Simultaneous reaction and separation technologies for biodiesel production derived from alternative feedstocks

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    งานวิจัยนี้ได้เน้นการผลิตไบโอดีเซลโดยใช้หอกลั่นที่มีปฏิกิริยาแบบไฮบริดไดซ์และเครื่องปฏิกรณ์แบบเหวี่ยงแยกจากน้ำมันปรุงอาหารที่ใช้แล้วเพื่อช่วยลดค่าใช้จ่ายในการผลิต อย่างไรก็ตาม น้ำมันปรุงอาหารที่ใช้แล้วโดยทั่วไปจะมีองค์ประกอบของน้ำปนเปื้อน ซึ่งเป็นสาเหตุหลักของการเกิดปฏิกิริยาการเกิดสบู่ โดยพบว่าการกำจัดน้ำโดยใช้เครื่องแลกเปลี่ยนความร้อนสองตัวร่วมกับหอกลั่นไฮบริดไดซ์เป็นวิธีที่ง่ายที่สุด แต่วิธีนี้ต้องการพลังงานสูงทำให้ต้นทุนการผลิตไบโอดีเซลสูง (1.63 ดอลลาร์ต่อกิโลกรัมไบโอดีเซล) การปรับปรุงด้วยการเพิ่มจำนวนชั้นหอของหอกลั่นเพื่อกำจัดน้ำจะต้องออกแบบและสร้างหอขึ้นใหม่โดยสามารถกำจัดน้ำและใช้พลังงานน้อยลงทำให้ต้นทุนการผลิตต่ำลง (1.07 ดอลลาร์ต่อกิโลกรัมไบโอดีเซล) และการปรับปรุงแบบรวมหน่วยเยื่อเลือกผ่านแบบซึมผ่านพบว่าเป็นตัวเลือกที่ดีที่สุดในเชิงปริมาณการกำจัดน้ำและการกู้คืนเมทานอลโดยใช้ต้นทุนการผลิตที่ต่ำที่สุด (1.04 ดอลลาร์ต่อกิโลกรัมไบโอดีเซล) นอกจากนี้ได้มีการออกแบบเครื่องปฏิกรณ์แบบเหวี่ยงแยกเพื่อใช้ตัวเร่งปฏิกิริยาวิวิธพันธุ์ ภาวะที่เหมาะในการผลิตไบโอดีเซลในเครื่องปฏิกรณ์นี้จาก การออกแบบส่วนประสมกลาง และ วิธีการพื้นผิวผลตอบ คือ อัตราส่วนของเมทานอลต่อน้ำมันคือ 12 ต่อ 1 ปริมาณแคลเซียมออกไซด์ร้อยละ 13 โดยน้ำหนัก และความเร็วรอบของการเหวี่ยงคือ 1,000 รอบต่อนาที ที่อุณหภูมิ 60 องศาเซลเซียส สามารถผลิตไบโอดีเซลได้ร้อยละ 95.01 และ 81.82 เมื่อใช้น้ำมันปาล์มบริสุทธิ์ และน้ำมันปรุงอาหารที่ใช้แล้วตามลำดับ การเร่งปฏิกิริยาทรานส์เอสเทอริฟิเคชันของแคลเซียมออกไซด์ในเครื่องปฏิกรณ์เหวี่ยงแยกที่อ้างอิงจากผลการทดลองพบว่าเป็นปฏิกิริยาอันดับสองเทียม ที่มีค่าพลังงานก่อกัมมันต์และตัวแปรเอกโพเนนเชียลเท่ากับ 26.53 กิโลจูลต่อโมล และ 98.5 ต่อนาที ตามลำดับ

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This research focused on the production of biodiesel using hybridized reactive distillation (hybridized RD) and centrifugal contractor reactor (CCR) from waste cooking oil (WCO) to reduce the operating cost. However, WCO contains some water which can cause saponification. The study showed that using two heat exchangers with hybridized RD is a simple method for water removal but it required the highest energy and cost (1.63 $/kg biodiesel). The extended spacing stage for water removal required a new hybridized RD construction with additional spacing stages. This method can handle and require less energy, resulting in lower cost (1.07 $/kg biodiesel). The integration of pervaporation unit was found to be the best option offering in terms of water removal and methanol recovery, resulting in the lowest cost (1.04 $/kg biodiesel). Additionally, CCR was designed for heterogeneously catalyzed biodiesel production. The optimal conditions were a methanol-to-oil ratio of 12:1, CaO catalyst loading of 13 wt%, and rotating speed of 1,000 rpm at 60°C, based on the center composite design and response surface methodology, offering the biodiesel yield of 95.01 and 81.82 % for refined palm oil and WCO feedstocks, respectively. The CaO catalyzed transesterification in the CCR was found to be a pseudo-second-order reaction with an activation energy and pre-exponential factor of 26.53 kJ/mol and 98.5 min^{-1}, respectively.

Field of Study:	Chemical Engineering	Student's Signature	....
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		Co-advisor's Signature	....

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CHAPTER 1

INTRODUCTION

1.1 Rationale

Fossil fuels (e.g., petroleum, natural gas and coal) are major feedstocks for our economic development. They are non-renewable and could be exhausted within the next 50 years based on the current rate of consumption [1]. Moreover, acceleration of growth of civilization and global trends and transformation can accelerate the depletion of the fossil fuels [2]. Therefore, an alternative energy resource is a crucial importance for seeking substitution of the non-renewable resource. Biodiesel currently poses as a remarkable alternative providing an overall positive life cycle in term of energy balance. The total emissions derived from biodiesel is less than that of the petro-diesel fuel [3,4]. Various reasons for using biodiesel instead of petro-diesel based on the environmental issue are lowering of greenhouse gas (GHG) emissions and less impact on global climate providing the sustainable and renewable energy solution. Biodiesel is a more promising alternative fuel for transportation to support the current energy demand. This can be concluded that using biodiesel can drive to the eco-friendly, renewability, biodegradability and nontoxicity fuel which is overcome to petro-diesel fuel [5]. For the above mentioned, the similar properties of petro-diesel with higher flash point, can make biodiesel as a promising alternative solution to petro-diesel fuel especially in the transport sector [6,7].

Biodiesel can be produced via various methods including of dilution, thermal cracking (pyrolysis), transesterification, and micro-emulsification using renewable feedstocks as vegetable oils. The major components in vegetable oil are triglycerides consisting of glycerol backbone connecting with 3 esters of fatty acid chains [8,9]. The fatty acid chain can have different numbers in bonds and carbon chain lengths. In addition, the transesterification of triglycerides derived from vegetable oil or animal fat and short chain alcohol (mainly as methanol) is the simplest method to produce a high quality of biodiesel or mono alkyl ester of a fatty acid (FAME) [10–13]. Nevertheless, these types of feedstock are usually utilized for food chain materials as

edible oils [14,15]. Large amount of edible oil for conversion to biodiesel can cause a food crisis. Non-edible oil or waste cooking oil is an interesting one to substitute the edible feedstock to produce biodiesel as well as algae oil [16–18], microalgae [19,20], jatropha oil [21] and grease oil [22]. Many research proposed that biodiesel production cost can be reduced by 60-90% using waste edible oil as feedstocks [23,24]. Numerous waste cooking oil source is discarded from household, restaurant and food industry. However, the water and free fatty acid (FFA) containing in the waste cooking oil give a significantly negative influence on the transesterification with presence of side reactions [25,26]. Hydrolysis and saponification can take place in the presence of water and free fatty acid with existing of heat, resulting in increased percent of FFA in the oil and emulsion impurity of biodiesel [27]. Therefore, in order to produce high quality biodiesel, the amount of FFA and water should be eliminated or reduced before transesterification. Transesterification of waste cooking oil requires a catalyst to carry out at mild condition which can be homogeneous or heterogonous one. While non-catalytic transesterification requires sever condition (high pressures and high temperature) to produce biodiesel such as supercritical transesterification.

Heterogeneously catalyzed transesterification is a potential method for the economical biodiesel production where the phase of the solid catalyst is different from that of the liquid reactants. Besides that, the different phase can be the immiscible liquids likely oil-water system or oil-short chain alcohol. The mechanism of heterogeneous catalysis initiates with the adsorption of reactants on the active site of catalyst surface and reacts with the neighbor reactant to form the new product. After the surface reaction, the product is desorbed from the surface of the catalyst to complete the cycle. Mass transfer resistance is more dominate on the reaction rate for the heterogeneous catalysis system which comes by multiphase reaction system including of oil-alcohol-solid catalyst. Several research studies have attempted to improve the mass transfer limitation for biodiesel production using intensification technology. Multi-functional reactors have been proposed to improve mass transfer limitation and production rate such as ultrasonic irradiation (US) [28], microwave (MW) [29], supercritical condition [30], oscillatory flow reactor (OFR) [31],

microchannel reactor [32], laminar flow reactor-separator [33], liquid-liquid flow reactor [34], zigzag micro-channel reactor [35], slit channel reactor [36], spiral reactor [37], spinning disc reactor (SDR) [38], and rotating tube reactor (RTR) [39]. However, these reactors require a subsequent separation unit to purify crude biodiesel.

Reactive distillation [40] combines the reaction by loading catalyst inside a column and separation take place similar to normal distillation. Recently, the development of reactive distillation has been proposed to carry out 2 reactions in a single column, namely hybridized reactive distillation (hybridized RD) [42]. This novel technology is beneficial for feedstock containing high free fatty acid which requires a pretreatment step via esterification to remove free fatty acid using acid catalyst before transesterification of triglycerides using base catalyst. The hybridized RD unit was operated by packing solid acid catalyst to catalyze esterification at the top section of column while transesterification zone was at the bottom section of column using solid base catalyst packing. As already known that a reactive distillation can shift reaction equilibrium with continuous removal of the low boiling point product. Therefore, this technology should be satisfactory for feasible biodiesel production with the third-generation feedstocks. However, this hybridized RD could be reduced only FFA which might not be carried out for the high moisture content feedstocks.

In addition, a centrifugal contractor reactor (CCR) [41] becomes a more gripping technology for biodiesel production. This technology also provides the simultaneous reaction and separation using a centrifugal force in a single unit which is suitable for the nature of biodiesel reaction mixture. The centrifugal force is generated between the space form the outer vessel wall and inner side. For transesterification products, high specific gravity liquid as glycerol phase will be centrifuged to the outer border of the vessel while the lighter phase of biodiesel travels at the inner side. Biodiesel and glycerol could be mechanically separated due to their different density. Therefore, this technology would be helpful for separation and purification of biodiesel production.

As mentioned above, this research aims to develop suitable and green technologies for biodiesel production using heterogeneous catalyst. This study has

been divided into two parts; the simulation of improvement biodiesel production performance of hybridized RD to carry out the feedstocks with high FFA and moisture content and the design and performance testing of bench scale CCR for biodiesel production from the alternative feedstocks using heterogeneous catalyst. The optimum condition and energy consumption of each process are compared with the conventional process. In addition, waste cooking oil (WCO) will be utilized in the above-mentioned reactors.

1.2 Objective

To develop intensification technologies including hybridized reactive distillation (hybridized RD) and centrifugal contractor reactor (CCR) for biodiesel production using heterogeneous catalyst and alternative feedstocks as WCO. The effects of operation parameters on the performance of the proposed reactors are investigated. The energy consumption and total production cost of each process is also compared with the conventional process.

1.3 Scope of work

- Two intensification technologies including hybridized RD column (simulations) and bench scale CCR (experiments) are designed and developed.
- Hybridized RD is designed for feedstocks containing high moisture contamination for biodiesel production.
- The simulation results of hybridized RD are obtained using Aspen Plus software and its performance is compared with other processes using different water removal methods (including integration of heat exchanger, extended stage spacing, and integration of pervaporation unit).
- To design CCR as a modification of normal Berty reactor.
- To characterize results of the CaO heterogeneous catalyst by scanning electron microscope (SEM), Brunauer, Emmett and Teller method (BET) and Hammett indication method.

- To determine the optimum condition of biodiesel production using CCR. Refined palm oil is used to produce biodiesel with various operating conditions including of methanol to oil molar ratio 6:1 – 12:1, reaction temperature (50-65°C), catalyst loading (5-15 wt%), and rotational speed (500-1500 rpm). WCO is also used to produce biodiesel at similar conditions for comparison.

- To investigate the energy consumption and total production cost of each process.

1.4 Expected outputs

- An efficient hybridized RD process to increase a flexibility of biodiesel production via simultaneous esterification and transesterification from alternative generation feedstocks.

- The optimum condition, optimum biodiesel purity and yield efficiency of the CCR using heterogeneous catalyst.
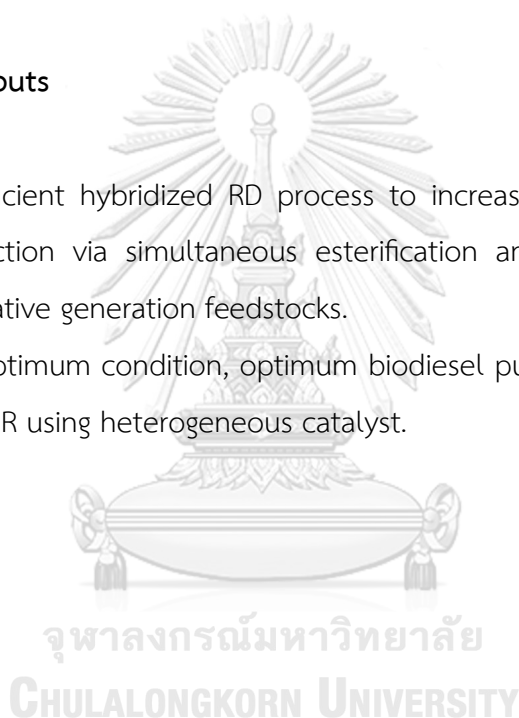
CHAPTER 2

THEORY AND BASIC KNOWLEDGE

This chapter provides the necessary theory and the basic knowledge of biodiesel production using process intensification technology including a trend of world energy consumption and the statistics of fuel energy consumption, the overview of biodiesel production, basic principle of reactive distillation and centrifugal contractor reactor technology, principle of shear force assisting biodiesel production, and the separation-purification of biodiesel process were mentioned.

2.1 Biodiesel

2.1.1 Definition

Biodiesel is an alternative energy that can replace fossil energy. Biodiesel properties are similar to petro-diesel and lower emission which can be used for diesel engines without modification. The mainly component of biodiesel is mono alkyl ester (methyl or ethyl ester) of long chain fatty acid such as methyl palmitate, methyl linoleate, methyl oleate, methyl stearate etc. depended on the parent feedstocks. Properties of the mono alkyl ester of long chain fatty acid is shown in the Table 2.1 [42]. There are 4 methods to produce biodiesel including blending with petroleum diesel, pyrolysis, micro-emulsification (co-solvent blending), and transesterification [43]. In general, biodiesel is produced from triglyceride and alcohol using homogeneous catalyst or heterogeneous catalyst via transesterification. The advantages of biodiesel compared to petro-diesel fuel are ecofriendly, renewability, high flash point, biodegradability and nontoxicity [5]. Moreover, the commercial standard of biodiesel based two types are American Society for Testing and Materials (ASTM) D6751 or the European EN 14214 as shown in Table 2.2.

Table 2.1 Properties of fatty acid alkyl eaters [43].

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

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

Table 2.2 Selected specification from American (ASTM D6751) and European Union (EN 14214) biodiesel standards [44]

	ASTM D6751	EN 14214
Acid value (mg KOH g^{-1})	< 0.50	< 0.50
Free glycerol (mass %)	< 0.020	< 0.020
Total glycerol (mass %)	< 0.240	< 0.250
Cloud point (°C)	Report	-[a]
Pour point (°C)	-	-
Cold filter plugging point (°C)	-	Variable[b]
Oxidative stability		
Induction period, 110 °C (h)	> 3	> 6
Onset temperature (°C)	-	-
Kinematic viscosity, 40 °C (mm^2s^{-1})	1.9 – 6.0	3.5 – 5.0

	ASTM D6751	EN 14214
Specific gravity	-	-
Sulfur (ppm)	< 15	< 10
Phosphorous (mass %)	< 0.001	< 0.001
Cetane number	> 47	> 51
Wear scar, HFRR, 60 °C (µm)	-[c]	-[c]
Gardner color	-	-
Iodine value (g I_2/100 g)	-	< 120

[a] Not specified

[b] Variable by location and time of year

[c] Maximum wear scars of 520 and 460 µm are specified in petro-diesel standards ASTM D975 and EN 590, respectively

2.1.2 Biodiesel feedstock characteristics

The common biodiesel is produced from triglyceride. A regular triglyceride consists of three fatty acid units attached to a glycerol backbone. The structure of fatty acid containing in triglyceride have many types such as stearic acid, oleic acid, palmitic acid, etc. Figure 2.1 shows the fatty acid compositions containing in the different oil sources.
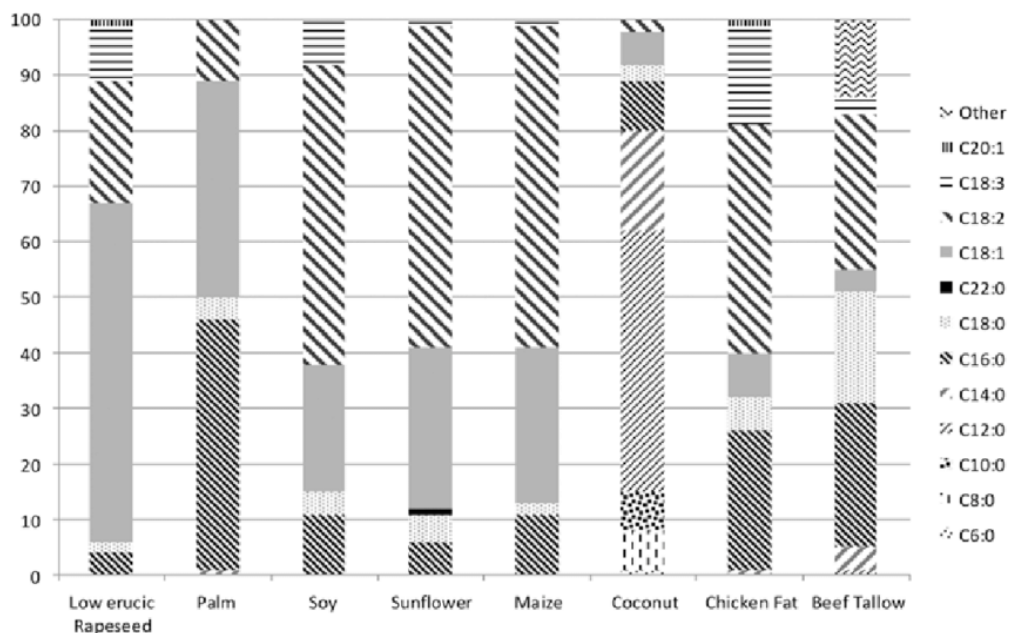
Figure 2.1 Typical fatty acid compositions of biodiesel feedstocks [45]

The fatty acid profile can predict physical properties and performance of the biodiesel product. For example, biodiesel produced from tallow (a highly saturated fat) has a higher freezing point which can prevent cold flow properties. Generally, fatty acid is a carboxylic acid group with a long unbranched aliphatic tail (chain), which can be saturated or unsaturated molecules. Most common fatty acids contain a chain of an even number of carbon atoms, from 4 to 28 [46]. Fatty acids connected with glycerol backbone are triglycerides while the individual or free fatty acid chain is called free fatty acid (FFA). This molecule can react with alcohol in presence of alkali catalyst to form soap via saponification as a side reaction of transesterification process. The FFA content of an oil sample could affect to the quality of produced biodiesel. All carbon atoms of the fatty acid are connected in single bonds which is saturated fatty acid. Monosaturated contains only one chain of saturated fatty acid while the polysaturated present more than one double bond of triglycerides as illustrated in Figure 2.2.
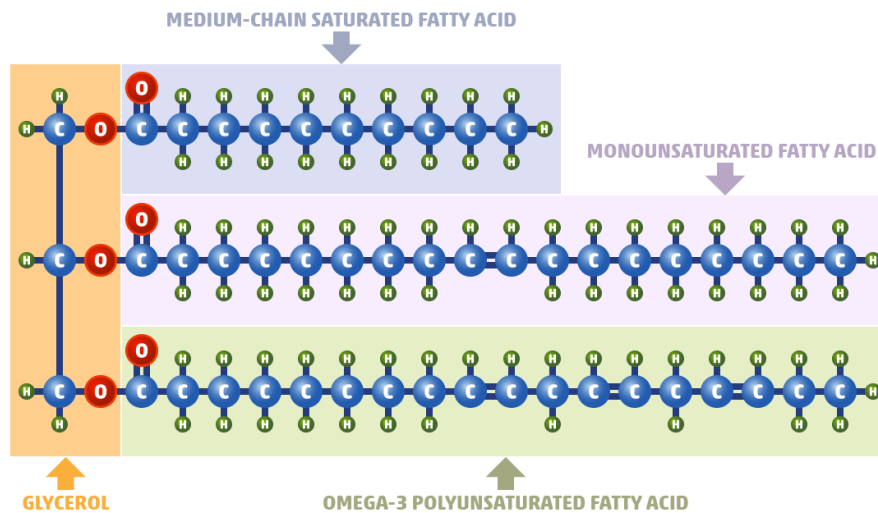
Figure 2.2 Example of triglyceride structure [47]

2.1.3 Classification of biodiesel feedstocks

Since biodiesel was introduced in 1978, many researchers attempt to produce biodiesel from many alternative feedstocks including edible oils, non-edible oils and waste oils. Generally, these feedstocks have a specifically technique to convert to biodiesel. Major issue regarding feedstock for biodiesel production could be divided into each generation base from the origin chemical component in each feedstock. According to the EASAC report 2012, biodiesel feedstocks can group into 4 generations.

First generation

The first generation of biodiesel feedstock is edible oil feedstock such as soybean oil, coconut oil, rapeseed oil, corn oil, palm oil, olive oil, etc. which is renewable and local available source are shown in Table 2.3 [48]. Reason for using edible feedstock to produce biodiesel is a conventional feedstock in this generation because the main composition of edible oil feedstock is triglyceride. Meanwhile, this process could be easier convert to biodiesel. However, the limitation in food supply

must be concerned as main drawback for using these feedstocks. Adaptability to environmental conditions, high cost of production, and cultivation limitation are also hindered for the biodiesel production from edible feedstocks. For these drawbacks, many researchers are shift on the further alternative sources.

Second generation

Second generation biodiesel feedstock has great attention as non-edible feedstock such as neem oil, nagchampa oil, jatropha oil, karanja oil, calophyllum inophyllum oil, rubber seed oil, etc. as shown in Table 2.3 [49,50]. (This generation feedstocks were proposed to reduce a production cost, eliminate food crisis problem and reduce a requirement of land for farming as the main benefits. However, in this generation still have a limitation as its lower farming yield. Even, these feedstocks can cultivate in insignificant lands. It refers to the forced cultivation of non-edible crops at farming lands. It directly influences economy of society and the food production. According to beat the socioeconomic issues of nonedible oil. The researchers were moving on the new alternative solution, which is economical feasible and simplified accessible.

Third generation

On third generation biodiesel feedstocks were introduced as a waste feedstocks and microalgae as shown in Table 2.3 [51]. Both feedstocks contain triglycerides and free fatty acid. Waste cooking oils are cheap as its considerate to be disposed. Moreover, microalgae oil are aquatic plants that having only one cell and has a possibility to generate an amount lipid for biodiesel production. Thus, the advantage of this generation is to reduce the greenhouse effect, higher growth rate and higher productivity, higher amount of oil percentage and lower influence on food supply affect. The main issue of this generation is requirement of large amount

of investment, necessity of sunlight, the ability of a larger scale production at and the difficulties or complication in oil extraction [51–53]. At present the production of biodiesel from algal biomass or waste cooking oil are ongoing research to enhance production rate of biodiesel. However, both feedstocks might require the oil extraction and purification feedstocks. In case of algae feedstocks, some algae have a capability to survive and high lipid content while waste cooking oil is also obtained from virous feedstocks including waste oil, waste fish oil, waste animal tallow. Therefore, these feedstocks should be process or remove impurities before going to biodiesel production unit.

(4) Fourth generation

In this generation is call "advance oil", the key parameter behind this generation in biodiesel feedstock as its high energy content, inexhaustible, easily availability and low price. Most of 4th generation feedstocks are using photosynthesis or solar energy to harvest and combine with capturing carbon dioxide (CO_2). These feedstocks could require a minimum number of steps between solar providing energy and transformation composition into biodiesel. Therefore, this generation is an emerging field, and extensive research is being undertaken to discover new technique for the sustainable conversion of energy to fuel. Due to the growing or harvesting of these feedstocks are still ongoing research resulting to lacking amount of this feedstock for biodiesel production study.

Table 2.3 Summary of example feedstock in different generation [54]

Edible oil (1st generation)	Non-edible oil (2nd generation)	Waste oils and micro algae oil (3rd generation)
Cashewnut	Aleutites fordii	Animal tallow
Coconut	Babassu tree	Biomass pyrolysis
Corn	Calophyllum inophyllum	Botryococcus braunii
Cotton seed	Castor	Chicken fat
Hazelnut	Cerbera odollam	Chlorella vulgaris algae
Mustard	Crambe abyssinica	Dunaliella salina algae
Olive	Jatropha curcus	Poultry fat
Palm	Jojoba	Fish
Pistachio	Karanja	Waste cooking oil
Raddish	Mahua indica	
Rapeseed	Milk bush	
Rice bran	Nagchampa	
Sunflower	Rubber seed	
Walnut	Sapindus mukorossi	
	Silk cotton tree	
	Tall	
	Thevettia peruviana	

For above mentioned, the interesting feedstock was third generation because these feedstocks are simplified and flexible composition material. Thus, to received great potential to produce alternative energy for biodiesel production. Microalgae and waste cooking oil were selected to investigate in this research.

2.2 Biodiesel production

2.2.1 Conventional process and development for biodiesel production

There are many techniques to produce biodiesel. Conventional process can be divided into two systems including of batch and continuous process. Batch process is a suitable process for the various types of feedstocks as its flexible and easy to operate. The main reaction in this process is transesterification which can use an acid or alkali catalysts. Based on this manner operation, it will make high operation cost while the equipment cost is low. In the other sides, the continuous processes are preferred over batch processes for large-capacity commercial production scale because these processes can produce the consistent product quality with low capital and operation costs per unit of product. However, the disadvantages of the conventional process using homogeneous catalyst is more concerned. It requires the additional separation step and the large waste stream is generated into process.

