

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

[48] Meher, L.C., Dharmagadda, V.S.S., and Naik, S.N. Optimization of alkali-catalyzed transesterification of Pongamia pinnata oil for production of biodiesel. Bioresource Technology 97(12) (2006): 1392-1397.

[49] Leung, D.Y.C. and Guo, Y. Transesterification of neat and used frying oil: Optimization for biodiesel production. Fuel Processing Technology 87(10) (2006): 883-890.

[50] Rashid, U., Anwar, F., and Knothe, G. Evaluation of biodiesel obtained from cottonseed oil. Fuel Processing Technology 90(9) (2009): 1157-1163.

[51] Kondamudi, N., Mohapatra, S.K., and Misra, M. Quintinite as a bifunctional heterogeneous catalyst for biodiesel synthesis. Applied Catalysis A: General 393(1–2) (2011): 36-43.

[52] Zheng, S., Kates, M., Dubé, M.A., and McLean, D.D. Acid-catalyzed production of biodiesel from waste frying oil. Biomass and Bioenergy 30(3) (2006): 267-272.

[53] Goff, M., Bauer, N., Lopes, S., Sutterlin, W., and Suppes, G. Acid-catalyzed alcoholysis of soybean oil. Journal of the American Oil Chemists' Society 81(4) (2004): 415-420.

[54] Wang, Y., Ou, S., Liu, P., Xue, F., and Tang, S. Comparison of two different processes to synthesize biodiesel by waste cooking oil. Journal of Molecular Catalysis A: Chemical 252(1–2) (2006): 107-112.

[55] Patil, P.D. and Deng, S. Optimization of biodiesel production from edible and non-edible vegetable oils. Fuel 88(7) (2009): 1302-1306.

[56] Sahoo, P.K. and Das, L.M. Process optimization for biodiesel production from Jatropha, Karanja and Polanga oils. Fuel 88(9) (2009): 1588-1594.

[57] Son, S.M., Kusakabe, K., and Guan, G. Biodiesel synthesis and properties from sunflower and waste cooking oils using CaO catalyst under reflux conditions. Journal of Applied Sciences 10(24) (2010): 3191-3198.

[58] Kouzu, M., Tsunomori, M., Yamanaka, S., and Hidaka, J. Solid base catalysis of calcium oxide for a reaction to convert vegetable oil into biodiesel. Advanced Powder Technology 21(4) (2010): 488-494.

[59] Liu, C., Lv, P., Yuan, Z., Yan, F., and Luo, W. The nanometer magnetic solid base catalyst for production of biodiesel. Renewable Energy 35(7) (2010): 1531-1536.

[60] Yoosuk, B., Udomsap, P., Puttasawat, B., and Krasae, P. Modification of calcite by hydration–dehydration method for heterogeneous biodiesel production process: The effects of water on properties and activity. Chemical Engineering Journal 162(1) (2010): 135-141.

[61] Encinar, J.M., González, J.F., Pardal, A., and Martínez, G. Rape oil transesterification over heterogeneous catalysts. Fuel Processing Technology 91(11) (2010): 1530-1536.

[62] Li, Y., Zhang, X.-D., Sun, L., Xu, M., Zhou, W.-G., and Liang, X.-H. Solid superacid catalyzed fatty acid methyl esters production from acid oil. Applied Energy 87(7) (2010): 2369-2373.

[63] Petchmala, A., et al. Transesterification of palm oil and esterification of palm fatty acid in near- and super-critical methanol with SO4–ZrO2 catalysts. Fuel 89(9) (2010): 2387-2392.

[64] Jiménez-Morales, I., Santamaría-González, J., Maireles-Torres, P., and Jiménez-López, A. Calcined zirconium sulfate supported on MCM-41 silica as

acid catalyst for ethanolysis of sunflower oil. Applied Catalysis B: Environmental 103(1–2) (2011): 91-98.

[65] Tan, K.T. and Lee, K.T. A review on supercritical fluids (SCF) technology in sustainable biodiesel production: Potential and challenges. Renewable and Sustainable Energy Reviews 15(5) (2011): 2452-2456.

