



**Process Development of Two-Step Esterification on
Waste Vegetable Oil with very High Free Fatty Acid**

Songtham Photaworn

**A Thesis Submitted in Fulfillment of the Requirements for the
Degree of Doctor of Philosophy in Chemical Engineering
Prince of Songkla University**

2017

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บทคัดย่อ

การใช้น้ำมันบริโภคในการผลิตไบโอดีเซล ทำให้มีต้นทุนการผลิตที่สูงกว่าน้ำมันวัตถุดิบที่มีคุณภาพต่ำ เช่น น้ำมันพืชเสีย ซึ่งโดยทั่วไปมีกรดไขมันอิสระและความชื้นสูง แต่อย่างไรก็ตาม น้ำมันประเภทนี้ก่อให้เกิดสบู่ในขณะปฏิกิริยาทรานส์เอสเตอริฟิเคชัน เมื่อใช้ค่าเป็นตัวเร่งปฏิกิริยา ดังนั้นกระบวนการเอสเตอริฟิเคชันจึงใช้ในการปรับสภาพวัตถุดิบ โดยการลดกรดไขมันอิสระให้อยู่ในระดับที่เหมาะสม ก่อนการทำปฏิกิริยาทรานส์เอสเตอริฟิเคชัน สำหรับวัตถุประสงค์ของงานวิจัยนี้ เพื่อพัฒนากระบวนการผลิตไบโอดีเซลแบบต่อเนื่องจากน้ำมันพืชเสียกับเมทานอล โดยการทำให้ปฏิกิริยาแบบ 2 ขั้นตอน

ขั้นตอนแรกศึกษากระบวนการเอสเตอริฟิเคชันทั้งแบบกะและแบบต่อเนื่อง ในแบบกะนั้นแบ่งออกเป็น 4 การทดลอง คือ ปฏิกิริยาเอสเตอริฟิเคชันครั้งที่ 1 ปฏิกิริยาเอสเตอริฟิเคชันครั้งที่ 2 ปฏิกิริยาเอสเตอริฟิเคชันแบบ 2 ครั้ง และปฏิกิริยาเอสเตอริฟิเคชันแบบ 2 ครั้งร่วมกับการนำเฟสเมทานอลกลับมาใช้ใหม่ มีปัจจัยที่ศึกษาได้แก่ อัตราส่วนโดยโมลของเมทานอลต่อกรดไขมันอิสระ อัตราส่วนโดยโมลของกรดซัลฟิวริกต่อกรดไขมันอิสระ อุณหภูมิและเวลา นอกจากนี้ได้นำการวิเคราะห์หาค่าหลายตัวแปรและสมมูลมวลมาวิเคราะห์ข้อมูล และตรงกับแบบจำลองที่เป็นสมการกำลังสองอย่างมีนัยสำคัญ โดยมีตัวแปรที่มีผลกระทบมากที่สุดในปฏิกิริยาเอสเตอริฟิเคชันครั้งที่ 1 คือ ผลคูณระหว่างอัตราส่วนโดยโมลของเมทานอลต่อกรดไขมันอิสระและอัตราส่วนโดยโมลของกรดซัลฟิวริกต่อกรดไขมันอิสระ ส่วนผลกระทบมากที่สุดในปฏิกิริยาเอสเตอริฟิเคชันครั้งที่ 2 คือ อัตราส่วนโดยโมลของกรดซัลฟิวริกต่อกรดไขมันอิสระ สำหรับการทำให้ปฏิกิริยาเอสเตอริฟิเคชันแบบ 2 ครั้ง โดยใช้สภาวะที่เหมาะสมจากปฏิกิริยาเอสเตอริฟิเคชันครั้งที่ 1 และปฏิกิริยาเอสเตอริฟิเคชันครั้งที่ 2 พบว่า สามารถเกิดการเปลี่ยนกรดไขมันอิสระได้อย่างมีประสิทธิภาพ และทำให้กรดไขมันอิสระมีค่าต่ำกว่า 1% โดยน้ำหนัก ซึ่งเป็นค่าที่กำหนดไว้สำหรับปฏิกิริยาทรานส์

เอสเทอริฟิเคชัน ส่วนปฏิกิริยาเอสเทอริฟิเคชันแบบ 2 ครั้งร่วมกับการนำกลับมาใช้ใหม่ของเฟสเมทานอลนั้น สามารถลดค่ากรดไขมันอิสระได้เช่นเดียวกับปฏิกิริยาเอสเทอริฟิเคชันแบบ 2 ครั้ง

กระบวนการเอสเทอริฟิเคชันแบบต่อเนื่อง ได้ศึกษาโดยใช้ถังปฏิกรณ์ชนิดที่มีการแยกน้ำออกในขณะที่เกิดปฏิกิริยา และถังปฏิกรณ์ชนิดกวนผสมอย่างเดี่ยว พบว่าการทำปฏิกิริยาเอสเทอริฟิเคชันแบบ 3 ครั้ง โดยใช้ถังปฏิกรณ์ชนิดแยกน้ำออก จำนวน 2 ถัง และถังปฏิกรณ์แบบธรรมดา จำนวน 1 ถัง ร่วมกับการนำกลับมาใช้ใหม่ของเฟสเมทานอล สามารถลดค่ากรดไขมันอิสระต่ำกว่า 0.5 % โดยน้ำหนัก ประโยชน์ที่ได้จากการทำปฏิกิริยาเอสเทอริฟิเคชันแบบต่อเนื่องร่วมกับการนำกลับมาใช้ใหม่ของเฟสเมทานอล คือ มีปฏิกิริยาทรานส์เอสเทอริฟิเคชันที่ใช้กรดซัลฟิวริกเป็นตัวเร่งปฏิกิริยา ทำให้ได้ปริมาณเอสเทอร์เพิ่มขึ้น

ขั้นตอนที่สอง คือ ปฏิกิริยาทรานส์เอสเทอริฟิเคชัน ซึ่งนำมันวัตถุดิบได้จากการผสมน้ำมันที่ผ่านการเอสเทอริฟิเคชันแล้วกับน้ำมันพืชใช้แล้วในอัตราส่วน 50/50 โดยน้ำหนัก ไตรกลีเซอไรด์จะทำปฏิกิริยากับเมทานอลโดยมีด่างเป็นตัวเร่งปฏิกิริยา โดยศึกษาปัจจัยต่างๆ เพื่อหาสภาวะที่เหมาะสมในการทำแบบกะของปฏิกิริยาทรานส์เอสเทอริฟิเคชันแบบ 2 ครั้ง ได้แก่ ปริมาณตัวเร่งปฏิกิริยา และอัตราส่วนของสารละลายตัวเร่งปฏิกิริยาในการทำปฏิกิริยาทรานส์เอสเทอริฟิเคชันครั้งที่ 1 และ ครั้งที่ 2

กระบวนการทรานส์เอสเทอริฟิเคชันแบบต่อเนื่อง ได้ศึกษาโดยใช้ถังปฏิกรณ์ชนิดกวนผสมอย่างเดี่ยว การทำปฏิกิริยาทรานส์เอสเทอริฟิเคชันแบบ 2 ครั้ง ใช้ถังปฏิกรณ์จำนวน 2 ถัง ร่วมกับถังบรรจุวัสดุ ณ สภาวะที่เหมาะสมพบว่าได้เมทิลเอสเทอร์ที่มีความบริสุทธิ์สูง (99.69 % โดยน้ำหนัก) และมีผลได้สูง (98 % โดยน้ำหนัก) คุณสมบัติทางเชื้อเพลิงโดยส่วนใหญ่ของเมทิลเอสเทอร์อยู่ในเกณฑ์มาตรฐานของ EN 14214 ดังนั้น น้ำมันพืชเสียสามารถใช้เป็นวัตถุดิบทางเลือกที่มีประสิทธิภาพทางด้านราคา

Thesis Title	Process Development of Two-Step Esterification on Waste Vegetable Oil with very High Free Fatty Acid
Author	Mr. Songtham Photaworn
Major Program	Chemical Engineering
Academic Year	2016

ABSTRACT

The use of edible oils in biodiesel production has higher cost than use of lower grade feedstocks such as waste vegetable oils (WVOs). However, WVOs usually contain high free fatty acids (FFAs) and moisture contents; and soap forming via saponification in base-catalyst transesterification. Esterification is a pretreatment step to reduce FFA down to a desirable level before transesterification. The aim of this research is to develop a continuous process to produce biodiesel from WVO with methanol (MeOH) by a two-stage process.