A- Mixer 1	1- Methanol	9- Glycerol + impurities
B- Reactor	2- Catalyst	10- Distilled water
C- Decanter 1	3- Methanolic solution	11- HCl 0.2%
D- Rotary evaporator	4- Oil	12- Biodiesel + water
E- Decanter 2	5- Products from the reaction	13- Sodium sulphate anhidrous
F- Mixer 2	6- Biodiesel + methanol + impurities	14- Biodiesel + hydrated sodium sulphate
G- Vacuum filtration unit	7- Glycerol + methanol + impurities	15- Biodiesel
	8- Biodiesel + impurities	16- Hydrated sodium sulphate

Figure 2.3 Process flow diagram of the conventional homogeneous acid/alkaline catalyzed for transesterification [55]

Figure 2.3 shows process flow diagram of the conventional of biodiesel production. This conventional process can divide into 2 steps including production (biodiesel synthesis) and purification. The production of biodiesel is usually produced via transesterification. Methanol is pre-mixed with the different homogeneous catalyst (A). The reaction was started when the mixture of alcohol and catalyst was added to the reactor (B) and operated at the reaction temperature is 60 $^{\circ}$C. The reactor set consists of a mixing vessel which immerses in the oil bath for controlling the temperature and a cooling condenser to recovery the vaporization of alcohol. At the end of the reaction, product is left to ensure the separation to oil-rich phase and glycerol-rich phase. After settlement, the reaction mixture is separated to three phases including methanol in the upper phase, biodiesel in the middle phase, and glycerol in the bottom phase. In additional, methanol could be recovered by a rotary evaporator under reduced pressure.

The biodiesel phase is washed with 10 – 50 vol.% of water until the pH of washing water is similar to distillation water. To remove residual water, biodiesel is dried over 100 $^{\circ}$C. Then anhydrous sodium sulfate is added (leave overnight). Finally, biodiesel is filtered to obtain the final product.

Table 2.4 Research studies of conventional process for biodiesel production

Oil source	Catalyst	Methanol/oil molar ratio	Temperature (°C)	Reaction time(min)	Ester content (%)	Ref.
Rice bran oil	0.75 wt.% of NaOH	9	55	60	90.18	[13]
Sunflower seed oil	2 wt.% of NaOH	7	60	60	96	[56]
Rapeseed oil	1 wt.% of KOH	6	65	120	95 - 96	[57]
Crude palm oil (CPO)	1 wt.% of KOH	6	60	60	88	[58]
Waste frying oil (WFO)	0.83 wt.% of KOH	9.5	50	20 and 40	98	[59]
waste frying oil (WFO)	0.5 wt.% of NaOH	7.5	50	30	∼97	[60]

Table 2.4 summarizes the study of conventional process for biodiesel production using a conventional mixing. The optimum conditions of catalyst loading, methanol to oil molar ratio, reaction temperature, and reaction time with various oil sources were presented. Although the high purity of fatty alkyl ester content was achieved in the conventional process, however, it could not be ready to scale-up for increasing the productivity of biodiesel.

2.2.1.1 Reactive distillation
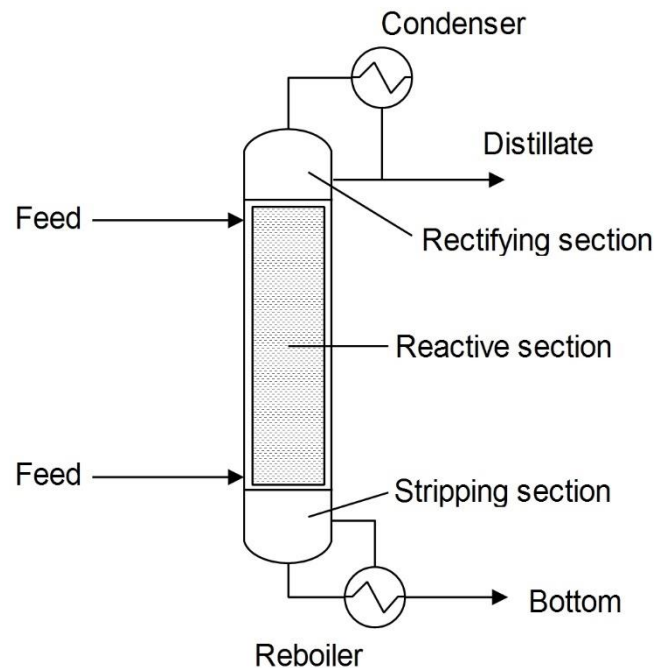
Figure 2.4 Schematic diagram of reactive distillation conceptual design.

The above-mentioned issues, conventional biodiesel production process could be divided into two steps. The first step is reaction step, this step is production via some reactions that converts feedstock to biodiesel. The separation step is next to this step to separate or increase the purity of the main product (biodiesel) by using some technique such as filtration unit, decanter or distillation column. Apart of operating expenses are also a barrier for industrialization of biodiesel production resulting to high biodiesel price compared with that diesel from petroleum [61]. To overcome that barrier, a method for the transesterification of low-cost feedstocks containing with any free fatty acid can be conducted in the reactive distillation column. The reactive distillation (RD) is an integration of reaction and separation in a single unit and provide high conversion, selectivity, and flexibility. Additionally, the energy requirement could be reduced in term of the utility consumption and its

capital cost [62,63]. Many researchers investigated the feasibilities and improvement dealing with the new technologies in reactive distillation. Considering reactive distillation column can be divided into three sections consisting of rectifying, stripping, and reactive section. At the rectifying section, the more volatile component is obtained through contacting the rising vapor with the down-flowing liquid. At the stripping section, the down-flowing liquid is stripped of the more volatile component by the rising vapor and the reaction section is always packed the catalyst to carry out the reactive equilibrium surface (reaction space) [64]. This section represents the subset of mole fraction space for which both phase and reaction equilibrium conditions are satisfied. This kind of technology is advantageous for equilibrium-controlled reactions as it offers product removal with reduced investment and production cost [65]. Most of suitable reaction for reactive distillation column is transesterification because this reaction is a reversible process and requires excess alcohol to shift the reaction equilibrium in the forward direction [23]. In the top of column uses to recovery of the extra alcohol (unreacted alcohol) and then recycle back into column. Thus, the reactive distillation column may consider as an efficient process in biodiesel production.

2.2.1.2 Centrifugal contractor reactor
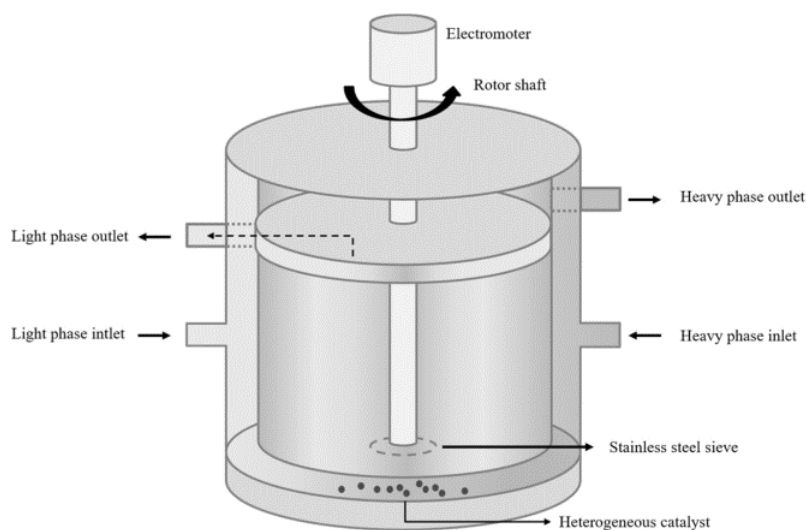
Figure 2.5 Schematic representation of the CCR reactor

In other aspect, centrifugal contractor reactor (CCR) could be designed for simultaneous mixer-separator reactor. This design was fabricated exclusively for biodiesel production due to the different nature of biodiesel and glycerol. From the conventional process, biodiesel production was performed by stirred tank reactor. This reactor types are simple conceptual design but there are suffer from long reaction time and quite high energy requirement. CCR is one of the process intensification reactors that has been carrying out the transesterification, similar to the conventional process. The original CCR was designed for cleaning-up nuclear waste [66] Subsequently, this reactor was applied in liquid-liquid separation process [67].

Figure 2.6 shows the schematic of CCR conceptual design. This reactor was contained by a hollow rotor positioned in a large vessel with spacing between the outside vessel part and inside of stator (this zone is called the mixing zone). Two immiscible liquid (oil and alcohol) phases enter in mixing zone and continuously. This zone should be intense and optimal mixing condition to achieve highest yield. In the lowest part of this reactor has perforate hole to allow the travelling of reaction mixture inside. Then, the removing of product by centrifuge force is applied after holding proper residence time in the mixing zone. Based on the difference density of each product chemical component in the vessel, i.e., the biodiesel and glycerol could leave the device through light phase and heavy phase outlets, respectively. This conceptual design could be fabricated exclusively for liquid-liquid phase like biodiesel production.

CHAPTER 3

LITERATURE REVIEWS

3.1 Current biodiesel production process using third generation feedstocks

There are many researchers considering biodiesel production using the third generation of feedstocks. To simplify the details of feedstocks in this generation it could be defined this kind of feedstocks containing high free fatty acid and moisture content. Since, the applications of heterogeneous acid and alkali catalysts could be their own limitations. Therefore, the combination of acid and base catalysts is a way for improving catalytic properties to synthesize biodiesel. Acid and alkali catalysts are utilized for a two-step process. First, free fatty acids in the waste cooking oil are converted to the corresponding FAMEs through esterification and then transesterification using acid and alkali catalysts, respectively.

3.1.1 Waste cooking oil feedstock

For this feedstock, waste cooking oil contains two major components including triglyceride (TG) and free fatty acid (FFA). FFA contents might be generated during heating, frying or cooking process of triglyceride content in vegetable oil. This FFA content should be concerned because it could be produced soap through saponification in the presence of this specie in alkali condition (as shown in Figure 3.1). Thus, some researchers have suggested or modified the biodiesel process to handle this feedstock.

$$H - O - \overset{\overset{\displaystyle O}{\|}}{C} - R_1 \quad + \quad X - OH \quad \rightleftharpoons \quad X - O - \overset{\overset{\displaystyle O}{\|}}{C} - R_1 \quad + \quad H_2O$$

Free fatty acid   Base   Soap   Water

$$X = Na, K, etc.$$
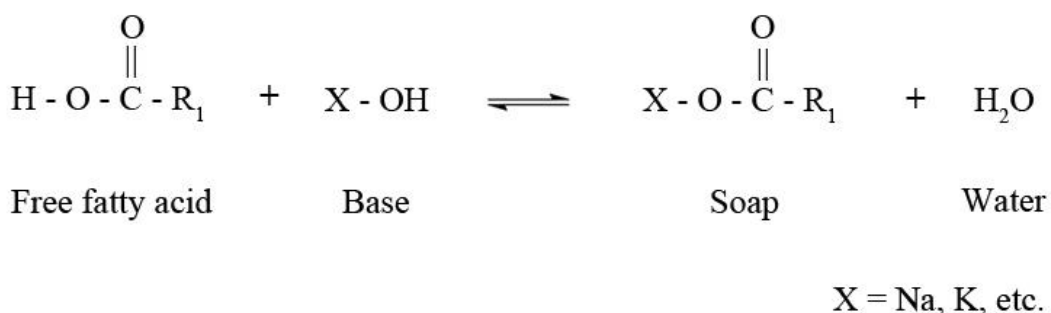
Figure 3.1 Undesired saponification

Zhang and Dube [68] purposed the conventional process (simulation calculation) of biodiesel production from waste cooking oil feedstock using homogeneous catalyst. Four different continuous processes for biodiesel production from virgin oil and waste cooking oil using alkaline and acidic catalysts on a commercial scale were proposed. From the technical assessment, Zhang and Dube's work showed the feasible of producing a high-quality biodiesel product and a top-grade glycerol (by-product). These processes were performed via 2 mixing reactors to productive each reaction (esterification and transesterification). The aim of this work was focus on to remove the number of free fatty acid content in feedstock before going to transesterification and purification biodiesel. Moreover, this work also suggested an alternative separation process to replace water washing via hexene as a solvent to avoid the formation of emulsions which is technically feasible with a less complex process.

3.1.2 Algae/micro-algae feedstock

Algal is a disruptive conventional biodiesel feedstock. This feedstock could provide sustainability with regard to the world's current issues. In commercial aspect, algal oil is still a bottleneck and a challenge due to difficult harvesting process. De Gruyter's work [69] investigated a simpler and effective transesterification process. Microalgae *Spirulina* sp was selected and produced in a batch-stirred reactor with the

mixture of palm oils and algae oil using methanol as reactant and co-solvent. Potassium hydroxide was utilized as a catalyst with a percentage of 1 wt% (w/w of palm oil). The effective result showed that 58.28 % of the obtained biodiesel yield (99.01 % of partial biodiesel yield from palm oil and 16.69% of partial biodiesel yield from dry microalgae) using 10:1 methanol to palm oil molar ratio, a 5:1 palm oil-micro algae weight ratio, and temperature 60 °C. However, for the simultaneous extraction transesterification is still hampered by low biodiesel yield of 16.69 %. It is still recommended to use the mixture of palm oil and microalgae to achieve higher overall biodiesel yield.

3.1.3 Catalysts for biodiesel production

The common homogeneous catalysts for biodiesel production are alkali catalysts because these catalysts are cheap, readily available and can produce biodiesel at mild condition with high biodiesel yield in a short reaction time. However, alkali catalyst is very sensitive to water and FFA content. Using high FFA content feedstocks cause a saponification to decrease biodiesel yield. Similarly, acid homogeneous catalyst can be used to produce biodiesel via the simultaneous esterification of FFA and transesterification of TG. However, the activity of this catalyst is 4,000 times lower than base catalyst based on transesterification resulting to very slow reaction rate and longer reaction time. In addition, the main problem of the homogeneous catalyst involves in the separation step of downstream purification and biodiesel recovery process.

Heterogeneous catalyst gains more attention that could replace the conventional homogeneous catalyst. More advantages in many aspects include; it improves the selectivity, diminishes the washing step of biodiesel, provides the easier separation of catalyst from the biodiesel product, reduces waste-water generation, obtains high product purity and can be regenerated. However, there are some

limitations in terms of high mass transfer resistance, slow reaction rate and possible obtained undesirable side reactions.

3.1.3.1 Acid catalysts

Acid catalysts are suitable for high FFA greater than 1 % and water contenting feedstock which is less favorable saponification. The mechanism of homogeneous acid-catalyzed transesterification of triglyceride has three steps follows; first, the protonation of carbonyl group followed by nucleophilic attach to alcohol producing tetrahedral intermediate. Finally, the proton migration and the tetrahedral intermediate was breakdown leaving glycerol backbone to generate a new ester and reforms the catalyst. [70]. The requirement of temperature, pressure, and alcohol to oil ratio for acid-catalyzed transesterification are higher than using alkali catalyst. The equipment for this process is required the specific and expensive material to avoid the acid corrosion. The common acid catalysts of transesterification are H_2SO_4, HCl, HF, H_3PO_4, and $\boldsymbol{\rho}$-sulfonic acid.

There are some researchers attempting to develop a powerful solid acid catalyst for biodiesel production. Usually, the biodiesel production form waste cooking oil (or feedstock has a high acid values and water content) was used solid acid catalyst which is suitable to catalyze esterification and transesterification or simultaneous reactions. The advantages of solid acid catalyst are that it is easy to remove from the reaction mixture, does not need water washing, could reduce a corrosion and insensitive to FFA content.

3.1.3.2 Alkali catalyst

Most of transesterification is used alkali catalyst than that of acid catalyst because its higher catalytic activity and faster reaction time under mild condition. The alkali catalyst could be corrosive to equipment and possibly reacts with FFAs to form by product soap resulting to require extensive and expensive separation when

feedstock have high water content. The most widely used method, especially for commercial biodiesel production, is the alkali-catalyzed process for the transesterification of the oil (with a low content of free fatty acids) with methanol, typically referred to as the "methyl ester process" [71]. Most of these catalysts are cheap and readily available such as Sodium hydroxide (NaOH), potassium hydroxide (KOH) or sodium methoxide (CH$_3$ONa). [51,72–74].

A heterogeneous alkali catalyst was proposed as it is more resistant to FFA content in the biodiesel feedstocks resulting in hindering the side reaction of saponification. Consequently, there is no emulsion phase which is easy for separation of glycerol from the methyl ester layer. Moreover, they are easily separated, high selectivity, and longer catalyst lifetime compared to homogeneous alkali catalyst. Metal-based oxides, including alkali metal, alkaline earth metal, and transition metal oxides have been selected as catalyst for transesterification. In the structure of metal oxides consists of cation ions that possess Lewis acid properties and negative oxygen ions as anions ions that possess Brønsted base properties [75,76]. Among the metal-based catalyst, CaO catalyst has been widely used to catalyze transesterification due to its superior properties such as long-life catalyst, high activity, low solubility in methanol, high basic strength, and require lower reaction condition. Moreover, CaO catalyst can be produced from waste material such as egg shell, calm shell and bone, etc. which could be a cheap catalyst.

3.1.3.3 Enzymes

Enzyme catalyzed biodiesel production has advantages and well-recognized as moderate operation, eco-friendliness and high product recovery. However, a few industries employ the enzyme catalyzed in biodiesel process because the cost of enzyme, and the problems related to its deactivation caused by feed impurities. The enzymatic alcoholysis of pure triglycerides with or without solvent has been well-

documented in the literature [77–79]. Efficient and low energy intensive protocols of the production of biodiesel from waste oils and animal fats combining lipases with alkali catalysts have also been reported [80]. However, the research dealing with enzyme catalyzed biodiesel forming reaction is still challenge. Table 3.1 illustrates the advantages and drawbacks of using acid, base and enzyme catalyst for biodiesel production.

Table 3.1 Summary of the advantages and disadvantages of different biodiesel catalysts [81]

Type of Catalyst	Example of catalysts	Advantages	Disadvantages
Acidic homogeneous catalysts	H_2SO_4, HCl, HF, H_3PO_4, sulfonic acid	• Insensitive to FFA and water content in oil • Catalyzed simultaneous esterification and transesterification reactions • Avoid soap formation	• Slow reaction rate • Long reaction time • Equipment corrosion • Higher reaction temperature and pressure • High alcohol to oil requirement
Acidic heterogeneous catalysts	ZrO, TiO, ZnO, ion-exchange resin, sulfonic modified mesostructured silica, sulfonated carbon-based	• Insensitive to FFA and water content in oil • Catalyzed simultaneous esterification and transesterification reactions • Recyclable, eco-friendly	• Weak catalytic activity • Catalyst is difficult to recycle • Slow reaction rate • Long reaction time • Higher reaction temperature and pressure • High alcohol to oil requirement • Weak catalytic activity • Low acidic site

Table 3.1 Summary of the advantages and disadvantages of different biodiesel catalysts [81] *Cont.*

Type of Catalyst	**Example of catalysts**	**Advantages**	**Disadvantages**
Acidic heterogeneous Catalysts (*cont.*)	catalyst, HPA, and zeolites	• Non-corrosive to reactor and reactor parts	• Diffusion limitation • Complex and expensive synthesis route • Low micro porosity • Leaching of active catalyst sites
Alkali homogeneous catalysts	NaOH, KOH, NaoCH$_3$, KOCH$_3$	• High catalytic activity • Faster reaction time • Low cost • Favorable kinetics • Modest operational conditions	• Low FFA requirement in the feedstock (<1 wt.%) • Highly sensitive to water and FFA • Saponification as side reaction • Soap formation • High volume of wastewater • Catalyst is non-recyclable • Equipment corrosion

Table 3.1 Summary of the advantages and disadvantages of different biodiesel catalysts [81] *Cont.*

Type of Catalyst	Example of catalysts	Advantages	Disadvantages
Alkali heterogeneous catalysts	CaO, MgO, SrO, mixed oxide and hydrotalcite	• Easy separation • Higher selectivity • Longer catalyst life • Noncorrosive • Environmentally benign • Recyclable • Fewer disposal problems	• Saponification as side reaction • Soap formation • High volume of wastewater • Slow reaction rate compared to homogeneous • Low FFA requirement in the feedstock (<1 wt.%) • Highly sensitive to water and FFA • Leaching of active catalyst sites • Diffusion limitation • Complex and expensive synthesis route

Table 3.1 Summary of the advantages and disadvantages of different biodiesel catalysts [81] *Cont.*

Type of Catalyst	Example of catalysts	Advantages	Disadvantages
Enzyme	Candida antarctica fraction B lipase, Rhizomucor miehei lipase	• Insensitive to FFA and water content in the oil • Avoid soap formation • Non-polluting • Easy purification • Possible reuse	• Very slow reaction rate • Highly expensive • Highly sensitive to alcohol • Denaturation of enzyme

3.2 Intensification processes for biodiesel production

To improve biodiesel production performance, the modification and development of reactor are investigated. The selected application of intensified reactors and their optimum condition results were reviewed. Multi-functional reactors are reactors which integrate one or more functions with reaction in a single vessel resulting in minimizing the capital and operation costs. As previous chapter, this research focused on hybridized RD and CCR as multifunctional reactors that could offer simultaneous separation and reaction.

3.2.1 Hybridized reactive distillation column.
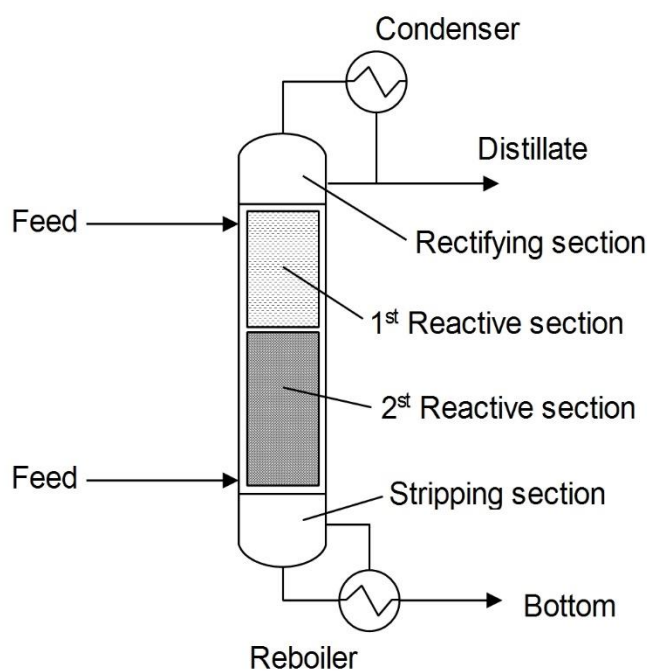
Figure 3.2 Conceptual design of hybridized reactive distillation column

The hybridized RD was proposed to produce biodiesel from high free fatty acid containing feedstock using heterogeneous catalyst [82]. In hybridized reactive distillation column contain two types of catalyst; an acid catalyst (Amberlyst-15) was loaded at the upper part of the column to eliminate free fatty acid (via

esterification), while an alkali catalyst (CaO/Al_2O_3) was loaded at the lower stage for biodiesel production (via transesterification). The simulation results found that this design is flexible to accommodate free fatty acid in feedstock, and requires lower methanol to oil molar ratio, lower energy requirement, and fewer number of unit operation as compared with the conventional process.

3.2.2 Centrifugal contractor reactor (CCR)
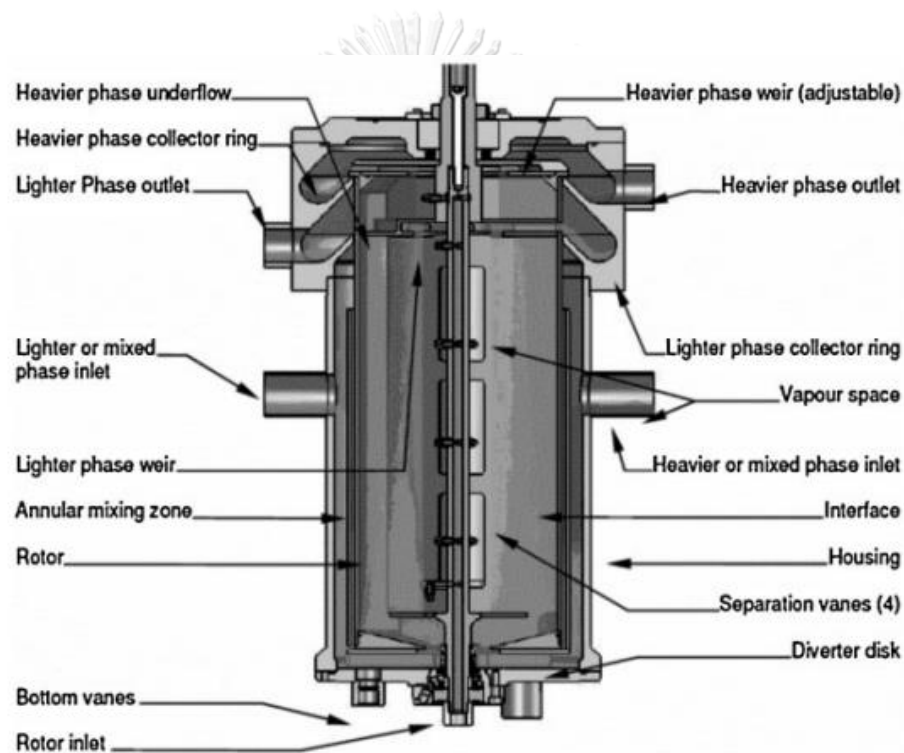
Figure 3.3 Schematic cross-sectional view of the centrifugal contractor purpose Muhammad et al. [83]

The centrifugal contractor is a new process intensification technology that has been explored for biodiesel production. This reactor combines transesterification and centrifugal separation in a single unit which this is a novel technology. Based on the reactor designed, the mass transfer and micro mixing efficiency was increased using centrifugal force. This reactor mainly comprises a hollow rotor positioned in a large

vessel. The space between the outer wall of the rotor and the inner side of the large vessel is called the mixing zone in two immiscible components (methanol and oil). Muhammad et al. [83] investigated the conversion of sunflower oil into biodiesel in a continuous centrifugal contractor reactor and using NaOH as a catalyst using various parameters of alcohol, oil flow rate, rotation speed, and catalyst loading. The optimized conditions (oil and methanol flow rate 31 and 10 mL/min, 34 Hz rotation speed, and 1.2 wt% NaOH loading can achieve 95 % biodiesel yield. The action of centrifugal forces could facilitate the separation of the immiscible liquids leaving the device with different distance in the radial direction depended on their densities. Ebrahim et al. [84] also proposed a simultaneous mixer separator reactor for the transesterification of WCO. The findings demonstrated that the biodiesel yield increased when the oil flow rate was raised from 10 to 15 mL/min, but it was dropped when increase oil flow rate to 30 mL/min. Moreover, enhancing the catalyst concentration from 0.5 to 1% had positive influence, resulting to increase biodiesel yield 35%. Additionally, elevating the temperature from 40 to 60℃ led to a substantial average increase in biodiesel yield from 42 to 88% and this research also achieved a 96 % biodiesel yield using 15 mL/min of oil flow rate and 1 wt% KOH catalyst loading. Moreover, Fayyazi et al. [85] also explored the natural material to synthesis a catalyst. This work was using chicken eggshell-derived to produce CaO as heterogeneous catalyst. An optimized 83.2 % biodiesel yield with a volumetric production rate of 638 kg_{FAME}/ ($m^3_{reactor}$.h) could be achieved in the CCR design at a 9 mL/min oil flow rate and 11:1 methanol to oil ratio, and a weight hourly space time (defined as the mass of catalyst over the oil mass flow rate) of 0.050 h.