[66] Feng, Y., Zhang, A., Li, J., and He, B. A continuous process for biodiesel production in a fixed bed reactor packed with cation-exchange resin as heterogeneous catalyst. Bioresource Technology 102(3) (2011): 3607-3609.

[67] Lu, P., Yuan, Z., Li, L., Wang, Z., and Luo, W. Biodiesel from different oil using fixed-bed and plug-flow reactors. Renewable Energy 35(1) (2010): 283-287.

[68] Chen, Y.-h., Chang, C.-y., Huang, Y.-h., and Lin, R.-h. Method of increasing transesterification of oils. 2008, NATIONAL KAOHSIUNH UNIVERSITY OF APPLIED SCIENCES (Kaohsiung City, TW): United States.

[69] Lafleur, C., Bouknight Jr., Harry, Bouknight Sr., Harry. System for creating a biofuel. 2008, Biofuels Allied, Inc. (Houston, TX, US),Powertech International Holding AG (Stans, CH): United States.

[70] Ji, J., Wang, J., Li, Y., Yu, Y., and Xu, Z. Preparation of biodiesel with the help of ultrasonic and hydrodynamic cavitation. Ultrasonics 44 (2006): E411-E414.

[71] Shin, J., et al. Effects of ultrasonification and mechanical stirring methods for the production of biodiesel from rapeseed oil. Korean Journal of Chemical Engineering 29(4) (2012): 460-463.

[72] Encinar, J.M., Gonzalez, J.F., and Pardal, A. Transesterification of castor oil under ultrasonic irradiation conditions. Preliminary results. Fuel Processing Technology 103 (2012): 9-15.

[73] Singh, A.K., Fernando, S.D., and Hernandez, R. Base-catalyzed fast transesterification of soybean oil using ultrasonication. Energy & Fuels 21(2) (2007): 1161-1164.

[74] Chand, P., Chintareddy, V.R., Verkade, J.G., and Grewell, D. Enhancing biodiesel production from soybean oil using ultrasonics. Energy & Fuels 24 (2010): 2010-2015.

[75] Kumar, D., Kumar, G., Poonam, and Singh, C.P. Fast, easy ethanolysis of coconut oil for biodiesel production assisted by ultrasonication. Ultrasonics Sonochemistry 17(3) (2010): 555-559.

[76] Avramovic, J.M., Stamenkovic, O.S., Todorovic, Z.B., Lazic, M.L., and Veljkovic, V.B. The optimization of the ultrasound-assisted base-catalyzed sunflower oil methanolysis by a full factorial design. Fuel Processing Technology 91(11) (2010): 1551-1557.

[77] Deng, X., Fang, Z., and Liu, Y.-h. Ultrasonic transesterification of Jatropha curcas L. oil to biodiesel by a two-step process. Energy Conversion and Management 51(12) (2010): 2802-2807.

[78] Na, Y., Su, Y., Wang, H., Wu, Z., and Huang, X. Experimental study on preparation of biodiesel through transesterification with ultrasonic assistant. in, pp. 284-287, 2011.

[79] Georgogianni, K.G., Kontominas, M.G., Tegou, E., Avlonitis, D., and Gergis, V. Biodiesel production: Reaction and process parameters of alkali-catalyzed transesterification of waste frying oils. Energy and Fuels 21(5) (2007): 3023-3027.

[80] Babajide, O., Petrik, L., Amigun, B., and Ameer, F. Low-cost feedstock conversion to biodiesel via ultrasound technology. Energies 3(10) (2010): 1691-1703.

[81] Hingu, S.M., Gogate, P.R., and Rathod, V.K. Synthesis of biodiesel from waste cooking oil using sonochemical reactors. Ultrasonics Sonochemistry 17(5) (2010): 827-832.

[82] Hanh, H.D., Dong, N.T., Okitsu, K., Nishimura, R., and Maeda, Y. Biodiesel production through transesterification of triolein with various alcohols in an ultrasonic field. Renewable Energy 34(3) (2009): 766-768.