The first stage was studied both of a batch and continuous esterification. In the batch type, the first esterification stand-alone, the second esterification stand-alone, the two-step esterification, and the two-step esterification with recycled MeOH-rich phase were studied. Parameters investigated were: MeOH-to-FFA molar ratio, H₂SO₄-to-FFA molar ratio, reaction temperature and time. Multiple regression analysis and material balance were employed. Quadratic model was proven more significant and the major coefficients impacted on FFA conversion are the 'multiplication of MeOH-to-FFA molar ratio to H₂SO₄-to-FFA molar ratio' in the first step, and 'H₂SO₄-to-FFA molar ratio' in the second step. The batch two-step esterification with practical optimum conditions from the first and the second esterification was shown effectively in FFA conversion within the recommended value of not greater than 1 wt.%. The results from the batch two-step esterification with MeOH-rich phase recycling were similar to the batch type.

The continuous esterification was investigated with continuous dewater reactor (CDR) which removed water during reaction and continuous stirred-tank reactor (CSTR). The continuous three-step esterification with 2-CDRs and 1-CSTR could be reduce FFA content less than 0.5 wt.%. The benefit of the continuous esterification with MeOH-rich phase recycling was an acid transesterification and thus to increase an amount of ester.

In the second stage: transesterification, a feedstock was a mixed esterified waste vegetable oil (mixed EWVO) which blended between EWVO and used cooking oil (UCO) in 50/50 wt.% ratio. Triglycerides (TGs) in a mixed EWVO were transesterified with MeOH in the presence of an alkaline catalyst. Parameters

were studied and optimized in a batch two-step transesterification such as an amount of catalyst and an amount of catalyst solution ratio in the first and second transesterification.

The continuous transesterification was investigated with continuous stirred-tank reactor (CSTR). The continuous two-step transesterification with 2-CSTRs and packing tank could be obtain methyl ester in high purity (99.69 wt.%) and yield (98 wt.%) under the optimum condition. The fuel properties of methyl ester almost met the specifications of EN 14214 standards. WVO thus can be cost-effectively used as an alternative feedstock.

ACKNOWLEDGMENT

I would like to express my sincere and gratitude appreciation to my major advisor, Assoc. Prof. Dr. Chakrit Tongurai for his kindness, guidance, and expertise during this research and also to my co-advisor Asst. Prof. Dr. Suratsawadee Kungsanant for many useful advisories.

I am very grateful to my examination committees: Assoc. Prof. Dr. Penjit Srinophakun, Assoc. Prof. Dr. Sukritthira Ratanawilai, and Assoc. Prof. Dr. Kulchanat Prasertsit for their comments and useful suggestions.

I appreciate the help of the staff members in the Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops and the Department of Chemical Engineering, Faculty of Engineering, Prince of Songkla University.

I would like to thank all the members of the PSU-Biodiesel research group for their helpful discussion.

I also would like to thank Mr. Wiwat Sutiwipakorn for his advice on scientific writing of manuscript.

I especially wish to thank all the technicians at the Scientific Equipment Center, Prince of Songkla University, for their useful help in the laboratory and their technical support.

This research was provided by partial funding from a Prince of Songkla Graduate Studies and the Graduate School of Prince of Songkla University. The Department of Chemical Engineering, Faculty of Engineering, Prince of Songkla University is gratefully acknowledge for other supports.

Finally, I am indebted and thankful to Mrs. Patomporn Photaworn and my family for their love, encouragement and support throughout my study.

Songtham Photaworn

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LIST OF ABBREVIATION

		Definition in this thesis
CDR	Continuous Dewater Reactor.....	A reactor in which the heavy liquids are separated out of the reactor at the bottom.
conc.	concentrated	-
CSTR	Continuous Stirred-Tank Reactor..	A reactor in which the contents are well stirred and uniform throughout.
EWVO	Esterified Waste Vegetable Oil.....	A TG-rich phase from esterification process.
FFA	Free Fatty Acid.....	A fatty acid is a carboxylic acid with a long aliphatic chain
GC	Gas Chromatography.....	A technique used in analytical methyl ester.
H ₂ SO ₄	Sulfuric acid.....	An acid catalyst in esterification process.
KOCH ₃	Potassium Methoxide.....	A base catalyst in transesterification process.
ME	Methyl Ester.....	The finished product from biodiesel production was blended RPO and PFAD to prepare MO.
MeOH	Methanol.....	An alcohol was used in esterification and transesterification processes.
MO	Mixed Oil.....	A mixed oil with properties similar to TG-rich phase from the first esterification stand-alone at the optimum conditions was used as feedstock for the second esterification stand-alone
PFAD	Palm Fatty Acid Distillation.....	A by-product of palm oil production was blended with RPO and ME to prepare MO.
RPO	Refined Palm Oil.....	An oil derived from crude palm oil was blended with PFAD and ME to prepare MO.

LIST OF ABBREVIATION (continued)

		Definition in this thesis
TG	Triglyceride.....	An ester derived from glycerol and three fatty acids
UCO	Used Cooking Oil.....	An oil or fat has been used for cooking or frying. It was blended with EWVO to prepare feedstock for transesterification process.
WVO	Waste Vegetable Oil.....	An used cooking oil with FFA content from 10 to 25 wt.% (Canakci and Gerpen, 2001). In batch esterification process, it was used as feedstock for the first esterification stand-alone, two-step, and two-step with MeOH-rich phase recycling and in continuous esterification process, it was used as feedstock for the two-step, two-step with recycled the MeOH-rich phase, and three-step with recycled the MeOH-rich phase.

CHAPTER 1

INTRODUCTION

1.1 Rational/Problem Statement

Due to the world's fossil fuel reserves depletion, the highly fluctuating prices of crude oil, the increased demand for energy, and the increasing environmental impact are mainly the key factors leading to search for renewable energy (Leung et al., 2010; Math et al., 2010; Shahid and Jamal, 2011).

Biodiesel has become increasingly of interest in comparison with petroleum diesels due to its many merits such as eco-friendliness, non-toxicity, biodegradability and renewability (Marchetti and Errazu, 2008; Salamatinia et al., 2013; Tan et al., 2011). Chemically, biodiesel is composed of long fatty acid mono-alkyl esters via chemical reactions such as a transesterification reaction; generally involving a reaction of triglyceride (TG) with alcohol (methanol: MeOH or ethanol) to produce ester and glycerol, accelerated by a basic catalyst.

Generally, biodiesel is produced from feedstocks containing low content of free fatty acid (FFA) such as edible vegetable oils which are relatively expensive type. The main problem of commercial biodiesel is high production cost from raw material that reaches 60-80% of the total production cost (Bokhari et al., 2016; Diaz-Felix et al., 2009; Hassan and Vinjamur, 2014; Hayyan et al., 2011; Kumar and Math, 2016). Waste vegetable oils (WVOs) or non-edible oils are alternative sources to produce biodiesel because they are low-cost sources. Thus, it is effectively reducing the expense to compete with petroleum diesels (Berrios et al., 2010; Lotero et al., 2005).

The disadvantages of low-cost feedstocks are containing undesirable FFA and high moisture. The presence of water in the raw material, moreover, hydrolyzes TG to form FFA via hydrolysis reaction. FFA poses a major problem in a base-catalyst transesterification process since it reacts with the base catalyst to have soap formation by saponification. Both reactions cause catalyst consumption and lowering of yield, and complicated production process (Encinar et al., 2011).