In addition, Schuur et al. [86] developed CINC device from CINC Manufacturing (This model similar to centrifugal contractor reactor). This device was developed for oil spill cleanup, liquid–liquid separation and extraction. The

integration of reaction and separation processes holds significant potential for the CINC device. This work also purposed the impact of liquid flow rates (ranging from 18 to 100 mL/min) and rotor frequency (30 to 60 Hz) on the interfacial area of a liquid-liquid system in a CINCV02 continuous integrated mixer/separator. The interfacial area was determined using a chemical reaction method. The specific interfacial areas observed were within the range of 3.2×10^2 to 1.3×10^4 m^2/m^3 of liquid volume, which is similar to those seen in a continuously stirred tank reactor (CSTR). The results revealed a significant maximum in the interfacial area at approximately 45 Hz of rotor frequency. Increasing the aqueous phase flow rates led to a substantial increase in the interfacial area, while the organic phase flow rate had no notable effect. An empirical model was employed to represent the experimental data, and a good agreement was observed between the experimental results and the model.

The process intensification technologies are used to reduce number of separation unit as mentioned above. Centrifugal contractor reactor and hybridized reactive distillation column were selected because both technologies were combined reaction and separation process. In case of biodiesel production by using third generation of feedstocks should be required the pretreatment process to eliminate free fatty acid composition. Therefore, the aim of this research was designed to investigate the optimum condition that can be handle the variety impurity in feedstocks (FFA and moisture content) to produce high biodiesel yield.

CHEPTER 4

RESEARCH PROCEDURE

This chapter provides the details of research procedures. for simulation and experiment sections including of materials and equipment for biodiesel production, the experimental setup, biodiesel analysis and simulation calculation setup.

4.1 Materials

This research was conducted in two parts including simulation and experimental. Therefore, the material section was divided into 2 parts as follows.

4.1.1 Material for simulation

WCO used for Aspen plus® simulation was fixing the amount of FFA at 6 wt%. The mixture of oleic acid and triolein was used as a model compound of WCO with a varying amount of water content such as 4 wt% water, 6 wt% FFA, and balanced with 90 wt% triglyceride, or 6 wt% water, 6 wt% FFA, and balanced with 88 wt% triglyceride. The maximum water content in the WCO

Table 4.1 WCO composition from different country sources

Source of waste cooking oil	Composition							Reference
	FFA (wt%)	Water content (wt%)	C16:0 (%)	C18:0 (%)	C18:1 (%)	C18:2 (%)	C18:3 (%)	
Bakery oil (Brazil)	1.5	6.2	11.6	3.9	25.5	51.9	4.8	[87]
Chinese Restaurant (UK)	1.53	1.2	6.1	1.8	64.2	19.4	8.4	[88]
Waste frying oil (Malaysia)	5.5	6	60.1	10.8	27.2	1.14	NI	[89]
Local restaurant (Mexico)	1.05	0.4	17.82	5.75	40.98	28.77	4.51	[90]

Source of waste cooking oil	Composition							Reference
	FFA (wt%)	Water content (wt%)	C16:0 (%)	C18:0 (%)	C18:1 (%)	C18:2 (%)	C18:3 (%)	
Waste frying oil (Mumbai)	2.40	NI	9.08	6.82	30.6	53.5	-	[91]
Local restaurant (Malaysia)	1.88	2	34.80	7.90	53.30	4.00	-	[92]

feedstock in this work was 10 wt%, which could cover all possible WCO feedstocks as summarized in Table 4.1 [93].

* NI-Not informed

Table 4.1 shows the various compositions in WCO from different sources. WCO was obtained from the immersion of foods oils or fat at high temperature (150 to 200 °C) in the presence of oxygen, moisture, pro-oxidant, and antioxidants of food [94,95]. The heating during the cooking process can lead to the formation of various compounds such as free fatty acid, the composition of the acyl group, or aldehydes [96,97]. Several reactions can occur during the cooking process including oxidation [98], polymerization, isomerization, hydrolysis [99], and decomposition [100]. The water content in WCO was found in the range of 0.4 to 6.2 wt% which should be removed before being introduced into the reaction unit because the presence of water can diminish the biodiesel production performance such as the saponification side reaction and the emulsion of water and reaction mixture resulting in decreased biodiesel yield and purity. Usually, the limitation of water or moisture content in WCO should be less than 1 wt% before feeding to the conventional biodiesel production process [101]. WCO must be treated before entering the process by filtration to remove all insoluble impurities and then heating to 120 °C to remove water or some moisture as a conventional method for the pretreatment of WCO. Therefore, the different water removal processes for the hybridized RD were proposed including of the conventional evaporator, the extended reactive stage and the pervaporate membrane.

4.1.2 Material for experimental

The main reactants for experimental research included a short chain alcohol, refined palm oil and WCO as a third generation of biodiesel feedstock. The short chain alcohol was methanol (analytical grade 99.8 % purity) which was purchased from Loba Chemie Pvt. Ltd. Commercial refined palm oil (Morakot) was purchased from a convenient store and used without further pretreatment. WCO was obtained from a restaurant in Chulalongkorn university's engineering canteen. WCO was filtrated to remove solid impurity and suspended food then it was heated to 110 °C for 2 h to remove moisture and water content. Commercial calcium oxide (CaO) fine powder was purchased from Sigma-Aldrich. After that, it was calcined in a muffle furnace with a heating rate of 10 °C/min to 900 °C and hold for 5 h then kept in a desiccator cabinet before use.

4.2 Research procedure

The research procedure was also divided into two parts including of the hybridized RD simulation and CCR experimental setup as follows.

4.2.1 Biodiesel production from low-cost waste cooking oil containing high water content in hybridized RD

4.2.1.1 Models and simulation properties

Based on the previous work [82], the Dortmund modified UNIFAC model [102] was selected to predict vapor-liquid equilibrium (VLE) and liquid-liquid equilibrium (LLE). Kuramochi et al. [103] also proved that the Dortmund modified UNIFAC model was most suitable for the prediction of the thermodynamic properties of various mixtures associated with the design of biodiesel processes corresponding to the experimental results for VLE of mixtures of methanol-biodiesel and methanol-glycerol systems, and LLE of mixtures of water, biodiesel, methanol-biodiesel, glycerol, and methanol-water-biodiesel systems. Ternary diagram of biodiesel-related

substances including of triolein-methanol-oleic acid, methyl oleate-methanol-glycerol and methyl oleate-methanol-oleic acid was shown in Figure 4.1 All of ternary diagram was generate by Aspen Plus programing through Aspen Plus Ternary Maps functions. This analysis was calculated based on thermodynamic properties that we selected the Dortmund modified UNIFAC (same as main process model calculation).

Modified hybridized RDs with different water removal methods were simulated by Aspen plus® simulation program version 8.0 in steady state operation. This program offers a comprehensive thermodynamic foundation for accurate calculation of physical properties, transport properties and phase behavior for the oil and gas refinery industries. There is a comprehensive library of unit operation models including distillation, reactors and heat transfer operation. To avoid the side effect or the side reaction that could reduce the biodiesel production performance, all water content should be removed before entering the transesterification section, and this is a constraint for the operation of all of the modified hybridized RDs. Biodiesel yield and its purity were also concerned to conform the EN 14214 standard to allow comparison of the process performance. Biodiesel yield is defined in Equation (4.1).

$$\text{Biodiesel yield (\%)} = \frac{F_{\text{Methyl oleate}}}{\left(3 \times F_{\text{Triolein,initial}}\right) + \left(F_{\text{Oleic acid,initial}}\right)} \times 100\% \quad (4.1)$$

where $F_{\text{Methyl oleate}}$ is the molar flow rate of methyl oleate in the product stream, $F_{\text{Triolein,initial}}$ and $F_{\text{Oleic acid,initial}}$ are the molar flow rates of triolein and oleic acid in the feed stream, respectively.

Aspen process economic analyzer (APEA) was used to analyze the equipment cost estimation for economic analysis. Assigned default mapping and sizing algorithms of APEA were used to simplify the mapping and sizing step for the unit operation.
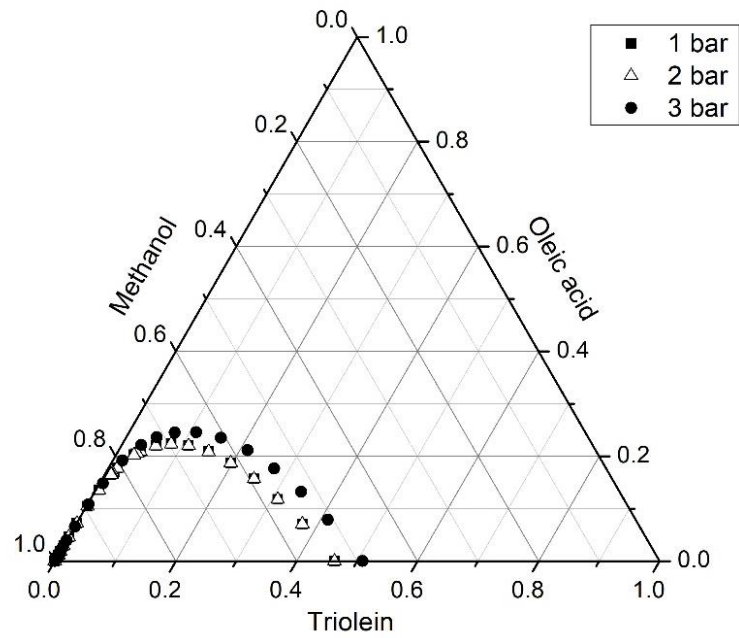
(a) Triolein-methanol-oleic acid
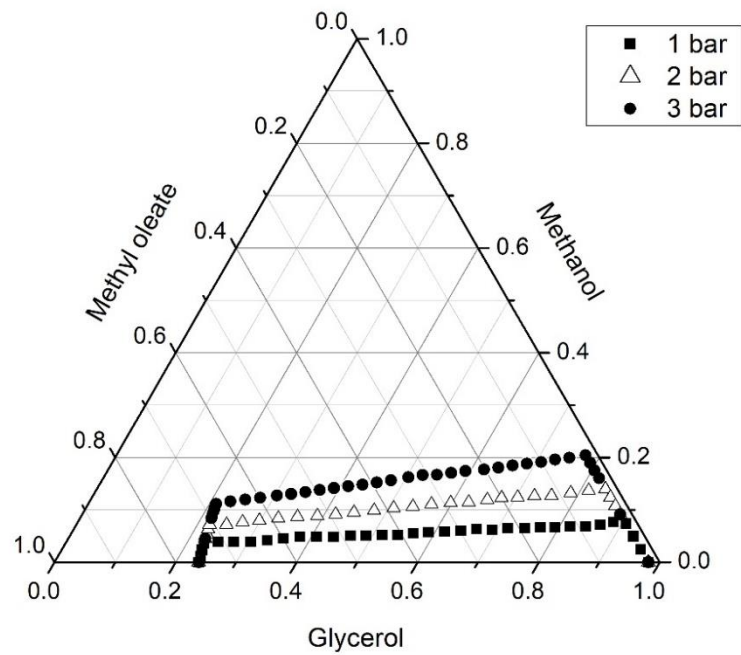
(a) Methyl oleate-methanol-glycerol
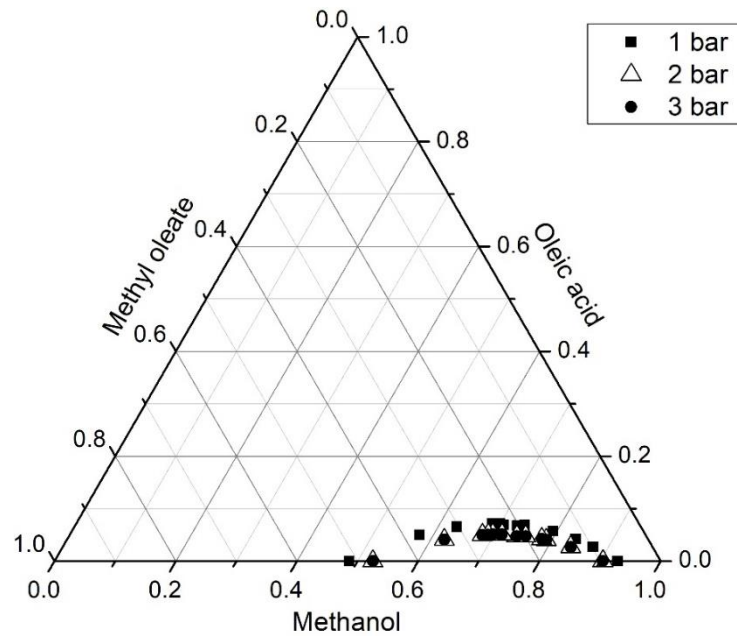
(b) Methyl oleate-methanol-oleic acid

Figure 4.1 Ternary diagrams of biodiesel-related substances: (a) triolein-methanol-oleic acid, (b) methyl oleate-methanol-glycerol and (c) methyl oleate-methanol-oleic acid

4.2.1.2 Kinetic model and data validation

The kinetic parameters of the reaction catalyzed by CaO/Al_2O_3 as a solid alkali catalyst was obtained from Pasupulety et al. [104] while the kinetic data for esterification in the pretreatment step using Amberlyst-15 as an acid catalyst was acquired from Steinigeweg and Gmehling [105]. Based on our previous work [82], both kinetic data were in good agreement with the experimental data. Therefore, the same set of kinetic data was also used for the prediction of the simultaneous esterification and transesterification in the hybridized RD using Aspen plus®.

4.2.1.3 Biodiesel production in hybridized RD

The hybridized RD flow diagram based on our previous work [82] is shown in Figure 4.2 The detail of the simulation based on our previous work was shown in Table 4.2. WCO was fed into the column at 1,050 kg/h (for the base case using 6 wt% FFA content) and methanol was fed at the methanol to WCO (triglyceride and FFA model compound) ratio of 4:1 into the bottom stage to produce biodiesel at 944 kg/h. The hybridized RD column (C-301) was pressurized to 3 bar to obtain the higher biodiesel production performance which does not require a reflux unit to recover unreacted methanol [82]. A partial condenser at the top column was used to remove some water contamination from esterification and also to recover unreacted methanol back to the system. A total of 10 actual stages (8 reactive stages, 1 stripping stage, and 1 rectifying stage) for the feedstock with 6 wt% FFA content were used. At the top column, the first 3 reactive stages were packed with Amberlyst-15 for esterification (pretreatment) to reduce FFA and the next 5 reactive stages were packed with CaO/Al$_2$O$_3$ to produce biodiesel via transesterification. After reaction completion, biodiesel and glycerol (bottom stream) were sent to the purifying unit (decantor-D401).

Figure 4.2 Hybridized RD for biodiesel production

Table 4.2 Hybridized RD column design parameters [20]

Parameter	Value	Unit
Rectifying section	1	stages
Reactive section	8	stages
Stripping section	1	stages
Total number of actual stages	10	stages
Column dimeter	0.30	m
Column height	6.00	m
Catalyst loading	Amberlyst-15 2.5 wt% CaO/Al$_2$O$_3$ 3 wt%*	-
Reflux ratio	0.1	-
Reboiler duty	216	kWh/kmol biodiesel
Reflux ratio	0.1	-
Column pressure	3	bar
Methanol to oil ratio	4:1	-
Free fatty acid in feedstock	6	wt%
Biodiesel production rate	944	kg/h

4.2.1.4 Selected water removal methods

In general, there are several processes for water removal from biodiesel production including vacuum drying [106], treatment with salt [107] and the use of coalescing filters [108]. However, these water removal processes are energy-extensive such as heating or vacuum flash with limited water content removal. In this study, the novel methods for water content removal are proposed based on their distinctive feature of three selected units combined with our earlier hybridized RD to produce biodiesel according to the ASTM or EN standard and to minimize the number of unit and energy consumption, as well as to be environmental-friendly. Based on this constraint, three combined units to remove water from the biodiesel production in the earlier hybridized RD have been selected. First, the heat exchanger with phase change (evaporator) unit was selected because it is a conventional process to remove the water content from the other components based on the difference in boiling points. However, as the evaporator requires high energy consumption, the other two novel water removal processes have been proposed. With the aim to minimize the energy requirement and the number of units, the second method using extended spacing stage modification from the earlier hybridized RD was adopt based on their vapor-liquid equilibrium. This modification process was firstly proposed to remove water content for biodiesel production. Moreover, the cost of the additional or modified process to produce eco-friendly and economical biodiesel was considered. Based on this reason, the integration of the pervaporation unit was proposed in this study because the pervaporation unit provides a high efficiency unit to remove water based on the selective permeation through molecular sieve membrane, which can be combined with the earlier hybridized RD next to the esterification stage.

4.2.2 Biodiesel production from refined palm oil and waste cooking oil using CaO catalyst in CCR reactor

4.2.2.1 Catalyst preparation and characterization

Commercial CaO catalyst was prepared by calcination in the static air using ramp rate of 10 °C /min with calcination temperature of 900 °C and holding time for 5 h. The catalyst characterizations for CaO were as follows.

4.2.2.1.1 X-ray diffraction (XRD) analysis

Crystallinity and phase of catalysts were characterized by XRD (Bruker D8 Advance, Cu K α at 0.154056 nm) between 5° and 90° with a step size of 0.0130° and a scan rate of 0.5 s per step.

4.2.2.1.2 Thermogravimetric analysis/differential scanning calorimeter (TGA/DSC)

Thermal stability of uncalcined CaO catalysts was analyzed by thermogravimetric analysis with differential scanning calorimeter (TGA/DSC, SDT Q600 Diamond Thermogravimetric and Differential Analyzer, TA Instruments). The analysis was operated from room temperature to 1,000 °C at a heating rate of 10 °C/min using 100 mL/min of air zero.

4.2.2.1.3 N_2 adsorption–desorption isotherms by using Brunauer - Emmett -Teller method (BET)

The surface area of each sample was determined by the Brunauer-Emmett-Teller (BET) method with nitrogen gas (Micromeritics Chemisorp 2750). Pore sizes and pore volumes of the samples were determined by desorption isotherm using Barret-Joyner-Halender (BJH) method.

4.2.2.1.4 Scanning electron microscope and energy dispersive X-ray spectrometer (SEM/EDX)

The morphologies of the CaO catalyst were analyzed using a scanning electron microscope, SEM, (Hitachi S-3400N) coupled with X-ray energy dispersive

spectroscopy, X-ray EDS, (AMETEK EDAX, APOLLO X) for analyzing the local dispersion of elements.

4.2.3   CCR design and construction
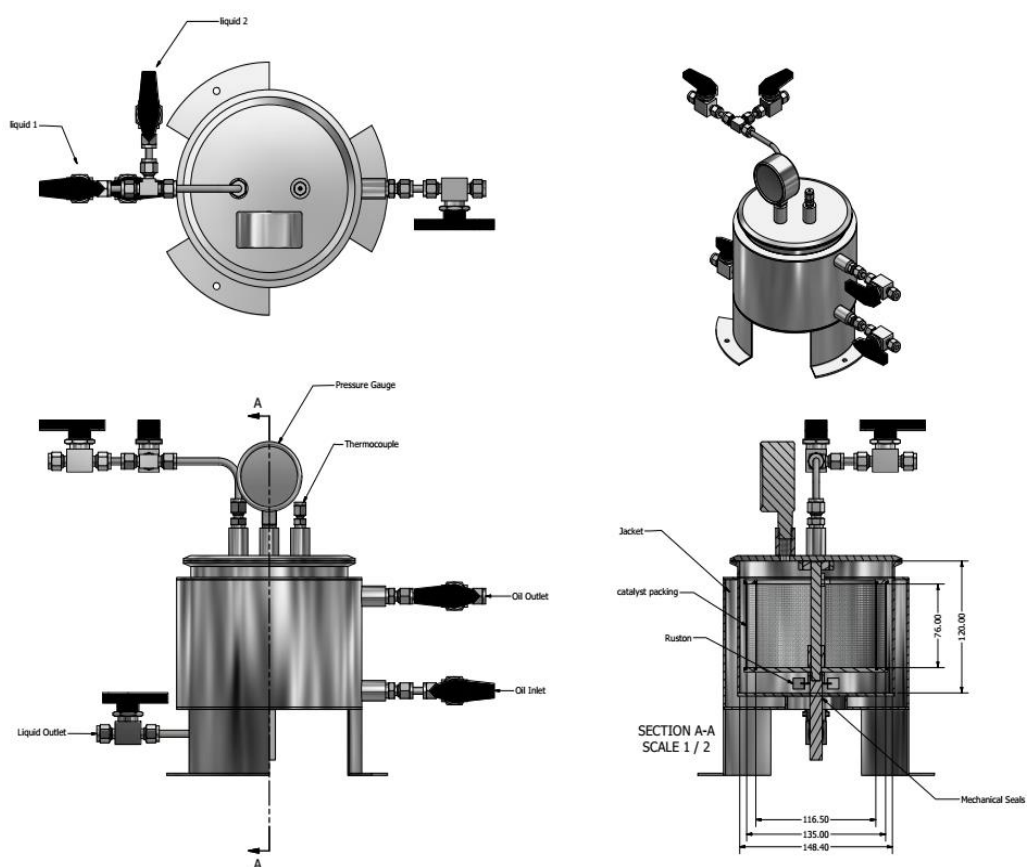
Figure 4.3 Schematic representation of the centrifugal contractor reactor design in this research

The simultaneous reactor and separator were modified from a berty reactor. This reactor was used to produce biodiesel using heterogeneous catalyst. Figure 4.3 shows the centrifugal contractor reactor design. This reactor was used to investigate the fundamentals of the centrifugal, mixing and separating process. Moreover, inside

this reactor was installed a basket to carry the heterogeneous catalyst and the end of motor shaft was connected with the adjustable mixing blades to generate and improve mixing of two immiscible fluids.
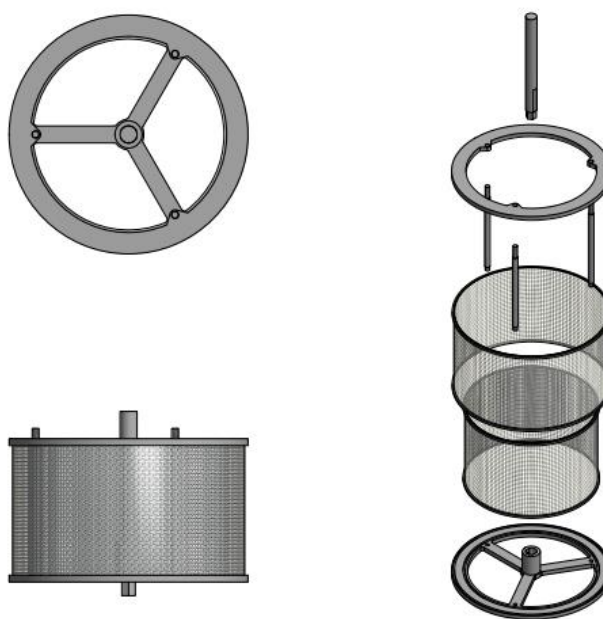
Figure 4.4 Schematic drawing of catalytic basket (inside reactor vessel)

To control the temperature, this reactor was equipped with a heat jacket on the outside of the vessel where hot fluid can be circulated to provide heat. As alkali catalyzed transesterification does not require a high temperature, this research was used hot oil as a heating source to control the temperature. The mixing zone is designed with a 2 L capacity (as shown in Figure 4.4 A basket with adjustable mesh wall is used to load catalysts with different sizes. Moreover, the distance between the basket and vessel wall were designed to have small gap to generate sufficient shear force for enhancing mixing of the reaction mixture. The picture of the designed and fabricated centrifugal contractor reactor is presented in Figure 4.5

Figure 4.5 Picture of the designed and fabricated centrifugal

4.2.4 Biodiesel production in CCR reactor

Figure 4.6 shows the overall process block diagram of the biodiesel production in CCR reactor consisting of three major parts including of preparation, reaction and analysis. The CaO powder was packed into the basket inside CCR reactor. The CaO was mixed with methanol for 30 min (using same rotating mixing speed condition) while palm oil was heated to the temperature of 70 °C. Then both of the reactants were fed into CCR reactor. The sample was periodically taken from the outlet bottom of the CCR in each experimental. Before analysis, sample was centrifuged to separate the layer of unreacted methanol, biodiesel, glycerol and CaO catalyst.
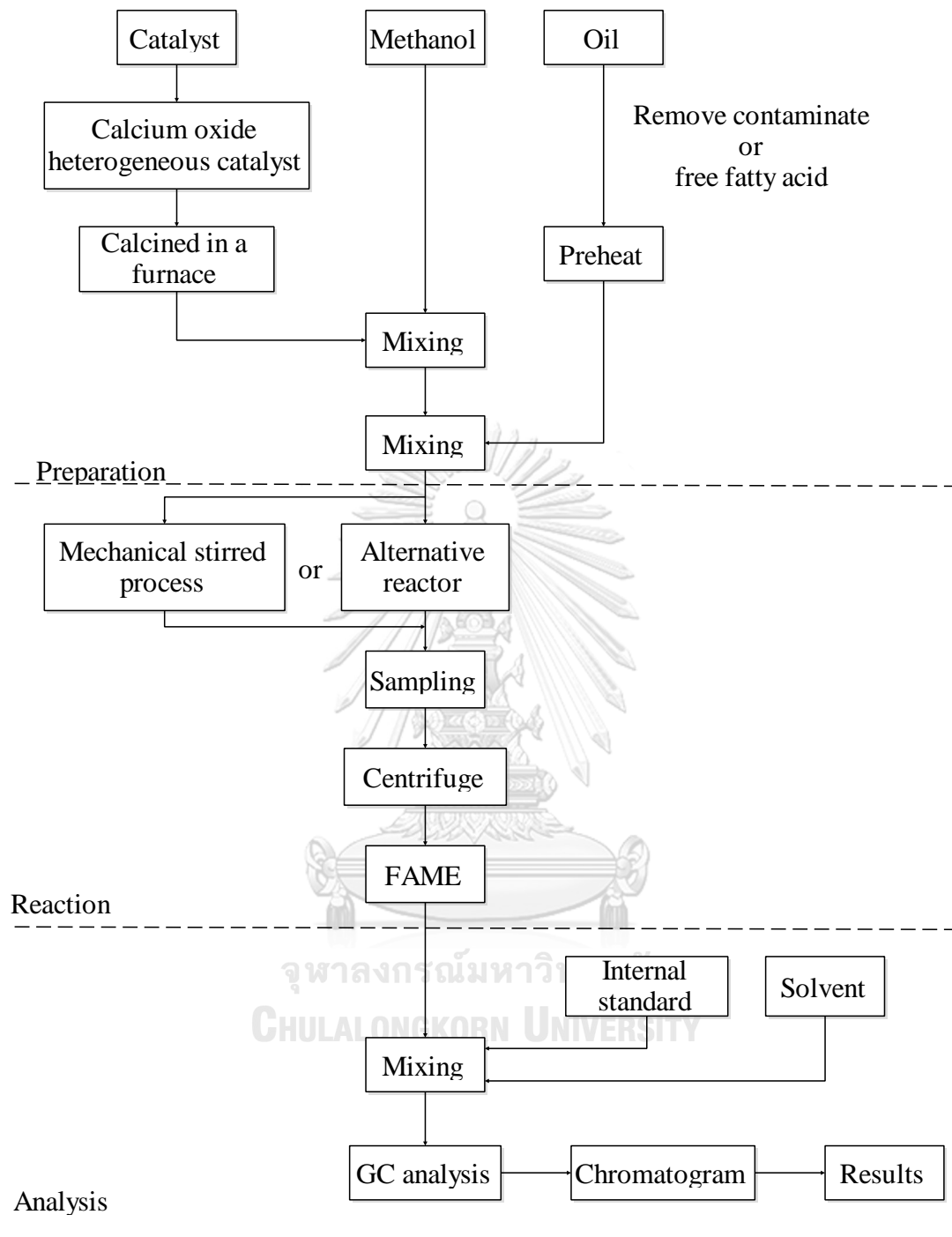
Figure 4.6 Overall experimental process block diagram.