[83] Van Manh, D., Chen, Y.-H., Chang, C.-C., Chang, M.-C., and Chang, C.-Y. Biodiesel production from Tung oil and blended oil via ultrasonic

transesterification process. Journal of the Taiwan Institute of Chemical Engineers 42(4) (2011): 640-644.

[84] Cintas, P., Mantegna, S., Gaudino, E.C., and Cravotto, G. A new pilot flow reactor for high-intensity ultrasound irradiation. Application to the synthesis of biodiesel. Ultrasonics Sonochemistry 17(6) (2010): 985-989.

[85] Riva, G., Toscano, G., Foppa Pedretti, E., and Duca, D. Refined soybean oil transesterification enhanced by sonication. Biomass and Bioenergy 35(7) (2011): 2867-2873.

[86] Hsiao, M.-C., Lin, C.-C., Chang, Y.-H., and Chen, L.-C. Ultrasonic mixing and closed microwave irradiation-assisted transesterification of soybean oil. Fuel 89(12) (2010): 3618-3622.

[87] Salamatinia, B., Mootabadi, H., Bhatia, S., and Abdullah, A.Z. Optimization of ultrasonic-assisted heterogeneous biodiesel production from palm oil: A response surface methodology approach. Fuel Processing Technology 91(5) (2010): 441-448.

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

[89] Salamatinia, B., Abdullah, A.Z., and Bhatia, S. Quality evaluation of biodiesel produced through ultrasound-assisted heterogeneous catalytic system. Fuel Processing Technology 97(0) (2012): 1-8.

[90] Georgogianni, K.G., Katsoulidis, A.P., Pomonis, P.J., and Kontominas, M.G. Transesterification of soybean frying oil to biodiesel using heterogeneous catalysts. Fuel Processing Technology 90(5) (2009): 671-676.

[91] Deng, X., Fang, Z., Liu, Y.-h., and Yu, C.-L. Production of biodiesel from Jatropha oil catalyzed by nanosized solid basic catalyst. Energy 36(2) (2011): 777-784.

[92] Azcan, N. and Danisman, A. Microwave assisted transesterification of rapeseed oil. Fuel 87(10–11) (2008): 1781-1788.

[93] Patil, P.D., Gude, V.G., Camacho, L.M., and Deng, S. Microwave-assisted catalytic transesterification of camelina sativa oil. Energy & Fuels 24 (2010): 1298-1304.

[94] Suppalakpanya, K., Ratanawilai, S.B., and Tongurai, C. Production of ethyl ester from crude palm oil by two-step reaction with a microwave system. Fuel 89(8) (2010): 2140-2144.

[95] Suppalakpanya, K., Ratanawilai, S.B., and Tongurai, C. Production of ethyl ester from esterified crude palm oil by microwave with dry washing by bleaching earth. Applied Energy 87(7) (2010): 2356-2359.

[96] Lin, Y.-C., Hsu, K.-H., and Lin, J.-F. Rapid palm-biodiesel production assisted by a microwave system and sodium methoxide catalyst. Fuel 115 (2014): 306-311.

[97] Farough, M. and Farid, N.A. The production of biodiesel from waste cooking oil using microwave irradiation. Mekanikal 32 (2011): 61-72.

[98] Chen, K.-S., Lin, Y.-C., Hsu, K.-H., and Wang, H.-K. Improving biodiesel yields from waste cooking oil by using sodium methoxide and a microwave heating system. Energy 38(1) (2012): 151-156.

[99] Rahmanlar, İ., Yücel, S., and Özçimen, D. The production of methyl esters from waste frying oil by microwave method. Asia-Pacific Journal of Chemical Engineering 7(5) (2012): 698-704.

[100] Perin, G., et al. Transesterification of castor oil assisted by microwave irradiation. Fuel 87(12) (2008): 2838-2841.