It is with these problems that technology such as a pretreatment process should be employed to reduce FFA content of low-cost oils, particularly to be less than 1.0 wt.% before using a base-catalyst transesterification (Canakci and Gerpen, 2001; Issariyakul et al., 2007; Kusdiana and Saka, 2004). The additional pretreatment method is a direct esterification of the FFA and an alcohol with an acid catalyst such as sulfuric acid (H_2SO_4) (Leung et al., 2010). The esterification step is

essential since it is an effective and efficient process to convert high FFA feedstocks to be suitable inputs for biodiesel production (Farag et al., 2011).

One-step esterification process commonly used usually requires large amounts of chemicals (such as MeOH and H₂SO₄) and a lengthy reaction time in order to obtain a high yield reaction. For example, the one-step esterification of mixed oil (crude palm oil and crude rubber seed oil) observed 97% FFA conversion after 5 h at 65 °C with 30:1 MeOH/FFA molar ratio and 0.09:1 H₂SO₄/FFA molar ratio (3.14 wt.% of FFA) and from used cooking oil obtained 95% FFA conversion after 2 h at 60 °C with 40:1 MeOH/FFA molar ratio and 0.28:1 H₂SO₄/FFA molar ratio (10 wt.% of FFA) (Chai et al., 2014; Khan et al., 2010). Moreover, the utilization of excess MeOH and H₂SO₄ requires complicated processes to recover or discharge and leads to increased production cost.

A two-step acid esterification, having water removed from the first esterification before subjected to the second one, has sometimes replaced the one-step process; some researchers seemed to concentrate on reducing FFA rather than the esterification steps and the excess chemicals consumption. For instance, the two-step esterification of mahua oil acquired 2.42% FFA after the first esterification at 1 h, 60 °C, 14:1 MeOH-to-FFA molar ratio and 0.30:1 H₂SO₄-to-FFA molar ratio (10.53 wt.% of FFA) and 0.80% FFA after the second esterification at 1 h, 60 °C, 47:1 MeOH-to-FFA molar ratio and 1.17:1 H₂SO₄-to-FFA molar ratio (41.32 wt.% of FFA) (Ghadge and Raheman, 2005). In an effort to reduce production cost, recycling was practiced on solid heterogeneous catalyst, but not on recycling of catalyst solution, if any.

In this study, a two-step alkali-catalyzed transesterification was studied to convert an esterified WVO and MeOH to biodiesel with Potassium methoxide (KOCH₃) catalyst.

Normally, batch processes is mostly performed in biodiesel production. In comparison with continuous processes, batch processes have several disadvantages such as high capital investment, low efficient of the products, and high labor costs (Darnoko and Cheryan, 2000). Thus, the biodiesel industry needs to develop large scale continuous processes to increase its production (Fonseca et al., 2010).

The purpose of this research was to develop a suitable and cost-effective continuous process for the two-stage conversion process: an acid-catalyzed esterification and alkali-catalyzed transesterification to produce high quality biodiesel, meeting international specifications, from WVOs containing high FFA content. The process development focused on the recycling of MeOH-rich phase as catalyst in the acid-catalyzed esterification. In this study, material balance was used to describe the amounts of components after a reaction was completed.

1.2 Theoretical Background

1.2.1 Biodiesel

Biodiesel is converted from transesterification of vegetable oil and animal oil/fat with a suitable alcohol (methanol or ethanol) and catalysts such as an acid, base, or enzyme (Fadhil et al., 2015). Properties of biodiesel are similar to petrodiesel. Biodiesel can be used to run diesel engines alone or with a blending of petrodiesel. The main merits of using biodiesel are renewability, biodegradability, and non-toxicity. It can be used without modifying existing engines, and emits less in harmful gases, e.g. sulfur oxide (Helwani et al., 2009; Tsolakis and Megaritis, 2004).

Moreover, biodiesel has better lubricant properties which improve engine yield and increase engine life (Demirbas, 2009). Biodiesel can be handled with the same procedure for conventional petrodiesel. In fact, biodiesel is safer than conventional petrodiesel because of a relatively high flash point (close to 150 °C) (Al-Zuhair, 2007). The physical properties of biodiesel are given in Table 1.1.

There are four methods (Table 1.2) that are used for biodiesel production: using alone or blending with raw material oils, micro-emulsions, thermal cracking, and transesterification (Leung et al., 2010). Generally, the transesterification is the most selected method for producing biodiesel.

Table 1.1 Physical properties of biodiesel

Common name	Biodiesel
Common chemical name	Fatty acid (m)ethyl ester
Chemical formula range	C ₁₄ –C ₂₄ methyl esters or C _{15–25} H _{28–48} O ₂
Kinematic viscosity range (mm ² /s, at 40 °C)	3.3–5.2
Density range (kg/m ³ , at 15 °C)	860–894
Boling-point range (°C)	>180
Flash-point range (°C)	145–180
Distillation range (°C)	190–350
Vapor pressure (mm Hg, at 22 °C)	<5
Physical appearance	Light to dark yellow, clear liquid
Odor	Light musty/soapy odor
Biodegradability	More biodegradable than petroleum diesel
Reactivity	Stable, but avoid strong oxidizing agents

(Demirbas, 2009)

1.2.2 Biodiesel feedstocks

Fig. 1.1 presents a variety of raw materials around the world which can be produced biodiesel and Table 1.3 shows the common name and structure of fatty

acids. The raw material of biodiesel depends considerably on particular weather, and type of soil (Lin et al., 2011). It can be seen that types of oil are many different such as soybean oil in USA, rapeseed oil in European countries, waste oil in China, palm oil in Malaysia, Indonesia, and Thailand, and jatropha oil in India and South East Asia.

However, a feedstock of biodiesel can be divided into four groups: (a) edible vegetable oil for example soybean oil rapeseed oil, palm oil, and canola; (b) waste vegetable oil e.g., yellow grease; (c) animal fats such as lard, tallow, and fish oil; (d) non-edible oils including jatropha, rubber seed oil, and castor oil (Demirbas, 2009).

Vegetable oils, edible oil, are mainly raw material for biodiesel production since they can be cultivated on a large area in many parts around the world. The fuel properties of biofuel are much suitable to be used as alternative energy to petro-diesel. Anyway, it may cause some obstacles e.g., the increase of the edible oil consumption. It can be increased the cost of vegetable oils and biofuel. In addition, it will deforest to plant more of energy crops in some countries. (Gui et al., 2008).

Table 1.2 Different methods for biodiesel production

Methods	Definition	Advantage	Disadvantage	Problems of using in engines
Direct use and blending	Direct use as diesel fuel or blend with diesel fuel	Liquid nature-portability	Higher viscosity	Coking and trumpet formation
		Heat content (~80% of diesel fuel) Readily available; renewability	Lower volatility Reactivity of unsaturated hydrocarbon chains	Carbon deposits Oil ring sticking; thickening and gelling of the lubricating oil
Micro-emulsions	A colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1–150 nm range formed spontaneously from two immiscible liquids and one or more ionic or non-ionic amphiphiles	Better spray patterns during combustion	Lower cetane number	Irregular injector needle sticking; incomplete combustion
		Lower fuel viscosities	Lower energy content	Heavy carbon deposits; increase lubrication oil viscosity
Thermal cracking	The conversion of long-chain and saturated substance (biomass basis) to biodiesel by means of heat	Chemically similar to petroleum-derived gasoline and diesel fuel	Energy intensive and hence higher cost	-
Transesterification	The reaction of a fat or oil with an alcohol in the presence of catalyst to form esters and glycerol	Renewability; higher cetane number; lower emissions; higher combustion efficiency	Disposal of by-product (glycerol and waste water)	-

(Leung et al., 2010)