4.2.5 Design of experiment and optimization for CaO catalyzed transesterification in CCR reactor

CaO catalyzed transesterification was performed in CCR reactor at fixed reaction temperature of 60 °C. Design of experimental was done by using center composite design (CCD) including the effect of (1) methanol to oil molar ratio for 12:1, 18:1 and 24:1, (2) CaO loading for 7, 10 and 13 wt% based on oil weight and (3) Rotation mixing speed for 700, 1,000 and 1,300 rpm as presented in Table 4.3 Minitab data analysis software was used for this work experimental design to efficiently analyze and interpret experimental data, making it an essential toll for RSM and CCD.

Table 4.3 Experimental design for CaO catalyzed transesterification in CCR reactor

Run	Methanol to oil (mol/mol)	Catalyst loading (wt%)	Rotation mixing speed (rpm)
1	12	13	700
2	24	13	700
3	12	7	1300
4	24	7	1300
5	12	13	1300
6	24	13	1300
7	12	10	1000
8	24	10	1000
9	18	7	1000
10	18	13	1000
11	18	10	700
12	18	10	1300
13	18	10	1000
14	12	13	700
15	24	13	700

4.2.6   Kinetic study of CaO catalyzed transesterification in CCR reactor.

The kinetic was investigated for CaO catalyzed transesterification of refined palm oil in the CCR reactor using the temperature of 40, 50, 60, and 65 °C. The experimental data of biodiesel yield along the reaction time was used to determine the pseudo-reaction order, the reaction rate constant (k) and the appearance activation energy (Ea) as well as frequency factor (A). The excess methanol was assumed based on the fixed ratio of methanol to refined palm oil of 12:1. The reaction of kinetics used as a pseudo-homogeneous because of this reaction mixture was not completely homogeneous. The linear fitted for the pseudo- first and second order are presented in Equations (4.2)-(4.3) as follow:

The linear pseudo first-order reaction is shown in Equation (4.2)

$$ln\frac{[TG0]}{[TG]} = kt \tag{4.2}$$

where k is reaction rate constant, t is reaction time (min), and [TG0] is initial oil concentration while [TG] is oil concentration at any time (t) in the unit of mol/L.

The reaction rate constant can be estimated from the slope of the linear dependence of [TG0]/[TG] with respect to time.

The linear pseudo second order reaction is shown in Equation (4.3)

$$\frac{1}{[TG]} = kt + \frac{1}{[TG0]} \tag{4.3}$$

where k is reaction rate constant, t is time (min), and [TG0] is initial oil concentration while [TG] is oil concentration at any time (t) in the unit of mol/L .

The reaction rate constant can be estimated from the slope of the linear dependence of 1/[TG] with respect to time.

Arrhenius equation is used based on the data obtained from the kinetics experimental plan as shown in Equation (4.4).

$$k = Aexp\left(\frac{-E_a}{RT}\right) \tag{4.4}$$

where k is reaction rate constant, A is frequency factor, Ea is activation energy (kJ/mol), R is gas constant (8,314 J/mol.K), T is absolute temperature (K).

4.2.7 CaO catalyzed transesterification of WCO in CCR reactor

The production of biodiesel from WCO has gained significant interest as a sustainable and environmentally friendly approach. The utilization of WCO as a feedstock for biodiesel production offers a promising solution for waste management and the promotion of renewable energy sources. WCO in this work was collected from fried chicken restaurant in Chulalongkorn university engineering canteen. WCO was filtered to remove solid contaminated and heat with hotplate to remove moisture before using in transesterification. WCO was contained 0.8 wt% of FFA. The transesterification of WCO was also performed in the three-neck flask with magnetic stirrer as conventional batch reactor for comparison. The optimal condition; methanol to oil molar ratio 12:1, 13 wt% of CaO catalyst loading and 1,000 rotation mixing speed was used.
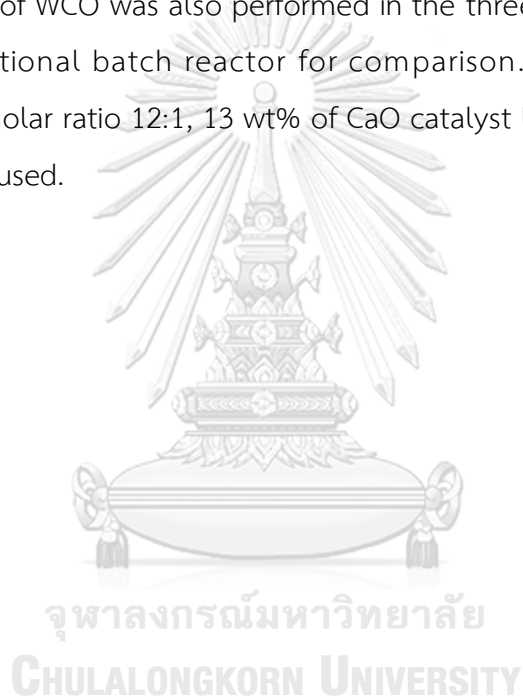
CHEPTER 5

RESULTS AND DISCUSSION

This chapter provide the results and discussion of the hybridized RD simulation for biodiesel production using waste cooking oil with high water content and biodiesel production using CaO catalyzed transesterification of refined palm oil and waste cooking oil in CCR reactor.

5.1 Biodiesel production from low-cost waste cooking oil containing high water content in hybridized RD
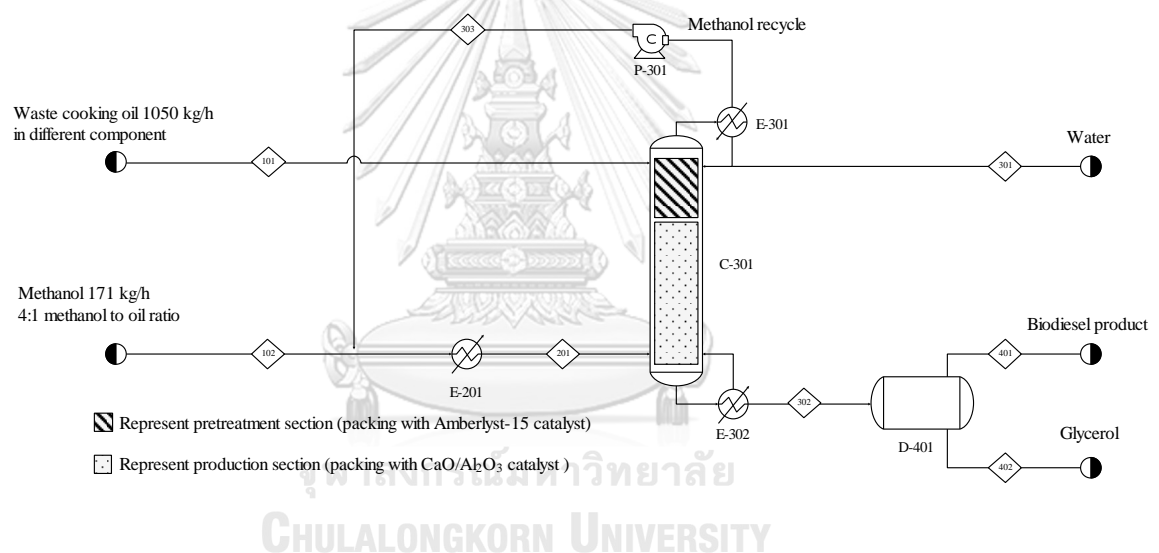
Figure 5.1 Earlier hybridized reactive distillation for biodiesel production

5.1.1 The earlier hybridized RD for biodiesel production

The earlier hybridized RD flow diagram based on our previous work [82] is shown in Figure 5.1 The detail of the simulation based on our previous work was shown in supplementary Table A1. WCO was fed into the column at 1,050 kg/h (for the base case using 6 wt% FFA content) and methanol was fed at the methanol to WCO (triglyceride and FFA model compound) ratio of 4:1 into the bottom stage to produce biodiesel at 944 kg/h as presented in Table 5.1 The earlier hybridized RD column (C-301) was pressurized to 3 bar to obtain the higher biodiesel production

performance which does not require a reflux unit to recover unreacted methanol [82]. A partial condenser at the top column was used to remove some water contamination from esterification, and also to recover unreacted methanol back to the system. A total of 10 actual stages (8 reactive stages, 1 stripping stage, and 1 rectifying stage) for the feedstock with 6 wt% FFA content were used. At the top column, the first 3 reactive stages were packed with Amberlyst-15 for esterification (pretreatment) to reduce FFA and the next 5 reactive stages were packed with CaO/Al_2O_3 to produce biodiesel via transesterification. After reaction completion, biodiesel and glycerol (bottom stream) were sent to the purifying unit (decantor-D401).

The 10 wt% water content in the WCO feedstock was used in this work to confirm that all of the proposed water removal methods can handle the feedstocks having the highest water content. It was found that oil containing water content higher than 17% obtained from the esterification section (4th stage in Table 5.1) could be present before the transesterification section which can cause the serious problem of operation and maintenance of the earlier hybridized RD. To avoid soap formation for CaO catalyzed transesterification, Lui et al. [109] reported that the water content in the methanol should be less than 2.8%, and therefore, the earlier hybridized RD was required the additional water removal process to minimize water level to be less than 1%. It should be noted that biodiesel purity was 98% even the large amount of water was entering to transesterification section due to the kinetics of CaO/Al_2O_3 catalyzed saponification of triglyceride, free fatty acid and biodiesel was not considered in the simulations of the earlier hybridized RD (Table 5.1).

In this study, the earlier hybridized RD with three methods of water removal were proposed. They include 1) addition of heat exchanger, 2) extended spacing stage modification and 3) integration with the pervaporation unit.

Table 5.1 Summary of data sheet and mass composition for hybridized RD for biodiesel production following Figure 5.1[a]

	101	102	201	301	302	303	401	402
Temperature (ºC)	25	25	35	114	180	114	30	30
Pressure (bar)	1	1	3	3	3	3	1	1
Vapor fraction	0	0	0	0	0	1	0	0
Mass Flows (kg/h)								
- Methanol	0.00	171.43	219.62	21.27	10.65	22.17	0.00	15.24
- Triolein	882.00	0.00	0.00	0.00	10.65	0.00	9.58	0.00
- Methyl oleate	0.00	0.00	0.00	0.00	950.79	0.00	950.78	0.00
- Glycerol	0.00	0.00	0.00	0.00	91.69	0.00	0.05	91.64
- Water	105.00	0.00	20.30	1.23	1.14	20.30	0.15	0.99
- Oleic acid	63.00	0.00	0.00	0.00	0.85	0.00	0.85	0.00

Mass fraction composition in hybridized RD[b]						
Stage	Methanol	Triolein	Methyl oleate	Glycerol	Water	Oleic acid
1	0.0721	0.0000	0.0000	0.0000	0.9279	0.0000
2	0.0337	0.7358	0.0350	0.0000	0.1763	0.0192
3	0.0386	0.7330	0.0481	0.0000	0.1737	0.0065
4	0.0417	0.7319	0.0527	0.0000	0.1716	0.0021
5	0.0432	0.5296	0.2509	0.0206	0.1537	0.0021
6	0.0549	0.3128	0.4597	0.0423	0.1282	0.0021
7	0.0730	0.1332	0.6294	0.0599	0.1024	0.0021
8	0.0930	0.0425	0.7130	0.0686	0.0809	0.0020
9	0.1900	0.0029	0.5541	0.0537	0.1977	0.0015
10	0.0562	0.0042	0.8041	0.0777	0.0556	0.0022

[a] Based-on water content of 10 wt%

[b] blue and green highlights indicate reactive stage of esterification and transesterification.

5.1.2 Addition of heat exchanger for water removing of hybridized RD for
biodiesel production
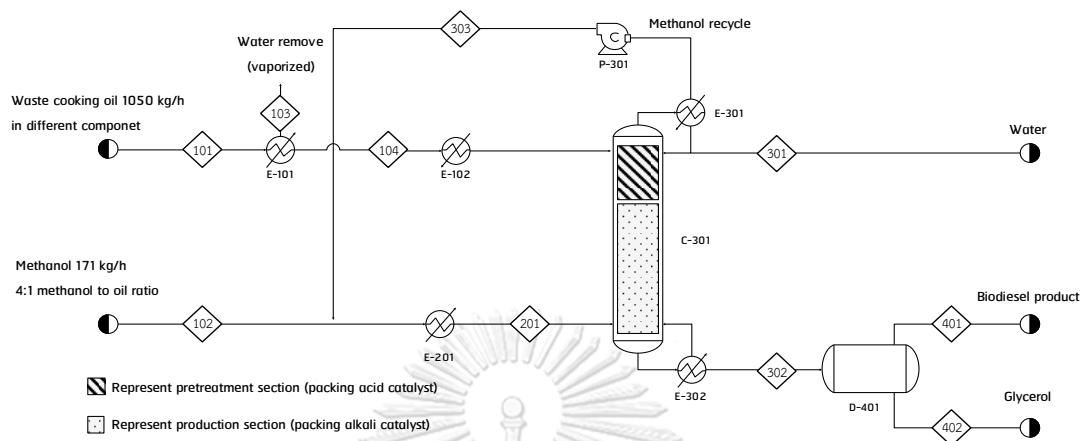
Figure 5.2 Addition of heat exchanger and hybridized RD to remove water content in
WCO feedstocks

The conventional methods usually employed to remove water from the
process like this method are such as heater under vacuum [110] or evaporator to
remove all water in the feedstock at 120 °C [111]. The combined heat exchanger unit
to remove some water or moisture content in WCO is the simple and basic process
for water removal in the industrial process because this method does not require
any intensification unit operation. However, the resulting stream from a single heat
exchanger could not be directly fed to the pressurized hybridized RD due to it was
too high temperature. Therefore, the cooling heat exchanger was required to cool
down feedstocks before entering the pressurized hybridized RD.
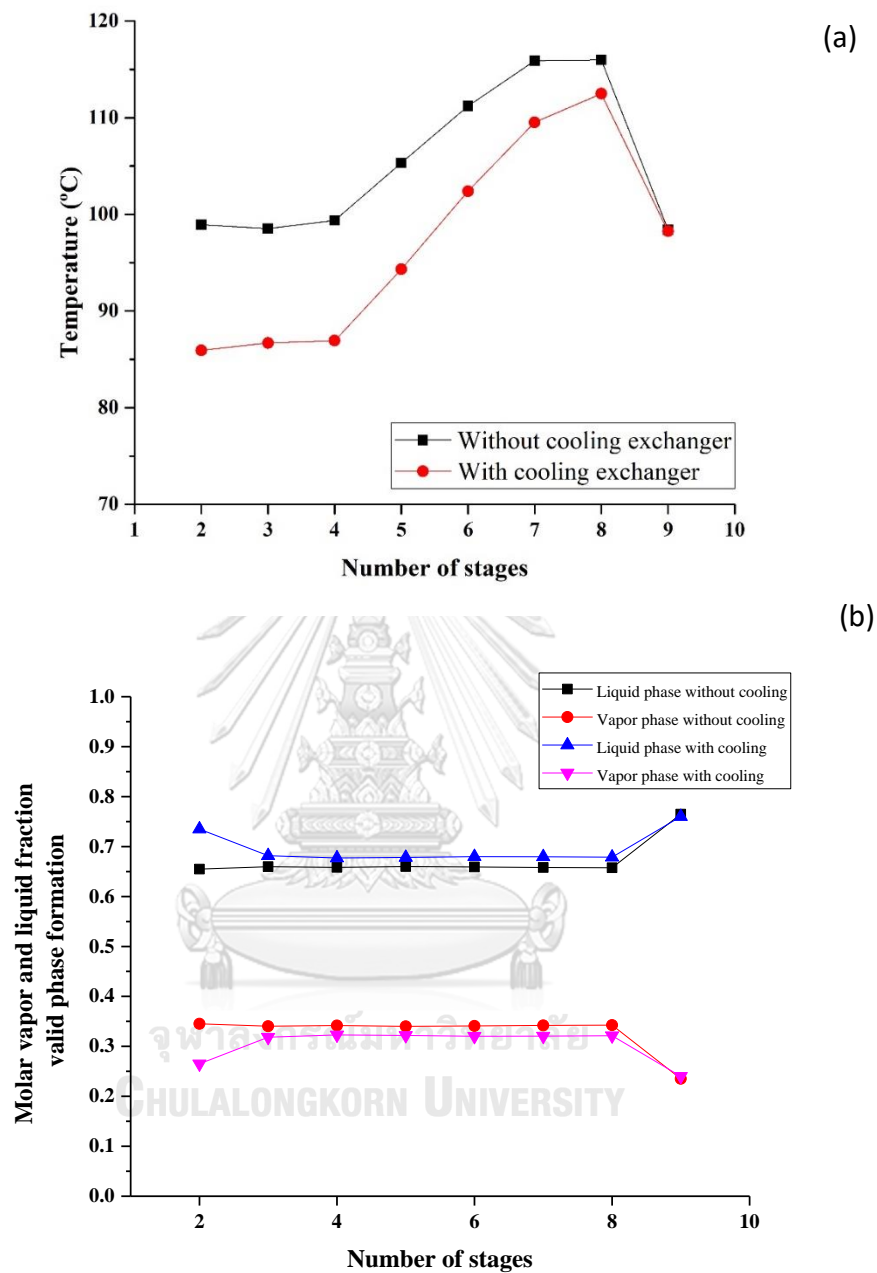
Figure 5.3 (a) Temperature profiles of hybridized reactive distillation column when modified by addition of heat exchanger and (b) Molar vapor and liquid fraction of hybridized reactive distillation column when modified by addition of heat exchanger

Two heat exchangers were installed to remove water or moisture content in WCO before feeding to the hybridized RD. The first heat exchanger (E-101) was heated to 120 °C to vaporize water or moisture content in the WCO stream, which then entered the next heat exchanger (E-102) to cool down to the feed stage temperature condition before feeding into the top column of the hybridized RD (Figure 5.2). If only one heat exchanger was used for heating to 120 °C, WCO was found to be vaporized at the top stages before flowing down to react in the reaction section of the column at the bottom section. Figures 5.3 (a) and (b) illustrate the temperature profiles and phase formation fraction in the hybridized RD combined with the heat exchanger (E-101) and the second heat exchanger for cooling (E-102) without the cooling exchanger. When using the cooling exchanger, the temperature along the hybridized RD can be reduced resulting in the higher liquid fraction of the WCO stream. The higher biodiesel yield and purity were obtained when using two heat exchangers because the heterogeneous catalyzed transesterification to produce biodiesel was carried out in the liquid phase. Therefore, this modification should require the cooling exchanger to reduce the temperature after pre-heating to vaporize water in the WCO stream. The addition of heat exchanger can remove amount of water more than 99% before flown down to transesterification section as seen in Table S2. The capital and energy consumption were an important constrain for this consideration. Table 5.2 summarizes the specification sheet of heat exchanger units determined from Aspen process economic analyzer.

Table 5.2 Specification sheet of exchanger units

Main process equipment			Estimated equipment cost*
Exchanger for heating	E-101	Vaporization temperature: 120 °C Specific energy requirement: 56.58 kWh/ton biodiesel	56,800 USD
Exchanger for cooling	E-102	Feed stage temperature (75 – 80 °C) Specific energy requirement: -49.63 kWh/ton biodiesel	70,500 USD

*Approximated by Aspen process economic analyzer

This combined heat exchanger can easily remove water or moisture content because the use of the first exchanger can vaporize all moisture as the de-moisturization process of the WCO consumes 56.58 kWh/ton biodiesel, while the second exchanger was used to cool down WCO feedstocks with the energy consumption of -49.63 kWh/ton biodiesel before going into the hybridized RD column. As can be seen, the heat exchanger is a simple unit to operate and can control the stream temperature so that all water content in the WCO stream can be removed before entering the hybridized RD. However, this modification required at least two additional heat exchangers (E-101 and E-102) which might not be appropriate for economical operation. More energy consumption for heat exchangers was required resulting in an increased operating cost. However, the use of heat integration can improve energy efficiency and reduce operating costs for the energy requirement. Traditionally, a sequential strategy is applied after performing the process optimization with heat integration. To simplify the calculation, the process was optimized by assuming that all heating and cooling loads are provided by utilities. An Aspen plus® calculation revealed that the hot utility cost was reduced to 10,317 USD/year representing 19.84 % of energy saving while the cold utility cost was reduced to 518 USD/year representing 87.04 % of energy saving by using heat

integration. However, the water can also produce in the hybridized RD in the esterification section using WCO feedstocks. This addition heat exchange might not be used to handle the producing water during the reaction [112].

5.1.3 Extended stage spacing modification for water removing of hybridized RD for biodiesel production
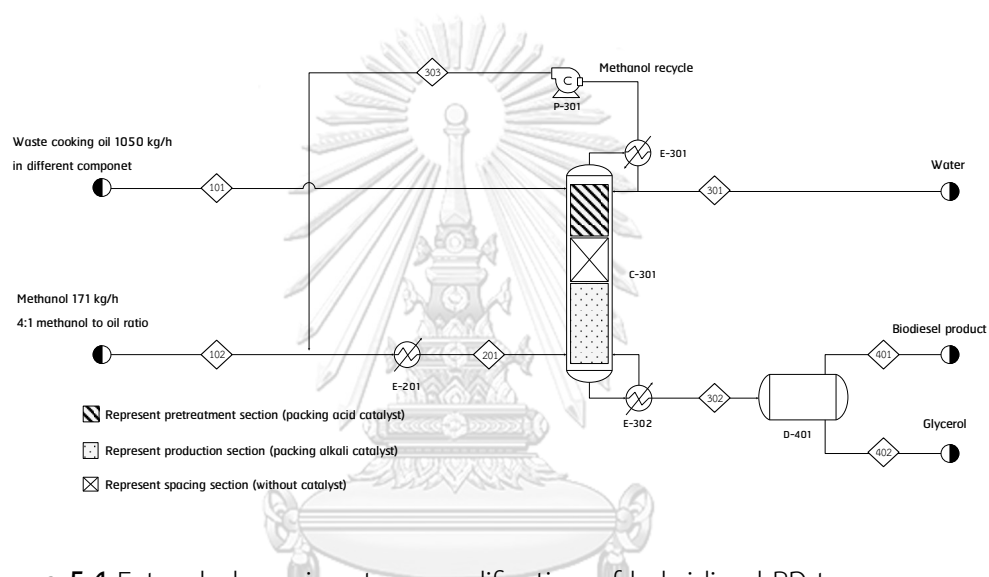
Figure 5.4 Extended spacing stage modification of hybridized RD to remove water content in WCO feedstocks.

The new concept of using RD for biodiesel production was proposed based on the fundamental theory of RD with various temperatures along the stage for separation as illustrated in Figure 5.4 The extended stage spacing modification does not require any additional unit operation. These additional spacing stages were used for the vaporization of highly volatile compounds (water and methanol) without any catalyst packing. Moreover, the large difference in the boiling point of the lighter compounds (water-methanol) and the heavier compounds (triglyceride and its derivative-biodiesel-glycerol) in this system was also encouraged. The extended stages spacing could be used to separate some lighter compounds from the heaviest compound [113]. Chuanhai et al. [114] demonstrated the addition of two spacing

stages in the RD can reduce the column diameter to obtain the lower operating cost and lower capital investment. Therefore, the addition of the spacing stage was applied between the pretreatment section stage (esterification) and the production section stage (transesterification) to allow some distillate stages for water content removal. Spacing stages without catalyst packing represent the common distillation stages. The vapor-liquid equilibrium of this liquid mixture took place in this stage, and the sufficient number of spacing stages resulted in the achievement of water separation from the liquid stream before flowing down to the transesterification section. Separation of mixture components from a liquid mixture via spacing stages depended on the differences in boiling points of the individual component and number of the equilibrium stage to obtain high purity of the top product which enhanced the light component separation or water separation efficiency. Moreover, the temperature profile in this extended stage hybridized RD can also vaporize methanol for the recovery of methanol. It should be noted that the temperature of the partial condenser was also adjusted to condense water out of the column and recycle unreacted methanol back to mix with the methanol feed stream before being preheated (E-201). The water content from the last stage of esterification section was reduced from 11.97 to 0.98 wt% at the last of 8 extended stages. The column temperature design was an important factor to control the amount of water in each stage. Therefore, the requirement of the reboiler duty was studied to determine the suitable column temperature sufficient to vaporize water up at the top column.