[101] Zhang, S., Zu, Y.-G., Fu, Y.-J., Luo, M., Zhang, D.-Y., and Efferth, T. Rapid microwave-assisted transesterification of yellow horn oil to biodiesel using a heteropolyacid solid catalyst. Bioresource Technology 101(3) (2010): 931-936.

[102] Kim, D., et al. Microwave-accelerated energy-efficient esterification of free fatty acid with a heterogeneous catalyst. Bioresource Technology 102(3) (2011): 3639-3641.

[103] Jin, L., et al. ZnO/$La_2O_2CO_3$ layered composite: A new heterogeneous catalyst for the efficient ultra-fast microwave biofuel production. Applied Catalysis B: Environmental 103(1–2) (2011): 200-205.

[104] Koberg, M., Abu-Much, R., and Gedanken, A. Optimization of bio-diesel production from soybean and wastes of cooked oil: Combining dielectric microwave irradiation and a SrO catalyst. Bioresource Technology 102(2) (2011): 1073-1078.

[105] Verziu, M., et al. Sunflower and rapeseed oil transesterification to biodiesel over different nanocrystalline MgO catalysts. Green Chemistry 10(4) (2008): 373-381.

[106] Yuan, H., Yang, B.L., and Zhu, G.L. Synthesis of biodiesel using microwave absorption catalysts. Energy & Fuels 23(1) (2008): 548-552.

[107] Melo Júnior, C.A.R., et al. Solid-acid-catalyzed esterification of oleic acid assisted by microwave heating. Industrial & Engineering Chemistry Research 49(23) (2010): 12135-12139.

[108] Wang, J., Chen, K., and Chen, C. Biodiesel production from soybean oil catalyzed by K_2SiO_3/C. Chinese Journal of Catalysis 32(9–10) (2011): 1592-1596.

[109] Hsiao, M.-C., Lin, C.-C., and Chang, Y.-H. Microwave irradiation-assisted transesterification of soybean oil to biodiesel catalyzed by nanopowder calcium oxide. Fuel 90(5) (2011): 1963-1967.

[110] Patil, P., Gude, V.G., Pinappu, S., and Deng, S. Transesterification kinetics of Camelina sativa oil on metal oxide catalysts under conventional and microwave heating conditions. Chemical Engineering Journal 168(3) (2011): 1296-1300.

[111] Terigar, B.G., Balasubramanian, S., Lima, M., and Boldor, D. Transesterification of soybean and rice bran oil with ethanol in a continuous-flow microwave-assisted system: yields, quality, and reaction kinetics. Energy & Fuels 24 (2010): 6609-6615.

[112] Lertsathapornsuk, V., Pairintra, R., Aryusuk, K., and Krisnangkura, K. Microwave assisted in continuous biodiesel production from waste frying

palm oil and its performance in a 100 kW diesel generator. Fuel Processing Technology 89(12) (2008): 1330-1336.

[113] Liao, C.-C. and Chung, T.-W. Analysis of parameters and interaction between parameters of the microwave-assisted continuous transesterification process of Jatropha oil using response surface methodology. Chemical Engineering Research & Design 89(12A) (2011): 2575-2581.

[114] Suppalakpanya, K., Ratanawilai, S., Nikhom, R., and Tongurai, C. Production of ethyl ester from crude palm oil by two-step reaction using continuous microwave system. Songklanakarin Journal of Science and Technology (2011).

[115] Encinar, J.M., Gonzalez, J.F., Martinez, G., Sanchez, N., and Pardal, A. Soybean oil transesterification by the use of a microwave flow system. Fuel 95(1) (2012): 386-393.

[116] Kanthale, P.M., Gogate, P.R., Pandit, A.B., and Marie Wilhelm, A. Mapping of an ultrasonic horn: Link primary and secondary effects of ultrasound. Ultrasonics Sonochemistry 10(6) (2003): 331-335.

[117] Berrios, M. and Skelton, R.L. Comparison of purification methods for biodiesel. Chemical Engineering Journal 144(3) (2008): 459-465.

[118] Gogate, P.R., Sutkar, V.S., and Pandit, A.B. Sonochemical reactors: Important design and scale up considerations with a special emphasis on heterogeneous systems. Chemical Engineering Journal 166(3) (2011): 1066-1082.

