Techno-economic and environmental assessment for enhancementbiodiesel production process using rotating tube reactor and dry washing

Mr. Arthit Jarungwongsathien

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การประเมินทางเศรษฐศาสตร์เทคโนโลยีและสิ่งแวดล้อมเพื่อเพิ่มประสิทธิภาพกระบวนการผลิตไบโอดีเซลโดยใช้เครื่องปฏิกรณ์แบบท่อหมุนร่วมกับการล้างแบบแห้ง

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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Thesis Title	Techno-economic and environmental assessment for enhancementbiodiesel production process using rotating tube reactor and dry washing
By	Mr. Arthit Jarungwongsathien
Field of Study	Chemical Engineering
Thesis Advisor	Professor SUTTICHAI ASSABUMRUNGRAT, Ph.D.
Thesis Co Advisor	Associate Professor Kanokwan Ngaosuwan, Ph.D.

Accepted by the FACULTY OF ENGINEERING, Chulalongkorn University in Partial Fulfillment of the Requirement for the Master of Engineering

.... Dean of the FACULTY OF ENGINEERING
(Professor SUPOT TEACHAVORASINSKUN, Ph.D.)

THESIS COMMITTEE

.... Chairman
(Assistant Professor APINAN SOOTTITANTAWAT, Ph.D.)
.... Thesis Advisor
(Professor SUTTICHAI ASSABUMRUNGRAT, Ph.D.)
.... Thesis Co-Advisor
(Associate Professor Kanokwan Ngaosuwan, Ph.D.)
.... Examiner
(MERIKA CHANTHANUMATAPORN, Ph.D.)
.... External Examiner
(Associate Professor Worapon Kiatkittipong, Ph.D.)

อาทฤต จรุงวงศ์เสถียร : การประเมินทางเศรษฐศาสตร์เทคโนโลยีและสิ่งแวดล้อมเพื่อเพิ่มประสิทธิภาพกระบวนการผลิตไบโอดีเซลโดยใช้เครื่องปฏิกรณ์แบบท่อหมุนร่วมกับการล้างแบบแห้ง. (Techno-economic and environmental assessment for enhancementbiodiesel production process using rotating tube reactor and dry washing) อ.ที่ปรึกษาหลัก : ศ. ดร.สุทธิชัย อัสสะบำรุงรัตน์, อ.ที่ปรึกษาร่วม : รศ. ดร.กนกวรรณ ง้าวสุวรรณ

การศึกษานี้มีวัตถุประสงค์เพื่อศึกษาความเป็นไปได้ในการใช้เครื่องปฏิกรณ์แบบท่อหมุน (RTR) และการวิเคราะห์ทางเศรษฐศาสตร์ ตลอดจนชี้ให้เห็นถึงความท้าทายที่เกี่ยวข้องจากการใช้วัตถุดิบตั้งต้นทั้งจากน้ำมันปาล์มบริสุทธิ์ (RPO) และน้ำมันใช้แล้ว (WCO) สำหรับการผลิตไบโอดีเซล วัตถุดิบที่แตกต่างกันมีผลอย่างมีนัยสำคัญต่ออุณหภูมิที่เหมาะสมในปฏิกิริยา ตัวอย่างเช่น น้ำมัน RPO สามารถใช้ผลิตไบโอดีเซลใน RTR ได้ที่อุณหภูมิห้อง ในขณะที่น้ำมัน WCO ต้องการแหล่งความร้อนภายนอกสำหรับการผลิตไบโอดีเซลที่อุณหภูมิ 65 องศาเซลเซียส นอกจากนี้ การผลิตไบโอดีเซลจากน้ำมัน WCO จะต้องใช้ปฏิกิริยาทรานส์เอสเทอริฟิเคชันสองขั้นตอน เพื่อให้ได้ผลผลิตไบโอดีเซล 95.16% ผลการจำลองพบว่าการใช้ RTR และการล้างแบบแห้งให้ผลผลิตไบโอดีเซลสูงสุดและใช้พลังงานต่ำสุดสำหรับน้ำมัน RPO และน้ำมันWCO ซึ่งแสดงในกรณี B1 และ B2 ตามลำดับ ในการผลิตไบโอดีเซล 100 ลิตรต่อวัน อย่างไรก็ตามการวิเคราะห์ทางเศรษฐศาสตร์พบว่ากรณี A2 (RPO, RTR-การล้างแบบเปียก) แสดงให้เห็นถึงต้นทุนการผลิตที่ต่ำที่สุดและมูลค่าปัจจุบันสุทธิ (NPV) สูงสุดที่ 61.6 และ 232.7 พันเหรียญสหรัฐ ตามลำดับ ในทางตรงกันข้ามการปล่อยแก๊สคาร์บอนไดออกไซด์ที่ได้จากการใช้ RTR สูงกว่ากระบวนการแบบดั้งเดิม เนื่องจากการใช้พลังงานต่อหน่วยของ RTR ได้จากการวัดในระดับห้องปฏิบัติการ การวิเคราะห์ความแปรปรวนพบว่าราคาน้ำมันและไบโอดีเซลมีผลอย่างมีนัยสำคัญต่อความเป็นไปได้ทางเศรษฐศาสตร์ของการผลิตไบโอดีเซล นอกจากนี้เพื่อให้มีความเป็นไปได้ทางเศรษฐศาสตร์จะต้องขายไบโอดีเซลในราคา 1.3 เหรียญสหรัฐต่อกิโลกรัม สำหรับกำลังการผลิตในโรงงานตั้งแต่ 4,000 ถึง 30,000 ลิตรต่อวัน โดยอ้างอิงจากกรณี A2 ทำให้สรุปได้ว่า RTR เป็นเครื่องปฏิกรณ์ที่เป็นไปได้สำหรับการผลิตไบโอดีเซลเมื่อพิจารณาในเชิงด้านเศรษฐศาสตร์และสิ่งแวดล้อม

สาขาวิชา	วิศวกรรมเคมี	ลายมือชื่อนิสิต	....
ปีการศึกษา	2565	ลายมือชื่อ อ.ที่ปรึกษาหลัก	....
		ลายมือชื่อ อ.ที่ปรึกษาร่วม	....

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KEYWORD: Biodiesel; rotating tube reactor; techno-economic analysis; waste cooking oil (WCO); dry washing process.

Arthit Jarungwongsathien : Techno-economic and environmental assessment for enhancementbiodiesel production process using rotating tube reactor and dry washing. Advisor: Prof. SUTTICHAI ASSABUMRUNGRAT, Ph.D. Co-advisor: Assoc. Prof. Kanokwan Ngaosuwan, Ph.D.

The study aims at exploring the potential use of rotating tube reactor (RTR) and performing economic analysis as wells as addressing the challenges associated with the utilization of different feedstocks including of refined palm oil (RPO) and waste cooking oil (WCO) for biodiesel production. The type of feedstock strongly influenced the optimum reaction temperature. For instance, RPO can produce biodiesel in the RTR at room temperature while WCO required the external heat source for biodiesel production at 65°C. In addition, two transesterification steps of WCO were required to achieve 95.16%. Simulation results found that the process intensification using RTR and dry washing gave the highest biodiesel yield and lowest energy consumption for both RPO and WCO feedstocks (B1 and B2 cases) based on 100 L/day of biodiesel production. However, the economic analysis revealed that A2 (RPO, RTR-wet washing) case demonstrated the lowest manufacturing cost and highest net present value of 61.6 and 232.7 thousand USD, respectively. On the other hand, the CO_2 emission obtained from the process intensification cases was higher than the conventional process because the specific energy consumption of RTR was measured from the lab scale. Sensitivity analysis confirmed the significant impact of oil and biodiesel prices on the economic feasibility for biodiesel production. Furthermore, the minimum biodiesel selling price of 1.3 USD/kg was required to achieve economically viable for all plant processing capacities from 4,000 to 30,000 L/day based on the A2 case. This can be concluded that RTR is a promising reactor for biodiesel production based on both economic and environmental consideration.

Field of Study:	Chemical Engineering	Student's Signature ....
Academic Year:	2022	Advisor's Signature ....
		Co-advisor's Signature ....

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Arthit Jarungwongsathien

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CHAPTER 1
INTRODUCTION

1.1 Introduction

Biodiesel has become increasingly popular because of its non-toxicity, biodegradability, and lubricity, making it a more attractive alternative compared to traditional diesel [1, 2]. Biodiesel is typically produced by transesterification, a process that involves reacting triglycerides with short-chain alcohols like methanol or ethanol. This results in the formation of fatty acid alkyl ester (FAAE) and glycerol as a by-product. This should be noted that, the cost of biodiesel production is much higher than that of fossil diesel, usually 1.5 to 2 times higher [3]. Vegetable oil, which serves as a typical feedstock, is the largest contributor to the total cost of biodiesel production, accounting for almost 70% of the cost. To make biodiesel production more economically feasible, research should focus on developing cost-effective feedstocks such as waste cooking oil (WCO) [4] and its purification methods [5]. Another method of producing FAAE is through the esterification of free fatty acids (FFAs), which are converted into FAAE and water as by-products. However, the transesterification process can be limited by the immiscibility of oil and alcohol, leading to a low mass transfer rate and long reaction times. This issue can be overcome by utilizing the intensification method [6]. One interesting intensification technology is a rotating tube reactor (RTR), which is used to increase mixing performance. The shear rate generated by the RTR not only facilitates mass transfer enhancement but also provides enough heat to decrease required residence time and lower energy consumption compared to other intensification reactors [7]. In a prior research study, the RTR was utilized for producing biodiesel via transesterification process of palm oil and methanol using sodium hydroxide (NaOH). The study found that a 97.5% biodiesel yield was achieved by utilizing a methanol-to-oil molar ratio of 6:1, a total flowrate of 30 mL/min, and a rotational speed of 1,000 rpm at room temperature [8].

Additionally, the operation and maintenance of an RTR do not require a specialized technical operator, making it a practical choice for small community and industrial-scale operations. Conventional biodiesel production typically involves homogeneous alkali-catalyzed transesterification, using either NaOH or KOH, of vegetable oil in a batch or continuous stirred tank reactor. Methanol recovery is achieved through a vacuum evaporation column, separation of biodiesel from glycerol is done in a settling tank or decanter. Finally, the purified biodiesel is obtained using a column in industrial scale plants [1]. Two methods are used for purifying biodiesel to meet international standards (e.g., EN and ASTM). Wet washing is utilized for industrial-scale production, while dry washing is used for pilot-scale production. Dry purification involving in the use of adsorbents such as Megnesol, silica, Amberlite BD10 DRY, and Purolite PD206 [9]. This process efficiently removes impurities from biodiesel through adsorption, resulting in a high quality and stable product. Purolite PD206 was an effective adsorbent due to its high adsorption capacity and selectivity for polar impurities such as water and glycerol. This method has potential to be applied in the industry because of its cost-effectiveness and simplicity, making it an attractive option for biodiesel production. The purification of biodiesel obtained through a two-stage synthesis process using higher fatty acid Jatropha curcas oil showed that the ability to adsorb methanol and glycerol was over 98 and 93%, respectively [10].

Techno-economic analysis (TEA) is a commonly used tool to evaluate the economic feasibility of process improvements. Several studies have used TEA to evaluate the biodiesel production process using various technologies, including plug flow reactors (PFR) [11], ultrasonic cavitation reactors (UC) [1], and continuous stirred tank reactors (CSTR) [12]. This could be a great way to draw attention to the feasibility of biodiesel production using an RTR reactor because it can operate at room temperature which could significantly reduce energy consumption. The use of RTR for biodiesel production has the potential to develop an economically viable system for small communities to achieve self-sufficiency. Therefore, the objective of this study is to assess the economic feasibility of homogeneous alkali-catalyzed transesterification using an RTR reactor for biodiesel production from refined palm oil

(RPO) and waste cooking oil (WCO) as feedstocks. Noted that FFAs in WCO could induce the side saponification and thus reduce biodiesel yield, when its content is greater than 0.5 wt% [13]. Esterification of FFAs using sulfuric acid (H_2SO_4) should also be performed to convert FFAs to biodiesel as the conventional recommendation [14]. Aspen Plus software is used to simulate the case studies of biodiesel production in an RTR reactor and compared to the conventional process. The purification methods, including wet and dry washing, are examined, along with sensitivity analysis of each case study to determine their impact on the economic index such as net present value (NPV) and internal rate return (IRR) of biodiesel production. In addition, various biodiesel production rate from small to industrial scale operation on the economic index is also considered. The indirect environmental assessment based on energy consumption and wastewater production is also considered.

1.2 Research objective

To investigate techno-economic and environmental impact of biodiesel production from refined palm oil (RPO) and waste cooking oil (WCO) using a rotating tube reactor (RTR) and dry washing process based on various biodiesel production rate from small to industrial-scale operations.

1.3 Scope of work

1.3.1 Perform the experiments for esterification-transesterification and transesterification-transesterification of WCO and methanol in a rotating tube reactor (RTR). For esterification as pre-treatment of WCO, the experiments are performed at a methanol to WCO ratio of 12:1, H_2SO_4 loading of 1 wt%, the total feed flowrate of 30 mL/min and reaction temperature of 60 ^{o}C. The condition of transesterification of RPO and pretreated WCO was a methanol to oil ratio of 6:1, NaOH loading of 1 wt%, a total feed flowrate of 30 mL/min and reaction temperature of 30 ^{o}C [8]. The obtained information is used for Aspen Plus simulations.

1.3.2 Propose a biodiesel production process using an RTR with homogeneous alkali catalysts for both refined palm oil (RPO) and waste cooking oil (WCO). Simulate the process using Aspen Plus V11 program.

1.3.3 Determine the performance of a process consisting of an RTR reactor and dry purification method using Purolite PD206 adsorbent [10] and compare with those of the conventional biodiesel production processes using RPO and WCO feedstocks.

1.3.4 Perform techno-economic analysis (TEA) and indirect environmental analysis of net CO_2 emission of the processes using Aspen Plus V11 program.

1.3.5 Investigate the economic index for the selected biodiesel process in term of biodiesel production rate from small to industrial scale operation.

1.4 Expected Outputs

An efficient and sustainable process for biodiesel production from RPO and WCO using homogeneous alkali catalysts in the RTR reactor and dry purification method is proposed based on the economic and environmental assessment for small to industrial scale operation.

CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 Biodiesel

2.1.1 Biodiesel and its properties

Biodiesel or fatty acid methyl ester (FAME) is a clean-burning alternative fuel produced from renewable resources. It can be defined as a mixture composed of mono-alkyl esters of saturated or unsaturated long-chain fatty acids produced via the chemical process, namely transesterification. In this process, oils react with alcohol in the presence of a homogeneous or heterogeneous catalyst. The standard of biodiesel in a commercial provided for two types which are the European EN 14214 or American Society for Testing and Materials (ASTM) D6751 as shown in Table 1.

Table 1 EN 14214 and ASTM D6751 specification of biodiesel [15].

Property(unit)	EN Limits	Test methods	ASTM Limits	Test methods
Ester content (wt%)	96.5	EN 14103	-	-
Pour point (°C)	-	-	-15 to -16	D97
Flash point (°C)	101 (Min)	EN ISO 2719/3679	130 (Min)	D93
Cloud point (°C)	-	-	-3 to -12	D2500
Cold filter plugging point (°C)	-	-	5 (Max)	D6371
Copper strip corrosion (3 h at 50 °C)	class 1	EN ISO 2160	No 3	D130
Cetane number	51 (Min)	EN ISO 5165	47 (Min)	D613
Iodine number (g I_2/100 g)	120 (Max)	EN 14111/16300	-	-
Acid value (mg KOH/g)	0.5 (Max)	EN 14104	0.5 (Max)	D664
Density at 15 °C (kg/m^3)	860-900	EN ISO	880	D1298

Property(unit)	EN Limits	Test methods	ASTM Limits	Test methods
		3675/12185		
Viscosity at 40 °C (mm^2/s)	3.5-5.0	EN ISO 3104	1.9-6.0	D445
Carbon residue (wt%)	-	-	0.05 (max)	D4530
Methanol content (wt%)	0.2 (Max)	EN 14110	0.2	EN 14110
Water content (mg/kg)	500 (Max)	EN ISO 12937	500 (Max)	D2709
Sulfur content (mg/kg)	10 (Max)	EN ISO 20884	S15 15 (Max) S500 500 (Max)	D5453
Sulfated ash content (%(m/m))	0.02 (Max)	ISO 3987	0.02 (Max)	D874
Phosphorus content (mg/kg)	4.0 (Max)	EN 14107	10 (Max)	D4951
Free glycerol (wt%)	0.02 (Max)	EN 14106	0.02 (Max)	D6584
Total glycerol (wt%)	0.25 (Max)	EN 14105	0.24 (Max)	D6548
Monoglyceride (wt%)	0.8 (Max)	EN 14105	0.40 (Max)	D6584
Diglyceride (wt%)	0.2 (Max)	EN 14105	-	-
Triglyceride (wt%)	0.2 (Max)	EN 14105	-	-
Distillation temperature, 90% recovered (°C)	-	-	360 (Max)	D1160
Oxidation stability at 110 °C (h)	8.0 (Min)	EN 14112	3 (Min)	EN 15751
Linolenic acid methyl ester (wt%)	12.0 (Max)	EN 14103	-	-
Polyunsaturated (≥ 4 double bonds) methyl esters (wt%)	1.0 (Max)	EN 15779	-	-
Alkaline metals (Na^+ K) (mg/kg)	5.0 (Max)	EN 14109	5 (Max)	EN 14538

Property(unit)	EN Limits	Test methods	ASTM Limits	Test methods
Alkaline earth metals (Ca^+ Mg) (mg/kg)	5.0 (Max)	EN 14538	5 (Max)	EN 14538
Total contamination	24 (Max)	EN 12662	-	-

2.1.2 Potential reaction involving for biodiesel production

(1) Transesterification

To convert triglycerides and alcohol into biodiesel and glycerol, a catalyst is used to facilitate a series of reactions. The overall reaction involves the triglyceride molecule reacting with three molecules of methanol and a catalyst to produce three molecules of biodiesel and one molecule of glycerol, as represented by Equation (1). In consecutive reaction, the conversion of triglycerides into diglycerides and monoglycerides occurs as intermediate steps, with the number of fatty acids or esters in the molecule determining whether it is a diglyceride or monoglyceride. As the reaction proceeds, the triglycerides release the fatty acid, which is replaced by a hydroxide group, leading to the formation of a diglyceride and biodiesel. This process is repeated, resulting in the formation of a monoglyceride and biodiesel. Finally, the monoglyceride is converted into glycerol and biodiesel, as represented by Equations (2)-(4) [16].

$$C_3H_5(OOCR)_3 + 3CH_3OH \leftrightarrow CH_3OOCR + C_3H_5(OH)_3 \qquad (1)$$
$$(TG) \qquad (Methanol) \quad (Biodiesel) \quad (Glycerol)$$

$$C_3H_5(OOCR)_3 + 3CH_3OH \leftrightarrow CH_3OOCR + Diglyceride \qquad (2)$$
$$(TG) \qquad (Methanol) \quad (Biodiesel) \qquad (DG)$$

$$Diglyceride + 3CH_3OH \leftrightarrow CH_3OOCR + Monoglyceride \qquad (3)$$
$$(DG) \qquad (Methanol) \quad (Biodiesel) \qquad (MG)$$

$$Monoglyceride + 3CH_3OH \leftrightarrow CH_3OOCR + C_3H_5(OH)_3 \qquad (4)$$
$$(MG) \qquad (Methanol) \quad (Biodiesel) \quad (Glycerol)$$

(2) Esterification

Free fatty acid (FFA) can be converted into biodiesel. A one mole of FFA reacts with methanol forming one mole of biodiesel and water as shown in Equation (5). Most catalysts use a strong homogeneous acid catalyst, such as H_2SO_4.

$$HOOCR + 3CH_3OH \leftrightarrow CH_3OOCR + H_2O \qquad (5)$$
$$(FFA) \quad (Methanol) \quad (Biodiesel)(Water)$$

(3) Saponification

Triglyceride and biodiesel can react with basic species (HO^-) leading to the formation of the sodium salt of a long-chained carboxylic acid, commonly known as soap [17]. This is highly undesirable due to catalyst consumption, which reduce biodiesel yield [18] as shown in Equations (6)-(7).

$$C_3H_5(OOCR)_3 + 3NaOH \leftrightarrow 3Soap + C_3H_5(OH)_3 \qquad (6)$$
$$(TG) \qquad\qquad\qquad\qquad\qquad\qquad (Glycerol)$$

$$CH_3OOCR + NaOH \leftrightarrow Soap + CH_3OH \qquad (7)$$
$$(Biodiesel) \qquad\qquad\qquad\qquad (Methanol)$$

(4) Hydrolysis

Low-quality raw materials such as waste cooking oil contain high moisture content, which leads to a significant hydrolysis rate of TG, as illustrated in Equation (8) [19]. This reaction results in the formation of FFA and glycerol. The increased presence of FFA leads to the production of more soap [20].

$$C_3H_5(OOCR)_3 + 3H_2O \leftrightarrow 3HOOCR + C_3H_5(OH)_3 \qquad (8)$$
$$(TG) \qquad (Water) \quad (FFA) \quad (Glycerol)$$

2.1.3 Catalysts for biodiesel production

Biodiesel production typically uses homogeneous base catalysts, such as NaOH and KOH, which can readily dissolve in methanol [21]. The advantage of using homogeneous base catalyst can produce high biodiesel yield in a short reaction time under mild operating conditions due to their higher catalytic activities compared to homogeneous acid catalysts with 4,000 times faster reaction rate. However, the major drawback of homogeneous catalysts is difficult to separate from the reaction mixture, making them non-reusable or non-regenerable. In addition, they are corrosive to reactors and their separation from the reaction mixture is more difficult [22].

The development and utilization of heterogeneous catalysts to produce biodiesel has gained significant attention. Solid or heterogeneous catalysts can be conveniently retrieved, rejuvenated, and reused, while also reducing the necessity for biodiesel and glycerol purification steps. Nevertheless, the existing three phases (oil/alcohol/catalyst) in the reaction mixture presents a mass transfer resistance challenge when using heterogeneous catalysts. When compared to a homogeneous catalyst, a solid catalyst generates lower conversions, which necessitates more stringent reaction conditions to achieve similar conversions [23]. Therefore, the conventional biodiesel production process is still used homogeneous catalyst based on the economical consideration.

2.1.4 Feedstocks

Biodiesel production can utilize various types of feedstocks, including both edible and non-edible vegetable oils as well as waste cooking oils. It is nonpolar and do not dissolve in water, but dissolve in organic solvents. The primary differences between feedstocks are the varying distributions of fatty acids and the elevated levels of FFA in the fats. Table 2 provides a reference for the fatty acid profiles and FFA content of certain various oils.

Table 2 Fatty acid composition and FFA of different feedstocks [24-30].

Feedstock	Palmitic (wt%, C16:0)	Stearic (wt%, C18:0)	Oleic (wt%, C18:1)	Linoleic (wt%, C18:2)	Linolenic (wt%, C18:3)	FFA (wt%)
Palm	45	4	39	11	-	0.1-5

Feedstock	Palmitic (wt%, C16:0)	Stearic (wt%, C18:0)	Oleic (wt%, C18:1)	Linoleic (wt%, C18:2)	Linolenic (wt%, C18:3)	FFA (wt%)
Sunflower	3-10	1-10	14-35	55-75	<0.3	0.1-1
Soybean	7-14	1.4-5.5	19-30	44-62	4-11	0.05-1
Coconut	7-10	1-4	5-8	1-3	-	0.1-0.5
Jatropha curcas	10-17	5-10	36-64	18-45	2.4-3.4	1-6
Waste cooking oil	24.6	18.4	46.0	3.9	0.3	2-15

2.2 Conventional biodiesel production process

Biodiesel production process can be conducted in batch, semi-batch/semi-continuous, or continuous modes, each with its own advantages and disadvantages, depending on how the steps are carried out. A typical biodiesel production plant consists of four steps as follows:

2.2.1 Biodiesel production unit

This step typically involves adding methanol or ethanol to the vegetable oil or animal fat, along with a catalyst such as NaOH or KOH. The mixture is heated to a temperature of 50-60 °C and allowed to react for one hour. In this step, the transesterification occurs under specific conditions, resulting in the production of biodiesel (FAME) and its by-products. In modern industrial facilities, which produce over 4 million liters per year, a continuous stirring reactor (CSTR) is used. However, smaller facilities use a batch reactor with a fixed volume [31].

2.2.2 Methanol recovery unit

The unreacted methanol present in the mixture can hinder the separation of products. However, excess methanol is usually not removed until complete separation of FAME and glycerol. To achieve high FAME production rate by shift the reaction equilibrium towards it, a higher amount of methanol feedstock than the stoichiometrically is required based on the Le Chatelier's principle. Although the reaction can also be shifted by increasing the temperature, the degradation of glycerol may limit the temperature range of operation [31] as well as high energy consumption. Vacuum distillation for methanol recovery is typically used because it takes advantage of the fact that reducing pressure lowers the flash point. The use of a vacuum reduces energy requirements, and the stream leaving the reactor is typically warm, making the separation process energy-efficient with only some vacuum needed. Moreover, it is a closed system, so there is minimal chance of methanol escaping into the environment.

2.2.3 Product separation unit

After the recovery of methanol comes the separation of biodiesel and glycerol. Biodiesel is non-polar and less dense than water, whereas glycerol is polar and higher density than water, allowing for separation. Due to the immiscible phase and huge differences in density between glycerol and FAME, a large portion of the glycerol produced from the reaction can be separated mechanically (centrifuge) or by a two-phase liquid-liquid separator (settling tank) [31].

(1) Settling tank

In settling tanks, gravity is utilized to separate substances according to their density. This is an inexpensive process, known as a passive system, that does not require significant energy input. The practicality of this method is largely determined by the flow rate of the reactor and the rate of separation. These factors dictate the necessary size of the settling tank to ensure sufficient separation of glycerol from FAME before it leaves the tank [32].

(2) Centrifuge

Effective separation is provided by centrifuges, as substances based on density difference could be separated, with the denser liquid (in this case, glycerol) being pushed toward the outside of a cylinder by centrifugal force imparted by a spinning rotor or by the cylinder itself rotating. However, centrifuges require more maintenance and come at a higher cost compared to settling tanks as they involve moving parts [32].

Further purification is required to achieve the high level of purity needed to meet standards. This is accomplished through the final biodiesel and glycerol purification system, which includes an important step of neutralizing and removing methanol from the FAME stream. The neutralization process reduces the pH level and produces salts, and the methanol impurities are then separated through a distillation column.

2.2.4 Biodiesel purification

The main objective of biodiesel washing is to eliminate any free glycerol, excess soap, alcohol, and leftover catalyst. To meet the standard requirements for water content in the purified biodiesel product, it is necessary to separate the biodiesel. Based on the main mechanism, the purification techniques used thus far to refine crude biodiesel can be categorized into two main groups:

(1) Wet washing

Distilled water or acidulated water (a solution of mineral acid in water) is used for wet washing to neutralize biodiesel as well as remove some glycerol using water at either room temperature or heated water. Comparing purified biodiesel from castor oil, it was found that washing with water at different temperatures and pH levels showed significant results at 30 and 70 °C with a pH of 2 and 7, as opposed to other temperatures (20-90 °C) within a pH range of 1-7 [33, 34]. The advantages of wet washing are a simple and effective method for purifying biodiesel and can remove glycerol and methanol effectively. However, it requires a large amount of water, and the washed product must be evaporated to remove trace amounts of water, which increases energy costs. Additionally, washing and settling tanks are necessary and occupy a large surface area.