The effect of water content on the number of extended spacing stages and the reboiler duty requirement were also investigated to determine the maximum number of spacing stages and the suitable operating condition as presented in Figures 5.5 (a) and (b), respectively.
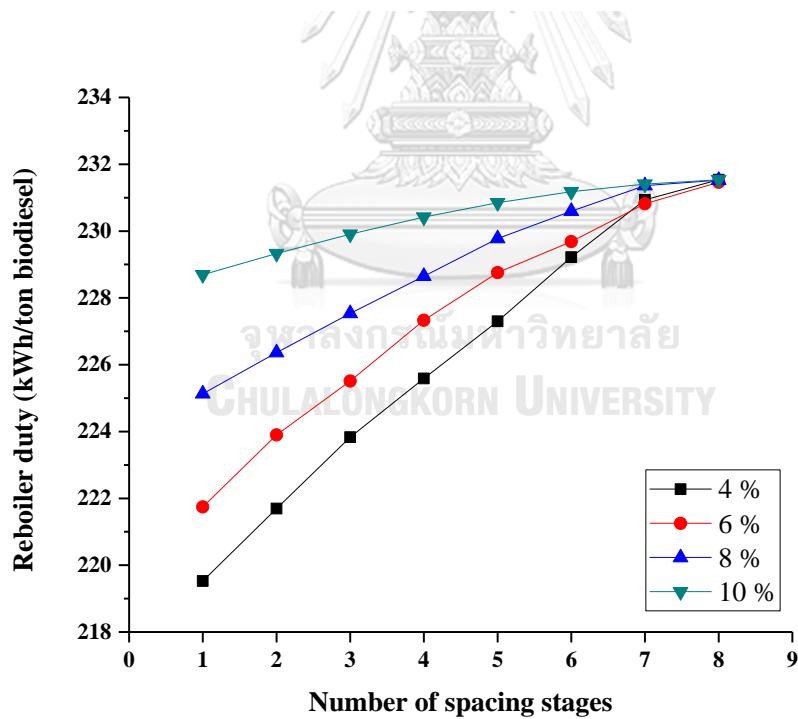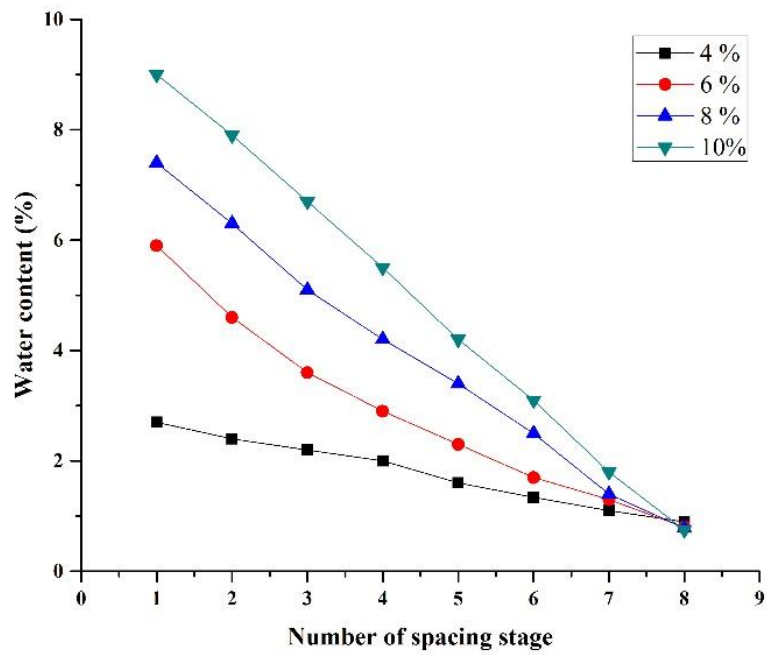
Figure 5.5 (a) Water content in WCO and (b) Reboiler duty requirement when increasing number of spacing stages with various water content in WCO feedstocks

The amount of water removal depended on the number of extended spacing stages due to their vapor-liquid equilibrium. Figure 5 (a) shows that the water content decreased with more spacing stages, corresponding to the total contact time of each stage allowing the water to vaporize up to the top column as the lighter component. This is because of the high volatility of water compared to other components. Our finding suggested that 8 extended stages would provide the highest water removal for 4 to 10 wt% of water content with less than 1 wt% water remaining due to their vapor-liquid equilibrium. It should be reminded that the increase in water content from 4 to 10 wt% increased the reboiler duty for the extended stages number of 1 to 8. However, the extended stages spacing modification required reboiler duty of 231.54 kWh/ton biodiesel using 8 extended stages to obtain the water content in WCO feedstocks less than 1 wt% before flowing down into the first stage of transesterification stages as can be seen from mass fraction composition of the hybridized RD in Table S3.

Based on the energy consideration, this modification required no significant different value of reboiler duty compared to the previous hybridized RD process even with the additional 8 spacing stages. This is most likely because of the similar components with relatively high volatile properties between the lighter phase (methanol and water) and the heavier phase (oil and its derivative, biodiesel, and glycerol). Based on the operating condition, the triglyceride and biodiesel were controlled in the liquid phase and flew down as the bottom product. This modification required the maximum of 8 extended spacing stages which is two times that of the primary hybridized RD. Therefore, this modification must be designed in a specific configuration before the construction of the hybridized RD for various feedstocks with the presence of FFA and water. This spacing stage modification has been originality proposed for the reactive distillation application to fulfill the limitation of low-cost feedstocks for the biodiesel production process.

5.1.4 Integration of pervaporation unit for water removing of hybridized RD for biodiesel production.
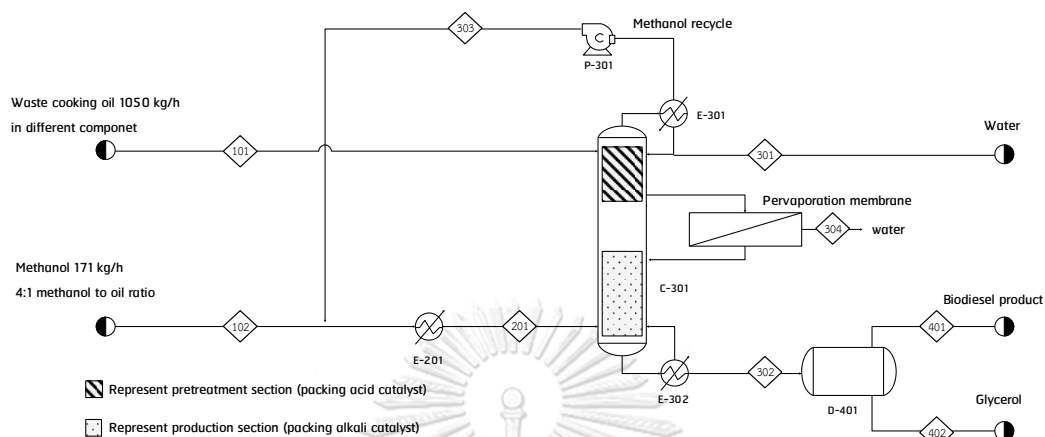
Figure 5.6 Integration of pervaporation unit and hybridized RD to remove water content in WCO feedstocks

Pervaporation has gained much attention for the separation of azeotropic mixtures and close-boiling point mixtures because this technique can overcome the limitation of the volatility of the components [115]. The advantages of using pervaporation comprise of low energy consumption, high selectivity, compact and modular design. The integration of the pervaporation unit has been proposed for the conceptual design at the last stage of the pretreatment section to remove liquid mixture using a membrane. The aim purpose to employ pervaporation membrane is to minimize energy consumption as only partial vaporization of liquid mixture and permeate through pervaporation membrane. For example, this application of the pervaporation membrane also applied to dimethyl ether (DME) production having three side stream products (DME product, methanol recovery, and wastewater) compared to the conventional process with the two-column requirement [116]. There are several types of membranes based on the experiments including the performance and selectivity reflecting the intrinsic properties of the membranes.

The composite of active polyvinyl alcohol (PVA) membrane namely Sulzer PERVAP-1510 could be utilized for this modification because the PVA composite provided the higher flux membrane to separate alcohol and water [117]. Thus, the

Sulzer PERVAP-1510 membrane was selected as the pervaporation unit for the removal of water content from WCO feedstocks before flowing down into the production stages. Haaz and Toth [118] proposed the performance model of this membrane compared to the experimental data as shown in Equations (5.2) - (5.4). The Sulzer PERVAP 1510 membrane is a composite of PVA flat sheet membrane. This membrane exhibited a good performance to remove water content in an aqueous solution from the dehydration reaction which is similar to the biodiesel production system comprising of water and alcohol [118]. Therefore, this model should be applied as the pervaporation model in Aspen plus® calculations.

$$J_i = \frac{1}{1+\left\{\frac{[\overline{D_i}\cdot\exp(B\cdot x_{i1})]}{p_{i0}\cdot\overline{\gamma_i}}\right\}} \cdot \frac{[\overline{D_i}\cdot\exp(B\cdot x_{i1})]}{\overline{\gamma_i}} \cdot \left(\frac{p_{i1}-p_{i3}}{p_{i0}}\right)$$

(5.2)

where J_i is partial flux, $\overline{D_i}$ is the transport coefficient of component i, B is a constant in the model (water = -6.51, MeOH = -2.40), $\overline{\gamma_i}$ is the average activity coefficient of component i, x_{i1} is the concentration of component i in the feed, p_{i1} is the input partial pressure of component i on the liquid phase membrane side, and p_{i3} is the input partial pressure of component i on the vapor phase membrane side.

Partial pressures (p_{i0}) are calculated according to the Antoine equation:

$$p_{i0} = \exp\left[A + \frac{B}{T} + C\ln T + DT^E\right] * 10^{-5}$$

(5.3)

where A, B, C, D and E are material-dependent constants in the Antonine equation.

$$\overline{D_\imath} = \overline{D_\imath^*} \exp\left[\frac{E_i}{R}\left(\frac{1}{T^*} - \frac{1}{T}\right)\right]$$

<div align="right">(5.4)</div>

where E_i is the activation energy of component i and T^* is the reference temperature (20 °C).

In this modification, the model (User2) was used in Aspen plus® model palette linking with Microsoft Excel for the integration of the pervaporation model and calculation. Microsoft Excel functioned as a stream calculator and fed results back into Aspen plus®. Some estimated parameters are shown in Table 5.3. The partial pressures of all components were obtained from Aspen plus® database.

Table 5.3 Estimated parameters for pervaporation model

Parameter	Component	
	Water	Methanol
$\overline{D_\imath}$, kmol/m^{2}h	1.67 x 10^{-1}	1.80 x 10^{-4}
E_i, kJ/kmol	23,498	30,795
B, -	-6.51	-2.40
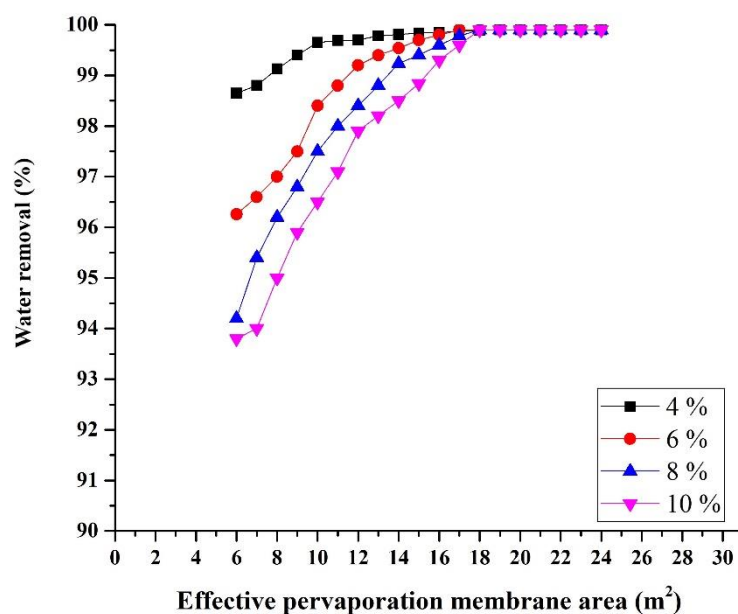
Figure 5.7 Mass fraction of water removal with various effective membrane surface using different water content in WCO feedstocks

The integration of the pervaporation membrane unit using the Sulzer PERVAP 1510 membrane was also evaluated on its performance to remove water contamination in WCO feedstocks. The feasibility of using pervaporation modification with the hybridized RD was investigated. It was found that the water of 99 wt% was reduced before entering to transesterification section as presented in mass fraction composition in the hybridized RD of Table A2. The effect of water content in the feed stream versus the effective pervaporation membrane area was also investigated (Figure 5.7). The water content in the retentate can be reduced with increasing membrane surface area. These results confirmed the possibility of purification using the pervaporation membrane. To obtain 99 wt% of water removal, WCO with low water content of 4 wt% required the effective PV membrane of 9 m^2 while WCO with the highest water content of 10 wt% required 17 m^2. Therefore, the selected PV membrane area should be 17 m^2 to achieve 99 wt% of water removal for water content from 4 to 10 wt% in WCO feedstocks. The benefit of using the pervaporation membrane to separate water from the liquid mixture in the transesterification section

of the hybridized RD is the ability to recycle high-purity methanol (93%) back into the hybridized RD (see data sheet in Table S4). Moreover, the side stream water should be of high purity to be utilized as a heating media in the process, fulfilling the green concept or cleaner technology for this biodiesel production technique. This membrane could not only provide high separation efficiency for water and methanol but also obtain high purity water for the side stream. Thus, this modification could be helpful to other similar processes. On the other hand, this process can remove some components which are unnecessary or needless in the system and this modification could shift the equilibrium to push the reaction forward by removing components from the pervaporation membrane [119]. This should be reminded that the pervaporation modification has a limitation of the lifetime of the membrane aside from assessing the economic perspective. Moreover, it was quite difficult to control the volumetric flow rate of the stage connecting to the pervaporation membrane in term of technical operation because the volumetric flow rate of the feed solution from the distillation column might be difficult to control in the steady state operation with the removal of the stream from the side of the column to the pervaporation membrane.

5.1.5 Process performance evaluation and comparison for water removing of hybridized RD for biodiesel production.

There are several parameters to evaluate and compare in the integration or modification process for water or moisture content removal in the hybridized RD including the amount of water removal, amount of methanol recovery, number of additional units, number of reactive stages, and total energy requirement based on the constrains of biodiesel quality according to EN 14103 standard as summarized in Table 5.4 The amount recovery methanol and its purity was also concerned as showed in Figures 5.8 and 5.9

Table 5.4 Performance comparison of different biodiesel production processes

	Heat exchanger addition	Extended stage spacing modification	Pervaporation integration
Water removal (%)	> 99	> 99	> 99
Biodiesel yield (wt%)	99.87	99.42	98.71
Biodiesel purity (wt%)	99.00	99.00	99.45
Methanol purity in recycle stream (%)	80.01	79.23	92.98
Modified equipment			
Exchanger	2 units	-	-
Stages of column	-	8 stages (Maximum)	-
Membrane	-	-	Sulzer PERVAP 1510
Energy requirement for			
Exchanger (kWh/ton biodiesel)	56.58 -49.63	-	-
Column (kWh/ton biodiesel)	- 12.81/237.56	-50.36/231.54	- 49.71/222.84
Total net specific energy requirement (kWh/ton biodiesel)	294.14	231.54	222.84
Total biodiesel production cost (USD/year)[a]	39,537	25,841	25,193
Additional unit operating cost for water removal (USD)	56,800 (E-101)	8,500[b]	221,000[c]

	Heat exchanger addition	Extended stage spacing modification	Pervaporation integration
Hybridized reactive distillation column	70,500 (E-102) 450,300	450,300	450,300
Total unit operating cost (USD)	577,600	458,800	671,300

[a] Utility cost was calculated by Aspen process economic analyzer considering only heat exchanger and PV unit input (other units such as decanter were used under a similar condition meaning no significant operating cost) based on the operating time of 24 hours per day and 360 days per year.

[b] This additional cost was calculated based on 16 stages of hybridized RD with the subtraction of the primary hybridized RD.

[c] Estimated cost of Sulzer PERVAP 1510 membrane with 17 m^2 obtained from Toth AJ.'s work [117]

(a)

(b)
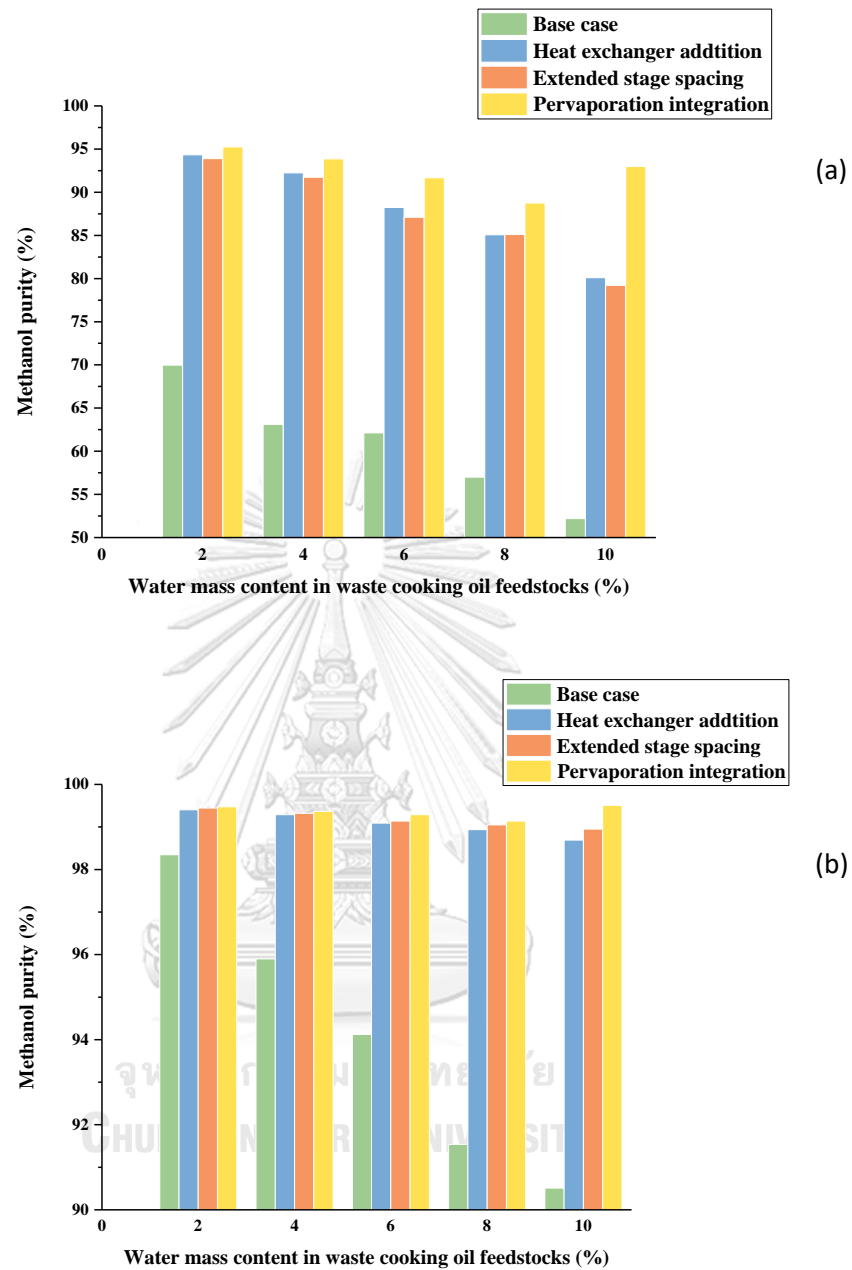
Figure 5.8 Methanol recovery purity in stream (a) residual methanol feed stream and
(b) mixed with methanol recycled with feed stream
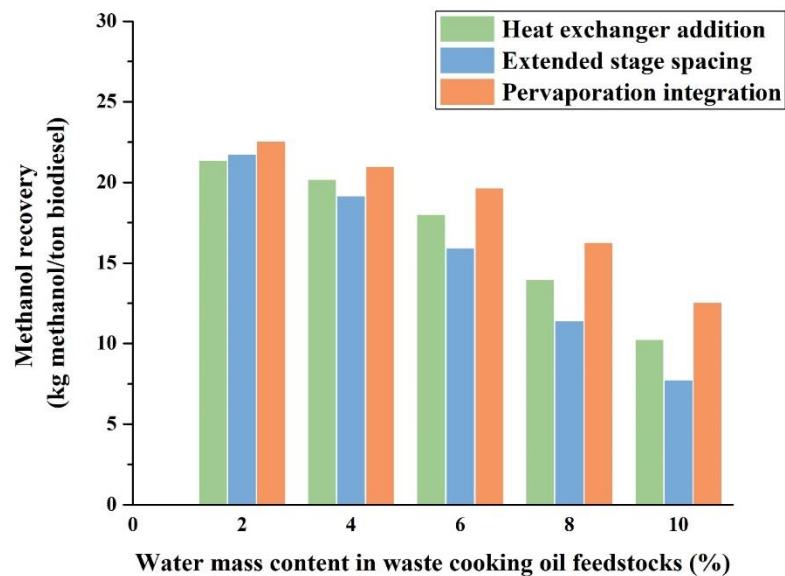
Figure 5.9 Methanol recovery content with various water contents in WCO feedstocks based on one tone of biodiesel production

Based on the requirement for all modification processes to remove water content before sending to the transesterification step from 17.15 wt% to 0.06, 0.09 and 0.08 wt% with respect to the base case hybridized RD, addition of heat exchanger, modification of extended stage and integration of pervaporation processes, respectively, this indicated that using the base case hybridized RD could not handle the minimization of water content as 1 wt% before entering the transesterification section. This process required the modification of the hybridized RD to reduce the water content to 1 wt%. All modification processes can produce biodiesel with the yield and purity conforming to the EN 14103 standard.

Moreover, based on the net specific energy consumption for the one ton of biodiesel production, the additional of heat exchanger required the highest energy consumption of 294.14 kWh/ton of biodiesel. For the other modifications, the required net specific energy consumption was 231.54 and 222.84 kWh/ton of biodiesel for the extended stage spacing modification and the pervaporation integration, respectively. For the capital cost or investment cost aspect, the additional exchanger modification requires adding two heat exchangers to the

hybridized RD process which resulted in the total additional capital cost of 127,300 USD (E-101 and E-102), while the integration of pervaporation membrane required the highest capital cost of 221,000 USD because of its intensification technology to fabricate this membrane. The total investment cost including capital and operating costs to produce a tone of biodiesel per year was 458,800, 577,600 and 671,300 USD for the modification of spacing extended stage, the addition of exchangers and the integration of pervaporation membrane, respectively.

The addition of the heat exchanger method was the simplest modification because of no modification to the hybridized RD. This process required only two additional heat exchangers for the water removal unit and preparation of the feedstock before going to the column. Even though the control aspect of this process should be easiest compared to the other processes, this modification required a highest operating cost. This biodiesel operating cost was 1.63 USD/kg biodiesel which is higher than the commercial diesel of 1.08 USD/kg [120]. This is because the high content of water in WCO required the high heat duty.

The second alternative process, the extended stage spacing modification method, does not need any additional equipment. This method required only the extra stage between esterification and transesterification stages for separation of water out of the liquid fraction. With the highest water content in WCO, this hybridized RD required 8 spacing stages to handle the water content before entering transesterification stages. Thus, the initial design of the hybridized reactive column should consider the spacing stage for handling different specifications of WCO with the additional cost of only 2% of the original hybridized RD. As can be seen, the number of spacing stages depended on not only the amount of free fatty acid and water content of WCO but also the catalytic activity of the selected catalyst. The advantage of using the spacing stage to separate water from the liquid fraction can be pronounced for the long-term use of the hybridized RD for biodiesel production using low-cost feedstocks. This finding was also in agreement with Chuanhai et al.'s work [114]. Using the separation of two-stage consecutive reversible reactions for two reaction operations was more advantageous than the conventional reactive distillation column because this separation stages provided the additional degrees of

freedom for the reinforcement of internal mass integration and/or internal energy integration between the reaction operations and the separation operation involved, which could reduce the operating cost and capital investment. This modification process can produce biodiesel with lower cost of 1.07 USD/kg biodiesel. However, the methanol purity in the recycle stream was only 76.33 wt% which is lowest compared to the other processes.

The last method, the pervaporation integration method, is regarded as the latest state of the art in the chemical industry dealing with the azeotrope compound separation, and the selection of an appropriate pervaporation membrane can achieve high water removal performance, and also obtain the highest purity of methanol residue. The biodiesel production cost obtained from the integration pervaporation membrane was lowest (1.04 USD/kg biodiesel) compared the other processes. The advantage of using a pervaporation membrane was not only the lower net specific energy consumption requirement but also the obtained highest methanol recovery per ton of biodiesel. However, the pervaporation membrane suffers from the operating time limitation resulting in the highest equipment cost (total unit operating cost is about 671,300 USD), and also the regeneration cost of the membrane. It should be noted that this method was the most efficient for water removal compared to the other processes. It can also handle all varieties of feedstocks (variable FFA and water content).

Moreover, the purity of residual methanol in the recycle stream for each process was different. It was found that using the integration of pervaporation unit provided the highest methanol purity of 93 wt% in the recycle stream while the methanol purity obtained from the addition of heat exchangers, the extended stage spacing modification and the base case of hybridized RD was 80, 79 and 52 wt%, respectively, as presented in Figure 5.9 (a). The purity of methanol recovery mixed with feed stream was presented in Figure 5.9 (b). All modification processes can use recovered methanol to obtain methanol purity in the mixed feed stream greater than 98 wt% except the base case for the highest water content of 10 wt%. The purity of mixed methanol recovery with feed stream of the base case was only 90.5 wt%, which could promote saponification in the transesterification section of the

hybridized RD [121]. This finding also referred to the amount of methanol which can be recovered back to the mixture of residual methanol with feed stream before sending to the hybridized RD as can be seen in Figure 5.10. At 10 wt% water content, the methanol recovery was found to be 10.26, 7.73 and 12.57 kg methanol per ton biodiesel for the addition of heat exchanger, extended spacing stage and integration of pervaporation unit, respectively.

Existing biodiesel production plants using WCO feedstock can use the only two options: the addition of heat exchangers and the integration of the pervaporation membrane. It was found that the total cost (investment and operating costs) for integration of pervaporation membrane was comparable to that of the addition of heat exchangers based on the calculation of payback period in terms of investment and operating costs per year for 7 years (without the maintenance expense). In addition, the feasibility of an industrial production not only includes both technological and economic aspects but also concerns on the environmental aspect. This finding suggested that the integration of the pervaporation membrane to the hybridized RD promoted the cleaner technology in terms of high water and methanol purity and the lowest energy consumption. While the addition of two exchangers is a simple process for the existing hybridized RD for the biodiesel production plant, this process required the highest biodiesel production cost. The extended stage is the best choice for the new biodiesel production plant using the hybridized RD or installation of the new hybridized RD to increase biodiesel production rate.