[119] Kouzu, M., Yamanaka, S.-y., Hidaka, J.-s., and Tsunomori, M. Heterogeneous catalysis of calcium oxide used for transesterification of soybean oil with refluxing methanol. Applied Catalysis A: General 355(1–2) (2009): 94-99.

[120] Yoosuk, B., Udomsap, P., Puttasawat, B., and Krasae, P. Improving transesterification acitvity of CaO with hydration technique. Bioresource Technology 101(10) (2010): 3784-3786.

[121] Verziu, M., Coman, S.M., Richards, R., and Parvulescu, V.I. Transesterification of vegetable oils over CaO catalysts. Catalysis Today 167(1) (2011): 64-70.

[122] Watcharathamrongkul, K., Jongsomjit, B., and Phisalaphong, M. Calcium oxide based catalysts for ethanolysis of soybean oil. Songklanakarin Journal of Science and Technology 32(6) (2010): 627-634.

[123] Sharma, Y.C., Singh, B., and Korstad, J. Application of an efficient nonconventional heterogeneous catalyst for biodiesel synthesis from pongamia pinnata oil. Energy and Fuels 24(5) (2010): 3223-3231.

[124] Kesić, Ž., et al. Mechanochemical preparation and characterization of CaO·ZnO used as catalyst for biodiesel synthesis. Applied Catalysis A: General 427–428(0) (2012): 58-65.

[125] Viola, E., et al. Biodiesel from fried vegetable oils via transesterification by heterogeneous catalysis. Catalysis Today 179(1) (2012): 185-190.

[126] Guan, G., Kusakabe, K., and Yamasaki, S. Tri-potassium phosphate as a solid catalyst for biodiesel production from waste cooking oil. Fuel Processing Technology 90(4) (2009): 520-524.

[127] López Granados, M., Alba-Rubio, A.C., Vila, F., Martín Alonso, D., and Mariscal, R. Surface chemical promotion of Ca oxide catalysts in biodiesel production reaction by the addition of monoglycerides, diglycerides and glycerol. Journal of Catalysis 276(2) (2010): 229-236.

[128] Kouzu, M., Hidaka, J.-s., Komichi, Y., Nakano, H., and Yamamoto, M. A process to transesterify vegetable oil with methanol in the presence of quick lime bit functioning as solid base catalyst. Fuel 88(10) (2009): 1983-1990.

[129] Al-Zaini, E.O.A. Biodiesel synthesis from spent frying vegetable oils over heterogeneous inorganic catalysts. Doctor of Philosophy, School of Chemical Engineering The University of New South Wales, 2012.

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

[131] Jain, S. and Sharma, M.P. Thermal stability of biodiesel and its blends: A review. Renewable and Sustainable Energy Reviews 15(1) (2011): 438-448.

[132] Araújo, B.Q., Nunes, R.C.d.R., de Moura, C.V.n.R., de Moura, E.M., Citó, A.n.M.d.G.a.L., and dos Santos Júnior, J.R. Synthesis and Characterization of Beef Tallow Biodiesel. Energy & Fuels 24(8) (2010): 4476-4480.

[133] Dou, B., Dupont, V., Williams, P.T., Chen, H., and Ding, Y. Thermogravimetric kinetics of crude glycerol. Bioresource Technology 100(9) (2009): 2613-2620.

[134] Refaat, A.A. and El Sheltawy, S.T. Comparing three options for biodiesel production from waste vegetable oil. in Waste Management and the Environment IV Conference, pp. 133-140, 2008.

[135] Zhou, H., Lu, H.F., and Liang, B. Solubility of multicomponent systems in the biodiesel production by transesterification of Jatropha curcas L. oil with methanol. Journal of Chemical and Engineering Data 51(3) (2006): 1130-1135.

[136] Rashid, U. and Anwar, F. Production of biodiesel through base-catalyzed transesterification of safflower oil using an optimized protocol. Energy & Fuels 22(2) (2008): 1306-1312.