(2) Dry washing

Dry washing is a water-free purification method developed as an environmentally friendly as alternative to wet washing. It involves using waterless washing agents, such as adsorbents and acid resins, to remove impurities from crude biodiesel. Dry washing has several advantages, including eliminating the risk of water in the fuel, enabling continuous operation, reducing the total production time, and significantly decreasing wastewater production. However, because it requires the use of absorbents and additional equipment, dry washing may not be cost-effective in certain industrial settings [35]. Therefore, the TEA should be performed as a guideline of dry washing process utilization.

2.3 Process intensification for biodiesel production

Biodiesel production is an essential process that requires several steps, including feedstock preparation, transesterification, separation, washing, and purification. However, these steps require significant amounts of energy and resources, which can make the biodiesel production process economically unsustainable and environmentally unfriendly. Process intensification (PI) has emerged as a promising approach to enhance the performance of each process in biodiesel production while minimizing energy consumption and reducing waste generation. One innovative PI technique is the rotating tube reactor, which has been shown to significantly increase the reaction rate and conversion of RPO or WCO to biodiesel (FAME).

2.3.1 Rotating tube reactor

RTR has attracted considerable attention as a process intensification technology that improves mixing performance, addressing the issue of immiscibility between vegetable oil and alcohol during transesterification and providing sufficient heat for biodiesel production [6]. The RTR mainly consists of two parts, namely, a rotor and a stator. The stator remains stationary while the rotor rotates at high speeds, creating a thin film of substances inside the reactor. This results in an increase in the interfacial area of the reactant and the generation of heat due to the shear force in the narrow gaps of the reactor [7]. Improving both mass and heat transfer can result in a reduced residence time for biodiesel production in the RTR. This reactor has a comparatively shorter residence time than other intensification reactors, which ultimately leads to decreased energy consumption [36].

Figure 1 shows the Tylor vortices generation inside RTR which is one of couette flow device.

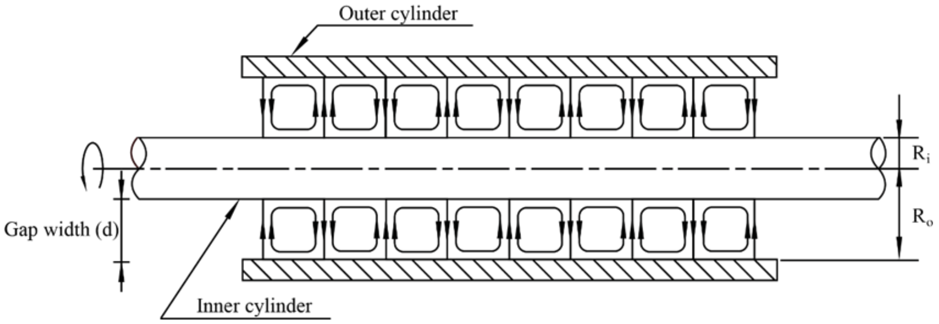


Figure 1 Tylor vortices generation inside RTR reactor [8].

2.4 Techno-economical assessment (TEA)

TEA is the total capital investment, cost of manufacturing, and revenue of a biodiesel production plant. The concepts and methods necessary for this evaluation can be found in specialized books by Turton et al. [37]. The key concepts and methods will be discussed below.

2.4.1 Total capital investment

The total capital investment (TCI) comprises fixed capital investment (FCI), working capital cost (WC), and land cost (L). The FCI is determined by adding the costs of auxiliary facilities to the total module cost (CTM), which is the sum of the bare module cost (CBM) and the costs of contingency and fees. The cost of auxiliary facilities can be assumed to be around 50% of CBM, within the range indicated by Turton [37], while the costs of contingency and fees are typically assumed to be 15% and 3% of CBM, respectively. FCI can be equated with the grassroots cost (CGR), which is approximated by Equation (9).

$$C_{\mathrm{GR}} = 1.68 \sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{C}_{\mathrm{Bm,i}}^{\mathrm{o}} \tag{9}$$

where $\mathrm{C}_{\mathrm{Bm,i}}^{\mathrm{o}}$ is the bare module cost of equipment i at base condition.

Therefore, the key parameter is C_{BM}, which related to the equipment purchase and subsequent installation. The method for calculation of the bare module cost is exponent estimation. The method involves utilizing operational plant data to estimate the capital cost of a new plant by applying the capacities ratio to a specific exponent. Generally, the six-tenths-factor rule is applied to all equipment in this process. It is very useful to scale up/down to a new capacity thus obtaining the impact of a plant size which is approximated by the following Equation (10).

$$\frac{C_n}{C_o} = \left(\frac{A_n}{A_o}\right)^n A_M A_T A_P \tag{10}$$

where: C: approximate cost of old and new equipment (\$, Baht, etc) as depicted Co and Cn, respectively., A: size factor of the equipment (m^2, kW, etc), n: size exponent (usually 0.6), A_M: correction factor due to the manufacturing material, A_T: Correction factor due to the operating temperature, and A_P: correction factor due to the operating pressure. Note that Equation (10) if A_M, A_T, and A_P are equal to 1.0 (carbon steel and room operating conditions).

As the cost of equipment purchases is typically obtained from previous years but can vary over time, it is necessary to update it to the current year by utilizing the chemical engineering plant cost index (CEPCI) for both the reference year and the current year. This can be estimated using Equation (11).

$$\mathrm{Cost}_{\mathrm{Current}} = Cost_{\mathrm{Ref}} \frac{\mathrm{CEPCI}_{\mathrm{Current}}}{\mathrm{CEPCI}_{\mathrm{Ref}}} \tag{11}$$

2.4.2 Manufacturing cost

The manufacturing cost (COM) refers to the annual expenses required to operate a plant. This cost can be divided into variable operating costs such as raw materials, utilities or services, and fixed operating costs including general and administrative expenses, maintenance and labor, insurance, management and operation services, marketing, logistics, and others. The COM for biodiesel production process includes expenses associated with raw materials (C_{RW}), utilities (C_{UT}), labor

(C_{OL}), waste treatment (C_{WT}), and other costs. The costs of utilities and waste treatment have been demonstrated in Turton et al. [37]. Equation (12) is used to calculate the manufacturing cost (COM) as follows.

$$COM = 0.180 * FCI + 2.73 * C_{OL} + 1.23 * (C_{UT} + C_{WT} + C_{RM}) \quad (12)$$

2.5 Profitability analysis

Profitability refers to the ability of a business to generate profit, which is which is determined by the disparity between the income earned and all costs and expenses incurred in earning that income. To measure profitability, businesses often use ratios such as return on assets (ROA) or return on investment (ROI) to evaluate the effectively utilized assets to generate profit of company. The profitability of a production process can be enhanced through effective cost management and increased productivity. Additionally, various economic parameters can be employed to assess the profitability of a specific biodiesel production process and to compare it with other available technologies for economic feasibility [1], including:

2.5.1 Net present value

To calculate the net present value (NPV), the present values of all cash flows, including the initial investment (C0), are summed up. The cash flows, represented by Cn, are discounted back to their present value at a suitable hurdle rate (r), considering the time value of money. The NPV is obtained by adding up each net present cash flow (cash inflow minus cash outflow) in year n over the total number of years, N. For a project to be accepted, both the cumulative and total NPV must be positive. [38], as demonstrated in Equations (13)-(14).

$$NPV = C_0 + \sum_{n=1}^{N} \frac{C_n}{(1+IRR)^n} = 0 \quad (13)$$

$$NPV = C_0 + \sum_{n=1}^{N} NPV_n = C_0 + \sum_{n=1}^{N} \frac{C_n}{(1+r)^n} = 0 \quad (14)$$

2.5.2 Internal rate of return

Internal rate of return (IRR) is the interest rate that equates the present value of cash inflows with the present value of cash outflows. In other words, it is the discount rate at which the net present value of a project is equal to zero. This metric provides the rate of return on an investment based on the cash flows generated over a specific period of time. To accept a project, the IRR must exceed a certain hurdle rate [38].

2.5.3 Payback period

Payback period (PBP) is the duration required to recover the initial investment with revenues generated from the project's start. Essentially, PBP represents the time, usually in years, it takes for the cash flows produced after discounting the working capital to recoup the initial investment [38].

2.5.4 Rate of return on investment

Rate of return on investment (ROI) is a measure of the effectiveness of an investment in a project, calculated as the difference between revenues and expenses, which have been discounted, in relation to the investment itself [38].

2.6 Literature review

2.6.1 Biodiesel production process

Zhang et al. [39, 40]. developed four distinct continuous processes for producing biodiesel at a rate of 8,000 tons per year using either virgin vegetable oil or waste cooking oil as the raw material. Two of them utilizing alkali catalysts with different feedstock including of virgin vegetable oil (process I) and waste cooking oil (process II). The other two processes (III and IV) used acid-catalyzed waste cooking oil as shown in Figure 2, 3, 4 and 5, respectively. All four methods were feasible for producing high-quality biodiesel and glycerol by-products under reasonable conditions, but it still had some limitations. The simplest process, process I, was the alkali-catalyzed process using virgin oil, which required fewer pieces of equipment but had a higher cost of raw material. Process II utilized alkali catalyzed WCO to lower raw material cost, but it required a pre-treatment unit for free fatty acid removal. Process III using an acid-catalyzed process for WCO, it required less equipment than process II, but also required more methanol supplement, resulting in a larger size of transesterification reactors as well as methanol/water distillation columns. Process IV was similar to process III, but it used of hexane solvent increased the number and size of some separation units such as hexane extraction and methanol/water recovery column in process IV. The economic viability of four continuous biodiesel production processes with an 8,000 ton/year capacity was assessed, and the results showed that the alkali-catalyzed process with virgin vegetable oil had the lowest fixed capital cost. However, the acid-catalyzed process with waste cooking oil was deemed more economically feasible overall due to its lower total manufacturing cost, more attractive after-tax rate of return, and lower biodiesel break-even price. Sensitivity analyses were performed based on these economic calculations, and it was discovered that the plant's capacity and the prices of feedstock oils and biodiesel were the most significant factors affecting the economic feasibility of biodiesel production.

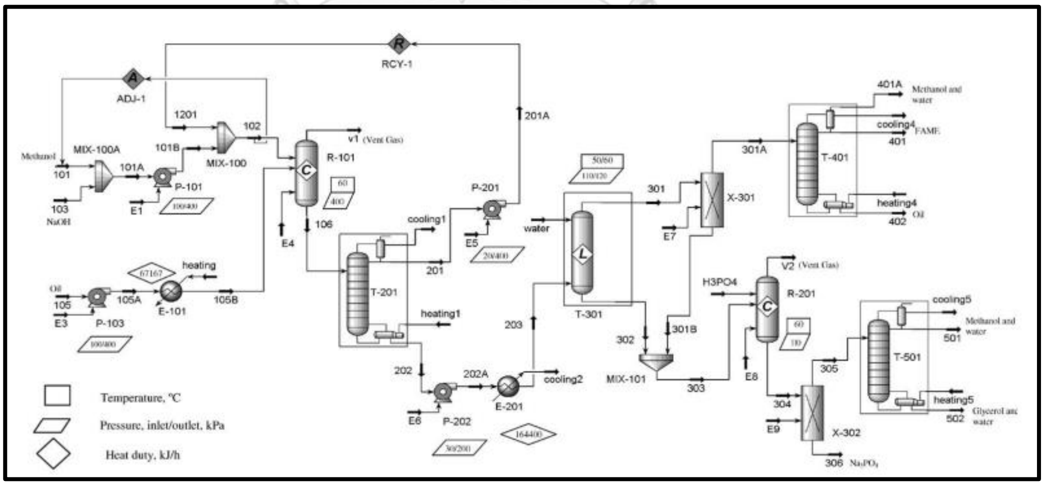


Figure 2 Alkali-catalyzed process to produce biodiesel from virgin oil [39].

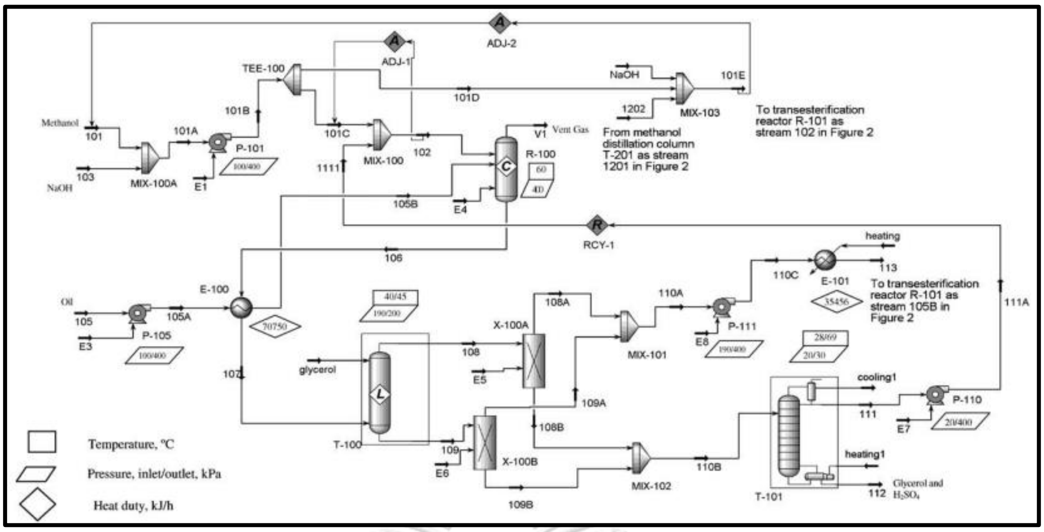


Figure 3 Acid-catalyzed process for pretreatment of WCO prior to alkali-catalyzed to produce biodiesel [39].

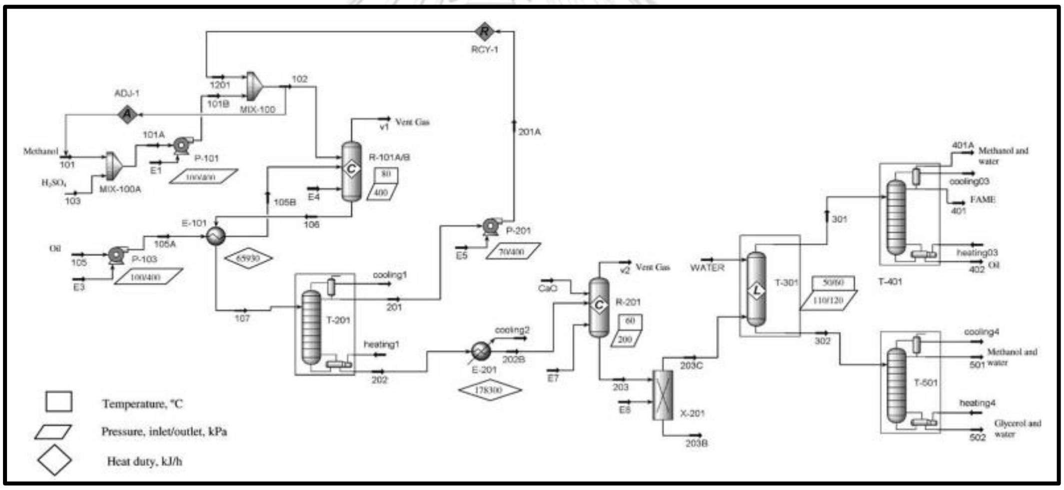


Figure 4 Acid-catalyzed process to produce biodiesel from WCO [39].

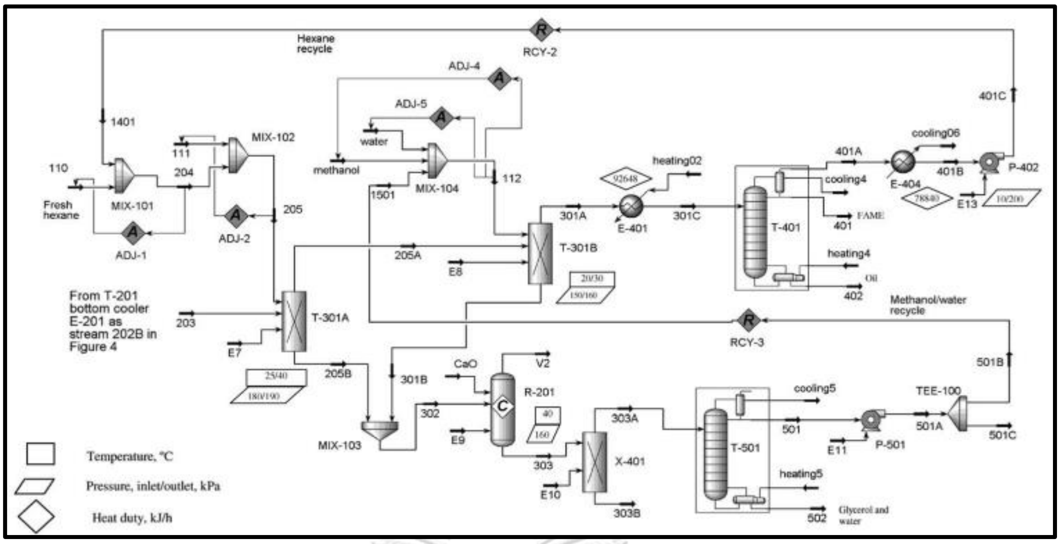


Figure 5 Alternative acid-catalyzed process to produce biodiesel from WCO using hexane extraction [39].

Boon-anuwat et al. [41] developed a continuous biodiesel production process using reactive distillation to overcome the thermodynamic limitations of conventional transesterification processes. The study involved designing and simulating four continuous biodiesel production processes, utilizing homogeneous alkali-based catalysts and heterogeneous acid-based catalysts for both conventional reactor/distillation and reactive distillation setups. The researchers analyzed important design and operating parameters to identify the best conditions for each process. The result showed that the homogeneous alkali-catalyzed RD process did not only eliminate the need for product separation and purification but also improve biodiesel yield while reducing methanol feedstock and energy consumption as compared to the sequential reaction and distillation method. Moreover, the homogeneous alkali-catalyzed RD process had the highest biodiesel productivity of 862 kg/h due to a lower methanol to oil molar ratio than the conventional RD process. In addition, using heterogeneous magnesium methoxide catalyst offers several benefits, including reducing the number of unit operations, lowering energy consumption, and eliminating the need for neutralization, wastewater disposal, or salt waste processing.

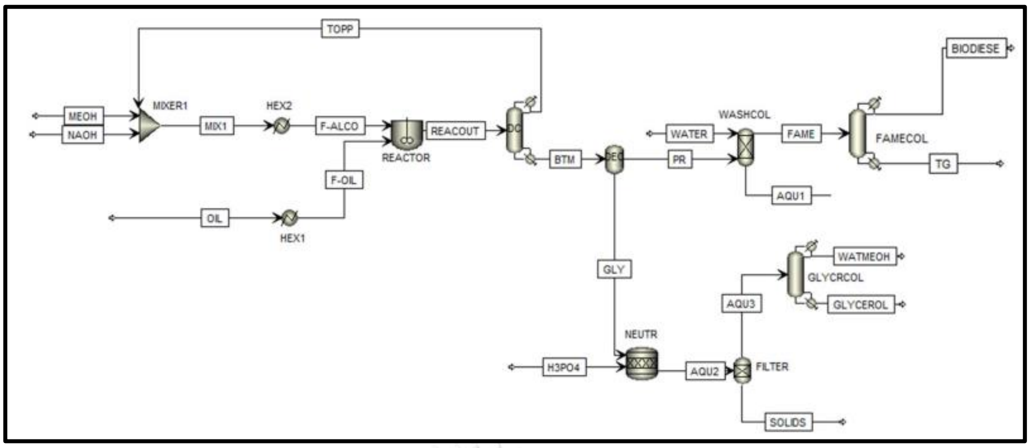


Figure 6 Conventional process for biodiesel production using homogeneous catalyst [41].

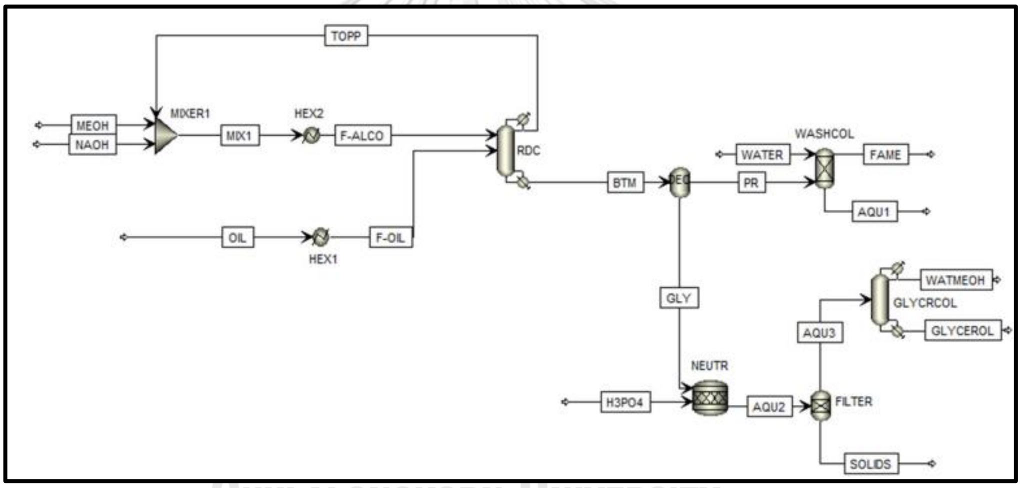


Figure 7 Biodiesel production process by reactive distillation column using homogeneous catalyst [41].

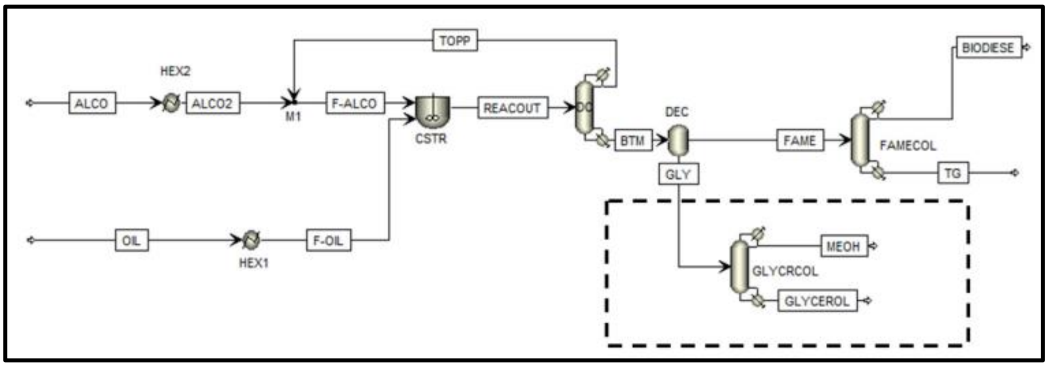


Figure 8 Conventional process for biodiesel production using heterogenous catalyst [41].

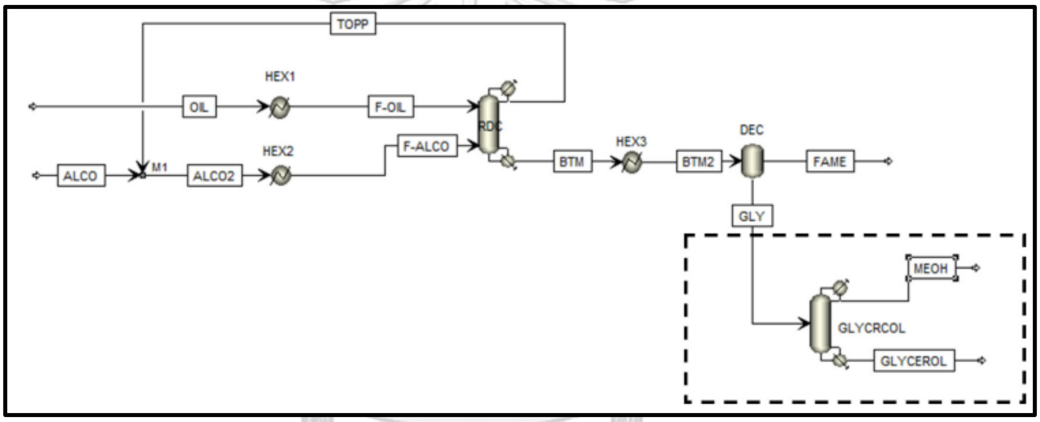


Figure 9 Biodiesel production process by reactive distillation column using heterogeneous catalyst [41]

2.6.2 RTR reactor for biodiesel production using alkali catalyst

Lodha et al. [42] investigated biodiesel production via transesterification of canola oils with alcohols and NaOH in the RTR reactor for continuous production by varying rotational speed, flow rate, temperature, and catalyst concentration. The result found that biodiesel yield of approximately 98% was obtained using the residence time of 45 s under the operating temperature range of 40–65 °C in RTR reactor. This was due to the RTR reactor was found to generate a thin liquid film due to strong shear forces, which enhanced heat and mass transport rates.

Chanthon et al. [8] explored hydrodynamic regime inside the RTR reactor to enhance the biodiesel production rate using alkali-catalyzed transesterification of RPO. The result showed optimal operating condition to be g 6:1 of methanol-to-oil molar ratio, 1 wt% of NaOH, total flowrate of 30 mL/min and rotational speed of 1,000 rpm operated continuously at room temperature giving the highest yield of 97.5% with yield efficiency of 3.75×10^{-3} g/J and the quality of biodiesel was conformed to the ASTM standard. It is worth noting that using the RTR (a tubular reactor) for biodiesel production offers the advantage of continuous operation with less energy consumption, as an external heat source is not required.

2.6.3 Biodiesel purification process

Banga et al. [10] compared the effectiveness of biosorbents and organic adsorbents in purifying biodiesel obtained through a two-stage synthesis process using higher fatty acid Jatropha curcas oil. The study utilized banana peel and Pleurotus species mushroom as biosorbents, and Amberlite BD10 DRY, Purolite PD 206, and Tulsion T-45BD as organic adsorbents. Uisng Purolite PD206 was highly efficient to purify biodiesel, with the ability to adsorb methanol and glycerol over 98 and 93%, respectively. Interestingly, the result also found that some naturally occurring adsorbents derived from bio-waste, such as banana peel, are equally effective in removing contaminants from biodiesel, and their effectiveness was comparable to that of other organic adsorbents. This may be attributed to the microporous nature of these adsorbents and the presence of functional groups in their structure. Unfortunately, the residual methanol, potassium content, and free and bonded glycerol levels were under the EN 14214 maximum limits for all the organic and natural adsorbents tested.

Santos et al. [43] studied of statistical design to optimize conditions for using chamotte clay as adsorbent for glycerol removal during the purification of biodiesel. The optimal conditions for maximum glycerol removal were achieved by using 5 w/v% chamotte at 50°C. The purified biodiesel met the established specifications of

EN 14214 and ASTM D6751 standards with over 98% glycerol removal from crude biodiesel and FAME content above 98.0 wt%. Chamotte clay showed a high adsorptive capacity, similar to conventional aqueous washing, attributed to its composition of silica and alumina as determined by EDX, XDR, and FT-IR analyses. Chamotte clay, a low-cost waste material, is readily available and could be used as a promising material in biodiesel purification processes or as packing for an extracting column to couple with processes that require simultaneous glycerol removal.

2.6.4 Techno-economic assessment (TEA) for biodiesel production

TEA provide a guideline with making informed decisions about future commercial developments by evaluating the economic viability and potential technical improvements of the process. This makes TEA a valuable tool for decision-making [38].

Apostolakou et al. [44] investigated the affecting of the critical profitability indicators on the production capacity of biodiesel production using traditional alkali-catalyzed transesterification of vegetable oil. According to the findings, the cost of raw materials makes up 75% of the total production expenses for small scale biodiesel plants producing 5 ton/year, and this process can rise to 90% for large scale plants that produce between 30,000 to 140,000 ton/year. Additionally, operating small scale plants with a capacity of less than 15,000 ton/year is not recommended because of its profitability. However, plants with capacities greater than 50,000 to 80,000 ton/year are considered economically viable based on economic analysis.