5.2 Biodiesel production from refined palm oil and waste cooking oil using CaO catalyst in CCR reactor

    5.2.1   Catalyst characterization

          5.2.1.1 X-ray diffraction (XRD) analysis

X-ray powder diffraction (XRD) is a rapid technique primarily used to examine the degree of crystallization i.e., size, composition and crystal structure. Uncalcined calcium oxide catalyst in this study have some of calcium hydroxide ($Ca(OH)_2$) contaminated. The calcium hydroxide was defined as an impurity because it was not an active phase for transesterification. The components of catalyst were also confirmed by X-ray diffractometer (XRD) as shown in Figure 5.10. It was noted that there was no peak of calcium carbonate ($CaCO_3$) contaminated for all catalysts. The observed CaO was detect at the angle 2θ = 32.20°, 37.35°, 53.90°, 64.15°, 67.37°, 79.66° and 88.54°. The average crystallite size of uncalcined CaO was calculated using the Debye-Scherrer equation and found to be 72.94 nm and similar peaks were observed with those reported in the literature [122,123].
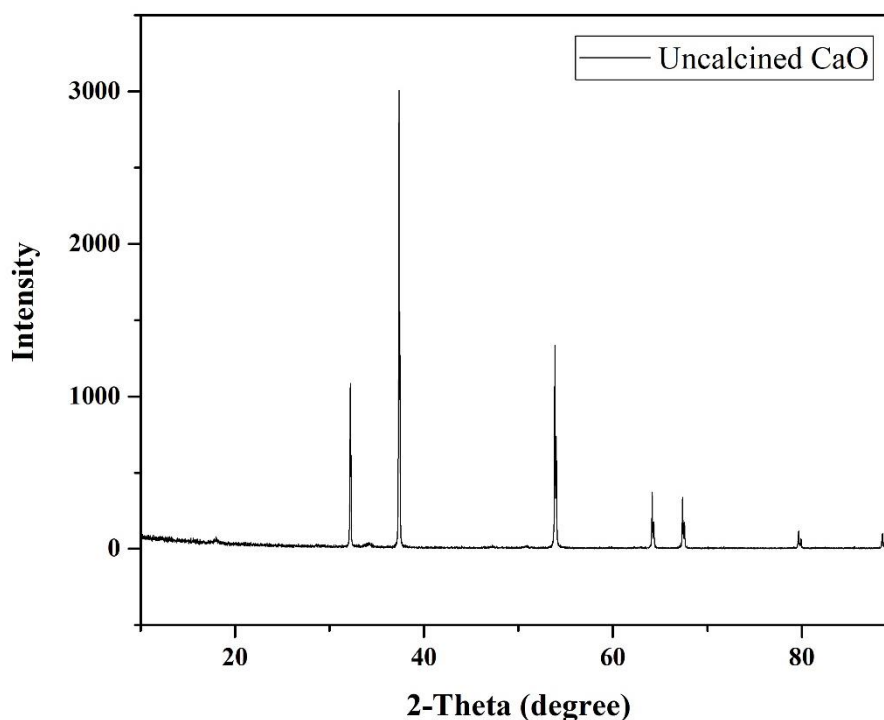
Figure 5.10 XRD profile for uncalcined CaO

5.2.1.2 Thermogravimetric analysis (TGA)
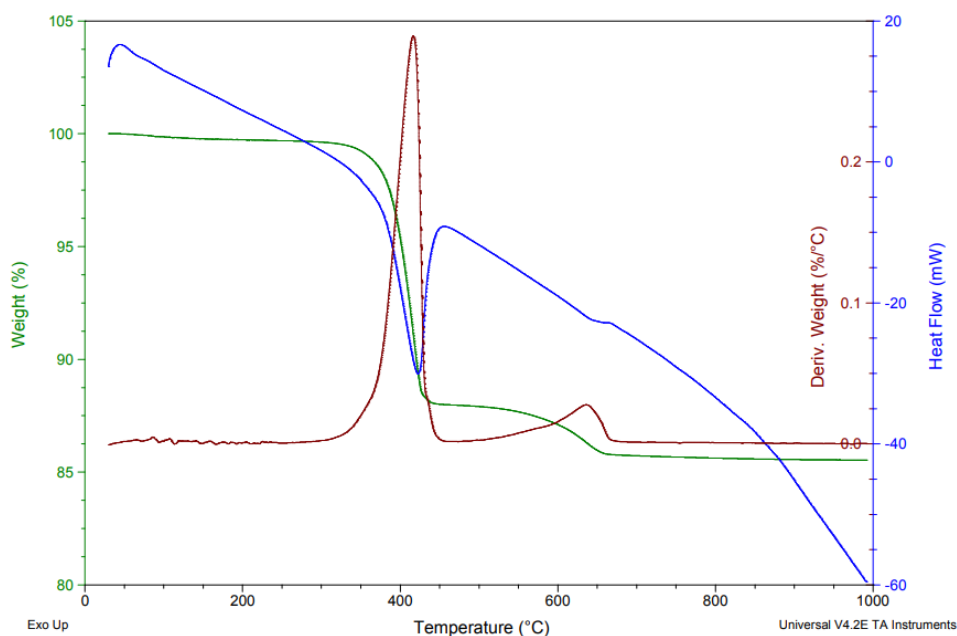
Figure 5.11 TGA-DTA curve for commercial CaO

Thermogravimetric analysis was employed to determine the calcination temperature of the commercial CaO. Thermogravimetric curves for commercial CaO were displayed in Figure. 5.11 The weight losses of commercial CaO obtained from TGA measurement (Green line) was initially observed in TGA curve remained constant from 35 °C to 340 °C. In the temperature range 340 - 480 °C, indicated the decomposition of Ca(OH)$_2$ [124,125]. This phenomenon was due to a chemical reaction occurring. The DSC curve showed an exothermic peak appearing between 340 °C – 450 °C. This reaction might be the decomposition of Ca(OH)$_2$ as derived from the moisture adsorption on the commercial CaO surface. The second weight loss was occurs at temperatures range 500 – 650 °C whole of calcium carbonate (CaCO$_3$) decomposed into calcium oxide and carbon dioxide [126]. From the thermal analysis result, it suggests that 650 °C temperature was sufficient to completely convert to CaO catalyst. However, CaO was calcined in the static air furnace which

could not provide the homogenous heat. Therefore, the CaO catalyst was calcined at the higher calcination temperature of 900 °C for 5 h to obtain the highest CaO phase.

   5.2.1.3 BET (Brunauer – Emmett – Teller) surface area and pore volume
   analysis

   The nitrogen adsorption-desorption isotherms and BET surface area, average pore sizes, and total pore volume of the calcined CaO catalyst. BET surface area of the calcined CaO catalyst was 5.3604 m²/g with an average pore diameter and pore volume of 2.79 nm and 0.003735 cm³/g respectively. It could be observed that most of the average pore sizes are in the range 2-50 nm, hence triglycerides molecules will easily penetrate into the catalyst, thus for transesterification reaction occurs with contact of most of the active sites of catalyst particles. Priti et al. [124] conducted a study where they obtained a surface area of 16.4 m²/g, a pore volume of 0.0207 cm³/g , and a pore diameter of 5.07 nm by synthesizing CaO from eggshell waste. This CaO derived from eggshell also reported an impressive 86.41% biodiesel yield from microalgae. Ashish et al. [126] synthesized CaO using snail shells, resulting in a specific surface area of 24 m²/g and a pore volume of 0.0582 cm³/g . Biodiesel yield of 87.28% was achieved from the snail shell CaO catalyzed transesterification of the utilizing waste frying oil. The difference in the surface area could be due to the different source of CaO.

   5.2.1.4 Scanning electron microscopy (SEM) and energy dispersive X-ray
   spectroscopy (EDS) analysis

   SEM images and surface morphology analysis of the calcined CaO catalyst were shown in Figure 5.12 The SEM micrograph shows few amorphous structures with spherical in shape with significant agglomeration of the catalyst particle to obtain different particle size in the range of 5-1 μm. The calcined CaO catalyst demonstrates a complex porous structure with three crystallographic surfaces, which could be offer numerous active sites available for catalytic reaction [123,127]. To ascertain the atomic/weight content of the calcined CaO catalyst, an analysis of the

EDS spectrum was conducted, as depicted in Figure 5.13. The intensity of peaks in the spectrum corresponds to the concentration of elements within the sample. For EDS of the calcined CaO. Oxygen (O), Platinum (Pt) – for coating catalyst and Calcium (Ca) elements appeared in 0.5 keV, 2.0 KeV and 4.0 KeV respectively. The amount of each element was found at 34.57 wt% of O and 65.43 wt% of Ca
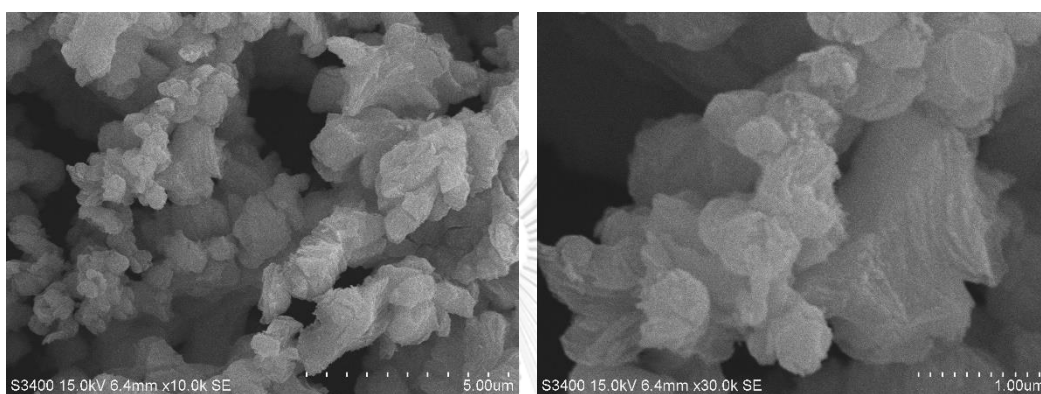
Figure 5.12 SEM images of synthesized CaO at different magnifications
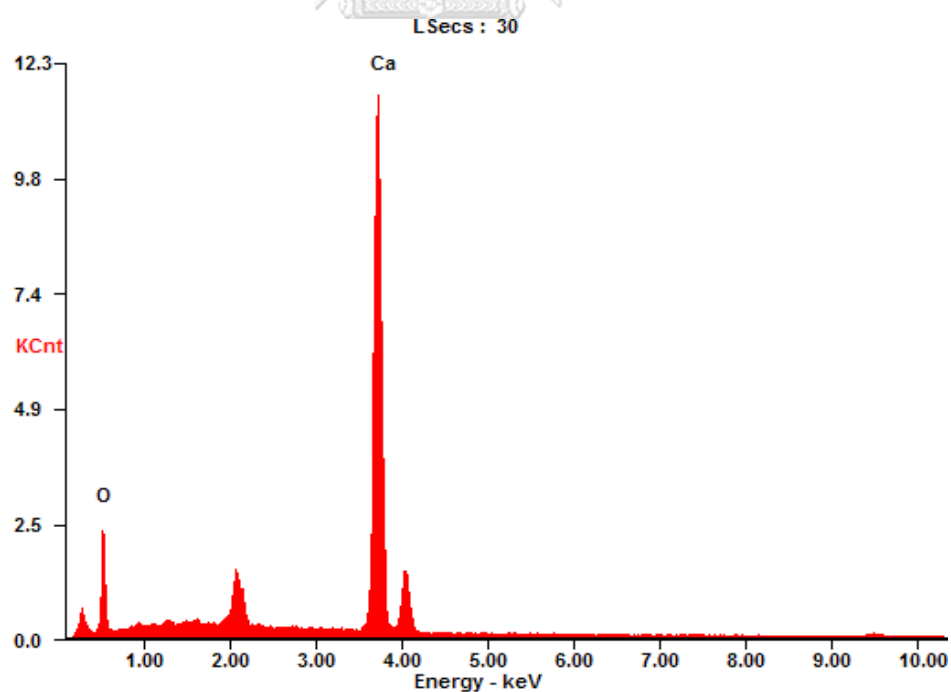
Figure 5.13 Energy dispersive X-ray spectrometry (EDS) with table of elements of the calcined CaO catalyst

5.2.2 Modeling and optimization of CaO catalyzed transesterification in CCR reactor using central composite design (CCD) and response surface methodology (RSM)

5.2.2.1 CaO catalyzed transesterification in CCR reactor using central composite design (CCD)
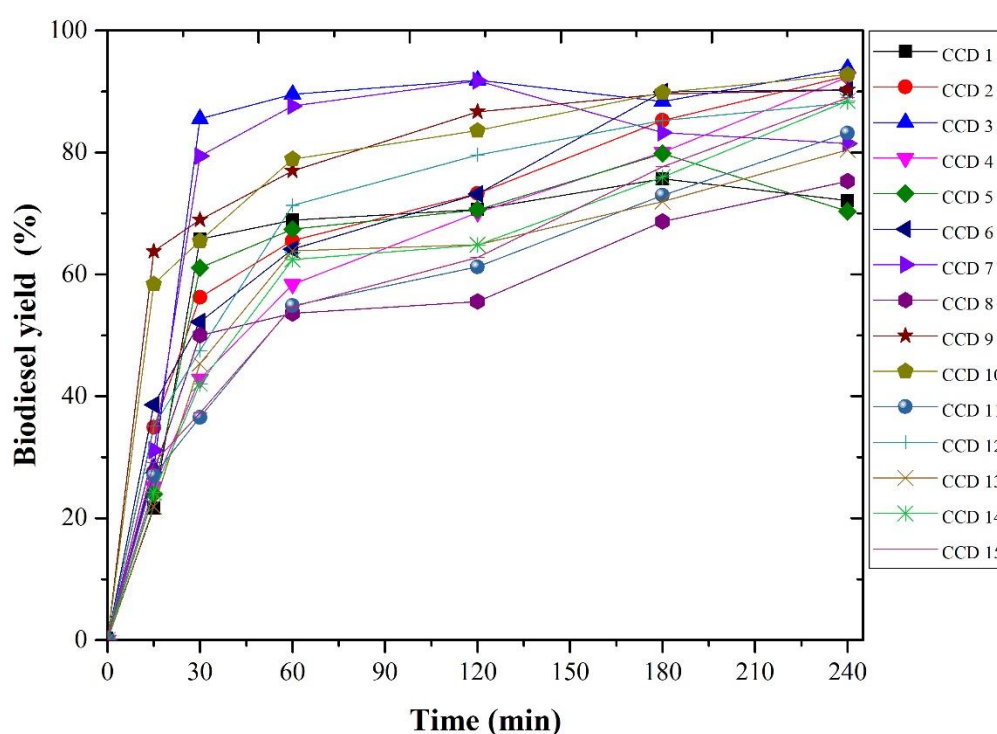
Figure 5.14 Biodiesel yield obtained from CaO catalyzed transesterification in CCR reactor using CCD as presented in Table 4.3

Figure 5.14 illustrated the biodiesel yield along the reaction time at the temperature of 60 °C. The CaO catalyst was packed into basket then pre-mixed with methanol for 30 min to activated CaO catalyst. The pre-heated refined palm oil was fed into at the top or bottom of CCR reactor. No induction period was observed for all experimental run because of the CaO was activated with methanol before transesterification. The parametric operating condition including of methanol to oil molar ratio, CaO loading and rotation mixing speed can influence on the

transesterification rate and equilibrium as indicated in the different slope of biodiesel yield profile and the equilibrium biodiesel yield, respectively. However, looking at the biodiesel yield after 120 min, the biodiesel yield was drop for several runs which could be due to reaction mixture solubility and reversible transesterification [128]. Methanol is as short chain polar molecule; the excess methanol can dissolve in both biodiesel (non-polar phase) and glycerol (polar phase). This leads to increase the amount of glycerol in the biodiesel phase resulting to decrease biodiesel yield. For the reversible transesterification, biodiesel could convert back to monoglyceride, diglyceride or triglyceride to reduce biodiesel yield. Therefore, the actual biodiesel yield used in the CCD prediction was selected at the reaction time of 120 min.

Table 5.5 summarizes the complete experimental and predicted responses for 15 runs for CaO catalyzed transesterification in CCR reactor at the reaction time of 120 min at different interacting variables. The maximum biodiesel yield from the experiment was obtained from 91.87% condition (CCD 3). The predicted biodiesel yield and actual biodiesel yield was slightly different with the maximum error of 13.89%.

Table 5.5 Experimental design based on CCD and results obtained actual biodiesel yield and predicted biodiesel yield for CaO catalyzed transesterification in CCR at reaction time of 120 min

CCD Run	Methanol to oil ratio	Catalyst loading (wt%)	Rotation mixing speed (rpm)	Actual Biodiesel yield (%)	Predicted Biodiesel yield (%)
1	12	13	700	70.670	70.500
2	24	13	700	73.260	75.204
3	12	7	1300	91.870	94.284
4	24	7	1300	70.140	67.452
5	12	13	1300	70.590	67.560

CCD Run	Methanol to oil ratio	Catalyst loading (wt%)	Rotation mixing speed (rpm)	Actual Biodiesel yield (%)	Predicted Biodiesel yield (%)
6	24	13	1300	73.180	72.264
7	12	10	1000	91.770	91.344
8	24	10	1000	55.550	64.512
9	18	7	1000	86.670	88.212
10	18	13	1000	83.600	77.148
11	18	10	700	61.230	65.694
12	18	10	1300	79.590	73.710
13	18	10	1000	64.900	63.882
14	12	13	700	64.830	60.942
15	24	13	700	62.800	69.702

5.2.2.2 Analysis of variance (ANOVA)

To complete design matrix, utilizing the CCD was utilized to explore the optimal combination of various operating parameters such as the methanol to oil molar ratio, catalyst loading and rotating mixed speed in order to maximize the biodiesel production. The significance of each reaction parameter could be investigated using analysis of variance (ANOVA) as shown in Table 5.6.

Table 5.6 Analysis of Variance (ANOVA).

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	6	1478.43	246.41	7.32	0.007
Linear	3	493.99	164.66	4.89	0.032
Methanol to oil molar ratio	1	311.81	311.81	9.26	0.016
Catalyst loading	1	159.92	159.92	4.75	0.061
Rotating mixing speed	1	22.26	22.26	0.66	0.440
Square	2	486.27	243.13	7.22	0.016

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Methanol*Methanol	1	471.54	471.54	14.00	0.006
Mixing*Mixing	1	148.92	148.92	4.42	0.069
2-Way Interaction	1	498.17	498.17	14.79	0.005
Methanol*Catalyst	1	498.17	498.17	14.79	0.005
Error	8	269.44	33.68		
Total	14	1747.87			

The ANOVA for the quadratic regression model was carried out using a 95% confidence interval and with a significance level of 0.05. The P-value < 0.05 demonstrates high significance with high confidence interval in predicting the biodiesel yield results and the suitability of the development regression model. The regression equation to determine biodiesel yield for CaO catalyzed transesterification in CCR reactor at the reaction time of 120 min was given in Equation (5.5).

$$\text{Biodiesel yield (\%)} = 34.8 - (9.52)A + (9.22)B + (0.1571)C + (0.3605)A^2 - (0.000081)C^2 - (0.438)AB \tag{5.5}$$

where, A is methanol to oil molar ratio, B is the CaO catalyst loading (wt%) and C is rotation mixing speed (rpm).
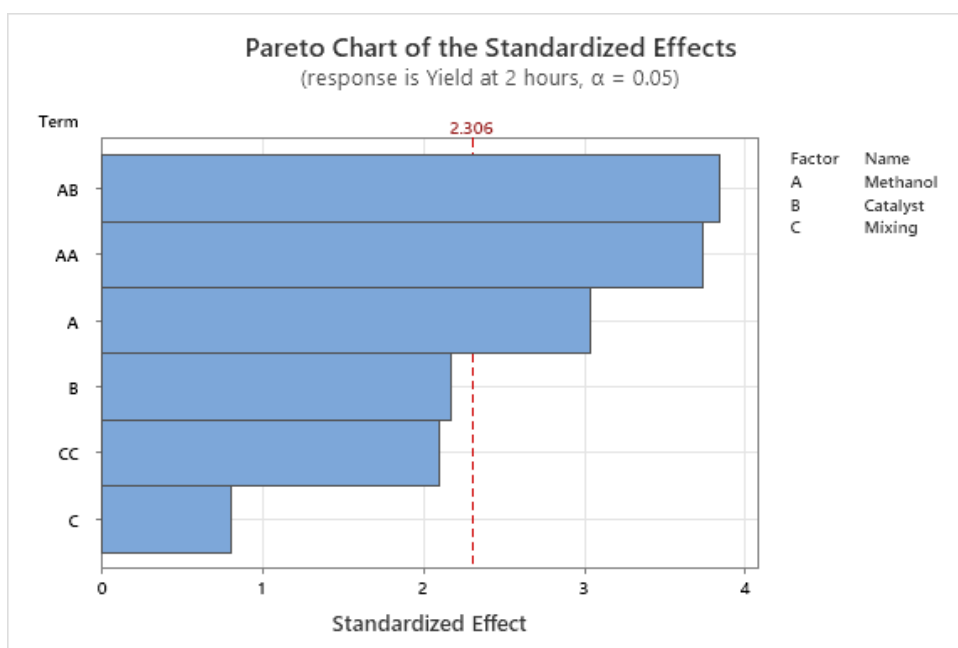
Figure 5.15 Pareto chart showing the significance of regression terms.

The regression equation consists of variable of the predictor; methanol to oil molar ratio, amount of catalyst loading and rotation mixing speed. The predicted yield along with experimentally calculated biodiesel yield obtained via regression equation are given in Table 5.6. According to the ANOVA results and regression equation results the highly significant variables that influence biodiesel yield response were A, AA, and AB. The value of determination of coefficient (R^2) indicated the model reliability, by comparing the results of the predicted with reasonable accuracy of the model to the real experimental results by the statistical method. The value of R^2 was 84.58 %. Normally, the value or $R^2 > 0.8$ there is a good agreement between the observed and predicted values [129] and when the R^2 value is close to unity (1.0) that the empirical models closely fit to the experimental data. An example in CCD 3; (12:1 of methanol to oil molar ratio, 13 wt% catalyst loading and 700 rpm rotation mixing speed) was achieved 91.87 % biodiesel yield and the predicted biodiesel yield was 94.28 % biodiesel yield which was greater than the actual biodiesel yield of 2.414% (2.56 % error). This indicated a better signal to noise ratio which conforms the model's desirability.

5.2.2.3 RSM analysis for interactive effects of independent variables

The present study aimed to explore the synergistic impact of the independent variables on the proportion of response variables. This investigation was carried out by generating three-dimensional surface curves (3D), which visually depicted the intricate relationships among the variables. Meanwhile, the remaining variables were held constant at their central (0) level throughout the analysis. The 3D plots are graphically represented of the biodiesel yield obtained from terms of various parameters. In this work selected three parameters (methanol to oil molar ratio, CaO catalyst loading and rotation mixing speed). Figure 5.16 (a) shows the interactive effect of methanol to oil molar ratio and rotation mixing speed on biodiesel yield at constant 10 wt% of catalyst loading. The biodiesel yield increased with an increase in the excess methanol to oil molar ratio for all rotation mixing speed. The excessive of methanol to oil molar ratio can drive the forward transesterification to produce more biodiesel yield which was in agreement to Ngadi' work [130]. On the other hand, the maximum biodiesel yield of 97 % was obtained at rotation mixing speed of 1,000 rpm. The increment of rotation mixing speed could refer to enhance the shear rate to provide more mixing performance as well as separation of glycerol from biodiesel based on the centrifugal force resulting to increase biodiesel yield [131]. However, biodiesel yield was drop at the highest rotation speed which could be attribute to higher rotation mixing speed, stronger reduction of the hold-up of the dispersed phase in the CCR reactor, leading to lower liquid contact times of reactant and active site of CaO catalyst to lower biodiesel yield [84-85]

(A)

Biodiesel yield (%)

90
80
70
60

1200
1000
800

Rotation mixing speed

15
20
25

Methanol to oil molar ratio

(B)

Biodiesel yield (%)

100
90
80
70

12
10
8

Catalyst loading (%wt)