[137] Choudhury, H.A., Chakma, S., and Moholkar, V.S. Mechanistic insight into sonochemical biodiesel synthesis using heterogeneous base catalyst. Ultrasonics Sonochemistry 21(1) (2014): 169-181.

[138] Tatake, P.A. and Pandit, A.B. Modelling and experimental investigation into cavity dynamics and cavitational yield: influence of dual frequency ultrasound sources. Chemical Engineering Science 57(22-23) (2002): 4987-4995.

[139] Kanthale, P.M., Gogate, P.R., and Pandit, A.B. Modeling aspects of dual frequency sonochemical reactors. Chemical Engineering Journal 127(1-3) (2007): 71-79.

[140] Gogate, P.R., Mujumdar, S., and Pandit, A.B. Sonochemical reactors for waste water treatment: comparison using formic acid degradation as a model reaction. Advances in Environmental Research 7(2) (2003): 283-299.

[141] Mahamuni, N.N. and Adewuyi, Y.G. Optimization of the synthesis of biodiesel via ultrasound-enhanced base-catalyzed transesterification of

soybean oil using a multifrequency ultrasonic reactor. Energy & Fuels 23 (2009): 2757-2766.

[142] Patil, P.D., et al. Power dissipation in microwave-enhanced in situ transesterification of algal biomass to biodiesel. Green Chemistry 14(3) (2012): 809-818.

[143] Kappe, C.O. Controlled microwave heating in modern organic synthesis. Angewandte Chemie-International Edition 43(46) (2004): 6250-6284.

[144] Lidstrom, P., Tierney, J., Wathey, B., and Westman, J. Microwave assisted organic synthesis - a review. Tetrahedron 57(45) (2001): 9225-9283.

[145] Perreux, L. and Loupy, A. A tentative rationalization of microwave effects in organic synthesis according to the reaction medium, and mechanistic considerations. Tetrahedron 57(45) (2001): 9199-9223.

[146] Tippayawong, N. and Sittisun, P. Continuous-flow transesterification of crude jatropha oil with microwave irradiation. Scientia Iranica 19(5) (2012): 1324-1328.

[147] Veera Gnaneswar Gude, P.P., Edith Martinez-Guerra, Shuguang Deng and Nirmalakhandan, a.N. Microwave energy potential for biodiesel production. Sustainable chemical process 1 (2013): 1-31.

[148] Hoque, M.E., Singh, A., and Chuan, Y.L. Biodiesel from low cost feedstocks: The effects of process parameters on the biodiesel yield. Biomass and Bioenergy 35(4) (2011): 1582-1587.

[149] Duz, M.Z., Saydut, A., and Ozturk, G. Alkali catalyzed transesterification of safflower seed oil assisted by microwave irradiation. Fuel Processing Technology 92(3) (2011): 308-313.

[150] Gao, L., Teng, G., Xiao, G., and Wei, R. Biodiesel from palm oil via loading KF/Ca–Al hydrotalcite catalyst. Biomass and Bioenergy 34(9) (2010): 1283-1288.

[151] Hassan, A.S.L., TX, US), Anthony, Rayford G. (College Station, TX, US), Borsinger, Gregory (Chatham, NJ, US), Hassan, Aziz (Sugar Land, TX, US), Bagherzadeh, Ebrahim (Sugar Land, TX, US). High shear process for air/fuel mixing. 2013, H R D Corporation (Houston, TX, US): United States.

[152] Chongkhong, S., Tongurai, C., Chetpattananondh, P., and Bunyakan, C. Biodiesel production by esterification of palm fatty acid distillate. Biomass and Bioenergy 31(8) (2007): 563-568.

[153] Yuan W, Hansen AC, and Q, Z. The specific gravity of biodiesel fuels and their blends with diesel fuel. the CIGR Journal of Scientific Research and Development 6 (2004): 1-11.

[154] Saifuddin, N., and K.H. Chua. Production of ethyl ester (biodiesel) from used frying oil: optimization of transesterification process using microwave irradiation. Malaysian Journal of Chemistry 6(1) (2004): 077-082.