Karmee et al. [4] investigated the feasibility of low-cost materials such as WCO used as feedstock for biodiesel production capacity of 8,000 ton/year. There are three different catalysts such as acid, base, and lipase were tested to determine the most cost-effective method of biodiesel production. The study conducted economic analyses and compared the results to identify the optimal approach. Additionally, sensitivity analyses were performed on the WCO and biodiesel prices to determine the internal rate of return (IRR). Using acid catalyst was the most economical, while the lipase catalyst process was the most expensive. Furthermore, the acid catalyst demonstrated an acceptable IRR even with fluctuations in WCO and biodiesel prices based on 15 years.

Gholami et al. [45] investigated the potential of ultrasonic cavitation as an intensification method in term of techno-economic perspective. Two plants for capacity of 50,000 ton/year, one using conventional mechanical stirring and the other using ultrasonic cavitation, were designed in Aspen HYSYS V8.4 for comparison. In order to compare two processes, the total investment, product costs, net present value, and internal rate of return were evaluated. The study found that the ultrasonic cavitation process required a lower total investment by approximately 20.8% and reduced product costs by 5.2% when compared to the mechanical stirring process. Moreover, the ultrasonic cavitation process achieved a positive net present value and an internal rate of return of 18.3%, indicating that it was a better option. Additionally, the ultrasonic cavitation process resulted in a significant decrease in energy consumption and waste production, with a reduction of 6.9% in energy consumption and only one-fifth of the waste produced by the mechanical stirring process.

Gholami et al. [46] evaluated the feasibility of utilizing hydrodynamic cavitation to enhance transesterification in industrial biodiesel plants. Aspen HYSYS V8.4 was used to simulate-based model that compared biodiesel production in the hydrodynamic cavitation to conventional mechanical stirring based on total capital investment, total product cost, net present value, modified internal rate of return, materials, and energy consumption. The producing biodiesel 33,000 ton/year from fresh sunflower oil was a basis of this simulation. Results showed that hydrodynamic cavitation provided the lower total capital investment and total product cost compared to mechanical stirring, with approximately 65% and 10% lower, respectively. The net present value was negative for the mechanical stirring process while the hydrodynamic cavitation resulted in a positive net present value and a modified internal rate of return of 25.61%. Sensitivity analysis using Box-Behnken design and response surface methodology showed that the sunflower oil price significantly affected the net present value. The hydrodynamic cavitation process also reduced materials and energy consumption by producing higher reactor yields and reducing alcohol and catalyst consumption.

Aydin et al. [47] investigated TEAs for small scale biodiesel production from transesterification of palm oil with methanol and homogeneous alkaline catalyst by conventional process, typically less than 1,000 L/day. This study found that the small-scale biodiesel production can be economically feasible and had the potential to provide significant economic benefits, particularly in rural areas having a high availability of feedstocks. However, the profitability of small-scale biodiesel production was highly depended on the feedstock cost, the type of technology used, and the availability of government incentives.

Zhang et al. [48] revealed the TEAs of medium scale biodiesel production from transesterification of soybean oil with methanol and homogeneous alkaline catalyst by conventional process, typically between 1,000 to 10,000 L/day. The medium scale biodiesel production can be economically viable, with the potential to provide significant economic benefits and create new jobs. However, the profitability of medium scale biodiesel production was also depended on the cost of feedstock, the efficiency of the production process, and the market price of biodiesel.

Verma et al. [49] presented the TEAs for large scale biodiesel production from transesterification of WCO with methanol and homogeneous alkaline catalyst using conventional process, typically greater than 10,000 L/day for industrial scale. Large scale biodiesel production can be economically viable and profitable, particularly when produced from low-cost feedstocks. However, the profitability of large-scale biodiesel production was still depended on the efficiency of the production process, the market price of biodiesel, and government incentives.

Overall, the TEAs of biodiesel production at various scales have demonstrated that biodiesel can be economically feasible and profitable, particularly when produced from low-cost feedstocks and using efficient production technologies. However, the profitability of biodiesel production is strongly depended on a range of factors, including the cost of feedstock, the type of technology used, and government incentives. Therefore, it is essential to conduct a thorough TEA before investing in biodiesel production to assess its economic feasibility and potential profitability [50].

CHAPTER 3

EXPERIMENTAL AND SIMULATION

3.1 Materials

Refined palm oil (RPO) was obtained from Morakot Industry Co. Ltd., while waste cooking oil (WCO) was acquired from a canteen located in the Faculty of Engineering at Chulalongkorn University, Thailand. The suspended food particles in the WCO were removed by filtration and subsequently heated to 110°C for 2 h to remove water. Sodium hydroxide (NaOH) with 99% purity, used as a catalyst for transesterification, was obtained from Supelco. In addition, sulfuric acid (H_2SO_4) with 98% purity, used as a catalyst for esterification, methanol (CH_3OH), and potassium hydroxide (KOH) were purchased from KEMAUS. Methyl heptadecanoate was purchased from Sigma-Aldrich. Heptane solvent (C_7H_{16}) with 99% purity was obtained from QRëC. Phenolphthalein ($C_{20}H_{14}O_4$) was purchased from LABCHEM.

3.2 Biodiesel synthesis

3.2.1 RPO feedstocks

Biodiesel production was carried out using a rotating tube reactor (RTR) with a methanol to palm oil molar ratio of 6:1, 1 wt% NaOH catalyst based on oil weight, a total flowrate of 30 mL/min and a rotational speed of 1,000 rpm as optimum condition obtained from the previous work [8]. Figure 10 illustrates the rotating tube reactor (RTR) set-up for the reaction.

3.2.2 WCO feedstock

Free fatty acids (FFAs) containing in WCO directly contributes to its acid value. If the acid value of WCO exceeds 2 wt% FFA, the probability of soap production via saponification is more dominated. Therefore, pretreatment process such as esterification was applied to reduce the FFA in WCO by converting to FAME. To address this, the esterification-transesterification study started with WCO pretreatment was carried out using a rotating tube reactor (RTR) with a methanol to

WCO ratio of 12:1, 1 wt% H_2SO_4 catalyst based on oil weight, and a rotational speed of 1,000 rpm and total flowrate of 30 mL/min. Figure 10 illustrates the rotating tube reactor (RTR) set-up for the reaction. The esterification of FFA was conducted at a temperature of 60 °C. H_2SO_4 catalyst was dissolved in methanol in a separate vessel. Then, two feed of oil and the mixture solution of H_2SO_4 and methanol were continuously sent to RTR reactor. The reaction period was tested for 0.5-2 h to ensure that the FFA content was lower than 0.5 wt% with steady state operation. The pretreated WCO was separated from the reaction mixture using a separatory funnel, where the methanol was in the upper layer and the pretreated WCO was in the lower layer due to the difference in density. Then, the pretreated WCO was placed on a hot plate to evaporate the residue of methanol at 70°C. Finally, the mixture was stored in a plastic bottle to prevent moisture absorption for the further transesterification following the similar step using RPO feedstock.

There were two steps for transesterification process to completely convert WCO to biodiesel. The first step was initiated using a methanol to WCO molar ratio of 6:1, a 1 wt% NaOH catalyst based on the oil weight, a total flow rate of 30 mL/min, and a rotational speed of 1,000 rpm in RTR reactor. These conditions were determined as the optimum condition based on previous work [8]. Additionally, various temperatures were tested to achieve high biodiesel yield. In the second step, a methanol to WCO molar ratio of 18:1, a 0.5 wt% NaOH catalyst based on the left-over oil weight, a total flow rate of 30 mL/min, and a rotational speed of 1,000 rpm was utilized to completely convert WCO to biodiesel in RTR reactor. This should be noted that the methanol to oil molar ratio of 18:1 was selected because of the limitation of pump for the minimum feeding methanol flow rate to the RTR reactor.

3.3 Free fatty acids (FFA) content analysis

The oil was weighed at 4.0 g and transferred into a 250 mL Erlenmeyer flask. Then, 50.0 mL of neutral ethyl alcohol was added to the flask. The neutral ethyl alcohol was prepared by adding phenolphthalein and neutralizing ethyl alcohol with potassium hydroxide (KOH) 0.1 N. Finally, the mixture was titrated with KOH 0.1 N until the endpoint was reached as indicated by the change of the mixture color to the pink solution for 1 min. The percentage of FFA in the sample was calculated using Equation (15).

$$FFA\% = ((V_{KOH} \times N_{KOH} \times 28.2) / W_{sample}) \times 100 \qquad (15)$$

where V_{KOH} is the volume of NaOH used (ml), N_{KOH} is normality of KOH, which is the concentration of KOH, 28.2 is the correction factor based on the molecular weight of oleic acid (the most common fatty acid in palm oils as well as WCO), and W_{sample} is weight of sample used (g).

3.4 Biodiesel yield analysis using gas chromatography.

The standard solution of methyl heptadecanoate was weighed at 0.05 ± 0.0005 g into a 5 mL bottle. The reaction mixture sample was weighed at 0.0250 ± 0.0015 g. using a micropipette and mixed with 5 mL of n-heptane. The bottle was immediately closed, and the solution was shaken to ensure complete mixing. Then, a 1 μL sample of the solution was injected into a gas chromatography system using a Shimadzu GC-2010 Plus fitted with a DB-WAX capillary column (30 m in length, 0.32 mm in diameter, and 0.25 μm in film coating) and detected by a flame ionization detector (FID). Helium and nitrogen were used as a carrier and make-up gas, respectively. For GC analysis, the temperature was initially set to 150 °C for a holding time of 5 min, then raised to 190 °C at a rate of 3° C/min and held for another 5 min. Finally, the temperature was increased to 220 °C at a rate of 3 °C/min and maintained for an additional 5 min. The yield of biodiesel was calculated using Equation (16).

$$\text{Biodiesel yield (\%)} = ((\sum A - A_{mh}) / A_{mh}) \times (C_{mh} \times V_{mh} / M_b) \times 100 \qquad (16)$$

where $\sum A$ is total area of fatty acid methyl ester, A_{mh} is area of methyl heptadecanoate (internal standard), C_{mh} is concentration of methyl heptadecanoate (mg/mL), V_{mh} is volume of methyl heptadecanoate (mL), and M_b is mass of biodiesel sample (mg).

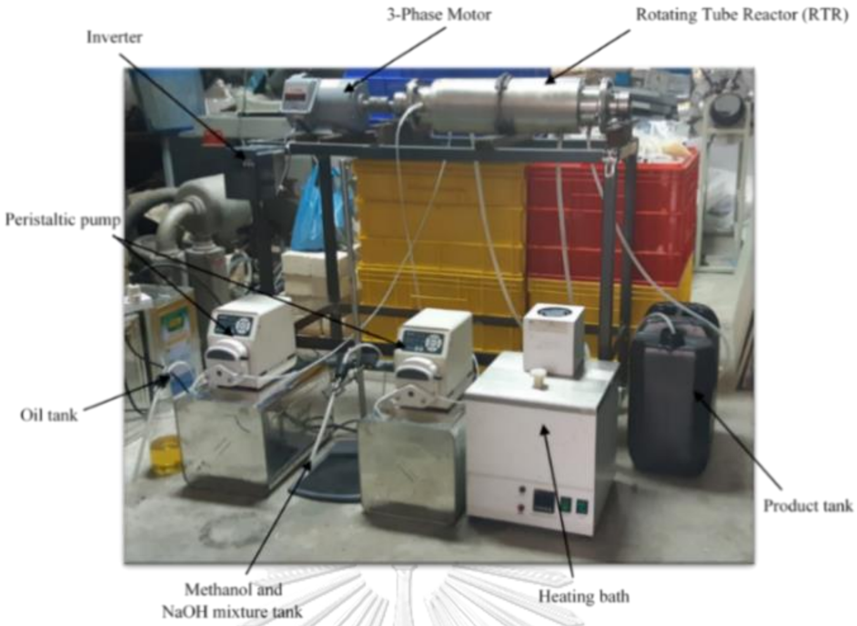


Figure 10 The rotating tube reactor (RTR) set-up for biodiesel production [8].

3.5 Process simulation

The simulation of the process was carried out using commercial process simulation software called Aspen Plus V11. The simulation was set-up by selecting the necessary chemical components and a thermodynamic model within the Aspen Plus V11 program. All components used in this work for simulation are available in the Aspen Plus library. Dortmund-modified UNIFAC model was used as the thermodynamic model to deal with liquid-liquid equilibrium (LLE), and vapor-liquid equilibrium (VLE) [51]. Moreover, non-random two liquid (NRTL) was also used for the interaction of reaction in the system such as transesterification, esterification, and chemical for precipitation. Feedstocks of this process comprised of RPO and WCO. The composition of RPO and WCO are shown in Tables 3 and 4, respectively. WCO was calculated based on the similar composition of RPO with addition of oleic acid as selecting for FFA model compound. The feedstock composition from Tables 3 and 4 was for A1, A2, B1, B2 and C1 cases while the WCO composition illustrated in Table 5 was used for C2 case.

Table 3 Components of RPO [52] for A1, B1 and C1 cases.

Main component	Mass composition (%)
Tripalmitin	45.0
Triolein	40.1
Trilinolein	10.3
Tristearin	4.6

Table 4 Components of WCO from experiment for A2 and B2 cases.

Main component	Mass composition (%)
Tripalmitin	44.6
Triolein	39.8
Trilinolein	10.2
Tristearin	4.6
Oleic acid	0.8

Table 5 Components of WCO from Zhang [39] for C2 cases.

Main component	Mass composition (%)
Tripalmitin	42.3
Triolein	37.7
Trilinolein	9.7
Tristearin	4.3
Oleic acid	6.0

3.5.1 Design process cases

Case A1: Biodiesel production using RPO in RTR reactor with wet purification method

(1) Transesterification

Transesterification was carried out at room temperature (30 °C) and 1 bar using methanol to oil molar ratio of 6 :1 and 1 wt% NaOH in RTR reactor (R-111) to achieve 97.5% of biodiesel yield and use for simulation based on the best condition from the previous results [8]. Fresh methanol (MEOH) and recycle methanol (steam 3) were fed to mix with sodium hydroxide (NaOH) in the mixer. Two streams of mixed methanol with NaOH and oil were sent to RTR reactor (R-111) to carry out transesterification. Steam 2 as a mixture of product and remaining reactant was also sent to recovery unit for methanol recovery. Since, the kinetic for NaOH catalyzed transesterification in RTR could not perform because of the different condition and mechanism was taking place at the higher temperature. When the temperature was increased the biodiesel yield was decreased due to the methanol vaporization from the excessive heat inside RTR [8]. Therefore, the transesterification condition was used to simulate as presented Table 6.

Table 6 Transesterification information

Reaction	Conversion
Triglyceride + 3Methanol → 3Fatty acid methyl ester + Glycerol	97.06%

(2) Methanol recovery

Distillation unit was used to purify methanol for methanol recovery as presented in Figure 11. 7 stages of distillation using 1.5 reflux ratio was used to separate 70% of methanol (stream 3) from the reaction mixture (stream 2) based on Boon-anuwat [41]. Stream 4 was recycled back to mixed with fresh methanol while the resulting product (stream 5) was sent to washing unit for biodiesel purification.

(3) Water washing (wet washing)

Water washing was used to separate biodiesel (stream 6) from remaining oil, glycerol, methanol and NaOH. The remaining product (stream 5) was sent to decanter (D-111) to separate glycerol methanol and NaOH (stream 10). However, the biodiesel purity in stream 6 was not achieved. The 5 stages of water scrubber unit (L-111) was used to remove glycerol from biodiesel according to EN standard using 6% water based on crude biodiesel weight operated at 30°C [41]. Process flow diagram is illustrated in Figure 11.

(4) FAME purification

Distillation unit was used to achieve biodiesel purity according to EN or ASTM standard. 6 stage of distillation unit (T-112) with reflux ratio of 2 was operated under vacuum to avoid decomposition of FAME. Unreacted oil (stream 9) was at bottom product while biodiesel product (BIODSEL) and mixture of methanol and water (stream 8) was at top of distillation unit as presented in Figure 11.

(5) Neutralization

Neutralization unit was used to remove NaOH from stream 11 using phosphoric acid (H_3PO_4). Sodium phosphate (stream 12) was produced in the neutralization reactor (R-212) at 50°C and 1 bar. 100% conversion of NaOH was basis for this unit. Sodium phosphate (stream 14) was separated from glycerol (stream 11) in the separation unit (S-211). Glycerol (stream 13) was then sent to distillation to increase its purity as presented in Figure11.

(6) Glycerol purification

Glycerol purification was used the increase glycerol purity in stream 14 to conform the commercial glycerol grade using 6 stages of distillation (T-213) where operated under vacuum to avoid glycerol decomposition based on Boon-anuwat [41]. Water and methanol (stream 15) were on the top of distillation and glycerol for sale (GLYCEROL), as presented in Figure 11.

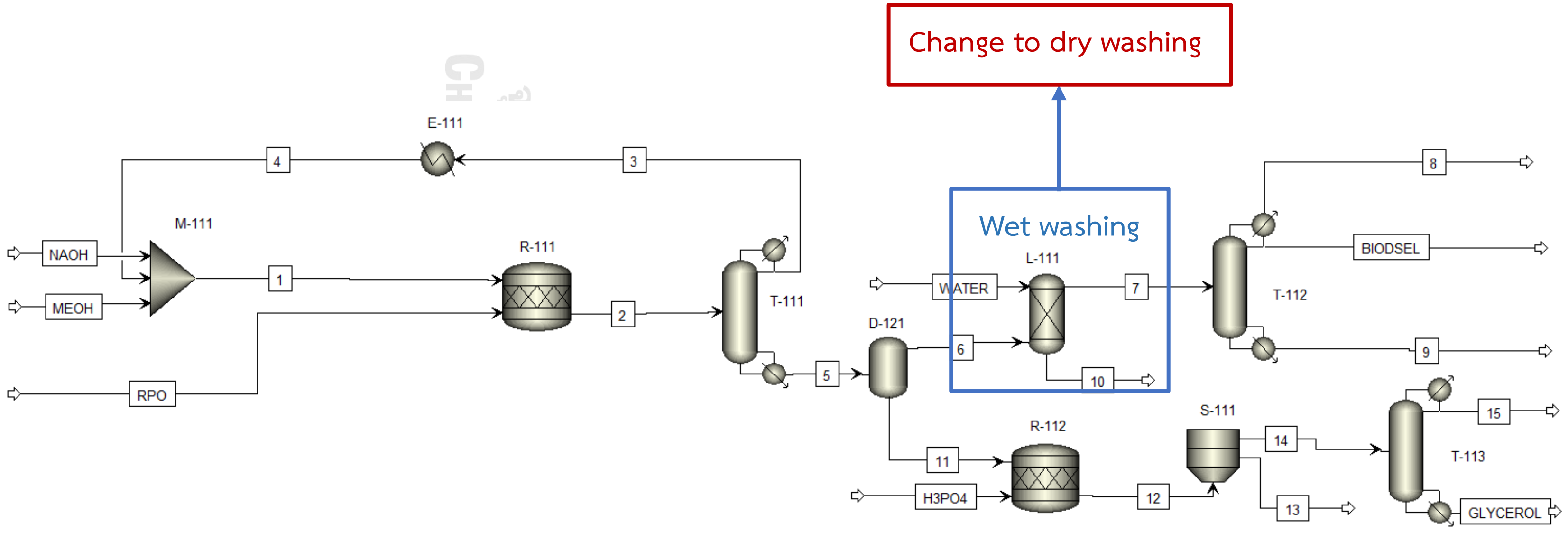


Figure 11 The overall process flow diagram of biodiesel production using RPO in RTR reactor with wet purification method (case A1)

Case A2: Biodiesel production using WCO in RTR with wet purification method.

(1) First step for transesterification of WCO

Transesterification of WCO was carried out at the reaction temperature of 65°C and 1 bar using methanol to oil molar ratio of 6 :1 and 1 wt% NaOH in RTR reactor (R-121). 90.88% of biodiesel yield as well as 91.18% of oil conversion was used to simulated based on the best condition of the experiment run as depicted in Table 7. Fresh methanol (MEOH) and recycle methanol (stream 10) were fed to mixed with sodium hydroxide (NaOH-1) in the mixer. Two streams of mixed methanol with NaOH and oil were heat to 65°C before sent to RTR reactor (R-121) to carry out 1st transesterification step. Steam 4 as a mixture of product and remaining reactant was also sent to decanter unit to separate oil-biodiesel (stream 5) from methanol-glycerol (stream 6) for 2nd transesterification step. Table 6 presents the information of 1st transesterification steps, respectively.

Table 7 1st Transesterification step using WCO feedstock.

Reaction	Conversion
Triglyceride + 3Methanol → 3Fatty acid methyl ester + Glycerol	91.18%

(2) Second step for transesterification of WCO

The 2nd Transesterification step was carried out at high temperature (65°C) and 1 bar using methanol to oil molar ratio of 18 :1 and 0.5 wt% NaOH in RTR reactor (R-122). The experimental result found the FAME content of 95.16% from GC analysis. Therefore, the biodiesel yield and oil conversion were calculated to be 96.51% based on the left-over oil. This value was used to simulated for the final conversion of 2nd transesterification in RTR reactor. Fresh methanol (MEOH-2) was fed to mixed with sodium hydroxide (NaOH-2) in the mixer. Two streams of mixed methanol with NaOH and oil were heat to 65°C before sent to RTR reactor (R-122) to carry out transesterification. Steam 9 as a mixture of product and remaining reactant was also sent to recovery unit for methanol recovery.

(3) Methanol recovery 1

Distillation unit was used to purify methanol for methanol recovery as presented in Figure 12. 7 stages of distillation using 1.5 reflux ratio was used to separate 70% of methanol (stream 9) from the reaction mixture (stream 8) based on Boon-anuwat [41]. Stream 10 was recycled back to mixed with fresh methanol and NaOH while the resulting product (stream 11) was sent to washing unit for biodiesel purification.

(4) Water washing (Wet washing)

Water washing was used to separate biodiesel (stream 13) from remaining oil, glycerol, methanol and NaOH. The remaining product (stream 11) was sent to decanter (D-121) to separate glycerol methanol and NaOH (stream 12). However, the biodiesel purity in stream 14 was not achieved. The 5 stages of water scrubber unit (L-121) was used to remove glycerol from biodiesel according to EN standard using 6% water based on crude biodiesel weight operated at 30°C based on Boon-anuwat [41]. Process flow diagram of wet washing illustrates in Figure 12.

(5) FAME purification

Distillation unit was used to achieve biodiesel purity according to EN or ASTM standard. 6 stage of distillation unit (T-122) with reflux ratio of 2 was operated under vacuum to avoid decomposition of FAME. Unreacted oil (stream 26) was at bottom product while biodiesel product (BIODSEL) and methanol and water (stream 15) was removed at top of distillation unit as presented in Figure 12.

(6) Neutralization

Neutralization unit was used to remove NaOH from mixture stream of stream 6 and 12 to stream 18 using phosphoric acid (H_3PO_4). Sodium phosphate (stream 19) was produced in the neutralization reactor (R-123) at 50°C and 1 bar. 100%

conversion of NaOH was basis for this unit. Sodium phosphate (stream 22) was separated from glycerol (stream 20) in the separation unit (C-121). Glycerol (stream 20) was then sent to distillation to increase its purity as presented in Figure 12.

(7) Glycerol purification

Glycerol purification was used to increase the glycerol purity in stream 20 to produce the commercial glycerol grade using 6 stages of distillation (T-124) under vacuum to avoid glycerol decomposition. Water and methanol (stream 21) were removed from the top of distillation column while glycerol for sale (GLYCEROL) as presented in Figure 12.

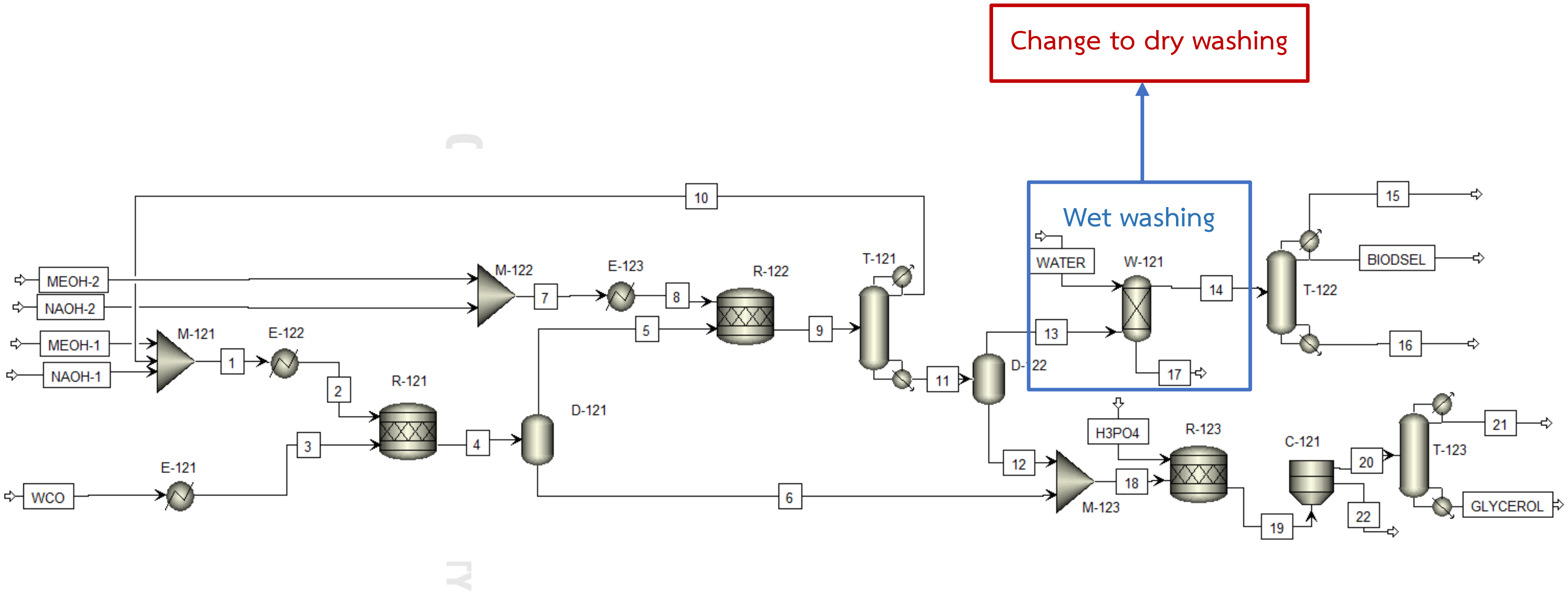


Figure 12 The overall process flow diagram of biodiesel production using WCO in RTR with wet purification method (case A2).

Case B1: Biodiesel production using RPO in RTR reactor with dry purification method (Purolite PD206 adsorbent).

Dry washing process was used to reduce wastewater and increase biodiesel purity instead of wet washing. Purolite PD206 was selected to use an adsorbent for dry washing to separate biodiesel (FAME) from glycerol and methanol because it can adsorb polar compounds such as glycerol and methanol from crude biodiesel. The literature found that using purolite PD206 adsorbent and adsorption temperature of 65 °C can remove glycerol and methanol from crude biodiesel over 93 and 98%, respectively [10]. Crude biodiesel (stream 6) was sent to flash drum (F-211) to vaporize methanol (stream 7). Then, stream 8 was sent to heat exchanger (E-212) to reduce temperature before sending to adsorption column (P-211). 3 wt% of purolite PD206) (based on crude biodiesel) was used to remove impurity of crude biodiesel. Biodiesel (stream 10) after treated with absorbent in P-211 was sent to distillation to increase purity. Process flow diagram of dry washing and the overall process flow diagram of wet washing shown in Figures 13 and 14, respectively. The additional equipment and details on the process simulation of this process are followed by case A1.