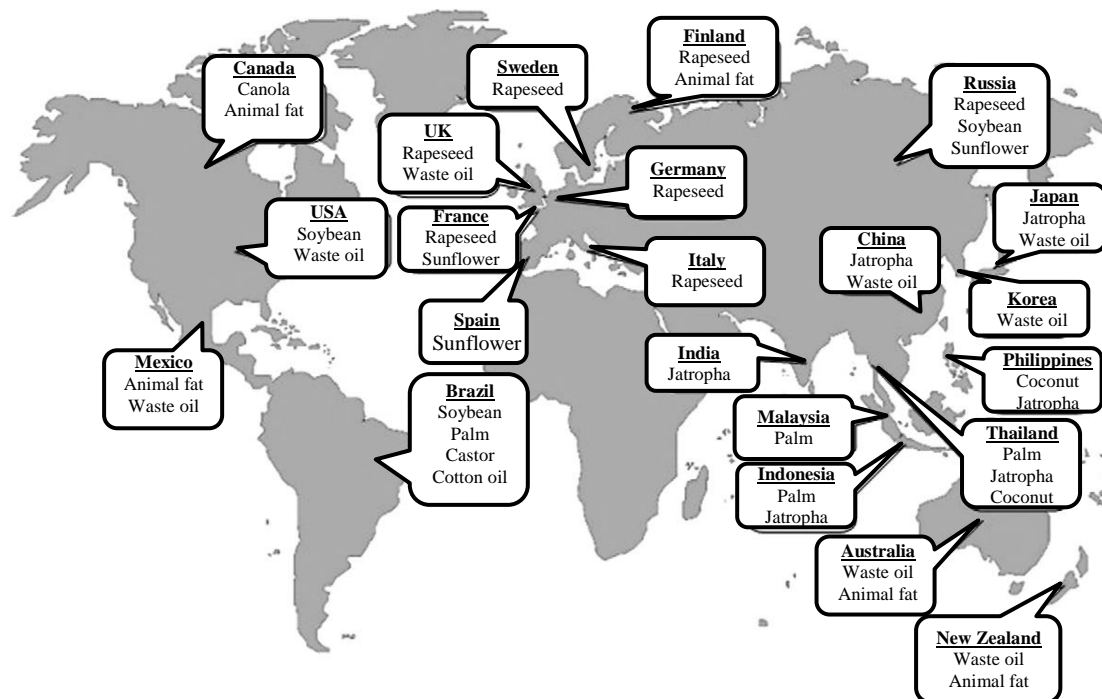


Fig. 1.1 FAME production around the world
(Lin et al., 2011)

Table 1.3 The chemical structures of common fatty acids

Fatty acids		Chemical structure
Lauric	C12:0	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$
Myristic	C14:0	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$
Palmitic	C16:0	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$
Stearic	C18:0	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
Oleic	C18:1	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
Linoleic	C18:2	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
Linolenic	C18:3	$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
Arachidic	C20:0	$\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$
Behenic	C22:0	$\text{CH}_3(\text{CH}_2)_{20}\text{COOH}$
Erucic	C22:1	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_{11}\text{COOH}$

To tackle these problems, many scientists are focused on alternative oils which are not in food chain such as waste oils, or waste cooking oil (WCO), and non-edible oils. Especially non-edible oil crops can be plant under lack of care in waste area and lead to low cost of operation to produce oils. Most of waste oils, WVO and non-edible oils contain high content of FFA and moisture. These oils need a pretreatment step to reduce FFA in biodiesel process. However, inferior quality WVO is a suitable for biodiesel production due to low-cost oils. It is significant reducing the overall biodiesel production because of cost of raw materials about 60-80%. Table 1.4 shows distribution of fatty acids in some raw material and Table 1.5 presents the fuel properties of some alkyl ester products.

1.2.3 Pretreatment of high FFA feedstocks

(Leung et al., 2010)

Generally, biodiesel is converted from oils or fats by transesterification with alkaline catalysts. The limit of transesterification is an amount of FFA in feedstocks because of soap formation. If the raw material has a FFA content over 1 wt.% (the acceptable FFA content in system), biodiesel production must employ a pretreatment process to reduce or remove FFA.

Many pretreatment processes have been suggested to reduce the high FFA content such as distillation, extraction, and esterification. However, the first method requires a high temperature to operation but it has low efficiency. The second one requires a high amount of solvent due to a low solubility and the complicated process. In comparison to the two former methods, acid catalyzed esterification is an effective pretreatment method because it is directly to convert FFA into alkyl ester.

Both of homogeneous acid catalysts and solid acid catalysts can be used in esterification reaction. Although, solid acid catalysts provide some advantages more than the tradition one such as separation from product, catalyst recycling, and safe environment, the reaction rate is slower.

FFAs will be esterified with alcohol to biodiesel and the water (by product) via acid catalyzed esterification. Normally, conventional one-step esterification cannot reduce the high FFA content feedstock to recommend level of the transesterification due to the high amount of water produced during the reaction and the progress of hydrolysis reaction. In this case, two-step esterification has replaced the one-step because of water removal from the first-step before fed to esterify with the fresh solution in the second-step.

Table 1.4 Distribution of fatty acid in some biodiesel feedstocks

Feedstock	Fatty acids (wt.%)						
	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3
Sunflower	-	-	6.08	3.26	16.93	73.73	-
Rapessed	-	-	3.49	0.85	64.40	22.30	8.23
Soybean	-	-	10.58	4.76	22.52	52.34	8.19
Palm	-	1	42.8	4.5	40.5	10.1	0.2
Peanut	-	0.3	12.3	4.6	53.6	29	0.1
Coconut	46.5	19.2	9.8	3	6.9	2.2	-
Soybean soapstock	-	-	17.2	4.4	15.7	55.6	7.1
Used frying oil	-	-	12	-	53	33	1
Tallow	-	3-6	24-32	20-25	37-43	2-3	-
Lard	-	1-2	28-30	12-18	4-50	7-13	-

(Lin et al., 2011)

Table 1.5 Some properties of diesel and biodiesel produced from different feedstocks

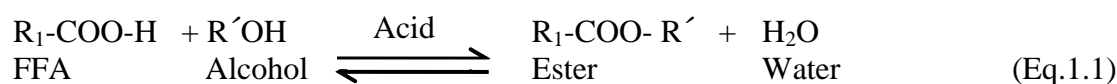
Parameter	Fuel							
	Diesel	Soybean ME	Rapeseed ME	Palm ME	Sunflower ME	Jatropha ME	Tallow ME	Soapstock ME
Kin. Viscosity, mm ² /s at 40 °C	2.0- 4.5	4.08	4.83	4.71	4.60	4.40	5.00	4.30
Density, g/cm ³ at 21 °C	0.820- 0.860	0.884	0.882	0.864	0.880	0.875	0.877	0.885
Cetane number	51.0	50.9	52.9	57.3	49.0	57.1	58.8	51.3
Flash point, °C	55	131	155	135	183	163	150	169
Cloud point, °C	-18	-0.5	-4	16	1	4	12	6
Pour point, °C	-25	-4	-10.8	12	-7	-	9	-

(Lin et al., 2011)

1.2.4 Esterification

(Clark, 2004)

Esterification is a chemical reaction of an alcohol and an acid with an acid catalyst to obtain an ester and water as the reaction product, as depicted in Eq. 1.1.



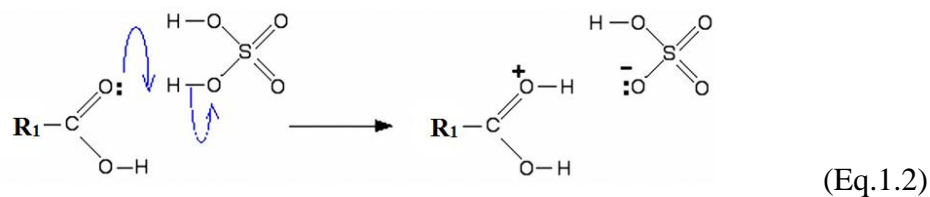
Where R₁ is long-chain hydrocarbons and R' is alkyl group of alcohol.

Generally, the concentrated sulfuric acid is employed as catalyst. Esterification is a reversible reaction. Thus water produced must be removed to shift the reaction to the right to obtain a higher FFA conversion yield.