[155] Santos, A.G.D., Souza, L.D., Caldeira, V.P.S., Farias, M.F., Fernandes Jr, V.J., and Araujo, A.S. Kinetic study and thermoxidative degradation of palm oil and biodiesel. Thermochimica Acta 592 (2014): 18-22.

[156] Marjanović, A.V., Stamenković, O.S., Todorović, Z.B., Lazić, M.L., and Veljković, V.B. Kinetics of the base-catalyzed sunflower oil ethanolysis. Fuel 89(3) (2010): 665-671.

APPENDICES

APPENDIX A

MATERIAL PROPERTIES

Table A.1 Chemical properties

Chemical	Molecular weight	Density (g/cm^3)	Heat capacity (J/kg K)
Palm oil	847	0.885	1,794
Methanol	32	0.791	2,566
Sodium hydroxide	40	2.130	-
Sulfuric acid	98	1.840	-
Calcium oxide	56	3.330	-
Potassium phosphate	212	2.564	-

Table A.2 Fatty acid methyl ester composition from palm oil

Fatty acid methyl ester composition	Amount (%)
Lauric acid methyl ester	0.3
Myristic acid methyl ester	0.9
Palmitic acid methyl ester	39.6
Palmitoleic acid methyl ester	0.5
Stearic acid methyl ester	4.1
Oleic acid methyl ester	42.6
Linoleic acid methyl ester	11.2
Linolenic acid methyl ester	0.3
Arachidic acid methyl ester	0.5

APPENDIX B

LIST OF PUBLICATIONS

B.1 International publications

1. Issara Choedkiatsakul, Kanokwan Ngaosuwan, Worapon Kiatkittipong, Navadol Laosiripojana and Suttichai Assabumrungrat. Patent Review on “Biodiesel Production Process”. Recent Patents on Chemical Engineering 4(3) (2011): 265-279.

2. Choedkiatsakul, I., Ngaosuwan, K., and Assabumrungrat, S. Application of heterogeneous catalysts for transesterification of refined palm oil in ultrasound-assisted reactor. Fuel Processing Technology 111 (2013): 22-28.

3. Choedkiatsakul, I., Ngaosuwan, K., Cravotto, G., and Assabumrungrat, S. Biodiesel production from palm oil using combined mechanical stirred and ultrasonic reactor. Ultrasonics Sonochemistry 21(4) (2014): 1585-1591.

B.2 International conferences

1. I. Choedkiatsakul, K. Ngaosuwan, S. Assabumrungrat. Promotion of heterogeneously catalyzed transesterification of refined palm oil using ultrasound-assisted reactor. The 9th European Congress of Chemical Engineering and the 2nd European Congress of Applied Biotechnology (ECCE9/ ECAB2), The Hague, The Netherlands, April 21-25, 2013 (Poster presentation).

2. I. Choedkiatsakul, K. Ngaosuwan, S. Assabamrungrat and G. Cravotto. New efficient flow system enhancing both mass and heat transfer for biodiesel production. The 23rd International Symposium on Chemical Reaction Engineering (ISCRE 23) and the 7th Asia Pacific Chemical Reaction Engineering Symposium (APCRE 7), Bangkok, Thailand, Sepember 7-10, 2014 (Oral presentation).

VITA

Miss Issara Choedkiatsakul was born in Sepember 5, 1985 in Chumphon, Thailand. She received the Bachelor's Degree in Chemical Engineering from King Mongkut's Institute of Technology Ladkrabang in 2007 and Master's Degree in Chemical Engineering from Chulalongkorn University in 2009. Afterward, she started her Doctoral Degree in Chemical Engineering since May 2010 under the scholarship of the Royal Golden Jubilee from Thailand Research Fund (TRF) and Chulalongkorn University. During her research years, she had collaborated with Professor Giancarlo Cravotto and spent one year as an exchange student to do some experiment in the University of Turin, Italy from June, 2013 to June 2014.