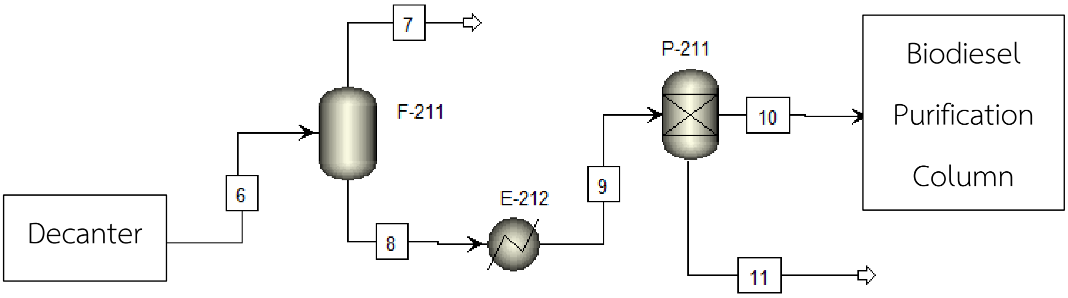


Figure 13 Process flow diagram of dry washing.

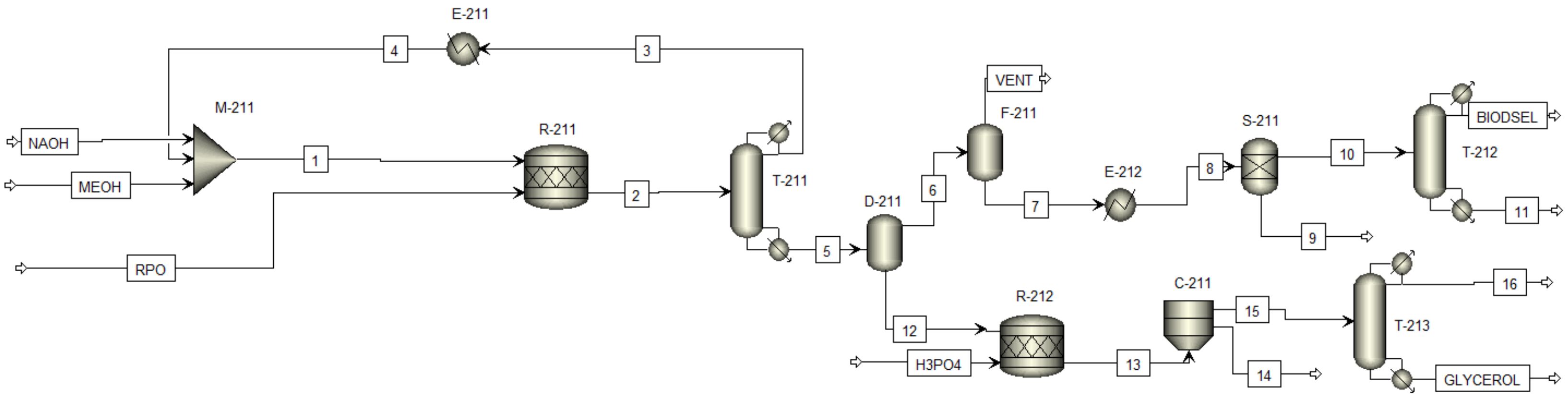


Figure 14 The overall process flow diagram of biodiesel production using RPO in RTR reactor with dry purification method (Purolite PD206 adsorbent) (case B1).

Case B2: WCO in RTR reactor using dry purification method (purolite PD206 adsorbent)

Purolite PD206 was used as adsorbent for dry washing. Process flow diagram of dry washing and the overall process flow diagram of wet washing shown in Figures 13 and 15, respectively. The additional equipment and details on the process simulation of this process are followed by **case A2**.

3.5.2 Conventional cases

CSTR as a conventional reactor for biodiesel production from RPO and WCO as feedstocks was used for transesterification reactor for comparison.

Case C1: Biodiesel production using RPO in a conventional reactor with wet purification method.

The conditions for transesterification included a methanol to oil molar ratio of 6:1, a temperature of 60°C, 0.2 wt% NaOH, and a residence time of 3 h [53]. The additional equipment and details on the process simulation of this process were described by Boon-anuwat et al. [41]. The overall process flow diagram of wet washing is shown in Figure 16.

Case C2: Biodiesel production using WCO in a conventional reactor with wet purification method.

The conditions for transesterification included a methanol to oil molar ratio of 6:1, a temperature of 60°C, 1 wt% NaOH using residence time of 1 h [39]. The additional equipment and details on the process simulation of this process were described by Zhang et al. [39]. The overall process flow diagram of wet washing is shown in Figures 17.

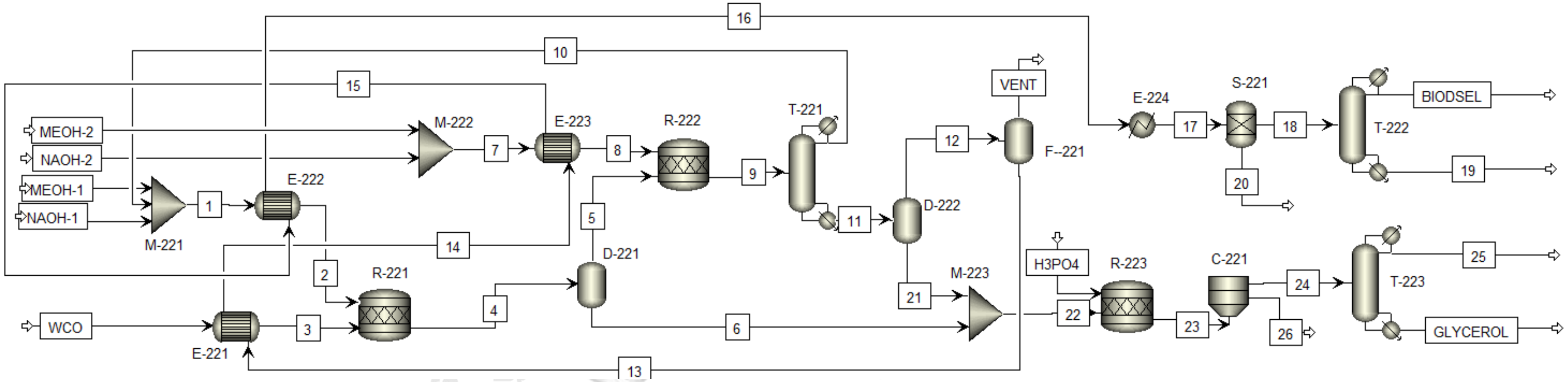


Figure 15 The overall process flow diagram of WCO in RTR reactor using dry purification method (purolite PD206 adsorbent) (case B2).

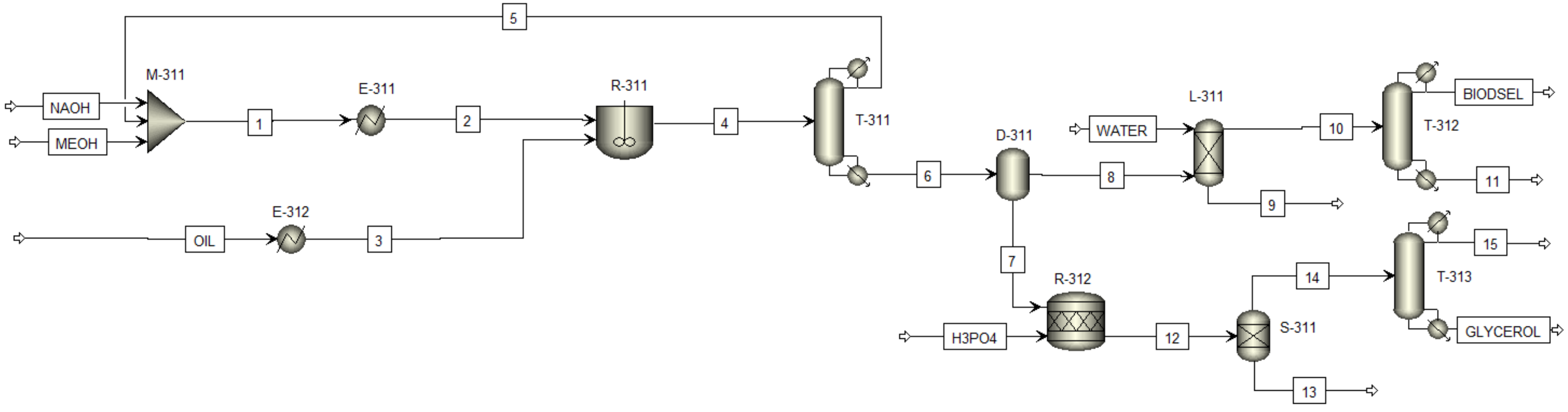


Figure 16 The overall process flow diagram of biodiesel production using RPO in a conventional reactor with wet purification method (case C1).

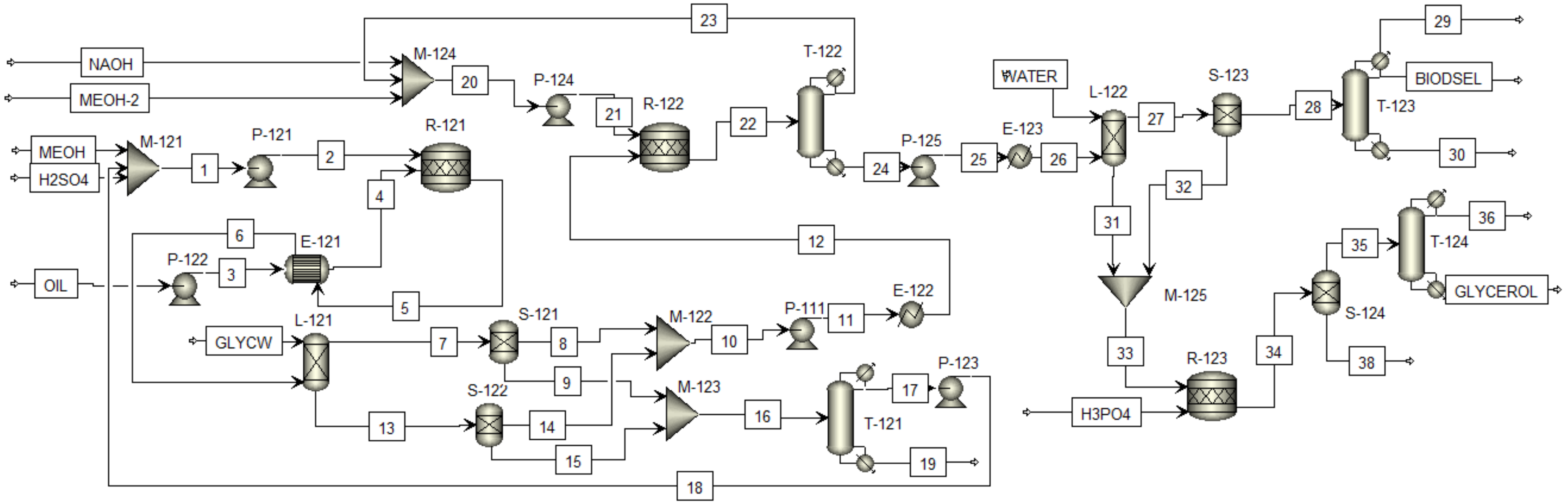


Figure 17 The overall process flow diagram of biodiesel production using WCO in a conventional reactor with wet purification method (case C2).

3.6 TEA analysis

TEA for the overall process provides the total capital investment (TCI) by summing up the fixed capital investment (FCI) and working capital (WC), cost of manufacturing (COM), and total annual revenue (R). The preliminary economic analysis in this study was based on the following assumptions:

- The plant capacity was set up based on a biodiesel production capacity for small scale plants of 100 L/day (3.6 kg/h) with 8,760 operating hours based on one year.
- The plant’s lifetime of the project was established in 10 years.
- The processing plant was assumed to operate at 100% of its capacity all the time.
- The selected process was simulated for the different plant capacity of 4,000, 8,000, 15,000, and 30,000 L/day.

The overall capital investment in the production of biodiesel was determined through the utilization of a module costing approach, as described in the previous work [37]. This method considers various factors that affect costs compared to the base conditions, such as the type of equipment used, the specific material used for construction, and the system pressure requirements. To calculate the manufacturing expenses, several elements were considered such as the estimation of capital investment, raw material costs, utility costs, labor costs, and waste treatment costs.

3.6.1 Total capital cost

In this study, the cost of purchased equipment was determined using Equation (17), with the corresponding parameters provided in Table 8. In order to compare the projected cost with the current cost, the Chemical Engineering Plant Cost Index (CEPCI), which was 798.0 in February 2023 [54], was utilized. This index is used to adjust costs to reflect changes in the overall economy and inflation, providing a more accurate representation of the present cost in the year 2023.

$$\log C_p^o = K_1 + K_2 \log_{10}(A) + K_3[\log_{10}(A)]^2 \qquad (17$$

where $\boldsymbol{C_p^o}$ represents the cost of purchased equipment constructed with carbon steel and operating at ambient pressure, as of January 2001 (CEPCI = 394.3, 2001). K_1, K_2, and K_3 are cost constants, while A is the equipment capacity.

Table 8 Parameters of estimated equipment cost [37].

Equipment	Unit of A	K_1	K_2	K_3
Reactor (agitated with jacketed)	m^3	4.1052	0.5320	-0.0005
Heat exchanger (spiral tube)	m^2	3.9912	0.0668	0.243
Pump (reciprocating)	kW	3.8696	0.3161	0.122
Tower tray	m^2	2.9949	0.4465	0.3961

The equipment bare module cost encompasses direct costs, including the purchase of equipment and installation expenses, as well as indirect costs such as freight, overhead, and engineering. Equation (18) was used to assess the bare module cost for each equipment. Working capital was estimated to encompass 15% of the total capital expenditure [37]. Fixed capital investment and total capital investment were represented by Equations (19) and (20) respectively.

$$C_{BM} = C_p^o\left[B_1 + B_2 F_p F_m\right] \tag{18}$$

$$FCI = 1.18 \sum_{i=1}^{n} C_{BM,i} \tag{19}$$

$$TCI = FCI + WCI \tag{20}$$

where C_{BM} represents equipment bare module cost. B_1 and B_2 are constants for bare module estimation. F_p and F_m denote the pressure factor and material factor, respectively. F_m=1 when material of construction is carbon steel. F_p =1 when pressure is ambient pressure. TCI, FCI, and WCI are total capital investment, fixed capital investment, and working capital investment, respectively.

3.6.2 Cost of manufacturing (COM)

(1) Cost of raw materials

In the biodiesel production process from transesterification of RPO and WCO, the cost of raw materials typically represents the highest operational expense. The prices of the product and raw materials are given in Table 9.

Table 9 Summary cost of raw materials and product.

Item	Specification	Price ($)	Ref.
Biodiesel	Qualified to meet ASTM D6751	$2.0/L	[55]
Glycerol	99 wt% vegetable glycerin	$10.0/kg	[56]
Glycerol	Washing grade	$5.0/kg	[57]
Refined palm oil	Free of water and solid impurity	$0.8/L	[58]
Waste cooking oil	Max 3 wt% FFA	$0.2/L	[59]
Methanol	99.85%	$0.4/kg	[60]
Sodium hydroxide		$2.4/kg	[61]
Phosphoric acid		$2.5/kg	[62]
Sulfuric acid		$2.1/kg	[63]
Purolite (PD206)		$2.1/kg	[64]

(2) Cost of utilities

The biodiesel production requires the utilities for operation. Electricity was used to power the pump and RTR reactor unit. To heat the system sufficiently, hot utilities such as low-pressure steam (0.6 MPa), medium-pressure steam (1.1 MPa), high-pressure steam (4.2 MPa), and fired heat (natural gas) were used. Cooling water and chilled water also required to cold the system. Moreover, electricity and steam can come from a variety of sources which produces a different amount of CO_2. The utility costs were summarized in Table 10.

Table 10 Cost of utility delivered to the process.

Utility	Specification	Price (USD/GJ)
Cooling water	30 °C to 40 °C	0.38
Chilled water	5 °C to 15 °C	4.77

Utility	**Specification**	**Price (USD/GJ)**
LP steam	6.2 barg, 160 ^{o}C	4.54
MP steam	10 barg, 184 ^{o}C	4.77
HP steam	41 barg, 254 ^{o}C	5.66
Fired heat	Natural gas	3.95
Electricity		16.90

(3) Cost of labor

In the study, the operating labor cost was estimated to be approximately 5,600 USD per year. This cost assumed of a single operator working for 49 weeks per year, with 5 shifts per week and 8 h per shift [65]. The labor rate used for this estimation was specific to Thailand, which served as a comparison.

(4) Cost of waste treatment

In the study, the wastewater from water washing column, glycerol purification column, and biodiesel purification column was estimated to be 56 USD/m^3 [37]. Solid waste from centrifuge and dry washing column was estimated to be 1.1$ /kg waste [37].

3.7 Profitability analysis

The calculation of biodiesel production profitability was performed using various methods, including the payback period (PBP), net present value (NPV), and rate of return on investment (ROI). The main assumptions used in these calculations are as follows:

- Plant construction time will not take into account. Therefore, production can start in the first year.
- Working capital can be estimated at 15% of total capital investment, which can be recovered in the last year.
- The salvage value of all equipment and land can be neglected.

- Depreciation is calculated using the modified accelerated cost recovery system (MARCS) with a recovery period of 7 years [44].
- The taxation rate was assumed to be 20% of the gross profits, including depreciation.

3.8 Sensitivity analysis

Sensitivity analysis was performed to understand the influence of the uncertain variables on the net present value (NPV) in each case. In this study, variations were investigated based on plant lifetime. The all prices of parameters were varied between -50% and +50% of the original values based on plant lifetime.

3.9 Environmental impact

Reducing greenhouse gas emissions have become more crucial issue due to the increasing levels of carbon dioxide in the atmosphere and their impact on the global warming. Energy consumption and waste generation are key factors in these emissions Equation (16) is used to calculate the equivalent CO_2 emissions [66]. The factors impact on the carbon dioxide emissions factors are listed in Table 11.

$$CO_2e\ (kgCO_2) = CEF\ (kgCO_2/\text{unit entity}) \times \text{utilization or generation rate (unit entity)} \quad (16)$$

Where CEF is carbon dioxide emission factor.

Table 11 Carbon dioxide emission factor value.

Index	Value	Unit	Ref.
LP steam	72.86	kg CO_2/GJ	[67]
MP steam	76.60	kg CO_2/GJ	[67]
Electricity	120.06	kg CO_2/GJ	[67]
Fired heat	55.89	kg CO_2/GJ	[68]
Wastewater	0.38	kg CO_2/m^3	[65]
Solid waste	3.7	kg CO_2/kg	[66]

CHAPTER 4

RESULTS AND DISCUSSION

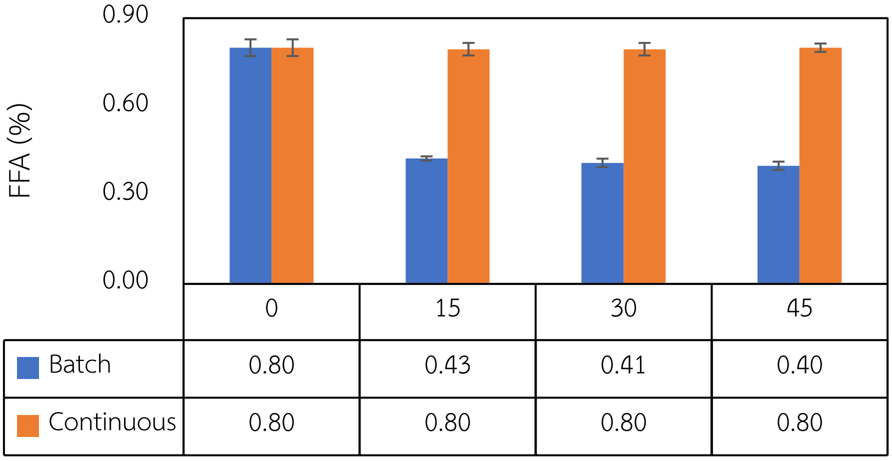
In this chapter, the experimental results and discussion of biodiesel production using WCO feedstock in RTR reactor are presented. Additionally, a techno-economic analysis of six biodiesel production cases is conducted. The simulation results are discussed in terms of performance analysis, energy consumption, environment impact cost analysis, and production capacity.

4.1 Biodiesel production using WCO in RTR reactor.

4.1.1 Esterification of WCO in RTR

WCO is a potential source for the economical biodiesel production. The primary concern with WCO is its high free fatty acid (FFA) content, leading to soap formation during the biodiesel production process. To solve this issue, a pretreatment process, namely esterification is employed to convert the FFA in WCO into FAME (biodiesel). Generally, the acid value of the WCO greater than 2% FFA is relatively high FFA content which could increase the chances of soap formation [2]. However, the FFA content in the WCO used in this study was approximately 0.8 %. To reduce the FFA content and mitigate the soap formation, esterification of WCO was carried out using a methanol to WCO ratio of 12:1, a sulfuric acid (H_2SO_4) loading of 1 wt%, a total feed flowrate of 30 mL/min, and a reaction temperature of 60 °C. This condition was used for a continuous RTR reactor as well as a batch reactor in a three-neck round-bottom flask. The inlet and outlet temperature during the esterification in RTR were also measured as illustrated in Figure C-1 in Appendix C. Figure 18 shows that the batch process achieved the reduction in FFA content to about 0.4%, while the FFA content was not reduced in the continuous RTR reactor. The batch process showed better results in terms of reducing the FFA content in WCO. One possible explanation might be due the feeding method of RTR there were two separated feeds as WCO and the mixture H_2SO_4 - methanol feed. Then, they were mixed, and the esterification took place in the continuous RTR reactor.

However, the mechanistic pathway for esterification of FFA is initiated by protonation from acid catalyst to FFA and then react with methanol to produce FAME [69]. Therefore, the mixture of H_2SO_4 with methanol might hinder the protonation step before contacting with WCO in RTR to reduce the esterification rate.



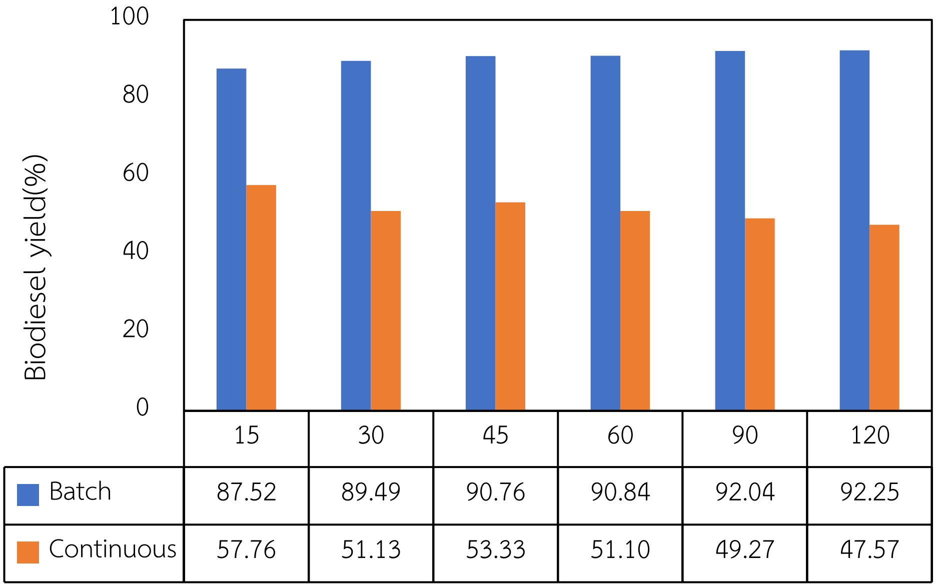
	0	15	30	45
🟦 Batch	0.80	0.43	0.41	0.40
🟧 Continuous	0.80	0.80	0.80	0.80

Figure 18 FFA content in both the batch and continuous RTR reactors.

The FFA containing in WCO for this study was below the standard value (2% FFA). This indicated that the WCO could be used for transesterification without the esterification pretreatment step [70]. Therefore, the transesterification of fresh WCO was performed in both batch and the continuous RTR reactor.

4.1.2 Comparison with batch process

In a previous study conducted on biodiesel production using the continuous RTR, the optimal condition of a methanol to oil molar ratio of 6:1, a 1 wt% concentration of NaOH, a rotational speed of 1,000 rpm at room temperature was reported [8]. Under this condition, when RPO and methanol were used as the feedstocks, the biodiesel production rate was obtained for 23.5 mL/min. The study then focused on investigating the feasibility for replacing the feedstock from RPO to WCO. The similar optimal parameter was tested for both the batch experiment conducted in a three-neck round-bottom flask and the continuous RTR reactor. In the batch process, the results of the study showed that a biodiesel yield ranging from 87 to 92% was achieved using the similar conditions except the reaction temperature, 60 °C, in batch reactor while only 50% of biodiesel yield was observed in the continuous RTR reactor. This means that the reaction temperature was more likely to dominate the transesterification rate in terms of kinetic and solubility [71]. In addition, the elevated temperatures used in the transesterification process gave the additional benefit of reducing the viscosity of the oil. Lower viscosity promotes better mixing and contact between the oil and the catalyst or reactants, leading to improve the reaction efficiency [72]. This explanation supported the higher biodiesel yield obtain from the batch process as shown in Figure 19. Furthermore, the study reported that the energy consumption of batch processes and continuous processes was measured to be 0.116 kWh and 0.223 kWh equally for the specific energy consumption of 0.643 and 0.0423 kW/kg WCO, respectively. These results indicated that the continuous RTR consumed less specific energy consumption compared to the batch process. This major energy consumption was derived from the heating system for the batch reactor operated at 60°C. Additionally, the continuous RTR reactor involves a larger volume of reaction mixture compared to the batch reactor further contributing to the higher total energy consumption with lower specific energy consumption.

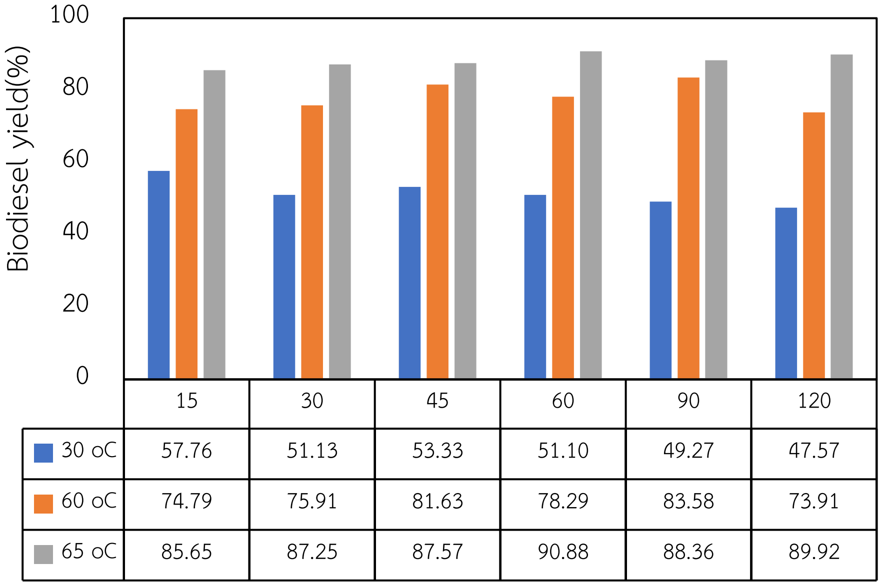


	15	30	45	60	90	120
🟦 Batch	87.52	89.49	90.76	90.84	92.04	92.25
🟧 Continuous	57.76	51.13	53.33	51.10	49.27	47.57

Figure 19 Biodiesel yield in batch at 60 ℃ and continuous RTR at room temperature.