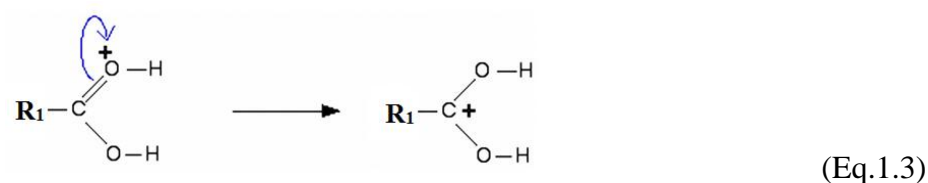
The mechanism for the formation of alkyl esters from carboxylic acids and methanol using conc. sulfuric acid catalyst shows in detail Eq.1.2-1.10. The mechanism is shown as one-way reaction steps to avoid of confusing in reverse reaction.

Step 1

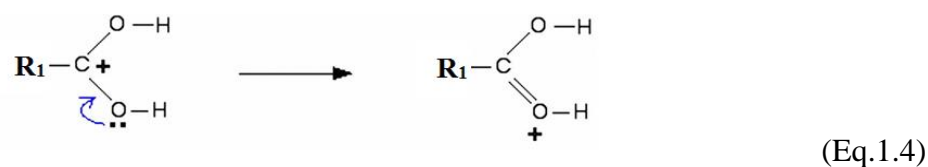
In the first step, the carboxylic acid takes a proton (a hydrogen ion) from the conc. sulfuric acid. The proton attacks to one of the lone pairs on the oxygen atom which is connected to double-bonded of the carbon atom.



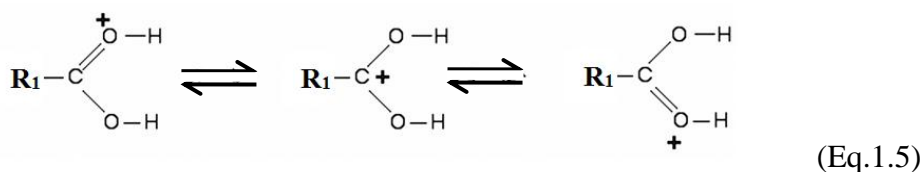
The proton transferring to the oxygen atom gives it a positive charge, but it is actually misleading to draw the structure in this way. The positive charge is delocalized over the whole of the right-hand end of the ion, with a fair amount of positiveness on the carbon atom. In other words, an electron pair shifting gives this structure:



Another lone pair electron can be located to form a third structure:



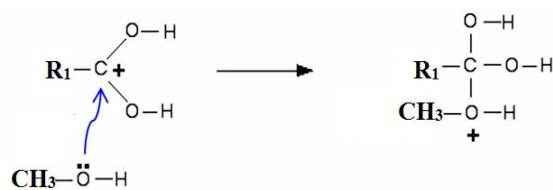
The correct structure of the ion formed is writing in the delocalized structure like this:



All of structures are known as resonance structures or canonical forms. The degree of positive charge on both of the oxygen atoms and the carbon atom will be the same - somewhere between a single bond and a double bond.

Step 2

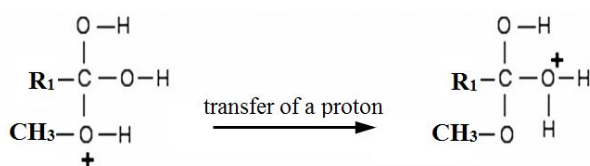
The lone pairs on the oxygen atom of the methanol molecule attack the positive charge on the carbon atom.



(Eq.1.6)

Step 3

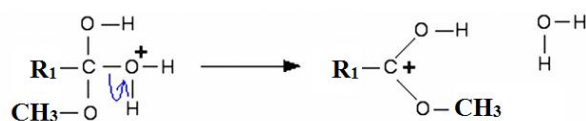
A proton (a hydrogen ion) gets transferred from the bottom oxygen atom to one of the others.



(Eq.1.7)

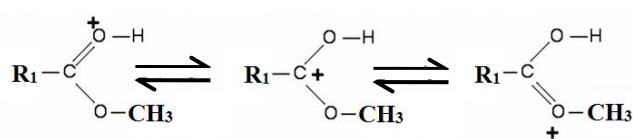
Step 4

Now a molecule of water is lost from the ion.



(Eq.1.8)

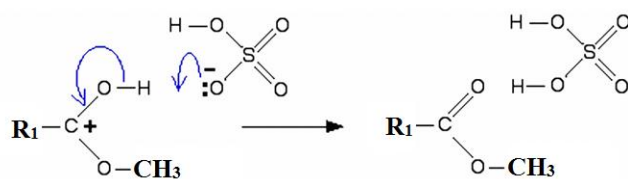
The product ion has been drawn in a shape to closely reflect the final product. The structure for the latest ion is just like the one discussed in step 1.



(Eq.1.9)

Step 5

The hydrogen is removed from the oxygen atom by reaction with the hydrogen sulfate ion which was formed way back in the first step.



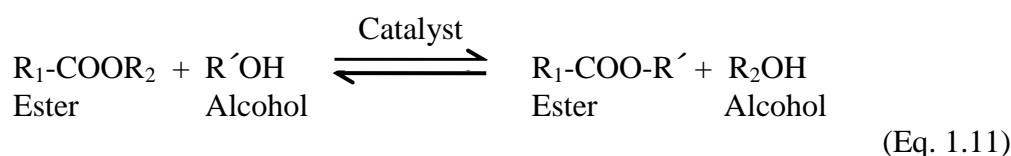
(Eq.1.10)

Finally, the alkyl ester has been formed and the sulfuric acid catalyst has been regenerated.

1.2.5 Transesterification

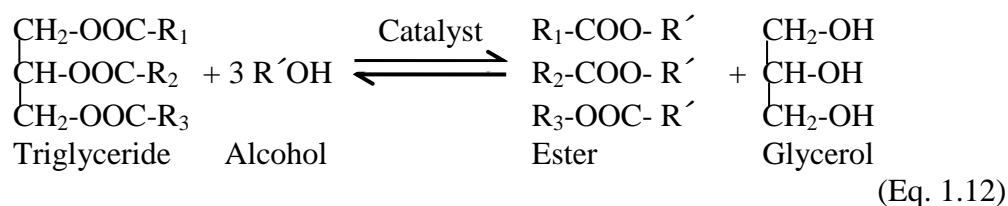
(Schuchardt et al., 1998)

Transesterification is an organic reaction where an origin ester is converted into another through interchange of the alkoxy functional group. If an ester is transformed with an alcohol, the reaction can be changed in particular name; alcoholysis (Eq. 1.11). The transesterification is a reversible reaction and the progress of reaction begins by mixing the reactants with a strong acid or base catalyst. For attaining a high yield of the ester, a high amount of alcohol has to be consumed more than stoichiometry ratio.



Where R_1 and R_2 are long-chain hydrocarbons. R' is alkyl group of alcohol.

Biodiesel is derived from the transesterification reaction of feedstocks: vegetable oils or animal fats (Eq. 1.12), a triglyceride (TG) reacts with an alcohol such as MeOH in the presence of a catalyst, to produce biodiesel (alkyl esters) and glycerol (by product). The overall process is a series of reactions in three consecutive and reversible reactions, which intermediates are di- and mono-glycerides. From the stoichiometric ratio, one mole of TG needs three moles of an alcohol but an excess of the alcohol is used to increase the yields of biodiesel and to allow its phase separation from the glycerol phase. Many factors including the type of catalyst (acid or base), alcohol/TG molar ratio, type of alcohol, temperature, time, purity of the reactants (mainly water content) and FFA content have an effect on the transesterification reaction.



Where R_1 , R_2 , R_3 are long-chain hydrocarbons and R' is alkyl group of alcohol.

1.2.6 Catalytic transesterification process

(Baskar and Aiswarya, 2016; Verma et al., 2016)

The catalytic transesterification process can be separated into two groups, the first is ‘catalytic transesterification reaction’ including homogeneous, heterogeneous and enzymes as catalyst and the second is ‘non-catalytic transesterification reaction’ with under supercritical conditions. Fig. 1.2 shows overall catalysts used in biodiesel production.