15
20
25

Methanol to oil molar ratio
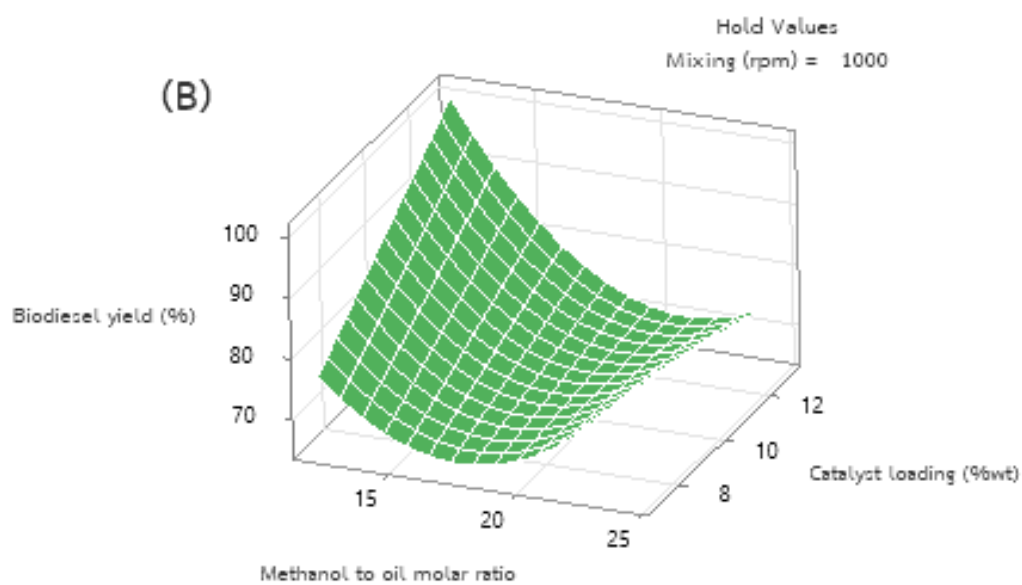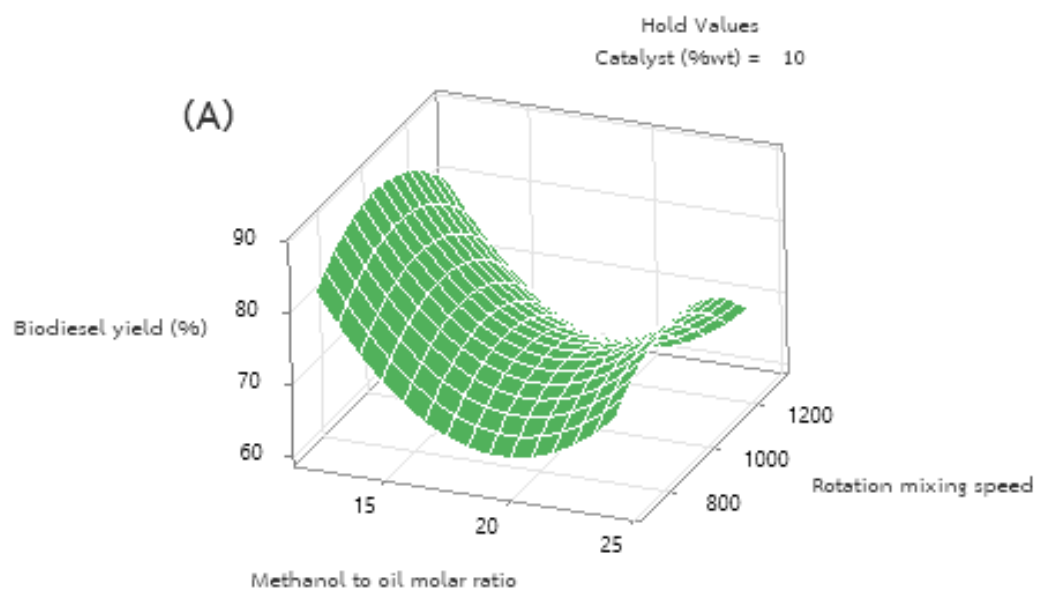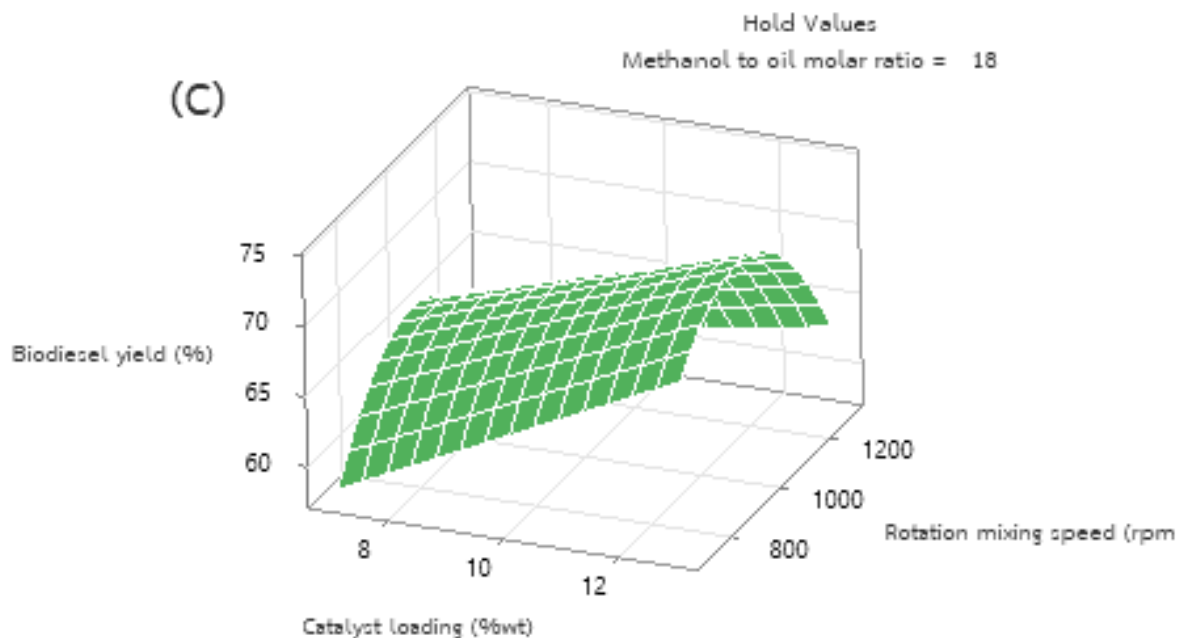
Figure 5.16 Surface plot of the interaction effect of operating parameter on CaO catalyzed transesterification in CCR reactor at 120 min. (A) methanol to oil molar ratio and rotation mixing speed on biodiesel yield at constant catalyst loading 10 wt% (B) methanol to oil molar ratio and catalyst loading on biodiesel yield at constant rotation mixing speed 1,000 rpm and (C) catalyst loading and rotation mixing speed on biodiesel yield at constant methanol to oil molar ratio of 18:1

Figure 5.16 (b) shows the combined effect of methanol to oil molar ratio and catalyst loading on the response biodiesel yield at 120 min. When increasing these both parameters the results the enhancement of transesterification rate to produce more biodiesel yield. As the concentration of CaO catalyst increased, the amount of molar ratio the number of active sites was also increased to facilitate more contact between reactants and catalyst to achieve higher biodiesel yield [132]. However, the higher dosage of CaO catalyst loading might be contributed to the lower yield because of the emulsion formation making more difficult of the reaction mixture phase separation [133].

Figure 5.16 (c) shows the influence of CaO catalyst loading and rotation mixing speed on biodiesel yield at methanol to oil molar ratio of 18:1. This was found that the similar result of rotation mixing speed and CaO catalyst loading on biodiesel yield were also observed at the constant methanol to oil molar ratio. The high rotation mixing speed not only generated high-speed shear force inside reactor but also decreased the contact time which can reduce the biodiesel yield [84] [85].The higher CaO loading provided higher active site to enhance biodiesel yield [132].
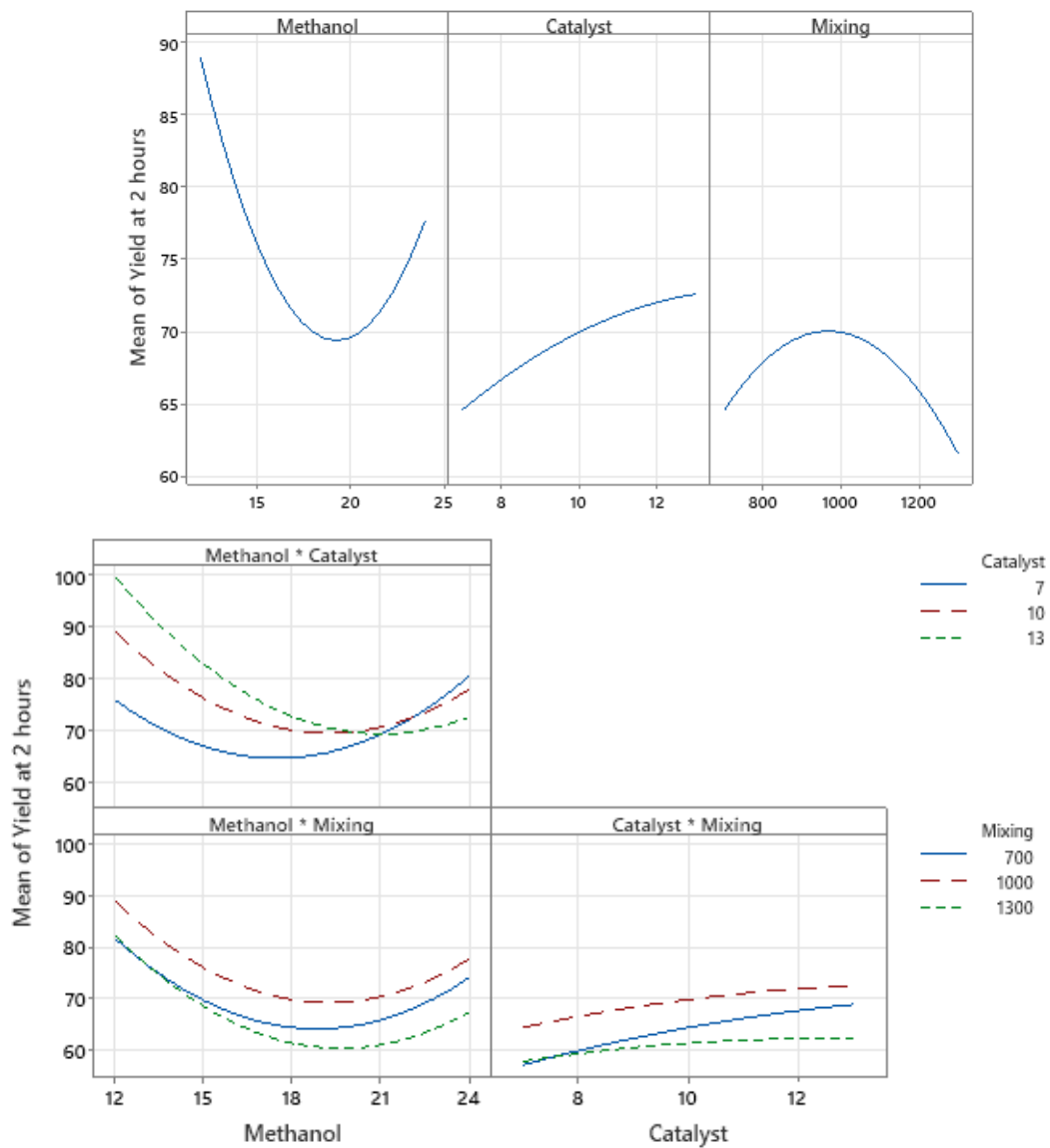
Figure 5.17 Individual design parameter effect plot and interaction parameters plot

Based on the CCD data and analysis of variance (ANOVA) which are standard statistical technique to provide a measure of confidence for the effect of individual design parameters to the biodiesel yield at 120 min reaction time as illustrated in Figure 5.17 This was found that when increasing methanol to oil molar ratio, biodiesel yield was increased. In contrast to CaO catalyst loading, the biodiesel yield was slightly reduced when CaO loading was higher than 10 wt%. The rotation mixing speed also had important effect on the biodiesel yield. When the rotation mixing speed was higher than 1,000 rpm, the negative effect on the biodiesel yield was observed.

5.2.2.4 Verification of optimal interacting parameters
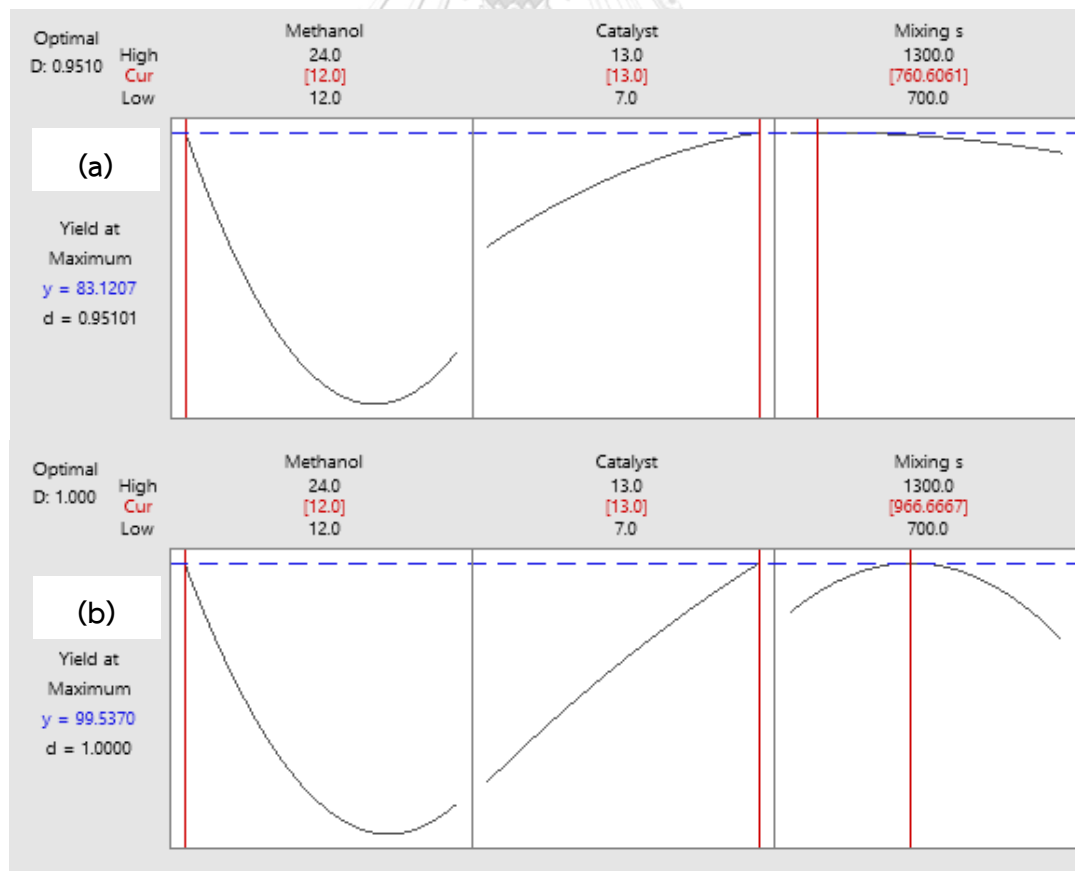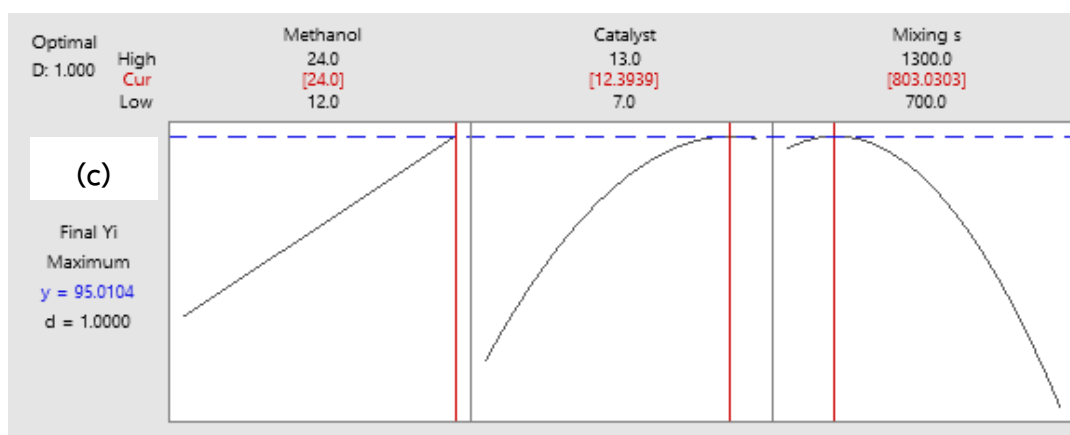
Figure 5.18 Response optimization of biodiesel yield from experimental in (a) 360 min, (b) 120 min and (c) 30 min

The optimization of reacting variables in this work using Minitab data analysis software was performed the response optimization of biodiesel yield with different reaction time (Figure 5.18). The highest biodiesel yield obtained from the optimal condition were 83.12, 99.54 and 95.01% for 360, 120 and 30 min, respectively. The highest biodiesel yield was found at 120 min. The optimum condition of CaO catalyzed transesterification of refined palm oil in CCR reactor was methanol to oil molar ratio of 12:1, 13 wt% of CaO catalyst loading and 996.67 rpm of rotation mixing speed. The condition using methanol to oil molar ratio of 12:1, 13 wt% of CaO catalyst loading and 1,000 rpm of rotation mixing speed (slightly different from the optimum rotation mixing speed) was performed to verify the predicted biodiesel model. This can be noted that the obtained experimental biodiesel with this small error was in good agreement with the predicted optimized conditions biodiesel yield (95.64 %). In addition, the catalytic activity of CaO catalyzed transesterification of refined palm oil in the conventional batch reactor at the similar condition was also tested for comparison. Figure 5.19 indicated that using CCR reactor can achieve higher transesterification rate as well as higher biodiesel yield (95.64%) when compared to the conventional batch reactor (84.25%). The hypothesis was due to the fact the CCR reactor provide more mixing based on the shear rate and the centrifugal force. Shear force was generated by suitable rotation mixing speed. CCR

reactor was design 1.27 cm distance between basket for packing catalyst and inside diameter of vessel reactor. The slightly space can generate shear stress when packing basket rotation was spinning. This shear force was expected to enhance mass transfer by promoting intimate contact and mixing between the reactants, thereby the efficiency of the reaction can be improved. Additionally, shear force was anticipated to facilitate the dispersion of catalysts or additives within the reactant mixture, resulting in more uniform distribution and potentially improving reaction kinetics [131]. Moreover, the application of shear force could contribute to the disruption of emulsions or phase separation that may occur during the reaction, thus aiding in the separation and purification of the biodiesel product. This is an advantage of CCR reactor for biodiesel production via transesterification. When biodiesel and glycerol were produced during the reaction the glycerol was simultaneously separate which can shift the reaction forward to enhance more biodiesel yield [63].
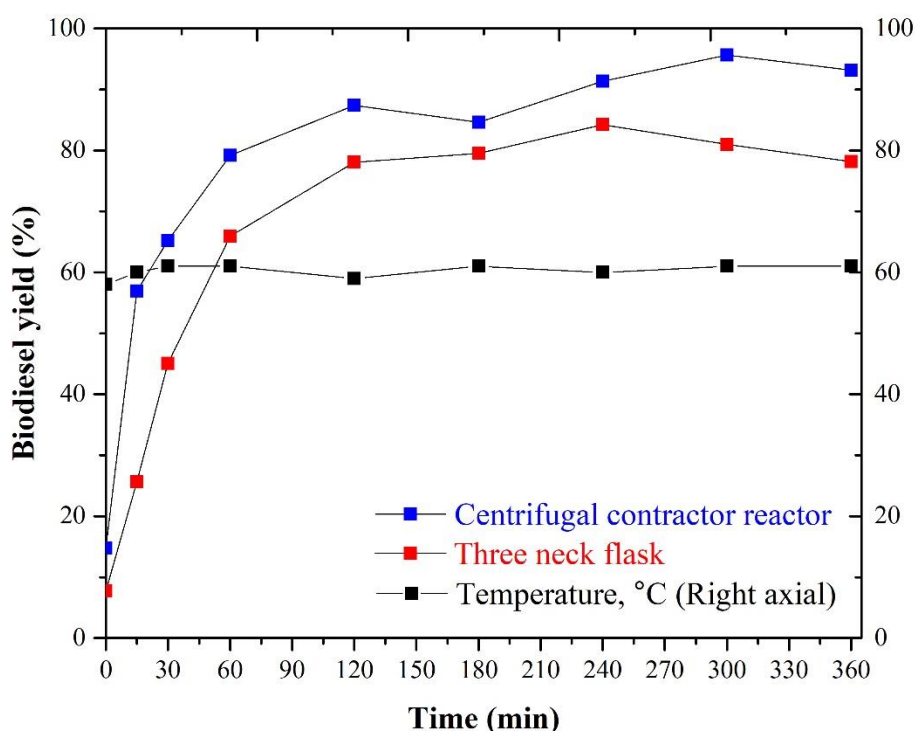
Figure 5.19 Response optimization of biodiesel yield from experimental in 6 h

5.2.2.5 Reusability and regeneration of CaO catalyzed transesterification in CCR reactor
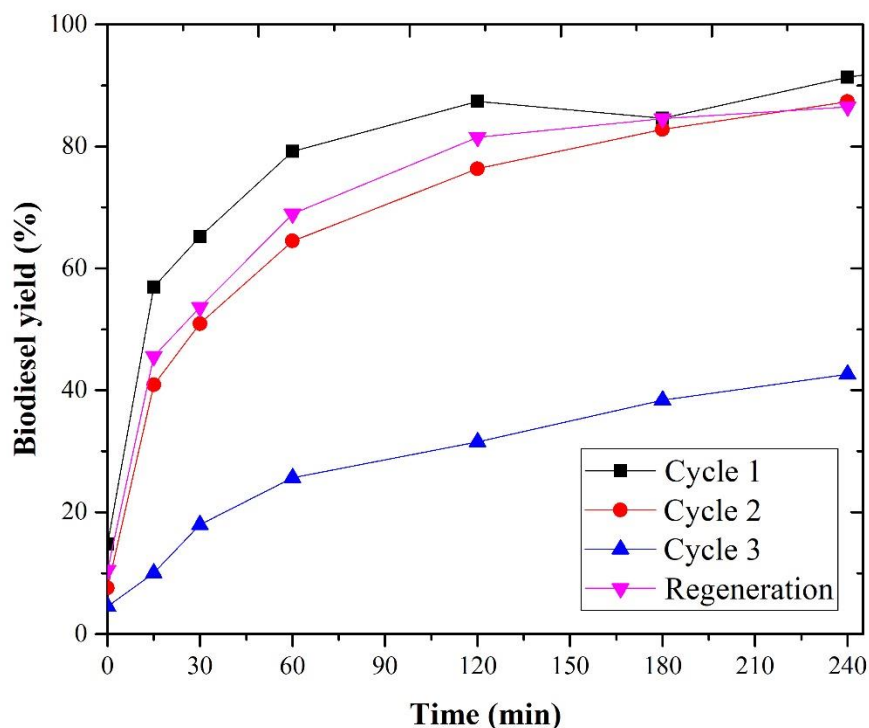
Figure 5.20 Reusability of CaO catalyzed transesterification in CCR reactor (methanol to oil ratio 12:1, catalyst loading 13 wt%, rotation mixing speed 1,000 rpm and reaction temperature 60 °C)

The reusability of heterogeneous catalyst is one of the most important tests required to assess its stability over repeated usage in the reaction. Transesterification or biodiesel production were setup as similar to the previous reaction process and the recovered CaO catalyst were filtered and separated the contaminated. Then, the used CaO catalyst was washed with methanol to remove the reaction mixture contaminate (oil or biodiesel). The process of methanol washing involved washing until the solution became clear and then washed CaO was dried to remove moisture for overnight [134]. The dried CaO catalyst should be powder form for the recovered catalyst reused at the obtained optimum condition from RSM. This reusability test CaO catalyst was done for 3 cycles as shown in Figure 5.20 Biodiesel yield was

continuously drop for every cycle. Biodiesel obtained from the 2nd cycle was 87.34% while the significantly dropped in biodiesel yield (only 42.64%) was observed at the 3rd cycle. This might be due to strong adsorption of reaction mixture on the active site of CaO which can reduce the number of active site to lower biodiesel yield [135].

5.2.2.6 Kinetic study of CaO catalyzed transesterification in CCR reactor

In this work, kinetic of CaO catalyzed transesterification in the CCR reactor using the optimum condition of methanol to oil molar ratio 12:1, 13 wt% catalyst loading and 1,000 rotation mixing speed was investigated as depicted in Figure 5.21 The similar biodiesel yield profile was observed at the reaction temperature of 60 and 65 °C which might be due to the more methanol was vaporized at high temperature of 65 °C resulting to influent on transesterification rate and biodiesel yield [128].
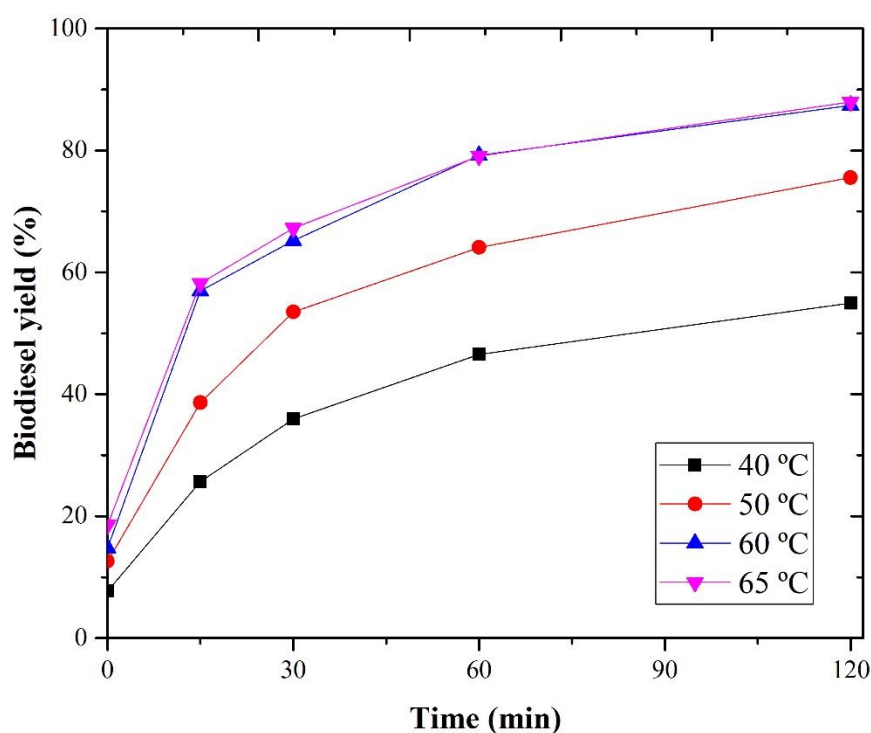
Figure 5.21 Biodiesel yield profile along reaction time for CaO catalyzed transesterification in CCR reactor with different temperature

To determine the reaction rate constant, the order of transesterification was determine based on the pseudo-first order and pseudo-second order of refined palm oil as shown in Figure 5.22
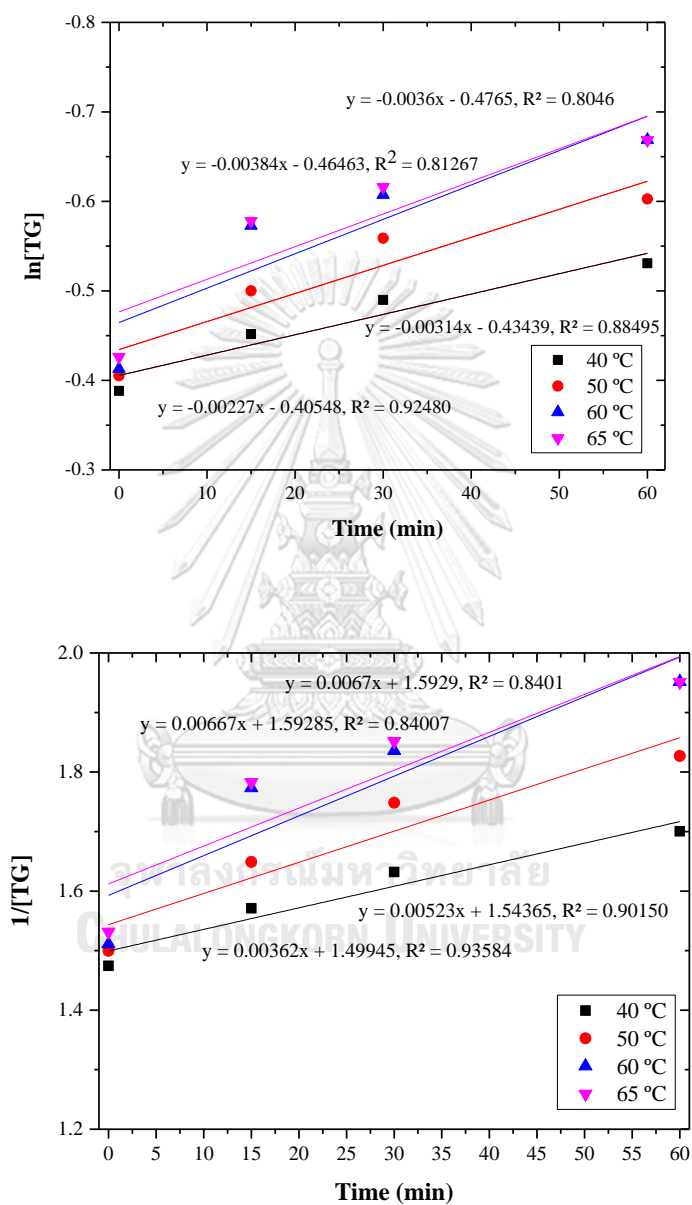
Figure 5.22 Linear plots of ln[TG] and 1/[TG] vs time (min) at different reaction temperature

Table 5.7 Calculated values of kinetic parameter values for CaO catalyzed transesterification of refined palm oil in CCR reactor

	T (°C)	k (min^{-1})	R^2	Ea (kJ/mol)	A (min^{-1})
1st order	40	0.00227	0.92480	22.8253	1.49 x 10^1
	50	0.00314	0.88495		
	60	0.00384	0.81267		
	65	0.00360	0.80460	-	-
2nd order	40	0.00362	0.93584	26.5267	9.85 x 10^1
	50	0.00523	0.90150		
	60	0.00667	0.84007		
	65	0.00670	0.8401	-	-

The Arrhenius plot was used to determine the activation energy (Ea) for CaO catalyzed transesterification in CCR reactor as illustrated in Figure 5.23. As mentioned before, the similar biodiesel yield profile was observed for 60 and 65 °C due the methanol vaporization. Therefore, the Arrhenius plot to determine the activation energy was excluded at 65 °C.