4.1.3 Effect of reaction temperature on biodiesel yield in the RTR reactor

The reaction temperature has a significant influence on the kinetics and equilibrium of the transesterification process. Higher temperatures provide multiple positive effects, including an increased reaction rate, improved heat and mass transfer. These factors contribute to an enhanced yield of biodiesel production in the transesterification process [73]. Transesterification of WCO was tested for 2 h with various temperature of 30, 60, and 65 °C using NaOH loading of 1 wt.% and make-up NaOH for neutralization of FFA in WCO and methanol to WCO molar ratio of 6:1 in the continuous RTR reactor. The inlet and outlet temperature during the transesterification of WCO in RTR were also measured as illustrated in Figure C-2 in Appendix C. The influence of reaction temperature on biodiesel yield over time on stream is presented in Figure 20. After 30 min, the steady state condition was reached for all runs because of the similar feed flowrate was used. The result clearly illustrated that raising the reaction temperature from 30 to 65 °C leads to an increase in the rate of biodiesel production. The highest biodiesel yield was achieved at 65 °C. Since, at this temperature, transesterification reached its optimal level compromising with transesterification rate and vaporization rate of methanol [74]. However, this condition gave a slightly increment in the biodiesel yield from 83.58 to 90.88% when the reaction temperature was raised from 60 to 65 °C. The higher transesterification rate indicates a more efficient conversion of triglycerides to biodiesel as it facilitates the reaction and improve the overall biodiesel yield. Furthermore, according to the study, the energy consumption at temperatures of 30, 60, and 65 °C was measured to be 0.223 kWh, 0.907 kWh, and 1.020 kWh or the specific energy consumption as 0.0423, 0.172, and 0.194 kW/kg WCO, respectively. This suggested that the significant higher energy consumption was mainly due to elevated reaction temperature.



	15	30	45	60	90	120
🟦 30 oC	57.76	51.13	53.33	51.10	49.27	47.57
🟧 60 oC	74.79	75.91	81.63	78.29	83.58	73.91
⬜ 65 oC	85.65	87.25	87.57	90.88	88.36	89.92

Figure 20 Effect of reaction temperature on the biodiesel yield for transesterification of WCO in the continuous RTR.

4.1.4 2^{nd} transesterification step

In the previous section, it was determined that the highest yield of biodiesel achieved at a reaction temperature of 65 °C was 90.88%. However, this yield did not meet the standard specification. To improve the yield, an additional step of transesterification (2^{nd} step) was performed. In this subsequent step, the reaction was carried out for 2 h using a catalyst loading of 0.5 wt% and a methanol to WCO molar ratio of 18:1 at the same reaction temperature of 65 °C. Biodiesel yield profiles of 1^{st} and 2^{nd} transesterification steps are presented in Figure 21. The inlet and outlet temperature during the transesterification of WCO in RTR were also measured as illustrated in Figure C-3 in Appendix C. Despite the improvement, the obtained biodiesel yield in this study still did not meet to the standard specification. Several factors could contribute to the lower biodiesel yield achieved in this study compared to the standard specification. One possible factor probably due to the impurities, such as water and FFA content, that can negatively affect the transesterification to reduce the biodiesel yield [75].

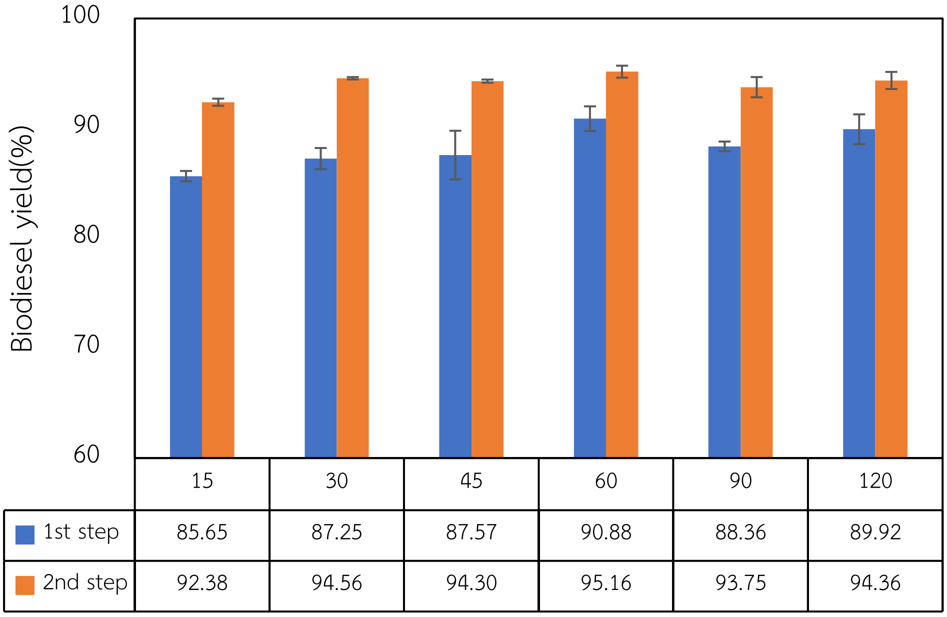


Figure 21 Biodiesel yield of 2 steps for transesterification of WCO in the continuous RTR reactor.

4.1.5 Comparative study of intensification process based on biodiesel yield and yield efficiency

The comparison of the intensification process for biodiesel production via transesterification using the alkaline catalyst with previous studies was presented in Table 12. NaOH and KOH are homogeneous catalysts mostly used in the biodiesel production process because of its low cost and higher transesterification rate to achieve higher yields. It was found that the biodiesel yield and yield efficiency obtained in this study was higher as compared to the conventional reactor. However, it was lower than that of a hydrodynamic cavitation reactor because using RTR can continuously produce biodiesel from WCO which required the energy for the continuous feeding reactant. Although the yield efficiency might be lower than that of a hydrodynamic cavitation reactor as in the batch operation, the RTR offers advantages in terms of scalability, ease of operation, and potential for large-scale production of biodiesel. This finding suggested that the continuous RTR reactor is a promising reactor for the continuous biodiesel production due to its higher yield efficiency and easier operation.

Table 12 Comparatives study of yield efficiency of intensification process for biodiesel production via transesterification from WCO.

Reactor	Process	Condition	Time (min)	Yield (%)	Yield efficiency (g/J) x 10^3	Ref.
Hydrodynamic cavitation reactor	Batch (10L)	6:1 methanol to WCO molar ratio in the presence of 1% KOH at 60 °C	60	95.0	1.28	[76]
Hydrodynamic cavitation reactor	Batch (50L)	6:1 methanol to treated rubber seed oil molar ratio in the presence of 1% KOH at 60 °C	18	97.0	0.91	[77]
Conventional reactor	Batch	6:1 methanol to treated rubber seed oil in the presence of 1% KOH at 60 °C	90	97.0	0.15	[77]
Rotating tube reactor	Continuous (30 mL/min)	6:1 methanol to oil molar ratio in the presence of 1% NaOH at 65 °C	120	90.9	0.66	This study

4.2 Process simulation

This section provides the simulation results of biodiesel production from RPO and WCO using process intensification and compared to the conventional process in terms of number of unit operation, energy consumption, economic and environmental analysis.

4.2.1 Comparison of performance

The simulation results were based on a biodiesel production capacity of 100 L/day (3.6 kg/h). The total feed flowrate of 90 mL/min was required based on 24 h/day operation. Therefore, three parallel RTR reactors were set up for the simulations in cases A1 and B1 while A2 and B2 required total six RTR reactors for the 1st and 2nd transesterification steps. Tables 13-14 and Figure 22 present a performance comparison in terms of product specifications and energy consumption. For RPO as feedstock, A1 case demonstrated a higher biodiesel yield of 97.5% compared to the conventional C1 case, which only achieved a biodiesel yield of 89.1%. Remarkably, transesterification in the A1 case was operate at room temperature using RTR reactor. The total energy consumption for the A1 case was 4.87 kW, which was lower than the 5.92 kW required for the C1 case. However, the A1 case still generated wastewater due to the water requirement for the wet washing step to achieve a biodiesel purity of 96.2%. To alleviate this issue and improve biodiesel purity, an integration of the RTR reactor and a dry washing process using Purolite PD206 or the B1 process was employed. This modification reduced wastewater production while increasing biodiesel purity according to the EN standard. The B1 case yielded biodiesel 97.5% and required a total energy consumption of only 3.70 kW to achieve a biodiesel purity of 97.0%. After passing through the distillation column, biodiesel purity reached 99.9% for both A1 and B1 cases.

For WCO as feedstock, the conventional C2 case gained 95.9%. biodiesel yield. However, this process required a high energy consumption of 9.12 kW. Interestingly, the total energy consumed for the A2 case was 5.58 kW, while the B2 consumed only 4.23 kW based on the similar biodiesel yield of 96.5%. After undergoing the distillation column, both the A2 and B2 cases can achieve a biodiesel purity of 99.2%. It is noteworthy that both the A2 and B2 cases are able to accomplish biodiesel purity greater than 99%, requiring a lower total energy consumption. This recommended that the utilization of the continuous RTR reactor and a dry washing unit not only provided high biodiesel quality but also reduced energy consumption.

Table 13 Comparison of the performance process for each case based on 100L/day of biodiesel production.

Item	A1	A2	B1	B2	C1	C2
Biodiesel yield (1st step) (%)	97.5	90.9	97.5	90.9	89.1	95.9
Biodiesel yield (2nd step) (%)	-	96.5	-	96.5	-	-
Biodiesel purity before washing (wt%)	95.2	96.4	95.2	96.4	86.3	85.0
Biodiesel purity after washing (wt%)	96.2	98.3	97.0	98.8	87.2	85.0
Biodiesel purity after distillation (wt%)	99.9	99.2	99.9	99.2	99.0	99.9
Biodiesel productivity (kg/h)	3.6	3.6	3.6	3.6	3.6	3.6
Glycerol purity before distillation (wt%)	81.5	52.2	81.5	52.1	78.3	43.0
Glycerol purity after distillation (wt%)	99.9	99.9	99.9	99.9	99.8	99.9
Glycerol productivity (kg/h)	0.4	0.4	0.4	0.4	0.4	0.4

4.2.2 Comparison of energy consumption

A comparison of total energy consumption, hot duty and cold duty between conventional reactors (C1 and C2 processes) and RTR reactors (A1, A2, B1, and B2 cases) is presented in Figures 22-24, respectively and Table 14. The energy consumption of a single RTR using both RPO and WCO as feedstocks were recorded from the experimental result for 2 h. The calculation of energy consumption was linear extended to 24 h/day operation and multiplied by the number of RTR used in each cased. When RPO was used as the feedstock, the energy consumption of three parallel RTR reactors for the C1, A1, and B1 cases were measured at 5.92, 4.87, and 3.70 kW, respectively. The biodiesel purification column took the main accounting for the largest portion of energy consumption in the C1 case, while the B1 case required nearly 50% reduction in the total energy consumption. It is worth noting that the C1 and A1 cases had higher energy requirements compared to the B1 case due to the higher water concentration in the crude biodiesel generated from wet washing step. This was mainly contributed to the increase energy demands for separation of unreacted oil and water. The utilization of dry washing step shows the significant benefits in terms of reducing wastewater and total energy consumption for biodiesel production, as similar findings with Alamsyah and Loebis [78].

When WCO was utilized as the feedstock, the methanol recovery unit accounted for a small portion of the energy consumption in the A2 and B2 cases. This is because these processes required two transesterification steps, with methanol being separated after the 1st transesterification step by decanter as illustrated in the process flow diagram in Figures 12 and 15, respectively. The recovery methanol was sent back to the 1st transesterification feed. The results indicated that a lower amount of methanol was sent to recovery in the distillation column compared to other cases. However, in the C2 case, the methanol recovery unit had a significant impact on the energy consumption. This was attributed to the esterification pretreatment step required high methanol to oil molar ratio of 6:1 or a methanol to FFA ratio of 36:1. The excess methanol was directly sent to the methanol recovery unit to achieve a methanol purity of 99.9% and then, it was recycled back to the esterification unit. This process posed the high energy consumption, as described in the process of Zhang et al. [39].

Table 14 Energy consumption and number of main equipment in each case (Heat duty-kW).

Equipment	Description	A1	A2	B1	B2	C1	C2
Heat exchanger	Heater	-	0.14	-	-	0.09	0.03
	Cooler	0.01	-	0.01	0.02	-	0.02
Reactor	Transesterification	0.33	0.67	0.33	0.67	0.16	0.06
	Esterification	-	-	-	-	-	0.07
	Neutralization	0.05	0.06	0.05	0.06	0.02	0.01
Distillation column	Methanol recovery	0.69	0.38	0.69	0.37	0.68	3.71
	Biodiesel purification	3.46	3.55	2.19	2.19	4.65	3.47
	Glycerol purification	0.28	0.78	0.28	0.79	0.30	1.76
Decanter		0.04	0.01	0.04	0.02	0.03	0.00
Flash drum		-	-	0.10	0.12	0	0
Total Energy Requirement (kW)		**4.87**	**5.58**	**3.70**	**4.23**	**5.92**	**9.12**

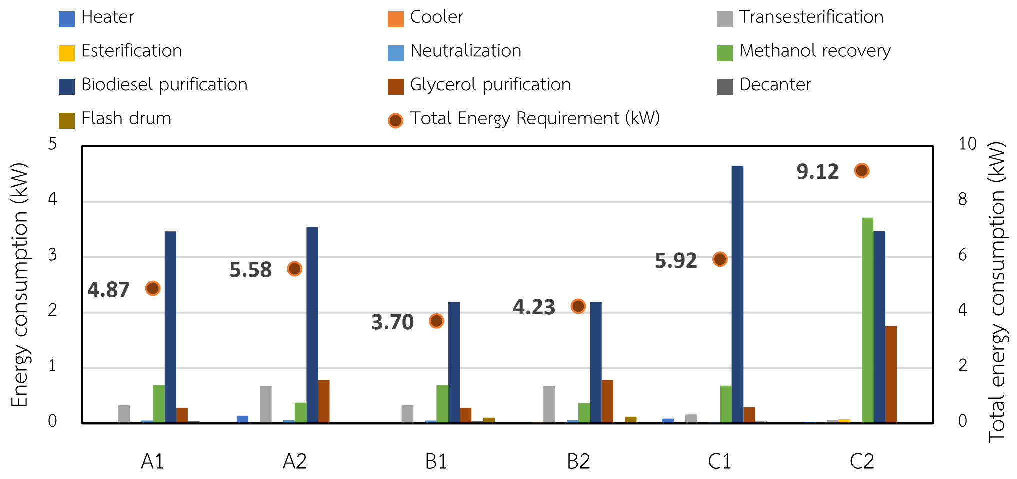


Figure 22 Energy consumption of each unit and total energy consumption for biodiesel production in all cases.

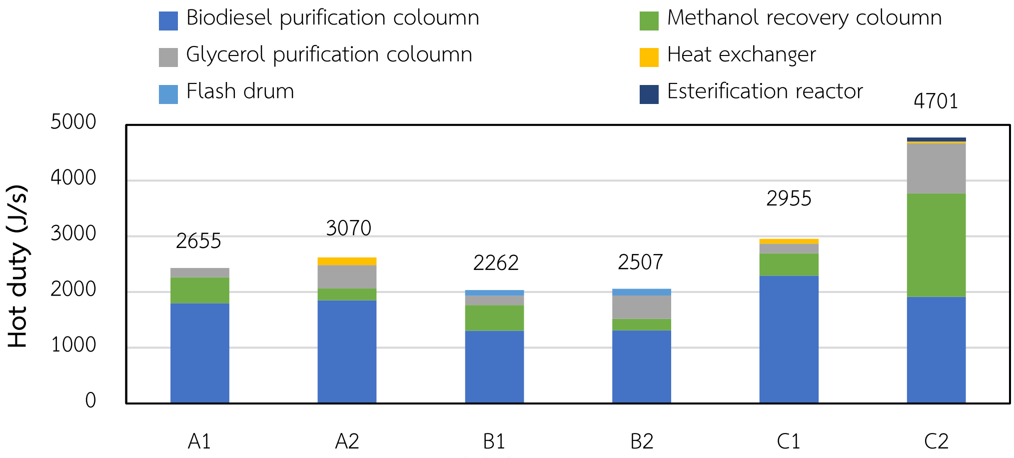


Figure 23 Hot duties of biodiesel production for each case

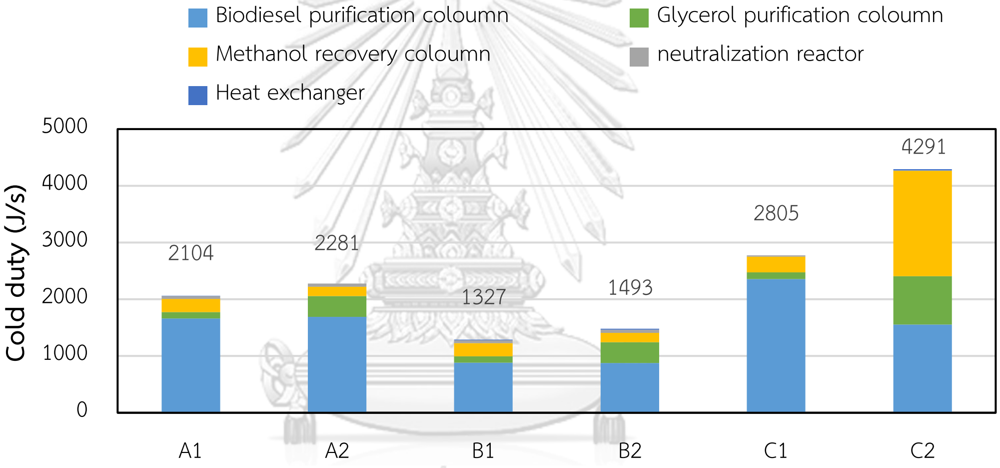


Figure 24 Cold duties of biodiesel production for each case

4.2.3 Environmental impact

The CO_2 emission was divided into 2 sections including of CO_2 emission from the utility (Fired heat, Electricity, Low-pressure steam (LP-steam), and medium-pressure steam (MP-steam)) and waste (solid waste and wastewater). Figure 25 presents the CO_2 emission in biodiesel production process. For the utility section, it was observed that fired heat had the most significant influence on CO_2 emissions for all cases except B1 and B2 cases. Since, the purification columns required fired heat from boilers to separate biodiesel and glycerol, having highest energy consumption on the hot duty. Additionally, the conventional C2 case showed the significant contribution of CO_2 emissions from LP-steam because LP-steam was used in the boiler of the methanol recovery column, which required high energy consumption on the hot duty for the C2 case, as depicted in Figure 23. The C2 case utilized two methanol recovery columns, leading to increased LP-steam usage. In the waste section, the B1 and B2 cases exhibited higher CO_2 emissions from waste treatment as compared to the A1, A2, C1, and C2 cases. This is attributed to the treatment of solid waste obtained from the neutralization stream after transesterification (Na_3PO_4) as well as the stream containing Purolite PD206 from the absorber unit. The increase waste treatment cost was further presented the cost of manufacturing (COM) in Table 15.

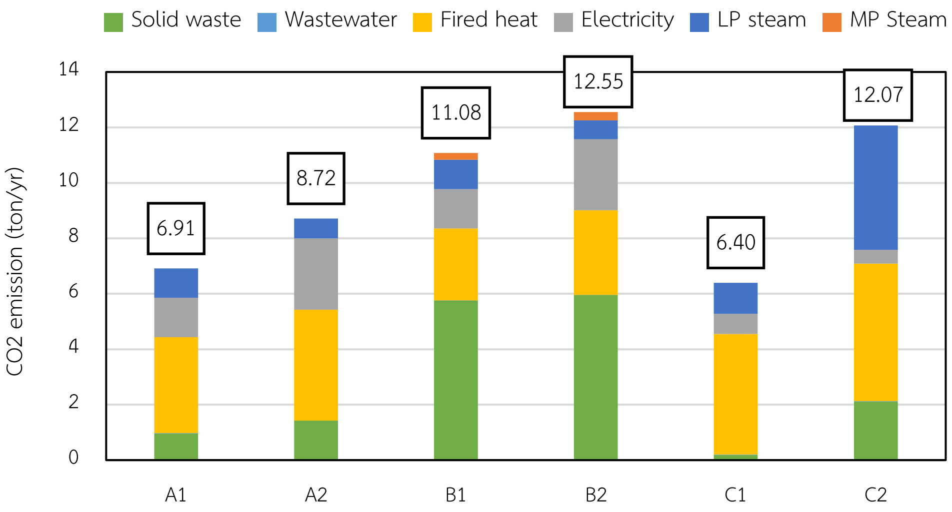


Figure 25 CO_2 emission in biodiesel production for each case.

4.3 Economic analysis

4.3.1 Total capital investment (TCI)

The results of the capital investment analysis in Table 15 and Figure 26 revealed that the C2 case had a higher total capital investment (TCI) compared to the C1, A1, A2, B1, and B2 cases. This difference in TCI can be attributed to the additional equipment required for the esterification process (pretreatment process). Specifically, the cost of adding a methanol recovery column after esterification was more expensive than that of adding a methanol recovery column after transesterification. As mentioned earlier, the distillation unit had to accommodate a larger size due to the large significant amount of methanol recovered from esterification. Among the processes, the TCI of B1 case was the lowest at 162.6 thousand USD, whereas the C1 and A1 cases had TCIs of 204.5 thousand USD and 166.2 thousand USD, respectively. One factor contributing to the lower TCI of B1 case was the use of dry washing in the B1 and B2 cases in absence of water utilization in the biodiesel washing step. As a result, the total mass of biodiesel entering the distillation column was reduced compared to the wet washing process employed in the C1, C2, A1, and A2 cases. Consequently, the cost of the biodiesel purification column in the B1 and B2 cases was cheaper compared to the other wet washing step.

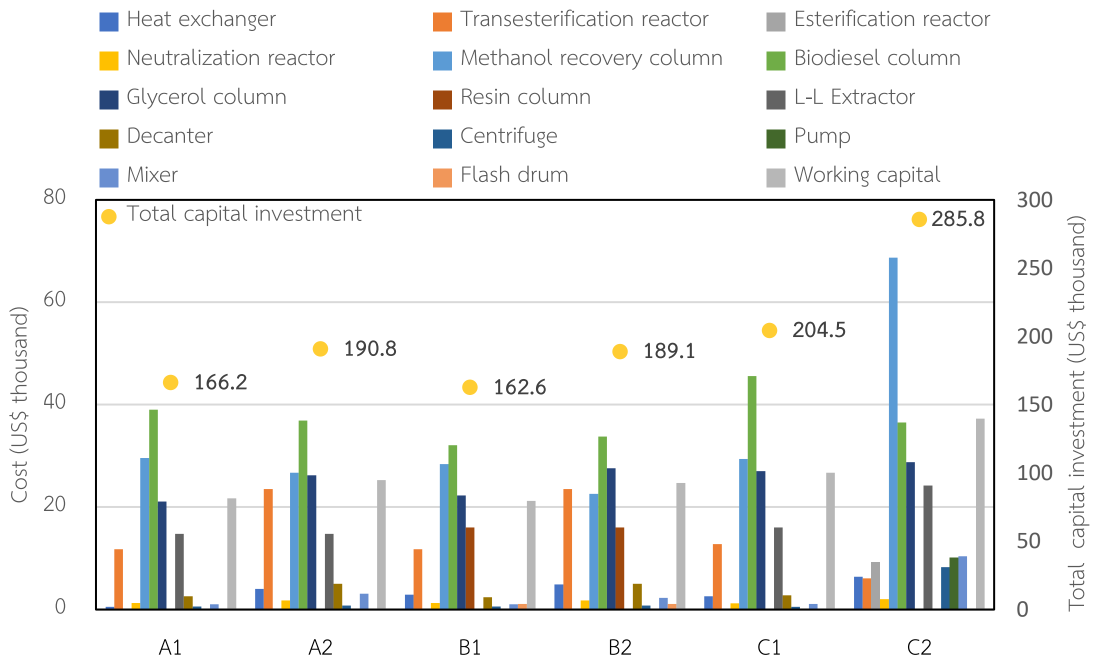


Figure 26 Total capital investment cost of biodiesel production for each case

Table 15 Total capital investment (TCI) for each case (thousand USD).

Item	A1	A2	B1	B2	C1	C2
Equipment cost						
Heat exchanger	0.5	4.0	2.9	4.9	2.6	6.4
Transesterification reactor*	11.8	23.5	11.8	23.5	12.8	6.1
Esterification reactor	-	-	-	-	-	9.2
Neutralization reactor	1.3	1.8	1.3	1.8	1.2	2.0
Methanol recovery column	29.6	25.9	28.4	22.6	29.4	68.7
Biodiesel column	39.0	36.9	32.1	33.8	45.6	36.5
Glycerol column	21.2	26.2	22.3	27.6	27.0	28.8
Purolite column	-	-	16.0	16.0	-	-
L-L Extractor	14.8	14.8	-	-	16.0	24.2
Decanter	2.6	5.0	2.4	5.0	2.8	-
Centrifuge (Separator)	0.6	0.8	0.6	0.8	0.5	8.3
Pump	-	-	-	-	-	10.1
Mixer	1.0	3.1	1.0	2.3	1.1	10.4
Flash drum	-	-	1.1	1.1	-	-
Total equipment cost	122.4	140.6	119.8	138.7	139.1	210.6
Fixed capital investment (FCI)	144.5	165.9	141.4	163.6	177.8	248.5
Working capital	21.7	24.9	21.2	24.7	26.7	37.3
Total capital investment	166.2	190.8	162.6	189.1	204.5	285.8

***** RTR was local made in Thailand with the price of 140,430 baht with the exchange rate for 35.79 Thai baht to 1 USD.

4.3.2 Cost of manufacturing (COM)

Table 16 and Figure 27 present the manufacturing costs for each process. It was noted that the raw material cost, especially the price of RPO, was the primary factor influencing the manufacturing cost. This finding agreed to the previous techno-economic analyses (TEA) using RPO as feedstock. They concluded that the oil price had the most significant impact on biodiesel production cost [79]. The B1 and B2 cases required the higher waste treatment costs as compared to the A1, A2, C1, and C2 cases due to the fact that dry washing step in B1 and B2 using absorbent to remove impurity of crude biodiesel. This step generated waste solids leading to additional costs. B2 required the highest solid waste treatment cost of 2.0 thousand USD /year due to the additional treatment cost for the neutralization stream after transesterification and the stream containing removed Purolite PD206. Table 17 summarizes the total revenue, which was similar for all cases, approximately USD107 thousand/year. Based on the manufacturing cost (COM), the revenues from A1, A2, B1, B2, and C1 cases were sufficient to generate profits, except for the C2 case due to its higher COM and TCI. Among the processes, the A2 case had the lowest manufacturing cost (COM), resulting in the highest net profit. This simulation result was interesting to highlight that biodiesel production in the continuous RTR using WCO feedstock can reduce COM costs and increase revenue for small-scale biodiesel production, similar to what has been observed in commercial-scale research [80]. Additionally, using the continuous RTR reactor combined with wet washing for biodiesel production from WCO feedstocks for small communities was proven to be a successful process both economically and environmentally. This should be noted that the adsorbent Purolite PD206 used in the dry washing process did not reuse resulting to increase material cost and waste treatment cost.

Table 16 Summary of manufacturing cost for each case (thousand USD/year.).