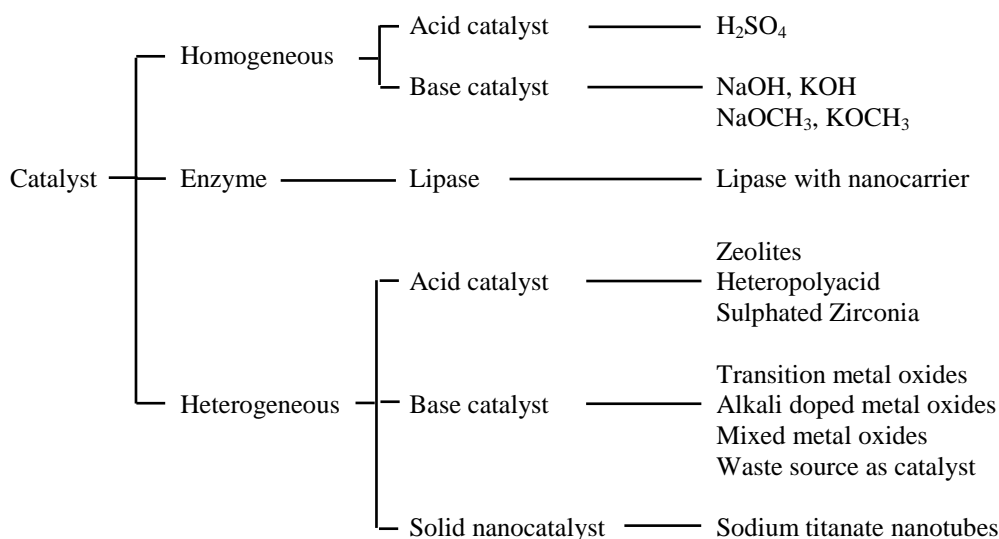


Fig. 1.2 Catalyst in biodiesel production

(Baskar and Aiswarya, 2016)

1.2.6.1 Homogeneous catalysis

Homogeneous catalyst is mainly used in transesterification to produce biodiesel. Two types of catalysts (acid and base) are generally used in transesterification system. The aim is to change TG in feedstocks into alkyl ester. By-products (glycerol) achievement must be removed off, in another way yield of conversion obtains lower by reversible reaction. The most of catalyst used are sulfuric acid (H_2SO_4) in acid catalyzed reaction, sodium hydroxide (NaOH) or potassium hydroxide (KOH) in base catalyzed reactions. Base catalysts: NaOH and KOH have been preferred in transesterification due to the reaction can be speeded up at normal temperature and pressure condition, yield can be achieved in short time, and the low cost.

The mechanism of transesterification reaction depends on type of catalysts (acid or base) since a base-catalyzed reaction begins with nucleophilic alkoxide from an alcohol attack the carbonyl group of the TG at the electrophilic part.

An acid catalysis starts with proton from catalyst attack the carbonyl group of the TG an alcohol attack at the protonated carbon.

The formation of ester consists of three steps. The first one is to create an unstable intermediate tetrahedral (Fig. 1.3) then it is broken into di-glyceride ion and fatty acid ester, finally proton is transferred to recover the catalyst. After this, each step is repeated and achieved three mole of alkyl esters and one mole of glycerol (Aransiola et al., 2014).

The undesirable components (FFA and water) in raw material oil have significant influence on the transesterification reaction because of soap formation (Eq. 1.13) and hydrolysis reaction. It is recommended that the base catalysts can be used in transesterification, if raw material oils contain FFA content to be less than 1 wt.% (Kulkarni and Dalai, 2006). Soap formation from high FFA raw materials in base catalyzed reaction causes complicated separation process of biodiesel and lead to loss of yield.

By comparison with an acid catalyst, activity of a base catalyst is faster than in transesterification. An amount of a base catalyst used for transesterification reaction is in between 0.5 wt.% to 5 wt.% of oil. The base catalysts are NaOH, KOH, CH₃ONa, CH₃OK, and so on but the acid catalyst is mostly used H₂SO₄ in reaction with raw materials having FFA content more than 6 wt.% (Takase et al., 2015). In transesterification process, the two types of catalyst both have been investigated in methanol and ethanol (Li et al., 2013).

Table 1.6 shows yield and production conditions in transesterification reaction with homogenous catalyst and Table 1.7 presents the merits and demerits of homogenous catalyst.

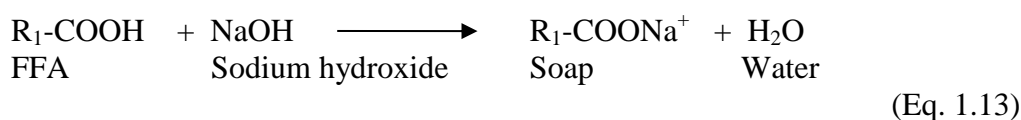


Table 1.6 Production parameters for homogenous-catalyzed transesterification

Feedstock	Alcohol	Catalyst wt.% of oil	Molar ratio (Alcohol:Oil)	Temperature °C	Time h	Yield wt.%	Reference
Waste canola oil	Methanol	0.5% NaOH	29:1	55	2	49.5	Hossain et al., 2010
	Ethanol					23.5	
	Butanol					19.5	
Canola oil	Methanol	0.8% KOH	6:1	50	0.5	92.5	Likoazar and Levec, 2014
	Ethanol					85.0	
	Isopropanol					89.7	
	Butanol					87.3	
Triolein	Methanol	1% KOH	6:1	25 under ultrasonic irradiation (40 kHz)	1	70	Hanh et al., 2009
	Ethanol					69	
	Propanol					64	
	Butanol					65	
Rapeseed oil	Biobutanol	1.1% KOCH ₃	6:1	78	1	96.9	Bouaid et al., 2014
Pongamia oil	Methanol	1.43% KOH	11:1	57	1.3	98.4	Dwivedi and Sharma, 2015
Crude palm oil	Methanol	9.3% H ₂ SO ₄	40:1	95	9	97	Crabbe et al., 2001

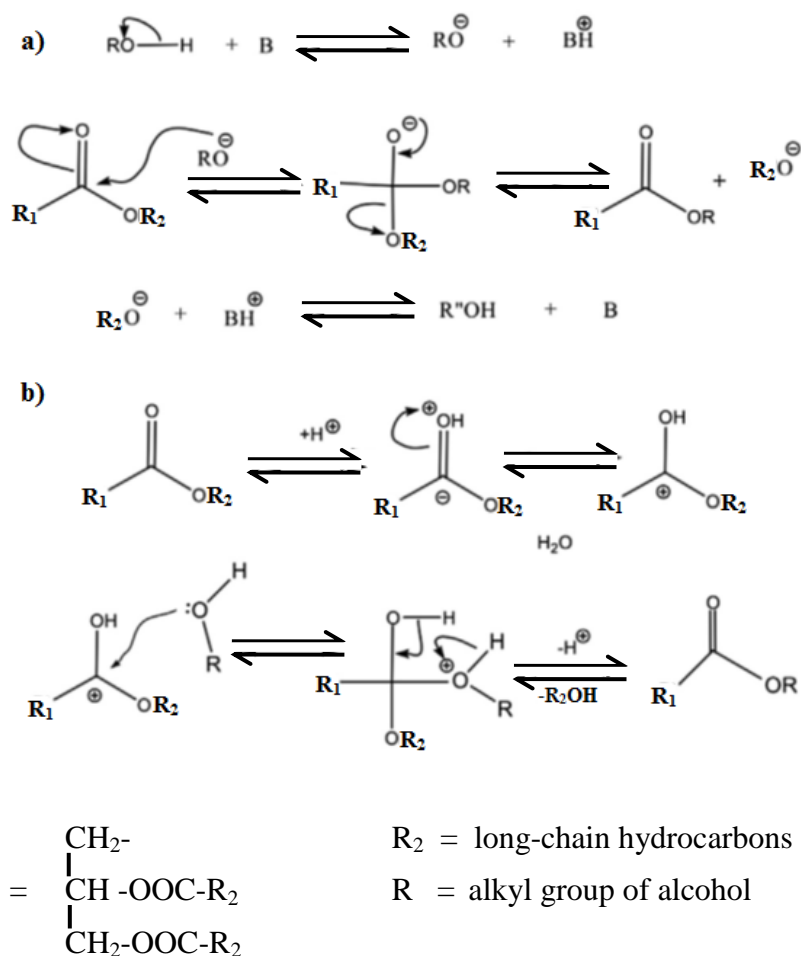


Fig. 1.3 Reaction mechanism of transesterification using base catalyst, a) and acid catalyst, b)