Table 5.7 summarizes the calculated kinetic values based on experiment results. The results revealed that CaO catalyzed transesterification of refined palm oil was more likely to be pseudo-second order with activation energy and pre-exponential factor of 26.53 kJ/mol and 9.85 x 10 min^{-1} respectively. Kadi et al. [136] also found that the reaction order of CaO catalyzed transesterification also followed the pseudo-second order.
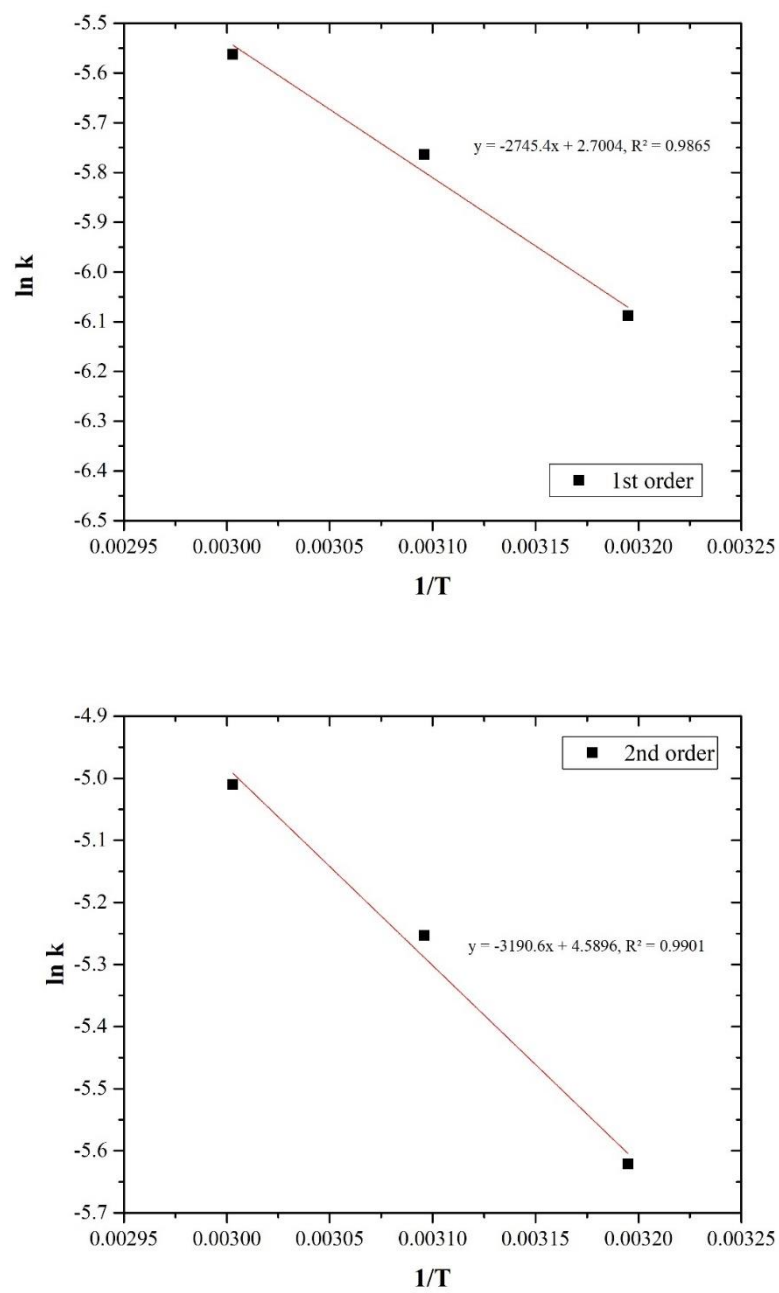
Figure 5.23 Arrhenius plot of lnk vs 1/T for 1st order and 2nd order of refined palm oil via CaO catalyzed transesterification in CCR

5.2.2.7 CaO catalyzed transesterification of WCO in CCR reactor
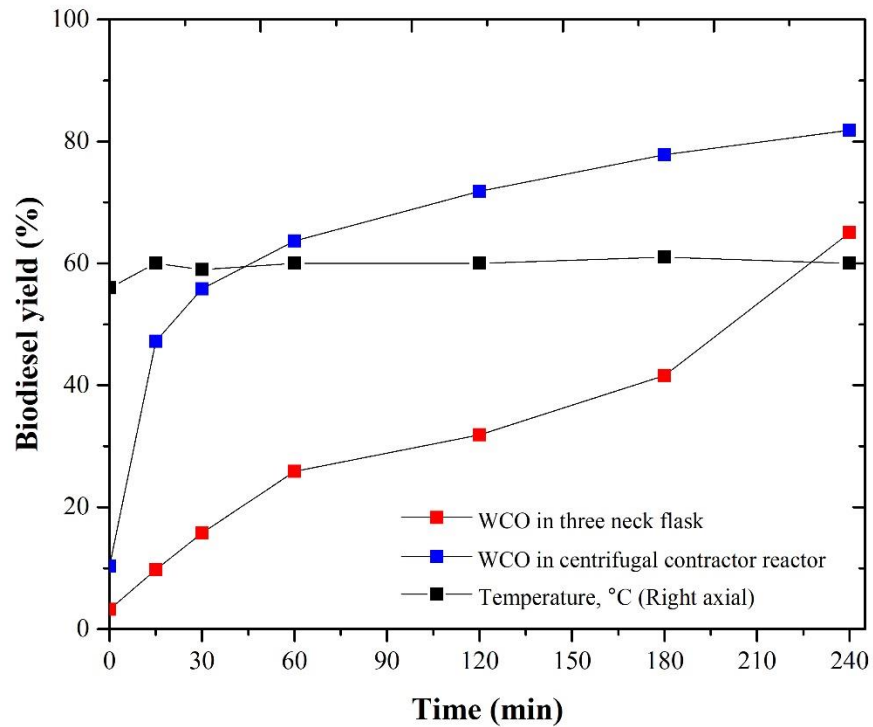
Figure 5.24 Biodiesel yield along the reaction time for CaO catalyzed
transesterification of waste cooking oil in CCR reactor

Figure 5.24 shows the highest biodiesel yield of 81.82% was achieved in the
CCR reactor. This result also supported that the biodiesel production in CCR reactor
is a promising process which can provide high biodiesel yields, improve reaction
rates, and reduce reaction times. Additionally, this reactor also shows great
advantage for handling impurities commonly found in WCO resulting to enhance the
mixing efficiency of reaction mixture and the catalyst to achieve more homogenous
phase.

Further research and optimization are necessary to fully exploit the
performance potential, optimize operating conditions, and scale up the technology
for commercial applications in the biodiesel industry. This should be noted that
these findings have the potential to inform the development of a pilot-scale system
that enables continuous biodiesel production.

5.2.3 Comparative reactor performance for heterogeneous catalyzed transesterification based on biodiesel yield and yield efficiency

Biodiesel production processes play a vital role in determining the efficiency and sustainability of this renewable fuel source. One crucial aspect of efficiency is energy consumption, as it directly impacts the overall cost and feasibility of biodiesel production as well as an environmental issue. This study aims to compare and evaluate the energy consumption profiles of two biodiesel production processes and their influence on biodiesel yield and yield efficiency. By comparing these processes, we can assess their respective energy requirements throughout feedstock preparation, pre-treatment, reaction, separation, and purification steps, as well as any auxiliary operations. The yield efficiency is defined in Equation (5.6).

$$\textbf{Biodiesel yield efficiency} = \frac{\textbf{Amount of product produced (g)}}{\textbf{Power supplied}\left(\frac{J}{s}\right)\textbf{x reaction time (s)}} \tag{5.6}$$

Table 5.8 Comparatives study of intensification process for intensification biodiesel production via transesterification

Process	Operate	Condition	Time (min)	Yield (%)	Yield efficiency 10^{-4} (g/J)	Ref
Vegetable oil (Mechanical stirring)	Batch Transesterification	- MeOH ratio 6:1 - Temperature 45°C. - Catalyst load 1 wt% (KOH) - Mixing speed 900 rpm	45	90.00	0.06	[137]
Nagchampa oil (Mechanical stirring)	Batch Transesterification	- MeOH ratio 4.5:1 - Temperature 50°C. - Catalyst load 1 wt% (KOH) - Mixing speed 350 rpm	40	90.60	0.05	[138]

Process	Operate	Condition	Time (min)	Yield (%)	Yield efficiency 10^{-4} (g/J)	Ref
Jatropha oil (microwave)	Batch Transesterification	- MeOH ratio 7.5:1 - Temperature 65°C. - Catalyst load 1.5 wt% (KOH) - Power 1,200 W	65	97.40	6.9	[139]
Vegetable oil (Homogenizer)		- MeOH ratio 6:1 - Temperature 60°C. - Catalyst load 10 wt% (CaO)	180	90.00	8.27	[140]
Vegetable oil (Magnetic stirrer – This work)	Batch Transesterification	- MeOH ratio 12:1 - Temperature 60°C. - Catalyst load 13 wt% (CaO) - Mixing speed 1,000 rpm	120	81.01	0.079	-
Vegetable oil (CCR – This work)	Batch Transesterification	- MeOH ratio 12:1 - Temperature 60°C. - Catalyst load 13 wt% (CaO) - Mixing speed 1,000 rpm	120	87.38	14.40	-

Table 5.8 reveals that the CCR process exhibited lower energy consumption compared to other processes under the optimal conditions. At CCR results were achieved 95.66 % of biodiesel yield with low yield efficiency. Because of the design of the CCR system, which employs shear forces for efficient mixing and enhances heat transfer via catalyst basket and station vessel wall, leading to higher temperatures then the oil bath would be reduced the energy usage.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATION

6.1 Conclusions

6.1.1 An efficient hybridized RD process to increase a flexibility of biodiesel production from alternative generation feedstocks.

The enhancement of the process performance of the hybridized RD was investigated in this study including the combination of the heat exchangers, extended stage spacing modification, and the integration of the pervaporation membrane. All alternative processes were proposed to use WCO as a biodiesel feedstock having different water contents (4-10 wt%). From the technical assessment, all processes can achieve the constrain of water removal below 1 wt% before entering the transesterification section. However, the selection of the alternative process combined with the hybridized RD depended on different aspects including of technical operation, economic and environment consideration. The integration of pervaporation membrane showed the highest performance to remove water content from the system and does not require more energy to operate the hybridized column corresponding to economic and environment aspects. While using the addition of double heat exchangers is the simplest technique. The extended stage spacing modification seems to be successfully met all requirement. However, it required the new construction cost which added only 2% to the capital cost to extend the hybridized RD with the extra 8 stages to remove all water content before flowing down. It should be noted that this modification probably requires the precise control of feedstock specification to eliminate another.

6.1.2 Biodiesel production from refined palm oil and waste cooking oil using CaO catalyst in CCR reactor

CCR reactor was successfully used to produce biodiesel via CaO catalyzed transesterification of refined palm oil. The CCD design of experiment was used to reduce the number of experiment and RSM was also used to determine the optimum condition of biodiesel production in the CCR reactor. It was found that the

methanol to oil molar ratio had a dominance effect on the biodiesel. The biodiesel yield was reduced when increase methanol to oil molar ratio than 12:1. In contrast to CaO loading, the biodiesel yield tended to enhance when increased CaO loading from 7 to 13 wt%. The rotation mixing speed required the optimum value to achieve high biodiesel yield. When the low rotation mixing of 700 rpm was utilized, the low transesterification rate was observed similar to the increase in rotation mixing speed to highest as 1,300 rpm, lower biodiesel yield was also observed as compared to that of the rotation mixing speed of 1,000 rpm. Since, low rotation mixing speed might not provide the efficiency mixing degree derived from shear and centrifugal force while highest rotation mixing speed gave the shorter contact time between active site and reactant to lower transesterification rate. Therefore, the optimum condition of CaO catalyzed transesterification of refined palm oil in the CCR reactor was methanol to oil molar ratio of 12:1, CaO loading of 13 wt% and rotation mixing speed of 1,000 rpm. enabling the identification of optimal conditions and determination of kinetic parameters. The kinetic experiments revealed that the CaO catalyzed transesterification of refined palm oil in the CCR reactor tended to be pseudo-second order reaction with respect to oil. The activation energy (Ea) and pre-exponential factor (A) were 26.53 kJ/mol and 9.85×10 min^{-1}, respectively. The reusability test found that the catalytic activity of CaO catalyst was continuously dropped with the consecutive run which could be due to the strong adsorption of the reaction mixture as well as moisture on the CaO surface. The re-calcination of used CaO is a potential method to re-activate the catalytic activity of used CaO catalyst. In addition, using CCR to produce biodiesel provided higher biodiesel yield as compared to the conventional batch reactor for both refined palm oil and waste cooking oil. The results supported that the CCR reactor is another intensification reactor for the efficient biodiesel production using heterogeneous catalyst.

6.2 Recommendations

The problems observed during the simulations and laboratory-scale experiments could be useful information for further studies in a larger scale or commercial scale production. The followings are some recommendations.

The integration of reaction and separation processes poses challenges in terms of controllability. Hence, it is crucial to establish plantwide process control measures to define the specifications of reactive distillation. These specifications may include determining the column diameter, selecting the appropriate type of packed catalyst, specifying the catalyst's lifespan, and identifying other effective catalyst options. Effective control strategies are necessary to ensure for the stable operation and optimization of the combined reaction and separation system. By carefully defining and implementing these specifications, it becomes possible to enhance the controllability of the process and achieve desired outcomes in terms of product quality, efficiency, and overall performance.

The reusability and regeneration of CaO catalyst were investigated in this work, and the reason why the performance of CaO catalyst dropped was provided. However, the reason should be proved by some characterization of the catalyst such as XRD for checking the composition after each cycle. Moreover, the continuous flow process system is preferable for larger or commercial-scale operations compared to batch processes. To facilitate this transition, the continuous flow process in CCR reactor for the biodiesel production using heterogeneous catalyst still faces many challenges. The design of heterogenous catalyst should be further studied. Moreover, for CCR reactor scale-up, the control system including of temperature control, monitoring input and output sample values, and optimizing catalyst packing to ensure efficient and reliable should be concerned. Simplifying and enhancing control measures will contribute to the successful implementation of the continuous flow process for commercial biodiesel production.

Appendix
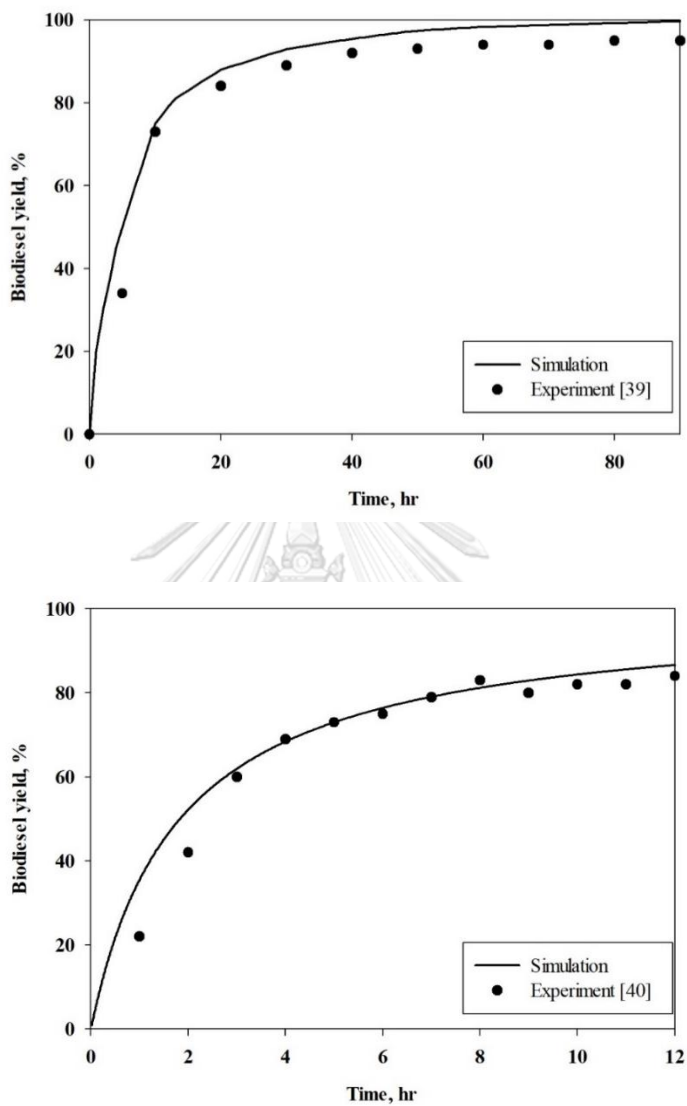
Figure A1 Model validations of (a) kinetic model catalyzed by sodium hydroxide in batch reactor (data adapted from Noureddini and Zhu [141], T= 50 ℃, methanol to oil = 6:1 at atmospheric pressure) and (b) kinetic model catalyzed by CaO/Al$_2$O$_3$ in batch reactor (data adapted from Pasupulety et al. [104], T= 150 ℃, methanol to oil = 9:1 at pressure = 1 bar)
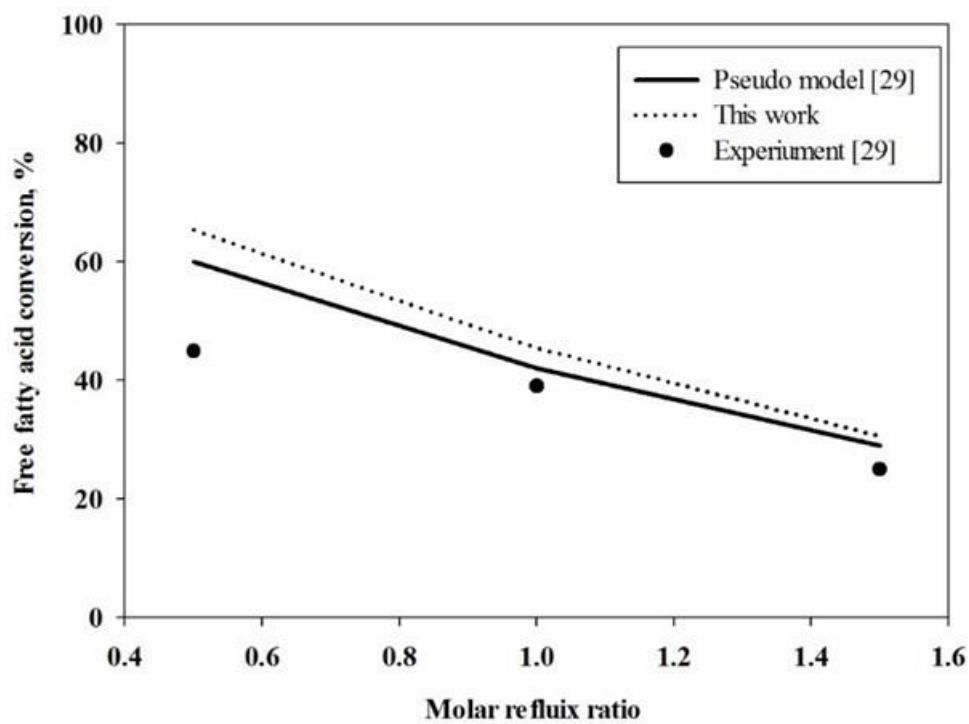
Figure A2 Model validation of kinetic data using Amberlyst-15 in term of free fatty

acid conversion as a function of reflux ratio using packing of Katapak-SP

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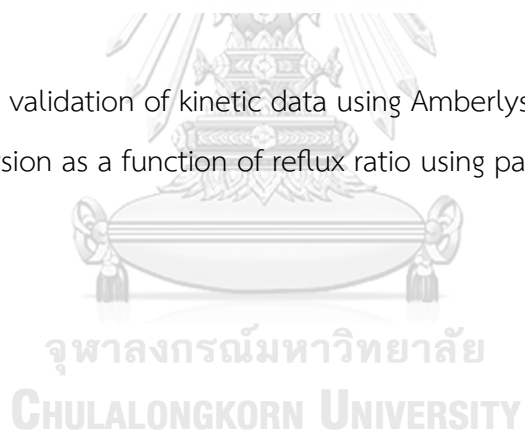
Table A1 Earlier hybridized RD column design parameter [20]

Parameter	Value	Unit
Rectifying section	1	stages
Reactive section	8	stages
Stripping section	1	stages
Total number of actual stages	10	stages
Column dimeter	0.30	m
Column height	6.00	m
Catalyst loading	Amberlyst-15 2.5 wt% CaO/Al_2O_3 3 wt%*	-
Reflux ratio	0.1	-
Reboiler duty	216	kWh/kmol biodiesel
Reflux ratio	0.1	-
Column pressure	3	bar
Methanol to oil ratio	4:1	-
Free fatty acid in feedstock	6	wt%
Biodiesel production rate	944	kg/h

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Table A2 Summary of data sheet and mass composition for extended spacing stage modification of hybridized RD following Figure 5[a]

	101	102	201	301	302	303	401	402
Temperature (°C)	25	25	35	114	194	194	30	30
Pressure (bar)	1	1	3	3	3	3	1	1
Vapor fraction	0	0	0	0	0	1	0	0
Mass Flows (kg/h)								
Methanol	0.00	171.43	178.25	9.33	20.17	7.25	0.00	39.02
Triolein	882.00	0.00	0.00	0.00	0.11	0.00	5.99	0.00
Methyl oleate	0.00	0.00	0.00	0.00	950.88	0.00	937.90	0.01
Glycerol	0.00	0.00	0.00	0.00	91.72	0.00	0.05	74.45
Water	105.00	0.00	1.90	30.68	0.45	1.90	0.41	3.60
Oleic acid	63.00	0.00	0.00	0.00	1.11	0.00	3.01	0.00

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Mass fraction composition in hybridized RD[b]					
Stage	Methanol	Triolein	Methyl oleate	Glycerol	Water	Oleic acid
1	0.3249	0.0000	0.0000	0.0000	0.6751	0.0000
2	0.0741	0.7330	0.0390	0.0000	0.1386	0.0152
3	0.0891	0.7272	0.0504	0.0000	0.1293	0.0039
4	0.1039	0.7223	0.0532	0.0000	0.1197	0.0009
5	0.1192	0.7174	0.0528	0.0000	0.1097	0.0009
6	0.1360	0.7120	0.0524	0.0000	0.0987	0.0009
7	0.1554	0.7057	0.0520	0.0000	0.0861	0.0009
8	0.1783	0.6981	0.0514	0.0000	0.0713	0.0009
9	0.2043	0.6895	0.0508	0.0000	0.0546	0.0009
10	0.2314	0.6803	0.0501	0.0000	0.0373	0.0009
11	0.2559	0.6718	0.0495	0.0000	0.0219	0.0008
12	0.2723	0.6678	0.0492	0.0000	0.0098	0.0008
13	0.2287	0.1666	0.5523	0.0521	0.0006	0.0008
14	0.2229	0.0297	0.6864	0.0660	0.0059	0.0008
15	0.2248	0.0049	0.7094	0.0685	0.0084	0.0008
16	0.2272	0.0008	0.7119	0.0687	0.0094	0.0008
17	0.3168	0.0001	0.6197	0.0692	0.0065	0.0007
18	0.0350	0.0001	0.8933	0.0862	0.0156	0.0010

[a]Based on water content of 10 wt%

[b]The blue and green highlighted indicate reactive stages of esterification and transesterification where non-highlighted are non-reactive stages with the simulation error less than 0.1%..

Table A3 Performance comparison of different biodiesel production processes

	Hybridization of RD
Overall methanol to oil feed molar ratio	4:1
Biodiesel purity, wt%	97.61
Overall biodiesel yield, %	99.87
Glycerol purity before purified, wt%	87.44
Glycerol purity after purified, wt%	
Lower reflux ratio	96.38
High reflux ratio	-
Energy requirement for glycerol purified, kW	
Lower reflux ratio	-4/10
High reflux ratio	-
Total net specific energy requirement (kWhr/kmol biodiesel)	216
Total net specific energy requirement allocates with technical grade glycerol production (kWhr/kmol biodiesel)	197

Parameter	Hybridization of RD	
	Column pressure 1 bar	Column pressure 3 bar
Column diameter (m)	0.82	0.30
Column height (m)	15.60	6.00
Number of reactive stage	24	8
Catalyst loading	Acid 2.5 wt%[1] and alkali catalyst 3 wt%[2]	

Table A4 Analysis of Variance (Full parameter)

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	1535.82	170.647	4.02	0.070
Linear	3	493.99	164.664	3.88	0.089
Methanol	1	311.81	311.811	7.35	0.042
Catalyst	1	159.92	159.920	3.77	0.110
Mixing	1	22.26	22.261	0.52	0.501
Square	3	491.02	163.673	3.86	0.090
Methanol*Methanol	1	459.36	459.355	10.83	0.022
Catalyst*Catalyst	1	4.75	4.752	0.11	0.751
Mixing*Mixing	1	122.58	122.583	2.89	0.150
2-Way Interaction	3	550.81	183.603	4.33	0.074
Methanol*Catalyst	1	498.17	498.175	11.75	0.019
Methanol*Mixing	1	26.25	26.245	0.62	0.467
Catalyst*Mixing	1	26.39	26.390	0.62	0.466
Error	5	212.05	42.410		
Total	14	1747.87			

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