Item	A1	A2	B1	B2	C1	C2
Raw material (C_{RM})						
RPO	28.1	-	28.1	-	30.7	-
WCO	-	7.7	-	7.7	-	9.2
Methanol	1.7	2.9	1.9	2.9	2.0	2.0
Glycerol (washing)	-	-	-	-	-	17.5
NaOH	0.8	0.8	0.8	0.8	0.2	0.8
H_3PO_4	0.4	0.6	0.4	0.6	0.1	0.7
H_2SO_4	-	-	-	-	-	0.7
Purolite (PD206)	-	-	3.1	3.0	-	-
Total raw material	31.0	12.0	34.3	15.0	33.0	30.9
Utilities (C_{UT})						
Electricity	0.23	0.42	0.23	0.41	0.11	0.10
Chilled water	0.01	-	0.06	-	0.36	0.28
Cooling water	0.02	0.03	0.02	0.02	0.01	0.03
Fired heat	0.24	0.28	0.18	0.22	0.31	0.35
LP steam	0.07	0.05	0.07	0.055	0.07	0.28
MP steam	-	-	0.02	0.02		-
Water	3E-03	3E-03	-	-	3E-03	6E-03
Total utilities	0.50	0.64	0.50	0.59	0.85	1.03
Operating labor (C_{OL})	5.6	5.6	5.6	5.6	5.6	5.6
Waste treatment (C_{WT})						
Wastewater	0.3	0.3	0.2	0.2	0.6	0.7
Solid waste	0.3	0.4	1.7	1.8	0.1	0.6
Total waste treatment	0.6	0.7	1.9	2.0	0.7	1.4
Total manufacturing cost (COM)	82.7	61.6	85.8	66.5	89.6	100.9

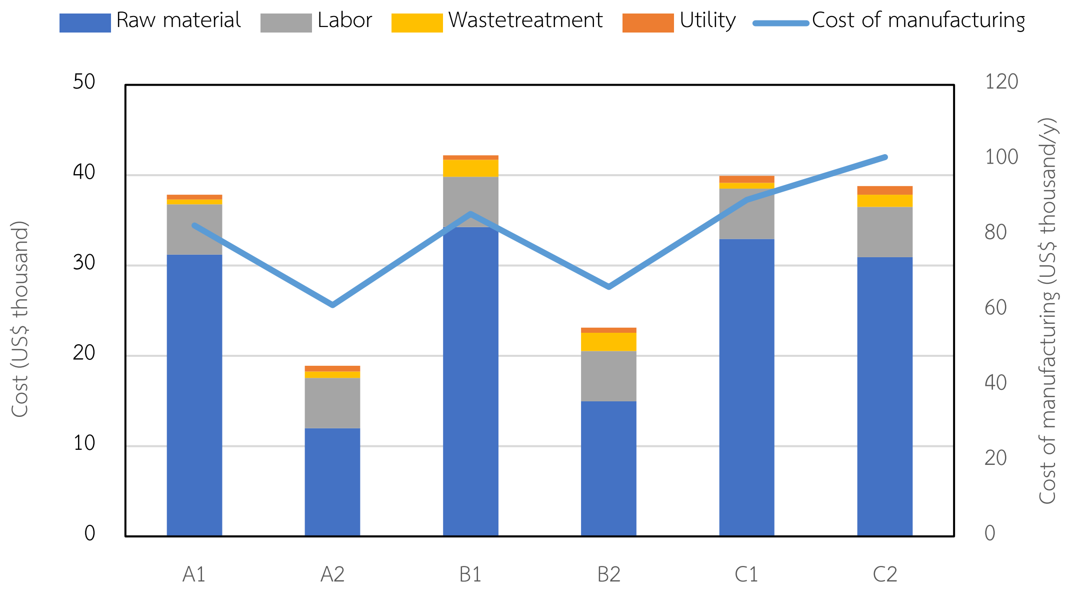


Figure 27 The cost of manufacturing (COM_d) of biodiesel production for each case

Table 17 Summary of revenue from selling biodiesel and glycerol for each case (thousand USD /year).

Item	A1	A2	B1	B2	C1	C2
Biodiesel	73.4	73.4	73.4	73.4	73.4	73.4
Glycerol	33.3	33.3	33.3	33.3	33.3	33.3
Total	106.7	106.7	106.7	106.7	106.7	106.7

4.4 Profitability analysis

To assess the profitability and efficiency of the biodiesel production project in a small community (100 L/day of biodiesel production), the internal rate of return (IRR) and net present value (NPV) were used as economic indicators. The calculations were carried out for a shorter duration of 10 years, considering that the project's sustainability may be challenging over a longer period compared to commercial-scale operations [3]. Table 18 presents the IRR and NPV values for each case. The short payback period of 4.4 and 4.8 years was found in the A2 and B2 cases, respectively. This should be noted that the C2 case did not gain the profitable. The positive values of NPV and IRR indicated that the project could generate profits without relying on government funding. Among the cases evaluated, the A2 case gave the highest NPV, amounting to 232.7 thousand USD. The NPVs of the B2, A1, B1, and C1 cases were 195.6, 94.6, 59.8 and 30.7 thousand USD, respectively. Considering a profitability threshold of 10% for the IRR, the A2 case using the RTR reactor and wet washing using water to produce biodiesel from WCO, emerged the most financially viable investment option for the 10-year timeframe under consideration. This research was corresponding the previous work [49] where addressed the utilization of WCO is more economical biodiesel production process.

Table 18 Profitability indicators for each case (10 years, USD thousand)

	A1	A2	B1	B2	C1	C2
Payback period (year)	6.5	4.4	7.6	4.8	-	-
NPV (10 year)	94.6	232.7	59.8	195.6	30.7	-144.2
IRR (%, 10 year)	6.5	14.0	4.2	11.9	0.0	-

4.5 Sensitivity analysis

A sensitivity analysis was conducted to evaluate the impact of key variables on the net present value (NPV) of biodiesel production using both the RTR and the conventional CSTR reactors. The variables considered in the analysis were the prices of WCO and RPO, methanol price, selling prices of biodiesel and glycerol, the price of Purolite PD206 in B1 and B2 cases, and the cost of glycerol in the conventional C2 case. These parameters were varied within a range of -50% to +50% of their original values, based on the plant's lifespan as depicted in Figure 28. The results of the sensitivity analysis showed that the RPO price had the most significant impact on the NPV of the A1 and B1 cases. In contrast, the WCO price and methanol price dictated the NPV of the A2 and B2 cases. Additionally, the price of Purolite PD206 had a similar effect to the methanol price in the B1 and B2 including in the raw materials cost because the Purolite PD206 was not reused (as indicated in Table 16). Furthermore, the selling price of biodiesel was the most significant influence on the economic analysis of all the processes. These findings conformed to the previous studies, which also highlighted the biodiesel selling price as the most crucial parameter affecting the NPV of biodiesel production using an alkali catalyst [79].

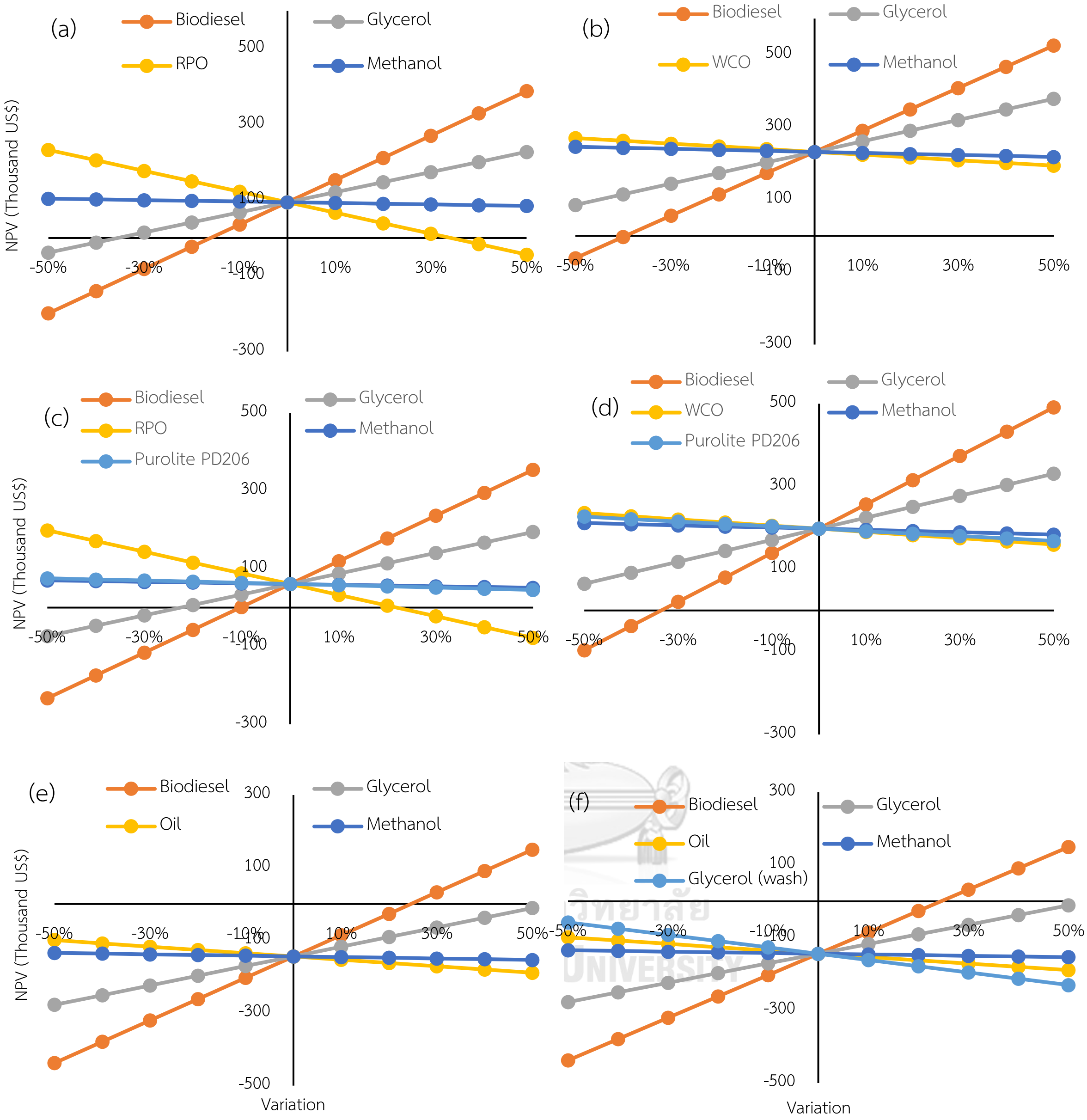


Figure 28 Sensitivity analysis in terms of net present value (NPV) of the biodiesel production process: (a) A1, (b) A2, (c) B1, (d) B2, (e) C1, and (f) C2 case

4.6 Plant capacity analysis

In the previous section, it was determined that the A2 case was the most financially viable investment option. Now, the increase the production capacity from 4,000 to 30,000 L/day was considered based on the assumption of the negligible for the economics of scale. Based on the design parameters obtained in the plant capacity analysis, the fixed capital and working capital investments can be estimated. The total capital investment for the biodiesel production plant ranges from 4,405,681 USD for a processing capacity of 4,000 L/day to 14,718,063 USD for a processing capacity of 30,000 L/day (Figure 29). It is worth noting that the cost of the RTR reactor has the most significant influence on the fixed capital investment for biodiesel production for all plant processing capacities as shown in Figure 30. This should be noted that the cost of RTR for this simulation was based on one RTR production cost. The price for the higher number of RTR can be reduced especially for feeding system.

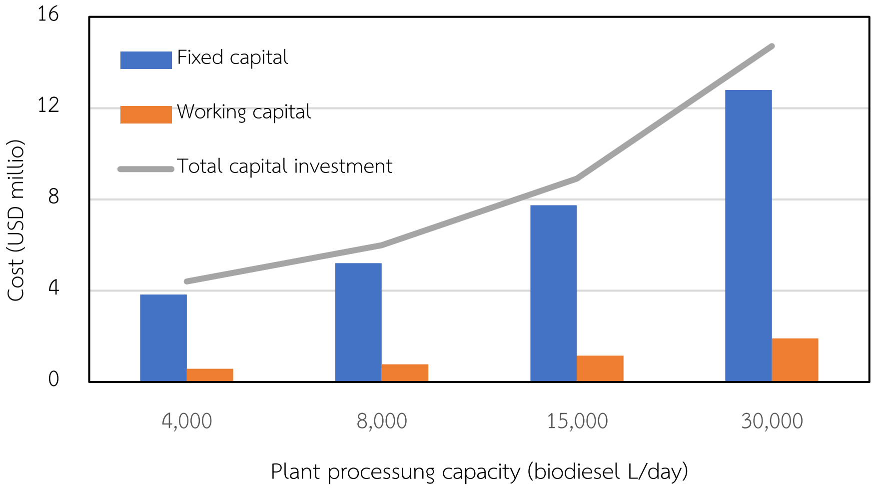


Figure 29 Total capital investment for each plant processing capacity.

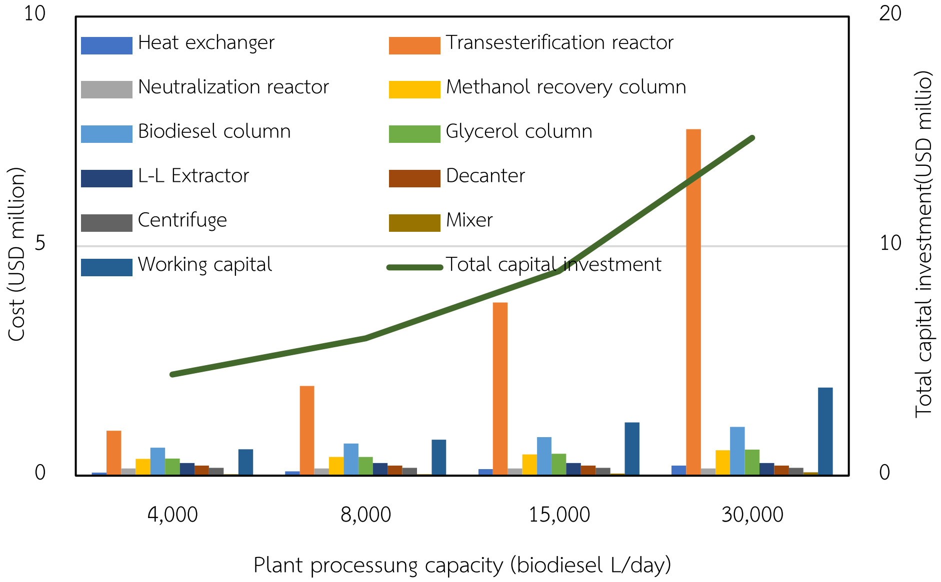


Figure 30 Total capital investment for each plant processing capacity.

Figure 31 depicts the total manufacturing cost at various plant processing capacities. It is evident that the raw material cost was the most crucial parameter impacting the manufacturing cost of biodiesel production for each plant processing capacity. Specifically, the cost of WCO had the most significant influence on the raw material cost across all plant processing capacities, as demonstrated in Figure 32.

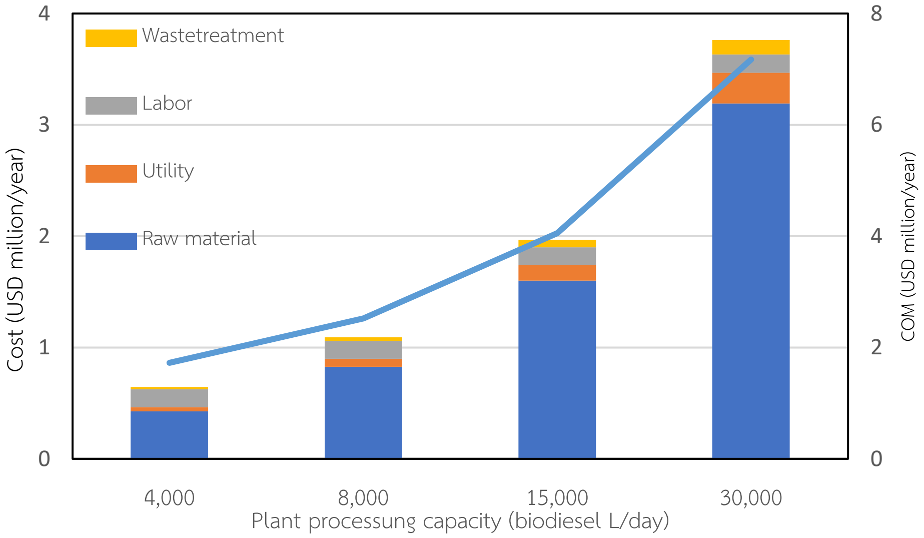


Figure 31 Cost of manufacturing for each plant processing capacity.

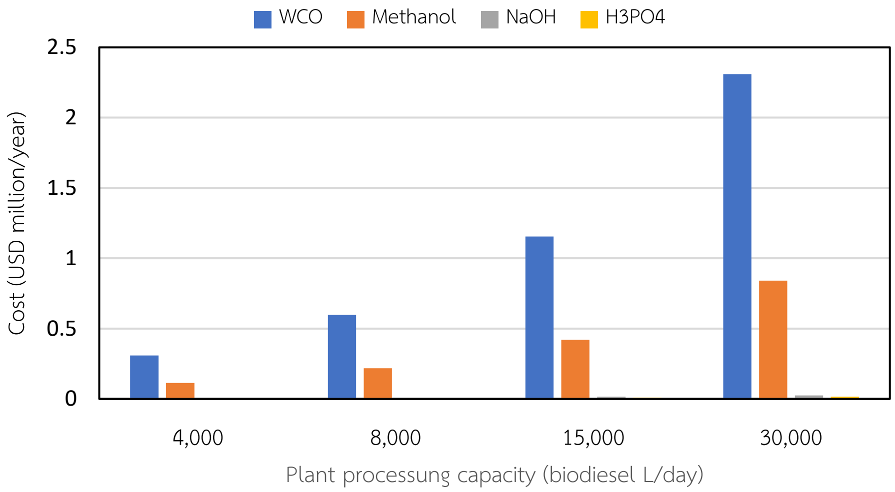


Figure 32 Cost of manufacturing for each plant processing capacity.

To assess the economic feasibility of the processing plant, the biodiesel selling prices were considered in the range of 0.9 to 1.7 USD/kg in 2023 [55]. Figures 33-35 show the NPV, IRR, and payback period, respectively. From the analysis, it can be observed that when the minimum price for biodiesel was set 1.3 USD/kg, the project becomes economically viable for all plant processing capacities in terms of IRR, NPV, and payback period. As the selling price of biodiesel increases, it becomes possible to achieve an economically viable process even with lower processing capacities. For other consideration, the plant capacity should be greater than 8000 L/day to achieve the positive value of the economic index which used the minimum biodiesel selling price of 0.9 USD/kg.

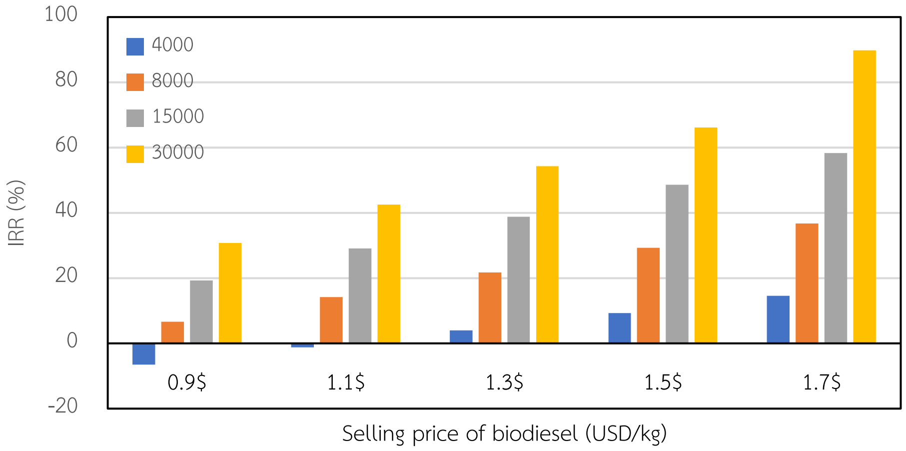


Figure 33 IRR for different selling price and plant processing capacity.

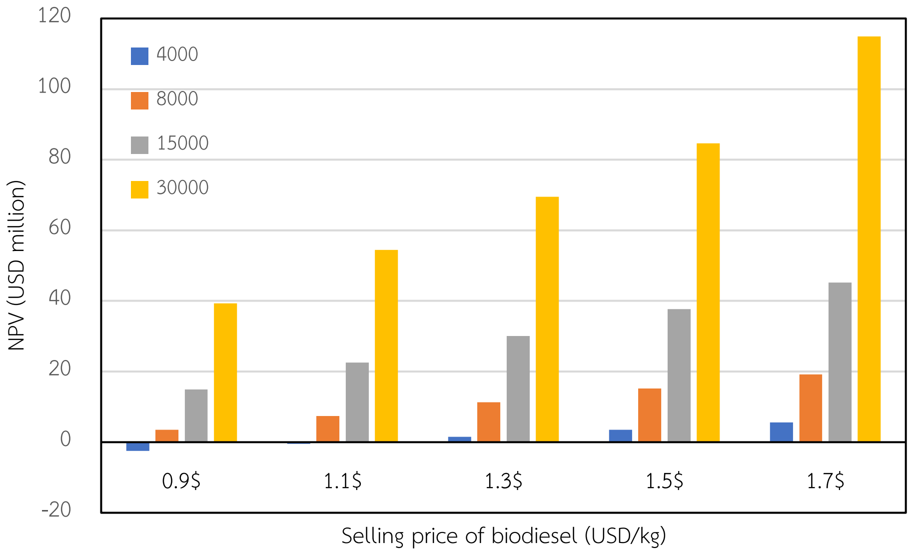


Figure 34 NPV for different selling price and plant processing capacity.

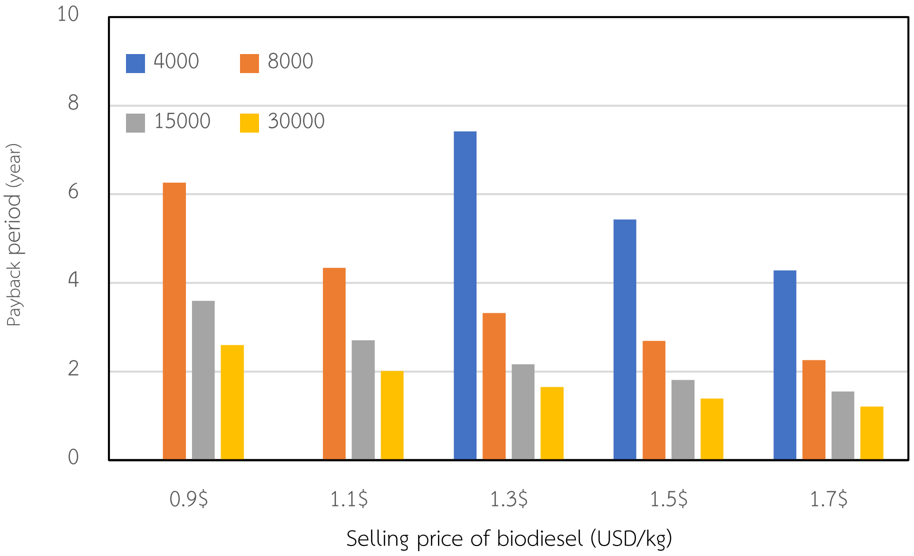


Figure 35 Payback period for different selling price and plant processing capacity.

CHAPTER 5

CONCLUSIONS AND RECOMENDATIOIN

5.1 Conclusions

The techno-economic analysis (TEA) was performed for biodiesel production in the intensified RTR reactor using RPO and WCO feedstocks. The experimental runs of biodiesel production from WCO in the RTR were carried out to obtain the information for the techno-economic simulation. FFA containing in the WCO used in this study was only 0.8%. Therefore, two steps transesterification of WCO was also performed under the operating conditions of methanol to oil molar ratio of 6:1 and 18:1, NaOH loading of 1 and 0.5 wt% for the 1st and 2nd transesterification steps, respectively, and similar rotational speed (1,000 rpm), total feed flowrate (30 mL/min) and reaction temperature of 65 °C. Biodiesel yields were 90.88 and 95.16% for the 1st and 2nd transesterification steps, respectively. The lower biodiesel yield might be attributed to impurities, such as water and FFA content, considered as the negatively affect for transesterification process.

The simulation results of biodiesel production from RPO and WCO using process intensification (RTR reactor and dry washing) were compared to the conventional process in terms of unit operations, energy consumption, economic analysis, and environmental impact. Using RPO feedstock with intensification RTR reactor and dry washing (B1 case) demonstrated a higher biodiesel yield (97.5%) with lowest total energy consumption of 3.70 kW. When using WCO as the feedstock in RTR reactor and dry washing (B2 case) also poses the similar trend as highest biodiesel yield of 95.2% and lowest energy consumption of 4.23 kW. The environmental impact analysis revealed that fired heat using in the re-boiler for distillation unit gave the highest CO_2 emissions for A1, A2, C1, and C2 cases. In addition, dry washing process in B1 and B2 cases also released higher CO_2 derived from the solid waste treatment for the neutralization and used purolite PD206.

TEA simulation results found that biodiesel production from WCO using RTR with wet washing process (A2 case) was the most cost-effective process providing minimum manufacturing cost as compared to A1 (RPO, RTR-wet washing) and B1 (RPO, RTR-dry washing) cases. The raw material cost of oil paly more important role on the NPV resulting to utilize WCO was more attractive than that of RPO. For dry washing process required the expensive cost for buying Purolite PD206 as well as solid treatment, resulting to lower profitability. Based on the 10-year time frame, the profitability assessment indicated that the A2 case had the shortest payback period (4.4 years) and highest NPV (232.7 thousand USD) and IRR (14.0%), making it the most financially viable option. The sensitivity analysis demonstrated that the prices of oil (RPO or WCO) had significant impacts on the NPV of biodiesel production. The biodiesel selling price was also identified as the most crucial parameter affecting the economic analysis.

The A2 cased was selected to investigate the effect of plant production capacity (4,000 to 30,000 L/day) on the fixed capital and working capital. The total capital investment from 4,405,681 USD to 14,718,063 USD was mainly from the RTR reactor cost. The raw material WCO cost was identified as the most crucial parameter impacting the manufacturing cost across different processing capacities. The economic feasibility of the processing plant was assessed by considering biodiesel selling prices ranging from 0.9 to 1.7 USD/kg. The analysis showed that at a minimum biodiesel selling price of 1.3 USD/kg, the project was economically viable for all plant processing capacities. As the selling price of biodiesel increased, even lower processing capacities became economically viable.

Recommendation

1. The design of experiment including the effect of the methanol-to-oil ratio, NaOH loading, rotating speed should also be performed to determine the optimum condition of transesterification of WCO in the RTR reactor.
2. The regeneration of Purolite PD206 as an important process to reduce absorbent costs as well as solid waste treatment should be considered in B1 and B2 cases.
3. The cost of RTR should be updated when the large number of RTR reactor was used for higher biodiesel production rate.

4. The economics of scale should be considered for the RTR reactor for a higher biodiesel production rate to reduce the cost of RTR.
5. The design of the esterification process should be considered in both B1 and B2 cases to reduce the FFA content in biodiesel product to meet the standard.
6. To compare the TEA of biodiesel production from WCO using RTR and conventional CSTR reactors based on the assumption of similar WCO containing FFA lower than 2%, the capital and operating cost of esterification unit in C2 case were neglected. The cost of RTR was calculated based on the actual construction cost was 23.5 greater than that of the conventional reactor as only 6.9 for C2 without esterification unit cases) resulting to higher total capital investment cost. The operating cost based on the similar WCO composition (FFA lower than 2%) was similar for A2, B2 and C2 without esterification cases as illustrated in Appendix D. The IRR and NPV values for the C2 without esterification case was 14.7% and 230.9 thousand USD, respectively which was similar to that of A2 case.

APPENDIX A

Example of calculations

A-1 Yield efficiency.