Table 1.7 Merit and demerit of homogenous catalyst reaction

Type of reaction	Merit	Demerit
Base-catalyzed	<ol style="list-style-type: none"> 1. Reaction is very rapid even 4000 folds rapid than acid-catalyzed transesterification. 2. Lesser energy required to achieve equilibrium and conditions are very mild. 3. Catalysts used are very economical in nature and available in abundance. 	<ol style="list-style-type: none"> 1. Ability of completion of reaction depends mainly on FFA content. 2. Not useful if when FFA content is greater than 2% due to formation of soap. 3. Lesser yield due to emergence of soap and waste water.
Acid-catalyzed	<ol style="list-style-type: none"> 1. In contrast to base catalysts, FFA composition and amount of water in oil does not matter much for acidic catalysts. 2. Able to produce biodiesel even from inferior quality raw material. 	<ol style="list-style-type: none"> 1. Takes longer time to achieve equilibrium. 2. Corrosive nature of catalysts like sulfuric acid used can lead to corrosion on reactor and pipelines. 3. Separation of catalyst from biodiesel is strenuous.

(Verma et al., 2016)

1.2.6.2 Heterogeneous catalysis

In homogeneous base catalyzed reaction, FFA poses a major problem due to soap formation and its leads to lesser in production yield. In contrast to the heterogeneous catalyst, NaOH and KOH, homogeneous catalyst, have the critical disadvantage which can be absorbed moisture from air and surrounding. Although heterogeneous catalysts cannot speed up the reaction and spend a longer time, biodiesel production cost is still lower due to the catalysts recycling.

The important of heterogeneous catalysts are including magnesium oxide (MgO), calcium oxide (CaO), barium oxide (BaO), strontium oxide (SrO), titanium oxide, zinc oxide, mixed oxides catalysts and hydrotalcites. The first-fourth catalysts are very well known which CaO is being adopted since it is made to cheap cost. Moreover, calcination of waste egg shells can provide CaO. The significant advantage of heterogeneous acid catalysts are no reaction with FFA in feedstock and simultaneously conduct esterification and transesterification reaction. The mixture of heterogeneous reaction is three phases which consists of alcohol, oil and catalyst.

From Table 1.8, the lists show that the conditions in transesterification of heterogeneous catalytic reaction: an amount of alcohol, temperature, and time are higher than homogeneous system.

1.2.6.3 Enzyme based catalysis

Enzyme catalysts have been used with biodiesel production, the results show that lipases are effective catalysts in aqueous or organic media. The major advantages of enzyme-catalyzed transesterification are: ability to high FFA feedstocks, ability to use un-treatment raw material oils, and elimination the post purification process. But the main disadvantages are including high cost of enzyme catalyst and slow conversion rate.

Table 1.8 Reaction yield as function of the heterogeneous catalyst

Feedstock	Alcohol	Catalyst wt.% of oil	Molar ratio (Alcohol:Oil)	Temperature °C	Time h	Yield wt.%	Reference
Sunflower oil	Methanol	7% CaO	6:1	65	1	67	Calero et al., 2014
Soybean oil	Methanol	0.4% CaO	7:1	60	2	83	Ferrero et al., 2015
Canola oil	Ethanol	2% Mg ₂ CoAl	16:1	200	5	96-97	Li et al., 2009
Waste cooking oil	Methanol	10% MgO/TiO ₂	50:1	170	6	91.6	Wen et al., 2010

Table 1.9 shows the production parameters for enzyme-catalyzed transesterification.

Table 1.9 Production parameters for enzyme-catalyzed transesterification

Feedstock	Alcohol	Catalyst wt.% of oil	Molar ratio (Alcohol:Oil)	Temperature °C	Time h	Yield wt.%	Reference
Rubber seed oil	Methanol	15% Lipase (<i>Rhizopus Oryzae</i>)	4:1	37	48	31	VC et al., 2016
Sweet basil seed oil	Methanol	6% Lipase (Novozym 435)	10:1	47	68	95	Amini et al., 2017
Canola oil	Methanol	0.23% Lipase (<i>Candida rugose</i>)	5:1	-	24	99	Bhangu et al., 2017
Microalgae oil	Methanol	0.3% Lipase (<i>Rhizomucor miehei</i>)	3:1	30	24	86	Huang et al., 2015

1.2.6.4 Super critical process

Biodiesel process is composed of pretreatment, transesterification reaction, and post-treatment processes. Biodiesel production is needed a larger amount of energy is used to produce biodiesel since multi steps of purification product are required such as separation, recover alcohol, and washing process.

Super critical fluid (SCF) is a condition of substance which behaved like as gas and liquid above its critical temperature and pressure. In comparison to acid or base-catalyzed transesterification, SCF process has many advantages such as no usage of catalyst, a short reaction time, and simultaneous transesterification and esterification. Table 1.10 shows the process parameters of super critical transesterification. Table 1.11 shows the merits and demerits of each technology in biodiesel production.

Table 1.10 Production parameters for super critical transesterification

Feedstock	Alcohol	Molar ratio (Alcohol:Oil)	Temperature °C	Time min	Pressure bar	Yield wt.%	Reference
Pongamia oil	Methanol	50:1	300	40	200	85	Rathore and Madras, 2007
	Ethanol					90	
Sea mango oil	Methanol	45:1	380	40	90	78	Ang et al., 2015
Sunflower oil	Ethanol	25:1	150-200	2-10	200	80	Santana et al., 2012
Palm oil	Methanol	40	372	16	150-200	81.5	Tan et al., 2010
	Ethanol	33	349	29		79.2	
Canola oil	Methanol	40:1	350	10	200	100	Farobie and Matsumura, 2015
	Ethanol			30		80	

Table 1.11 Comparison of different technology for biodiesel production

Parameter	Homogeneous catalyst		Heterogeneous catalyst	Enzyme	Super critical
	Base	Acid			
Temperature (°C)	60-70	50-80	60-200	30-50	200-350
Reaction Time (h)	0.5-2	4-70	Variable	8-70	2-40 min
Product from FFA	Soap	Ester	Ester	Ester	Ester
Effect of water	Interference	Interference	Interference	No influence	No influence
Yield of methyl ester	Normal	Normal	Normal	High	High
Recovery of glycerol	Difficult	Difficult	Simple	Simple	Simple
Ester Purification	Difficult	Difficult	Simple	Simple	Simple
Cost	Cheapest	Cheaper	Medium	Expensive	Expensive
Amount of equipment	High	High	Low	Low	Low

(Marchetti, 2012)

1.2.7 The factors affection on biodiesel production

(Takase et al., 2015)

1.2.7.1 Reaction temperature

The reaction temperature significantly affects the reaction rate since the viscosity of the raw material oil can be reduced in high temperature. In biodiesel process, reaction temperature should not over the boiling point of an alcohol due to preventing the loss of alcohol from system. Normally, reaction temperature is vary in range 60-80 °C which it depends on the type of alcohol.

1.2.7.2 Molar ratio of alcohol to oil

From stoichiometric ratio, one mole of TG in transesterification reaction requires three moles of alcohol to form and one mole of glycerol and three moles of alkyl ester. In practice work, an excess alcohol is used to shift a reaction to products side because of reversible reaction. The usage of alcohol in base-catalyzed transesterification reaction is 6:1 alcohol-to-oil molar ratio and in acid-catalyzed transesterification is 20:1 alcohol-to-oil molar ratio.

1.2.7.3 Catalyst concentration

An amount of catalyst in transesterification reaction is a one significant parameter which controls the production yield. When the amount of catalyst

increases, the progress of reaction and the yield of ester also increase until an equilibrium state. Base catalysts are mainly used in transesterification more than acid catalysts due to the high reactivity at mild conditions. The usage of base catalyst such as NaOH and KOH is in the range 0.55-2.0 wt.% of oil.