The biodiesel yield efficiency is defined in Equation below.

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

For example, calculate yield efficiency of RTR at 90.88% of biodiesel yield.

At first step, we change volume of WCO to mol of WCO.

So, mol of WCO = $2862\ ml\ x 0.92\ \frac{g}{ml}\ x\ \frac{1}{870}\ \frac{mol}{g}$ = 3.03 mol

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

So, mass of methyl ester = $3.03\ mol\ x\ 3\ x\ 294.9\ \frac{g}{mol}$ = 2677.35 g

Third step, 90% biodiesel yield was converted to g of actual methyl ester.

So, mass actual methyl ester is equal to $\frac{2677.35\ x\ 90.88\%}{100\%}$ = 2433.34 g

Forth step, find power supplied.

From in experiment, Use electricity 1.02 kWh in 2 h.

So, Power supplied (J) = $1.02\ kWh\ x\ 3.6\ x\ 10^6\ \frac{J}{kWh}$ = 3.67 x 10^6 J

Fifth step, Find Biodiesel yield efficiency.

So, Biodiesel yield efficiency = $\frac{2409.61\ g}{3.67\ x\ 10^6\ J} = 0.00066\ \frac{g}{J}$

A-2 Specific energy consumption.

The specific energy consumption is defined in Equation below.

$$\boldsymbol{Specific\ energy\ consumption} = \frac{\boldsymbol{Power\ supplied\ (kW)}}{\boldsymbol{Amount\ of\ oil\ (kg)}}$$

For example, calculate specific energy consumption of RTR

At first step, we change volume of WCO to mol of WCO.

So, mol of WCO = $2862\ ml\ x\ 0.92\ \frac{g}{ml}\ x\ \frac{1}{1,000}\frac{kg}{g}$ = 2.63 kg

Second step, find power supplied.

From in experiment, Use electricity 1.02 kWh in 2 hours.

So, Power supplied (kW) = $1.02\ kWh\ x\ \frac{1}{2}\frac{J}{h}$ = 0.51 kW

Third step, Find Biodiesel yield efficiency.

So, specific energy consumption = $\frac{0.51\ kW}{2.63\ kg} = 0.19\ \frac{kW}{kg}$

A-3 Bare module cost of RTR in each case.

At first step, find number of RTR per transesterification step.

From simulation results, Oil and methanol stream inlet RTR about 86 ml/min

And in experiment, Oil and methanol stream inlet RTR about 30 ml/min

So, Amount of RTR = $\frac{86\ \mathrm{ml/min}}{30\ ml/min}$ = 2.9 $\approx$ 3 reactors

Second step, find bare module cost of RTR in USD.

From RTR was local made in Thailand with the price of 140,430 baht with the exchange rate for 35.79 Thai baht to 1 USD.

So, Bare module cost of RTR = $140,430\ Baht\ x\ \frac{1}{35.79}\frac{USD}{Baht}$ = 3,924 USD

Third step, find bare module cost of RTR in each case.

For A1 and B1 cases, 1 transesterification step.

So, Bare module cost of RTR = $3,924\ \mathrm{USD} x\ 3$ reactors = 11,771 USD

For A2 and B2 cases, 2 transesterification steps.

So, Bare module cost of RTR = $3,924\ \mathrm{USD} x\ 6$ reactors = 23.542 USD

A-4 Energy consumption of RTR in each case.

At first step, Find energy consumption of RTR per reactor.

From in experiment, Use electricity 0.223 kWh in 2 hours.

So, Energy consumption = $0.233\ kWh\ x\ \frac{1}{2}\frac{J}{h}$ = 0.11 kW per reactor.

Second step, Energy consumption in each case.

For A1 and B1 cases, 1 transesterification step.

From previous section, Use RTR 3 reactors per transesterification step.

So, Energy consumption = 0.11 kW x 3 reactors = 0.33 kW

For A2 and B2 cases, 2 transesterification steps.

So, Energy consumption = 0.11 kW x 3 reactors x 2 step= 0.67 kW

APPENDIX B

Stream table

	Units	1	2	3	4	5	6	7	9	10	11	12	13	14	15	BIODSEL	GLYCEROL	H3PO4	MEOH	NAOH	RPO	8	WATER
From		M-111	R-111	T-111	E-111	T-111	D-121	L-111	T-112	L-111	D-121	R-112	S-111	S-111	T-113	T-112	T-113					T-112	
To		R-111	T-111	E-111		D-121	L-111	T-112			R-112	S-111		T-113				R-112	M-111	M-111	R-111		L-111
Temperature	C	31	30	64	30	108	108	100	309	106	108	50	50	50	47	148	262	20	30	30	30	148	30
Pressure	bar	1	1	1	1	1	1	1	0.1	1	1	1.1	1.1	1.1	0.4	0.1	0.5	1.1	1	1	1	0.1	1
Mole Flows	mol/hr	27.1	31.5	9.4	9.4	22.0	14.9	14.6	0.2	10.7	7.1	7.3	0.2	7.1	3.0	12.7	4.0	0.2	16.8	0.9	4.4	1.7	10.4
Mass Flows	kg/hr	0.9	4.6	0.3	0.3	4.3	3.8	3.8	0.1	0.2	0.5	0.5	0.0	0.5	0.1	3.6	0.4	0.0	0.5	0.0	3.7	0.0	0.2
Mass Fractions																							
MEOH		0.958	0.094	1	1	0.030	0.014	0.002	Trace	0.198	0.159	0.154	0	0.163	0.827	68 ppm	trace	0	1	0	0	0.185	0
TG1		0	0.010	Trace	Trace	0.010	0.012	0.012	0.356	Trace	Trace	0	0	0	0	Trace	0	0	0	0	0.401	trace	0
TG2		0	0.011	Trace	Trace	0.011	0.013	0.013	0.399	Trace	Trace	0	0	0	0	Trace	0	0	0	0	0.450	trace	0
TG3		0	0.002	Trace	Trace	0.003	0.003	0.003	0.091	Trace	Trace	0	0	0	0	Trace	0	0	0	0	0.103	trace	0
TG4		0	0.001	Trace	Trace	0.001	0.001	0.001	0.041	Trace	Trace	0	0	0	0	Trace	0	0	0	0	0.046	trace	0
FAME1		0	0.316	Trace	Trace	0.339	0.382	0.386	0.074	Trace	246 ppm	237 ppm	0	252 ppm	Trace	0.400	314 ppm	0	0	0	0	0.038	0
FAME2		0	0.355	Trace	Trace	0.380	0.429	0.433	0.005	1 ppm	591 ppm	570 ppm	0	606 ppm	5 ppm	0.451	753 ppm	0	0	0	0	0.131	0
FAME3		0	0.081	Trace	Trace	0.087	0.098	0.099	0.021	Trace	68 ppm	66 ppm	0	70 ppm	Trace	0.103	87 ppm	0	0	0	0	0.012	0
FAME4		0	0.036	Trace	Trace	0.039	0.044	0.044	0.013	Trace	26 ppm	25 ppm	0	27 ppm	Trace	0.046	33 ppm	0	0	0	0	0.004	0
GLYC		0	0.085	Trace	Trace	0.091	0.001	Trace	Trace	0.021	0.795	0.766	0	0.815	0.067	Trace	0.999	0	0	0	0	trace	0
NAOH		0.042	0.008	Trace	Trace	0.009	0.004	Trace	11 ppm	0.065	0.045	0	0	0	0	Trace	0	0	0	1	0	trace	0
WATER		0	0	0	0	0	0	0.007	Trace	0.715	0	0.020	0	0.021	0.105	243 ppm	trace	0	0	0	0	0.630	1
H3PO4		0	0	0	0	0	0	0	0	0	0	155 ppm	0	164 ppm	Trace	0	205 ppm	1	0	0	0	0	0
NA3PO4		0	0	0	0	0	0	0	0	0	0	0.059	1	0	0	0	0	0	0	0	0	0	0

Figure B-1 Stream table of A1 case.

	Units	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
From		M-121	E-122	E-121	R-121	D-121	D-121	M-122	R-122	T-121	T-121	D-122	D-122	W-121	T-122	T-122	W-121
To		E-122	R-121	R-121	D-121	R-122	M-123	E-123	T-121		D-122	W-121	M-123	T-122			
Temperature	C	41	65	65	65	65	65	30	65	64	88	88	88	81	148	286	87
Pressure	bar	1	1	1	1	1	1	1	1	1	1	1	1	1	0.1	0.1	1
Mole Flows	mol/hr	26.7	26.7	4.3	31.0	16.4	14.6	6.7	23.1	6.9	16.2	15.4	0.7	13.9	1.2	0.0	13.9
Mole Fractions																	
Mass Flows	kg/hr	0.9	0.9	3.6	4.5	3.8	0.7	0.2	4.0	0.2	3.7	3.7	0.0	3.6	0.0	0.0	0.3
Mass Fractions																	
MEOH		0.958	0.958	0	0.103	0.036	0.457	0.993	0.080	1	0.025	0.022	0.267	0.001	0.132	trace	0.273
TG1		0	0	0.398	0.028	0.034	trace	0	0.001	trace	0.001	0.001	trace	0.001	trace	0.307	trace
TG2		0	0	0.446	0.032	0.038	trace	0	0.001	trace	0.001	0.001	trace	0.001	trace	0.344	trace
TG3		0	0	0.102	0.007	0.009	trace	0	0.000	trace	301 ppm	305 ppm	trace	311 ppm	trace	0.079	trace
TG4		0	0	0.046	0.003	0.004	trace	0	0.000	trace	136 ppm	138 ppm	trace	140 ppm	trace	0.035	trace
FFA-1		0	0	0.008	0.006	0.008	49 ppm	0	0.007	trace	0.008	0.008	40 ppm	0.008	317 ppm	0.009	trace
FAME1		0	0	0	0.294	0.349	266 ppm	0	0.361	trace	0.382	0.387	173 ppm	0.394	0.039	0.148	trace
FAME2		0	0	0	0.330	0.391	0.001	0	0.405	trace	0.429	0.434	399 ppm	0.442	0.131	0.009	trace
FAME3		0	0	0	0.075	0.089	90 ppm	0	0.093	trace	0.098	0.099	54 ppm	0.101	0.012	0.041	trace
FAME4		0	0	0	0.034	0.040	23 ppm	0	0.042	trace	0.044	0.045	17 ppm	0.046	0.004	0.027	trace
GLYC		0	0	0	0.079	0.000	0.499	0	0.009	trace	0.009	0.001	0.706	trace	trace	trace	0.008
NAOH		0.042	0.042	0	0.008	0.001	0.043	0.007	0.002	trace	0.002	0.002	0.025	trace	trace	3 ppm	0.020
WATER		0	0	0	0	0	0	0	0	0	0	0	0	0.005	0.681	trace	0.699
H3PO4		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NA3PO4		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Figure B-2 Stream table of A2 case.

	Units	17	18	19	20	21	BIODSEL	GLYCEROL	H3PO4	MEOH-1	MEOH-2	NAOH-1	NAOH-2	S1	WATER	WCO
From		M-123	R-123	C-121	T-123	C-121	T-122	T-123						E-123		
To		R-123	C-121	T-123					R-123	M-121	M-122	M-121	M-122	R-122	W-121	E-121
Temperature	C	66	50	50	44	50	148	262	30	30	30	30	30	65	30	30
Pressure	bar	1	1	1	0.4	1	0.1	0.5	1	1	1	1	1	1	1	1
Mole Flows	mol/hr	15.4	15.7	15.4	11.2	0.3	12.7	4.2	0.3	18.9	6.7	0.9	0.0	6.7	12.3	4.3
Mole Fractions																
Mass Flows	kg/hr	0.8	0.8	0.7	0.3	0.0	3.6	0.4	0.0	0.6	0.2	0.0	0.0	0.2	0.2	3.6
Mass Fractions																
MEOH		0.446	0.431	0.456	0.956	0	48 ppm	4 ppm	0	1	1	0	0	0.993	0	0
TG1		trace	0	0	0	0	trace	0	0	0	0	0	0	0	0	0.398
TG2		trace	0	0	0	0	trace	0	0	0	0	0	0	0	0	0.446
TG3		trace	0	0	0	0	trace	0	0	0	0	0	0	0	0	0.102
TG4		trace	0	0	0	0	trace	0	0	0	0	0	0	0	0	0.046
FFA-1		48 ppm	47 ppm	49 ppm	trace	0	0.008	94 ppm	0	0	0	0	0	0	0	0.008
FAME1		260 ppm	252 ppm	266 ppm	243 ppm	0	0.398	288 ppm	0	0	0	0	0	0	0	0
FAME2		551 ppm	533 ppm	564 ppm	569 ppm	0	0.446	0.0006	0	0	0	0	0	0	0	0
FAME3		87 ppm	85 ppm	90 ppm	152 ppm	0	0.102	32 ppm	0	0	0	0	0	0	0	0
FAME4		23 ppm	22 ppm	24 ppm	11 ppm	0	0.046	35 ppm	0	0	0	0	0	0	0	0
GLYC		0.511	0.494	0.523	0.003	0	trace	0.999	0	0	0	0	0	0	0	0
NAOH		0.042	0	0	0	0	trace	0	0	0	0	1	1	0.007	0	0
WATER		0	0.018	0.019	0.041	0	257 ppm	trace	0	0	0	0	0	0	1	0
H3PO4		0	5 ppm	5 ppm	trace	0	0	10 ppm	1	0	0	0	0	0	0	0
NA3PO4		0	0.056	0	0	1	0	0	0	0	0	0	0	0	0	0

Figure B-2 Stream table of A2 case (continue).

	Units	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	BIODSEL	GLYCEROL	H3PO4	MEOH	NAOH	RPO	VENT
From		M-211	R-211	T-211	E-211	T-211	D-211	F-211	E-212	S-211	S-211	T-212	D-211	R-212	C-211	C-211	T-213	T-212	T-213					F-211
To		R-211	T-211	E-211		D-211	F-211	E-212	S-211		T-212		R-212	C-211		T-213				R-212	M-211	M-211	R-211	
Temperature	C	31	30	64	30	108	108	148	65	65	65	322	108	50	50	50	47	234	262	20	30	30	30	148
Mole Flows	mol/hr	27.1	31.5	9.4	9.4	22.0	14.9	13.9	13.9	0.9	12.9	0.3	7.1	7.3	0.2	7.1	3.0	12.7	4.1	0.2	16.8	0.9	4.4	1.0
Mole Fractions																								
Mass Flows	kg/hr	0.9	4.6	0.3	0.3	4.3	3.8	3.8	3.8	0.0	3.7	0.1	0.5	0.5	0.0	0.5	0.1	3.6	0.4	0.0	0.5	0.0	3.7	0.0
Mass Fractions																								
MEOH		0.958	0.094	1	1	0.030	0.014	0.005	0.005	0.553	86 ppm	trace	0.159	0.154	0	0.163	0.827	89 ppm	trace	0	1	0	0	0.984
TG1		0	0.010	trace	trace	0.010	0.012	0.012	0.012	0	0.012	0.347	trace	0	0	0	0	trace	0	0	0	0	0.401	trace
TG2		0	0.011	trace	trace	0.011	0.013	0.013	0.013	0	0.013	0.390	trace	0	0	0	0	trace	0	0	0	0	0.450	trace
TG3		0	0.002	trace	trace	0.003	0.003	0.003	0.003	0	0.003	0.089	trace	0	0	0	0	trace	0	0	0	0	0.103	trace
TG4		0	0.001	trace	trace	0.001	0.001	0.001	0.001	0	0.001	0.040	trace	0	0	0	0	trace	0	0	0	0	0.046	trace
FAME1		0	0.316	trace	trace	0.339	0.382	0.385	0.385	0	0.389	0.070	246 ppm	237 ppm	0	252 ppm	trace	0.400	314 ppm	0	0	0	0	0.003
FAME2		0	0.355	trace	trace	0.380	0.429	0.432	0.432	0	0.436	0.005	591 ppm	570 ppm	0	606 ppm	5 ppm	0.451	753 ppm	0	0	0	0	0.009
FAME3		0	0.081	trace	trace	0.087	0.098	0.099	0.099	0	0.100	0.019	68 ppm	66 ppm	0	70 ppm	trace	0.103	87 ppm	0	0	0	0	0.001
FAME4		0	0.036	trace	trace	0.039	0.044	0.044	0.044	0	0.045	0.013	25 ppm	25 ppm	0	27 ppm	trace	0.046	33 ppm	0	0	0	0	311 ppm
GLYC		0	0.085	trace	trace	0.091	0.001	0.001	0.001	0.126	79 ppm	4 ppm	0.795	0.766	0	0.815	0.067	81 ppm	0.999	0	0	0	0	0.003
NAOH		0.042	0.008	trace	trace	0.009	0.004	0.004	0.004	0.321	0.001	0.027	0.045	0	0	0	0	trace	0	0	0	1	0	trace
WATER		0	0	0	0	0	0	0	0	0	0	0	0	0.020	0	0.021	0.105	0	trace	0	0	0	0	0
H3PO4		0	0	0	0	0	0	0	0	0	0	0	0	0.000	0	164 ppm	trace	0	205 ppm	1	0	0	0	0
NA3PO4		0	0	0	0	0	0	0	0	0	0	0	0	0.059	1	0	0	0	0	0	0	0	0	0

Figure B-3 Stream table of B1 case.

	Units	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
From		M-221	E-222T	E-221T	R-221	D-221	D-221	M-222	E-223T	R-222	T-221	T-221	D-222	F--221	E-221S	E-223S	E-222S	E-224	S-221
To		E-222T	R-221	R-221	D-221	R-222	M-223	E-223T	R-222	T-221		D-222	F--221	E-221S	E-223S	E-222S	E-224	S-221	T-222
Temperature	C	41	65	65	65	65	65	30	65	65	64	88	88	133	105	80	72	65	65
Pressure	bar	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Mole Flows	mol/hr	26.7	26.7	4.3	31.0	16.4	14.6	6.7	6.7	23.1	6.9	16.2	15.4	13.6	13.6	13.6	13.6	13.6	12.7
Mole Fractions																			
Mass Flows	kg/hr	0.9	0.9	3.6	4.5	3.8	0.7	0.2	0.2	4.0	0.2	3.7	3.7	3.6	3.6	3.6	3.6	3.6	3.6
Mass Fractions																			
MEOH		0.958	0.958	0	0.103	0.036	0.457	0.993	0.993	0.080	1	0.025	0.022	0.007	0.007	0.007	0.007	0.007	109 ppm
TG1		0	0	0.398	0.028	0.034	trace	0	0	0.001	trace	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
TG2		0	0	0.446	0.032	0.038	trace	0	0	0.001	trace	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
TG3		0	0	0.102	0.007	0.009	trace	0	0	285 ppm	trace	301 ppm	305 ppm	310 ppm	310 ppm	310 ppm	310 ppm	310 ppm	310 ppm
TG4		0	0	0.046	0.003	0.004	trace	0	0	128 ppm	trace	136 ppm	138 ppm	140 ppm	140 ppm	140 ppm	140 ppm	140 ppm	140 ppm
FFA-1		0	0	0.008	0.006	0.008	49 ppm	0	0	0.007	trace	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008
FAME1		0	0	0	0.294	0.349	266 ppm	0	0	0.361	trace	0.382	0.387	0.393	0.393	0.393	0.393	0.393	0.397
FAME2		0	0	0	0.330	0.391	560 ppm	0	0	0.405	trace	0.429	0.434	0.441	0.441	0.441	0.441	0.441	0.444
FAME3		0	0	0	0.075	0.089	90 ppm	0	0	0.093	trace	0.098	0.099	0.101	0.101	0.101	0.101	0.101	0.102
FAME4		0	0	0	0.034	0.040	23 ppm	0	0	0.042	trace	0.044	0.045	0.045	0.045	0.045	0.045	0.045	0.046
GLYC		0	0	0	0.079	289 ppm	0.499	0	0	0.009	trace	0.009	0.001	0.001	0.001	0.001	0.001	0.001	41 ppm
NAOH		0.042	0.042	0	0.008	0.001	0.043	0.007	0.007	0.002	trace	0.002	0.002	0.002	0.002	0.002	0.002	0.002	371 ppm
WATER		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H3PO4		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NA3PO4		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Figure B-4 Stream table of B2 case.

	Units	19	20	21	22	23	24	25	1213	BIODSEL	GLYCEROL	H3PO4	MEOH-1	MEOH-2	NAOH-1	NAOH-2	S3	VENT	WCO
From		T-222	S-221	M-223	R-223	C-221	T-223	C-221	D-222	T-222	T-223							F--221	
To				R-223	C-221	T-223			M-223			R-223	M-221	M-222	M-221	M-222	M-221		E-221T
Temperature	C	286	65	66	50	50	44	50	88	231	262	30	30	30	30	30	64	133	30
Pressure	bar	0.1	1	1	1	1	0.4	1	1	0.1	0.5	1	1	1	1	1	1	1	1
Mole Flows	mol/hr	0.1	0.9	15.4	15.7	15.4	11.2	0.3	0.7	12.7	4.2	0.3	18.9	6.7	0.9	0.04	6.9	1.8	4.3
Mole Fractions																			
Mass Flows	kg/hr	0.02	0.03	0.75	0.78	0.73	0.35	0.04	0.04	3.59	0.38	0.03	0.61	0.21	0.04	0.00	0.22	0.06	3.59
Mass Fractions																			
MEOH		trace	0.781	0.446	0.431	0.456	0.957	0	0.267	109 ppm	4 ppm	0	1	1	0	0	1	0.993	0
TG1		0.196	0	trace	0	0	0	0	trace	trace	0	0	0	0	0	0	0	trace	0.398
TG2		0.219	0	trace	0	0	0	0	trace	trace	0	0	0	0	0	0	0	trace	0.446
TG3		0.050	0	trace	0	0	0	0	trace	trace	0	0	0	0	0	0	0	trace	0.102
TG4		0.023	0	trace	0	0	0	0	trace	trace	0	0	0	0	0	0	0	trace	0.046
FFA-1		0.027	0	48 ppm	47 ppm	49 ppm	trace	0	40 ppm	0.008	9 ppm	0	0	0	0	0	0	8 ppm	0.008
FAME1		0.280	0	260 ppm	252 ppm	266 ppm	231 ppm	0	173 ppm	0.397	299 ppm	0	0	0	0	0	0	0.001	0
FAME2		0.020	0	551 ppm	533 ppm	0.001	0.001	0	398 ppm	0.447	0.001	0	0	0	0	0	0	0.004	0
FAME3		0.067	0	87 ppm	84 ppm	89 ppm	150 ppm	0	54 ppm	0.102	34 ppm	0	0	0	0	0	0	371 ppm	0
FAME4		0.058	0	23 ppm	22 ppm	24 ppm	11 ppm	0	17 ppm	0.046	35 ppm	0	0	0	0	0	0	129 ppm	0
GLYC		2 ppm	0.072	0.511	0.494	0.523	0.001	0	0.706	41 ppm	0.999	0	0	0	0	0	0	0.001	0
NAOH		0.060	0.147	0.042	0	0	0	0	0.025	trace	0	0	0	0	1	1	0	trace	0
WATER		0	0	0	0.018	0.019	0.041	0	0	0	trace	0	0	0	0	0	0	0	0
H3PO4		0	0	0	5 ppm	5 ppm	trace	0	0	0	9 ppm	1	0	0	0	0	0	0	0
NA3PO4		0	0	0	0.056	0	0	1	0	0	0	0	0	0	0	0	0	0	0

Figure B-4 Stream table of B2 case (continue).

	Units	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	BIODSEL	GLYCEROL	H3PO4	MEOH	NAOH	OIL	WATER
From		M-311	E-311	E-312	R-311	T-311	T-311	D-311	D-311	L-311	L-311	T-312	R-312	S-311	S-311	T-313	T-312	T-313					
To		E-311	R-311	R-311	T-311		D-311	R-312	L-311		T-312		S-311		T-313				R-312	M-311	M-311	E-312	L-311
Temperature	C	44	60	60	60	64	102	102	102	100	93	321	50	50	50	47	21	262	20	30	30	30	25
Pressure	bar	1	1	1	1	1	1	1	1	1	1	0.1	1.1	1.1	1.1	0.4	0.1	0.5	1.1	1	1	1	1.1
Mole Flows	mol/hr	28.8	28.8	4.8	33.6	11.2	22.4	6.4	16.0	14.1	15.3	1.0	7.3	0.0	7.2	3.4	14.3	3.8	0.8	17.5	0.2	4.8	13.4
Mass Flows	kg/hr	0.9	0.9	4.0	5.0	0.4	4.6	0.4	4.2	0.3	4.1	0.5	0.5	0.0	0.4	0.1	3.6	0.4	0.0	0.6	0.0	4.0	0.2
Mass Fractions																							
MEOH		0.991	0.991	0	0.103	1	0.033	0.183	0.018	0.230	0.002	trace	0.176	0	0.178	0.813	0.002	5 ppm	0	1	0	0	0
TG-1		trace	trace	0.450	0.025	trace	0.027	trace	0.030	trace	0.030	0.236	0	0	0	0	trace	0	0	0	0	0.450	0
TG-2		trace	trace	0.401	0.020	trace	0.022	trace	0.024	trace	0.024	0.189	0	0	0	0	trace	0	0	0	0	0.401	0
TG-3		trace	trace	0.103	0.004	trace	0.004	trace	0.005	trace	0.005	0.037	0	0	0	0	trace	0	0	0	0	0.103	0
TG-4		trace	trace	0.046	0.002	trace	0.002	trace	0.002	trace	0.002	0.016	0	0	0	0	trace	0	0	0	0	0.046	0
DG-1		trace	trace	0	0.008	trace	0.008	trace	0.009	trace	0.009	0.074	trace	0	trace	trace	trace	trace	0	0	0	0	0
DG-2		trace	trace	0	0.006	trace	0.007	trace	0.007	trace	0.007	0.058	trace	0	trace	trace	trace	trace	0	0	0	0	0
DG-3		trace	trace	0	0.001	trace	0.001	trace	0.001	trace	0.001	0.008	0	0	0	0	trace	0	0	0	0	0	0
DG-4		trace	trace	0	0.000	trace	0.000	trace	0.000	trace	364 ppm	0.003	0	0	0	0	trace	0	0	0	0	0	0
MG-2		trace	trace	0	0.013	trace	0.014	0.001	0.015	trace	0.016	0.121	0.001	0	0.001	trace	60 ppm	0.001	0	0	0	0	0
MG-1		trace	trace	0	0.015	trace	0.016	196 ppm	0.018	trace	0.018	0.138	189 ppm	0	191 ppm	trace	4 ppm	245 ppm	0	0	0	0	0
MG-3		trace	trace	0	0.003	trace	0.004	110 ppm	0.004	trace	0.004	0.032	106 ppm	0	107 ppm	trace	4 ppm	137 ppm	0	0	0	0	0
MG-4		trace	trace	0	0.002	trace	0.002	9 ppm	0.002	trace	0.002	0.014	8 ppm	0	8 ppm	trace	trace	11 ppm	0	0	0	0	0
FAME-1		trace	trace	0	0.323	trace	0.348	430 ppm	0.385	trace	0.389	0.004	413 ppm	0	419 ppm	0.001	0.446	355 ppm	0	0	0	0	0
FAME-2		trace	trace	0	0.291	trace	0.313	183 ppm	0.346	trace	0.350	0.048	175 ppm	0	178 ppm	254 ppm	0.395	156 ppm	0	0	0	0	0
FAME-3		trace	trace	0	0.077	trace	0.083	54 ppm	0.091	trace	0.092	0.011	52 ppm	0	52 ppm	152 ppm	0.104	24 ppm	0	0	0	0	0
FAME-4		trace	trace	0	0.034	trace	0.037	19 ppm	0.041	trace	0.041	0.012	19 ppm	0	19 ppm	13 ppm	0.046	21 ppm	0	0	0	0	0
GLYC		trace	trace	0	0.072	trace	0.077	0.804	0.001	0.019	trace	trace	0.772	0	0.783	0.017	trace	0.998	0	0	0	0	0
NAOH		0.009	0.009	0	0.002	trace	0.002	0.010	0.001	0.013	trace	trace	0	0	0	0	trace	0	0	0	1	0	0
H2O		0	0	0	0	0	0	0	0	0.738	0.007	trace	0.036	0	0.037	0.168	0.008	trace	0.800	0	0	0	1
H3PO4		0	0	0	0	0	0	0	0	0	0	0	24 ppm	0.002	0	0	0	0	0.200	0	0	0	0
NA3PO4		0	0	0	0	0	0	0	0	0	0	0	0.013	0.998	0	0	0	0	0	0	0	0	0

Figure B-5 Stream table of C1 case.

	Units	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
From		M-121	P-121	P-122	E-121	R-121	E-121	L-121	S-121	S-121	M-122	P-111	E-122	L-121	S-122	S-122
To		P-121	R-121	E-121	R-121	E-121	L-121	S-121	M-122	M-123	P-111	E-122	R-122	S-122	M-122	M-123
Temperature	C	25	25	26	60	70	48	45	45	45	45	46	60	48	48	48
Pressure	bar	1	4	4	4	4	4	1.9	1.9	1.9	1.9	4	4	2	2	2
Mole Flows	mol/hr	30.8	30.8	4.8	4.8	35.6	35.6	18.9	4.4	14.5	4.8	4.8	4.8	21.7	0.4	21.3
Mole Fractions																
Mass Flows	kg/hr	1.1	1.1	3.7	3.7	4.9	4.9	4.3	3.5	0.8	3.8	3.8	3.8	1.0	0.3	0.8
Mass Fractions																
TG1		0	0	0.423	0.423	0.325	0.325	0.342	0.423	0	0.422	0.422	0.422	0.114	0.411	0.002
TG2		0	0	0.377	0.377	0.290	0.290	0.305	0.377	0	0.376	0.376	0.376	0.102	0.367	0.001
TG3		0	0	0.097	0.097	0.074	0.074	0.078	0.097	0	0.097	0.097	0.097	0.026	0.094	361 ppm
TG4		0	0	0.043	0.043	0.033	0.033	0.035	0.043	0	0.043	0.043	0.043	0.012	0.042	161 ppm
FFA1		0	0	0.060	0.060	0.060	0	0	0	0	0	0	0	0	0	0
MEOH		0.814	0.814	0	0	0.183	0.183	0.063	0	0.328	0	0	0	0.595	0	0.822
FAME1		0	0	0	0	0.022	0.022	0.022	0.027	0	0.028	0.028	0.028	0.011	0.039	149 ppm
FAME2		0	0	0	0	0.019	0.019	0.020	0.024	0	0.025	0.025	0.025	0.010	0.034	132 ppm
FAME3		0	0	0	0	0.005	0.005	0.005	0.006	0	0.006	0.006	0.006	0.002	0.009	34 ppm
FAME4		0	0	0	0	0.002	0.002	0.002	0.003	0	0.003	0.003	0.003	0.001	0.004	15 ppm
GLYC		0	0	0	0	0	0	0.103	0	0.536	0	0	0	0.019	0	0.027
NAOH		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H2SO4		0.186	0.186	0	0	0.043	0.043	0.025	0	0.131	0	0	0	0.098	0	0.135
H2O		0	0	0	0	0.003	0.003	0.001	0	0.006	0	0	0	0.009	0	0.013
H3PO4		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NA3PO4		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Figure B-6 Stream table of C2 case.

	Units	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
From		M-123	T-121	P-123	T-121	M-124	P-124	R-122	T-122	T-122	P-125	E-123	L-122	S-123	T-123	T-123
To		T-121	P-123			P-124	R-122	T-122	M-124	P-125		L-122	S-123	T-123		
Temperature	C	46	28	29	63	28	29	60	28	67	67	60	54	54	185	357
Pressure	bar	1.9	0.2	4	0.3	0.2	4	4	0.2	0.3	2	2	1.1	1.1	0.1	0.3
Mole Flows	mol/hr	35.8	25.3	25.3	10.5	23.5	23.5	28.2	8.9	19.3	19.3	19.3	36.6	14.0	1.9	0.2
Mole Fractions																
Mass Flows	kg/hr	1.6	0.8	0.8	0.8	0.8	0.8	4.5	0.3	4.2	4.2	4.2	4.2	3.8	0.1	0.2
Mass Fractions																
TG1		0.001	trace	trace	trace	trace	trace	0.018	trace	0.019	0.019	0.019	0.018	0.021	trace	0.413
TG2		0.001	trace	trace	trace	trace	trace	0.016	trace	0.017	0.017	0.017	0.016	0.018	trace	0.368
TG3		174 ppm	trace	trace	trace	trace	trace	0.004	trace	0.004	0.004	0.004	0.004	0.005	trace	0.095
TG4		78 ppm	trace	trace	trace	trace	trace	0.002	trace	0.002	0.002	0.002	0.002	0.002	trace	0.042
FFA1		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
MEOH		0.565	0.999	0.999	0.107	0.952	0.952	0.080	1	0.017	0.017	0.017	0.010	0	0	0
FAME1		71 ppm	trace	trace	147 ppm	trace	trace	0.358	trace	0.383	0.383	0.383	0.380	0.426	0.225	0.037
FAME2		64 ppm	trace	trace	131 ppm	trace	trace	0.319	trace	0.341	0.341	0.341	0.339	0.379	0.201	0.033
FAME3		16 ppm	trace	trace	34 ppm	trace	trace	0.082	trace	0.088	0.088	0.088	0.087	0.097	0.052	0.008
FAME4		7 ppm	trace	trace	15 ppm	trace	trace	0.037	trace	0.039	0.039	0.039	0.039	0.043	0.023	0.004
GLYC		0.291	trace	trace	0.598	trace	trace	0.077	trace	0.082	0.082	0.082	0.004	0	0	0
NAOH		0	0	0	0	0.048	0.048	0.008	trace	0.009	0.009	0.009	0.006	0	0	0
H2SO4		0.133	trace	trace	0.273	0	0	0	0	0	0	0	0	0	0	0
H2O		0.009	trace	0.001	0.018	0	0	0	0	0	0	0	0.094	0.008	0.499	trace
H3PO4		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NA3PO4		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Figure B-6 Stream table of C2 case (continue).

	Units	31	32	33	34	35	36	38	BIODSEL	GLYCEROL	GLYCW	H2SO4	H3PO4	MEOH	MEOH-2	NAOH	OIL	WATER
From		L-122	S-123	M-125	R-123	S-124	T-124	S-124	T-123	T-124								
To		M-125	M-125	R-123	S-124	T-124					L-121	M-121	R-123	M-121	M-124	M-124	P-122	L-122
Temperature	C	59	54	52	60	60	65	60	185	261	25	25	25	25	28	25	25	25
Pressure	bar	1.2	1.1	1.1	1.1	1.1	0.4	1.1	0.1	0.5	2	1	1.1	1	1	1	1	1.1
Mole Flows	mol/hr	4.9	22.6	27.5	27.8	27.4	23.6	0.4	11.9	3.8	5.0	2.1	0.3	3.3	13.6	0.9	4.8	22.2
Mole Fractions																		
Mass Flows	kg/hr	0.4	0.5	0.8	0.9	0.8	0.5	0.1	3.6	0.4	0.5	0.2	0.0	0.1	0.4	0.0	3.7	0.4
Mass Fractions																		
TG1		0.003	0	0.003	0.003	0	0	0.016	trace	0	0	0	0	0	0	0	0.423	0
TG2		0.002	0	0.002	0.002	0	0	0.014	0	0	0	0	0	0	0	0	0.377	0
TG3		0.001	0	0.001	0.001	0	0	0.004	0	0	0	0	0	0	0	0	0.097	0
TG4		274 ppm	0	274 ppm	274 ppm	0	0	0.002	0	0	0	0	0	0	0	0	0.043	0
FFA1		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.06	0
MEOH		0.083	0.090	0.087	0.084	0.091	0.159	0	0	trace	0	0	0	1	1	0	0	0
FAME1		0.019	0	0.009	0.009	0.002	0.004	0.087	0.9999	trace	0	0	0	0	0	0	0	0
FAME2		0.017	0	0.008	0.008	0.002	0.004	0.078	0	trace	0	0	0	0	0	0	0	0
FAME3		0.004	0	0.002	0.002	0.001	0.001	0.020	0	trace	0	0	0	0	0	0	0	0
FAME4		0.002	0	0.001	0.001	240 ppm	421 ppm	0.009	0	trace	0	0	0	0	0	0	0	0
GLYC		0.844	0.035	0.412	0.397	0.430	0.002	0	0	0.9998	1	0	0	0	0	0	0	0
NAOH		0.023	0.061	0.043	0	0	0	0	0	0	0	0	0	0	0	1	0	0
H2SO4		0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0
H2O		trace	0.814	0.435	0.439	0.475	0.831	0	52 ppm	191 ppm	0	0	0	0	0	0	0	1
H3PO4		0	0	0	0.001	0	0	0.009	0	0	0	0	1	0	0	0	0	0
NA3PO4		0	0	0	0.057	0	0	0.761	0	0	0	0	0	0	0	0	0	0

Figure B-6 Stream table of C2 case (continue).

APPENDIX C

Inlet and outlet temperatures of the RTR reactor

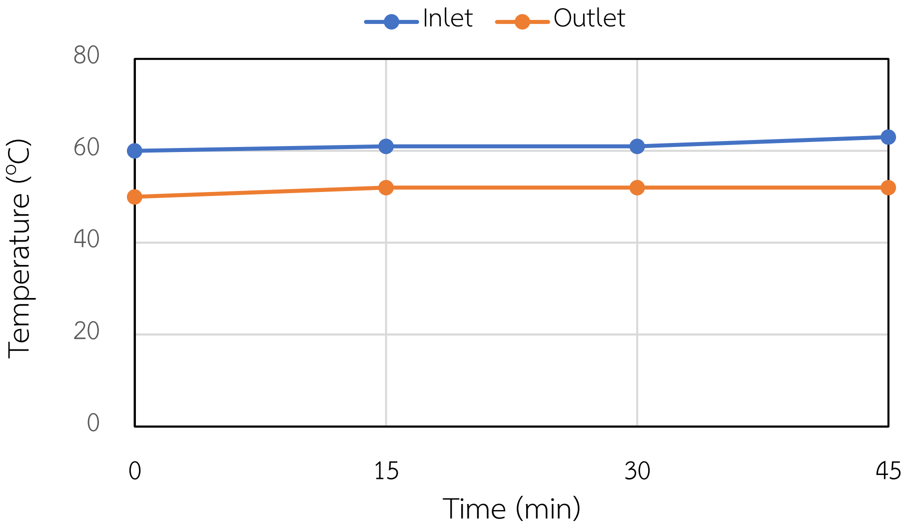


Figure C-1 Inlet and outlet temperature of the RTR reactor in esterification at 60 °C.

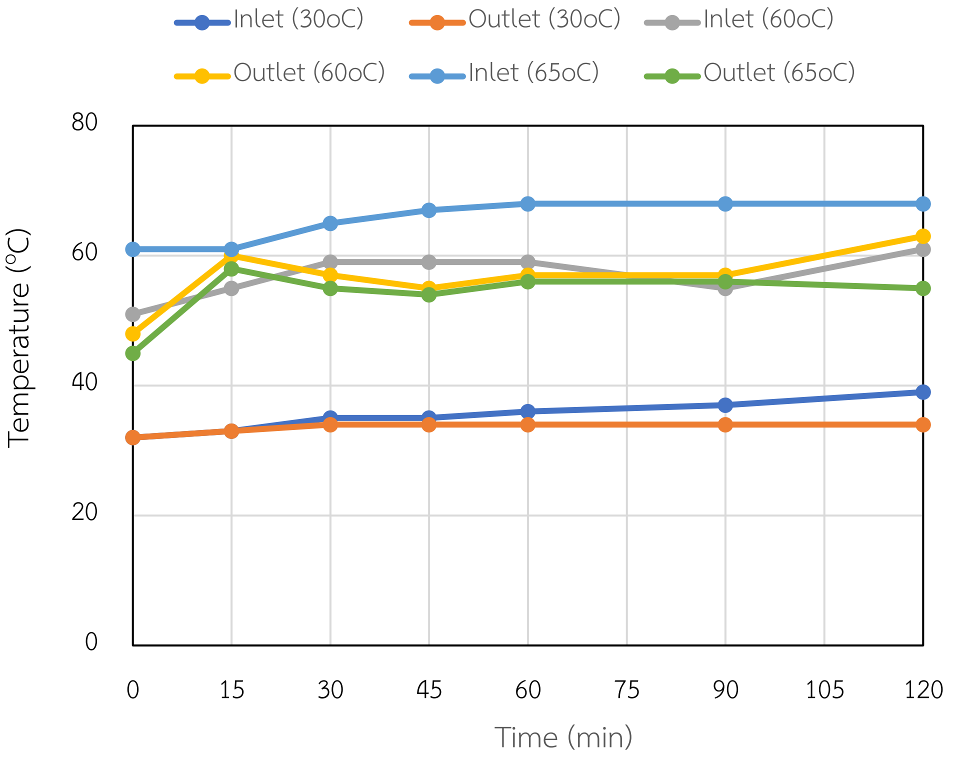


Figure C-2 Inlet and outlet temperature of the RTR reactor in transesterification

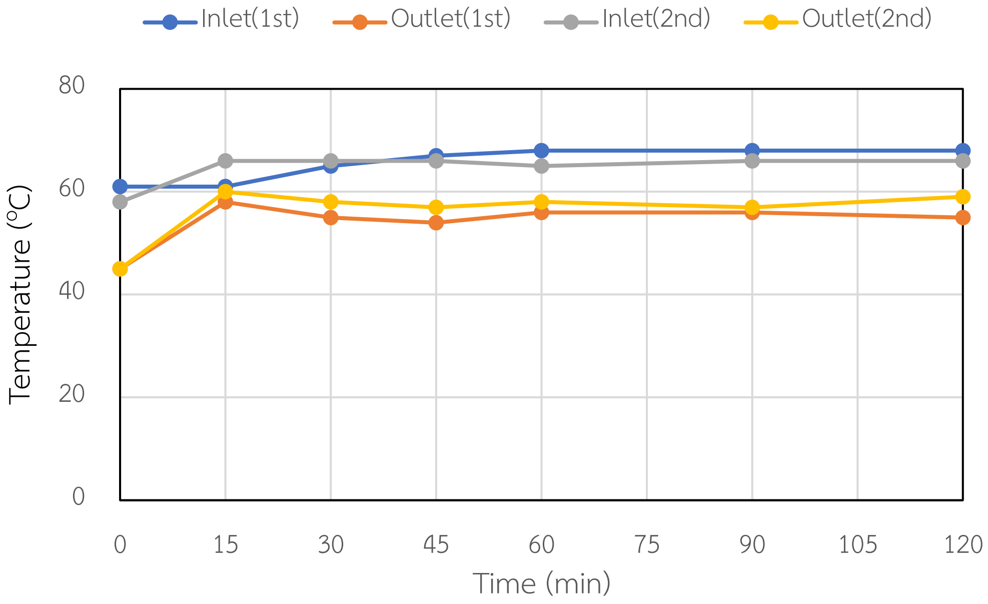


Figure C-3 Inlet and outlet temperature of the RTR reactor in 1st and 2nd transesterification step.

APPENDIX D

Case C2 without esterification

To compare the TEA of biodiesel production from WCO using RTR and conventional CSTR reactors based on the assumption of similar WCO containing FFA lower than 2%, the capital and operating cost of esterification unit in C2 case were neglected. The overall process flow diagram and stream table are depicted in Figures D-1 and D-2, respectively.

Tables D-1 and D-2 present the total capital investment and manufacturing costs for C2 case without esterification unit. The cost of RTR was calculated based on the actual construction cost as indicated in the transesterification reactor (A2 and B2 cases) was greater than that of the conventional reactor (C2 and C2 without esterification unit cases) resulting to higher total capital investment cost as compared to C2 case. The operating cost based on the similar WCO composition (FFA lower than 2%) was similar for A2, B2 and C2 without esterification cases as illustrated in Table D-2. Table D-3 shows the IRR and NPV values for the C2 without esterification case was 14.7% and 230.9 thousand USD, respectively which was similar to that of A2 case. This should be noted that the biodiesel product does not meet the required standard due to its FFA content higher than 0.5%.

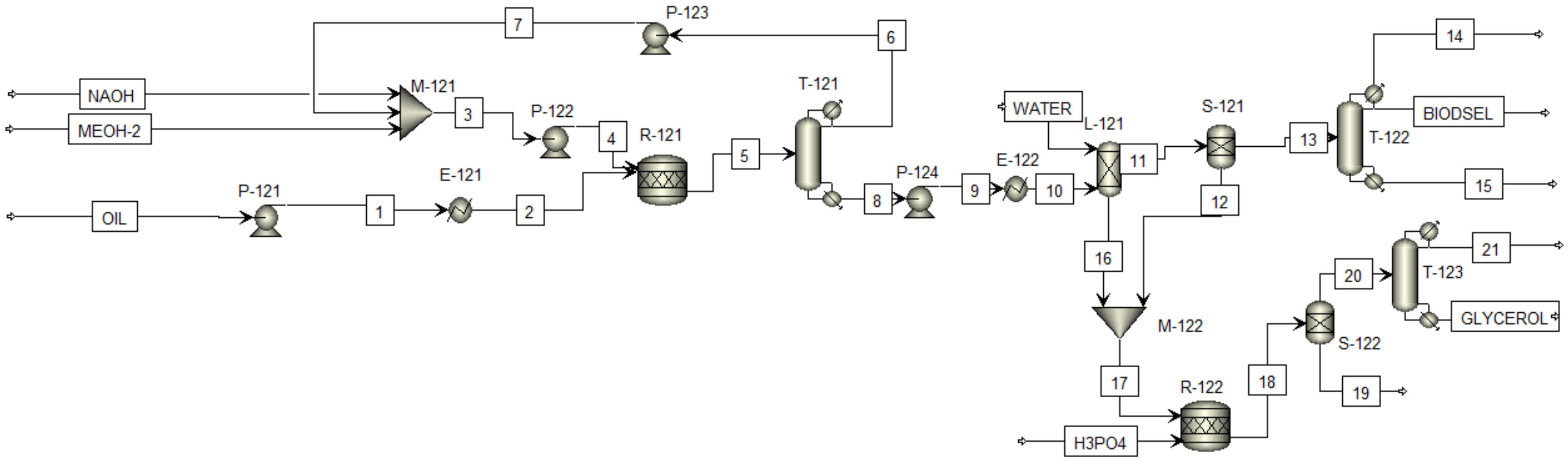


Figure D-1 The overall process flow diagram of biodiesel production using WCO (without esterification) in a conventional reactor with wet purification method (case C2(without Esterification)).

	Units	1	2	3	4	5	6	7	8	9	10	11	12	13	14
From		P-121	E-121	M-121	P-122	R-121	T-121	P-123	T-121	P-124	E-122	L-121	S-121	S-121	T-122
To		E-121	R-121	P-122	R-121	T-121	P-123	M-121	P-124		L-121	S-121	M-122	T-122	
Temperature	C	25.7	60.0	28.3	28.7	60.0	28.3	28.9	97.5	97.8	60.0	57.5	59.4	59.4	185.0
Pressure	bar	4	4	1	4	4	0.2	4	0.3	2	2	1.1	1.1	1.1	0.1
Mole Flows	mol/hr	5.7	5.7	35.3	35.3	41.0	19.4	19.4	21.7	21.7	21.7	15.9	0.1	15.8	1.0
Mole Fractions															
Mass Flows	kg/hr	4.3	4.3	1.1	1.1	5.5	0.6	0.6	4.9	4.9	4.9	4.4	0.0	4.4	0.0
Mass Fractions															
TG1		0.423	0.423	0	0	0.017	trace	trace	0.019	0.019	0.019	0.021	0	0.021	trace
TG2		0.377	0.377	0	0	0.015	trace	trace	0.017	0.017	0.017	0.019	0	0.019	trace
TG3		0.097	0.097	0	0	0.004	trace	trace	0.004	0.004	0.004	0.005	0	0.005	trace
TG4		0.043	0.043	0	0	0.002	trace	trace	0.002	0.002	0.002	0.002	0	0.002	trace
FFA1		0.060	0.060	0	0	0.048	trace	trace	0.054	0.054	0.054	0.059	0	0.059	0.006
MEOH		0	0	0.962	0.962	0.121	1	1	0.008	0.008	0.008	0.002	0.958	0.001	0.092
FAME1		0	0	0	0	0.320	trace	trace	0.360	0.360	0.360	0.400	0	0.400	0.153
FAME2		0	0	0	0	0.285	trace	trace	0.321	0.321	0.321	0.356	0	0.357	0.382
FAME3		0	0	0	0	0.073	trace	trace	0.083	0.083	0.083	0.092	0	0.092	0.037
FAME4		0	0	0	0	0.032	trace	trace	0.037	0.037	0.037	0.041	0	0.041	0.013
GLYC		0	0	0	0	0.076	trace	trace	0.086	0.086	0.086	trace	41 ppm	0	0
NAOH		0	0	0.038	0.038	0.008	trace	trace	0.009	0.009	0.009	42 ppm	0.042	0	0
H2O		0	0	0	0	0	0	0	0	0	0	0.003	0	0.003	0.317
H3PO4		0	0	0	0	0	0	0	0	0	0	0	0	0	0
NA3PO4		0	0	0	0	0	0	0	0	0	0	0	0	0	0

Figure D-2 Stream table of C2 case (without esterification).

	Units	15	16	17	18	19	20	21	BIODSEL	GLYCEROL	H3PO4	MEOH-2	NAOH	OIL	WATER
From		T-122	L-121	M-122	R-122	S-122	S-122	T-123	T-122	T-123					
To			M-122	R-122	S-122		T-123				R-122	M-121	M-121	P-121	L-121
Temperature	C	299.0	58.6	48.0	60.0	60.0	60.0	56.7	185.0	261.2	25.0	28.2	25.0	25.0	25.0
Pressure	bar	0.3	1.2	1.1	1.1	1.1	1.1	0.4	0.1	0.5	1.1	1	1	1	1.1
Mole Flows	mol/hr	2.20	8.53	8.67	9.03	0.36	8.67	4.13	12.54	4.54	0.36	34.22	1.08	5.70	2.78
Mole Fractions															
Mass Flows	kg/hr	0.8	0.5	0.5	0.6	0.1	0.5	0.1	3.6	0.4	0.0	1.1	0.0	4.3	0.1
Mass Fractions															
TG1		0.119	trace	trace	0	0	0	0	trace	0	0	0	0	0.423	0
TG2		0.106	trace	trace	0	0	0	0	trace	0	0	0	0	0.377	0
TG3		0.027	trace	trace	0	0	0	0	trace	0	0	0	0	0.097	0
TG4		0.012	trace	trace	0	0	0	0	trace	0	0	0	0	0.043	0
FFA1		0.152	33 ppm	33 ppm	31 ppm	293 ppm	0	0	0.040	0	0	0	0	0.060	0
MEOH		0	0.059	0.066	0.062	0	0.070	0.392	29 ppm	trace	0	1	0	0	0
FAME1		0.366	20 ppm	20 ppm	19 ppm	134 ppm	5 ppm	29 ppm	0.411	trace	0	0	0	0	0
FAME2		0.074	39 ppm	40 ppm	36 ppm	347 ppm	0	0	0.418	0	0	0	0	0	0
FAME3		0.094	7 ppm	8 ppm	7 ppm	63 ppm	0	0	0.092	0	0	0	0	0	0
FAME4		0.050	1 ppm	2 ppm	1 ppm	12 ppm	0	0	0.039	0	0	0	0	0	0
GLYC		0	0.793	0.786	0.737	0	0.823	0.006	0	1.000	0	0	0	0	0
NAOH		0	0.082	0.081	0	0	0	0	0	0	0	0	1	0	0
H2O		trace	0.066	0.066	0.096	0	0.107	0.603	220 ppm	223 ppm	0	0	0	0	1
H3PO4		0	0	0	24 ppm	233 ppm	0	0	0	0	1	0	0	0	0
NA3PO4		0	0	0	0.104	0.999	0	0	0	0	0	0	0	0	0

Figure D-3 Stream table of C2 case (without esterification) (continue).

Table D-1 Total capital investment (TCI) for each case (thousand USD).

Item	A2	B2	C2	C2 (without Esterification)
Equipment cost				
Heat exchanger	4.0	4.9	6.4	4.0
Transesterification reactor*	23.5	23.5	6.1	6.9
Esterification reactor	-	-	9.2	-
Neutralization reactor	1.8	1.8	2.0	-
Methanol recovery column	25.9	22.6	68.7	32.7
Biodiesel column	36.9	33.8	36.5	33.9
Glycerol column	26.2	27.6	28.8	25.3
Purolite column	-	16.0	-	-
L-L Extractor	14.8	-	24.2	12.7
Decanter	5.0	5.0	-	-
Centrifuge (Separator)	0.8	0.8	8.3	3.2
Pump	-	-	10.1	10.8
Mixer	3.1	2.3	10.4	1.8
Flash drum	-	1.1	-	-
Total equipment cost	140.6	138.7	210.6	132.6
Fixed capital investment (FCI)	165.9	163.6	248.5	156.5
Working capital	24.9	24.7	37.3	23.5
Total capital investment	190.8	189.1	285.8	180.0

Table D-2 Summary of manufacturing cost for each case (thousand USD/year.).

Item	A2	B2	C2	C2 (without Esterification)
Raw material (C_{RM})				
RPO	-	-	-	-
WCO	7.7	7.7	9.2	10.5
Methanol	2.9	2.9	2.0	1.7
Glycerol (washing)	-	-	17.5	-
NaOH	0.8	0.8	0.8	0.9
H_3PO_4	0.6	0.6	0.7	0.8
H_2SO_4	-	-	0.7	-
Purolite (PD206)	-	3.0	-	-
Total raw material	12.0	15.0	30.9	13.9
Utilities (C_{UT})				
Electricity	0.42	0.41	0.10	0.10
Chilled water	-	-	0.28	0.09
Cooling water	0.03	0.02	0.03	0.02
Fired heat	0.28	0.22	0.35	0.24
LP steam	0.05	0.055	0.28	0.01
MP steam	-	0.02	-	-
Water	3E-03	-	6E-03	6E-03
Total utilities	0.64	0.59	1.03	0.55
Operating labor (C_{OL})	5.6	5.6	5.6	5.6
Waste treatment (C_{WT})				
Wastewater	0.3	0.2	0.7	0.8
Solid waste	0.4	1.8	0.6	0.6
Total waste treatment	0.7	2.0	1.4	1.4
Total manufacturing cost (COM)	61.6	66.5	100.9	62.8

Table D-*3* Profitability indicators for each case (10 years, USD thousand).

	A2	**B2**	**C2**	**C2 (without Esterification)**
Payback period (year)	4.4	4.8	-	4.3
NPV (10 year)	232.7	195.6	-144.2	230.9
IRR (%, 10 year)	14.0	11.9	-	14.7

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VITA

NAME	Arthit Jarungwongsathien
DATE OF BIRTH	8 November 1998
PLACE OF BIRTH	Nan
INSTITUTIONS ATTENDED	Chemical Technology, Chulalongkorn University, Bankok, Thailand
HOME ADDRESS	173/2 Taksin Maharaj Road, Tha Pradu, Mueang Rayong District, 21000
AWARD RECEIVED	1st Runner Up, TIChE National Chemical Student Design Competition 2020-2021. The best oral presentation award, TIChE 2023.