1.2.7.4 Reaction time

The reaction progresses with time till an equilibrium state is reached. The reaction time in base-catalyzed transesterification reaction is 2 h or less and in acid-catalyzed transesterification is in range 18-24 h. It can be seen that base catalysts presented the high reactivity than acid catalyst.

1.2.8 Modern technologies for biodiesel production

(Verma et al., 2016)

Some novel technologies have been proposed into biodiesel production to compare with conventional transesterification process such as corona discharge plasma, ultrasound irradiation and microwave methods, membrane reactor, reactive distillation, and continuous deglycerolisation process (CD process). The advantage of novel technologies is summarized in Table 1.12.

From Table 1.12, CD process with atmospheric gravity separator of immiscible liquid is an economic and possible process to develop to industrial scale. It was used to produce ester from refined palm oil and ethanol with KOCH_3 catalyst. The results presented that ethyl ester from a single step transesterification with CD process could be achieved a high yield (93.1 wt.%) and purity (98.0 wt.%). The optimum conditions were: 5.5:1 ethanol-to-oil molar ratio, 1.2 wt.% KOCH_3 of oil and 0.5 h retention time (Nikhom and Tongurai, 2014).

The two immiscible liquid A (heavy liquid or glycerol) and B (light liquid or biodiesel) are separated in a continuous gravity separator (Fig. 1.4) which the initial mixture of the two liquids fed into the separator, then separated into two phase and overflowed out of the separator.

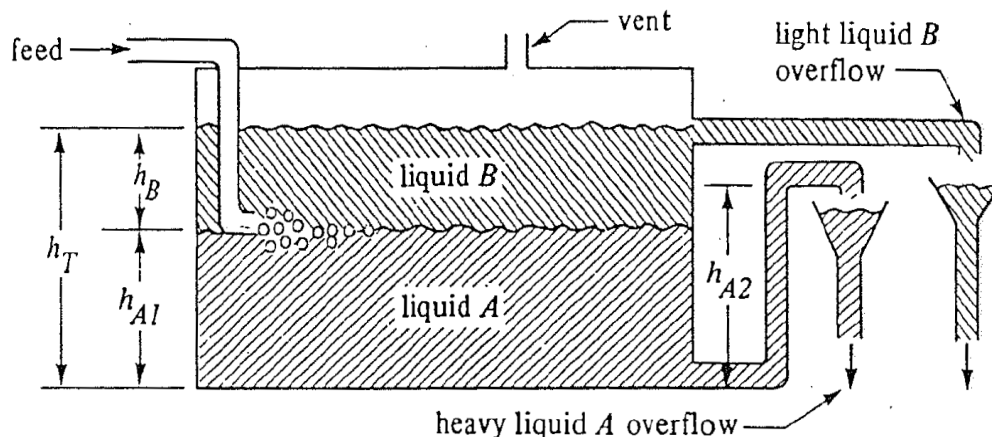
In Fig. 1.4, the height of the phase of heavy liquid A is h_{A1} and that of light liquid B is h_B . The total height $h_T = h_{A1} + h_B$ and is fixed by position of the overflow line for light liquid B. The heavy liquid A releases as an overflow line h_{A2} above the vessel bottom line. The vessel bottom and the overflow lines are vented to the atmosphere.

A hydrostatic balance gives

$$h_B \rho_B g + h_{A1} \rho_A g = h_{A2} \rho_A g \quad (\text{Eq. 1.14})$$

Table 1.12 Summary of some non-tradition production process

Feedstock	Technology	Finding	Merit	Reference
Yellow horn oil	Microwave-assisted transesterification	High yield of 96% was obtained	Rapid conversion of triglycerides into biodiesel	Zhang et al., 2010
Food industry waste	Corona discharge plasma technology	Acid value indicates the content of FFAs in the biodiesel and the value obtained in this study was 0.43 mg KOH/g	1. Acceleration of the esterification reaction 2. Easy separation of the biodiesel 3. Elimination of waste generation	Cubas et al., 2016
Canola oil	Ultrasonic assisted Enzyme catalytic transesterification	Conversion of 100% was achieved in 15 min	The presence of ultrasound is ascribed to the physical effects of ultrasound, which help the formation of fine emulsion between immiscible fluids resulting in an increase in the rate of transesterification reaction.	Bhangu et al., 2017
Canola oil	Membrane	Highly pure biodiesel	1. Reduction of cost incurring in separation of products and recycling 2. Higher conversion in single reaction 3. Products obtained are rich in purity	Cao et al., 2007 Xu et al., 2015
High FFA oil	Reaction distillation	Reduces the usage of alcohol in excess	1. Less time required to achieve equilibrium 2. Less usage of alcohol 3. Reduced energy requirement for reaction	Kiss et al., 2008
Palm oil	Continuous deglycerolisation process (CD process)	Conversion of 98% was obtained	Removal of glycerol during reaction can drive the equilibrium to the product side in order to obtain high conversion	Nikhom and Tongurai, 2014

**Fig. 1.4** Continuous atmospheric gravity separator for immiscible liquid (Geankoplis, 1993)

Substituting $h_B = h_T - h_{A1}$ into Eq.1.14 and solving for h_{A1}

$$h_{A1} = \frac{h_{A2} - h_T \left(\frac{\rho_B}{\rho_A} \right)}{1 - \left(\frac{\rho_B}{\rho_A} \right)} \quad (\text{Eq. 1.15})$$

1.2.9 Biodiesel standards

(Barabás and Todorut, 2011)

Biodiesel standard in many countries are presented in Table 1.13.

Table 1.13 Comparison of various biodiesel standards

Specification/ Standards	Unit	European EN 14214	USA ASTM D6751	South African SANS 1935	Brazil ANP 42	Thailand TIS 2313
Ester content	wt. %	≥ 96.5	-	≥ 96.5	report	≥ 96.5
Density 15°C	kg/m ³	860-900	-	860-900	report	860-900
Viscosity 40°C	mm ² /s	3.5-5.0	1.9-6.0	3.5-5.0	report	3.5-5.0
Flash point	°C	≥ 120	≥ 130	≥ 120	≥ 100	≥ 120
Sulfur content	mg/kg	≤ 10.0	≤ 500	≤ 10.0	≤ 10.0	≤ 10.0
Carbon residue	%wt	≤ 0.30	≤ 0.05	≤ 0.30	≤ 0.05	≤ 0.30
Cetane number	number	≥ 51	≥ 47	≥ 51	≥ 45	≥ 51
Sulfated ash content	wt. %	≤ 0.02	≤ 0.02	≤ 0.02	≤ 0.02	≤ 0.02
Water content	mg/kg	≤ 500	-	≤ 500	-	≤ 500
Water & Sediment	vol. %	-	≤ 0.05	-	≤ 0.05	-
Total contamination	mg/kg	≤ 24	-	≤ 24	report	≤ 24
Copper strip corrosion	number	≤ 1	≤ 3	≤ 1	≤ 1	≤ 1
Oxidation stability	h	≥ 6	≥ 3	≥ 6	≥ 6	> 10
Total acid number	mg KOH/g	≤ 0.5	≤ 0.8	≤ 0.5	≤ 0.8	≤ 0.5
Iodine value	g Iodine/100g	≤ 120	-	≤ 140	report	≤ 120
Linolenic acid methyl ester	wt. %	≤ 12.0	-	≤ 12.0	-	≤ 12.0
Content of FAME with ≥ 4 double bonds	wt. %	≤ 1	-	≤ 1	-	-
Methanol content	wt. %	≤ 0.2	-	≤ 0.2	≤ 0.2	≤ 0.2
Monoglyceride	wt. %	≤ 0.8	-	≤ 0.8	≤ 1.0	≤ 0.8
Diglyceride	wt. %	≤ 0.2	-	≤ 0.2	≤ 0.25	≤ 0.2
Triglyceride	wt. %	≤ 0.2	-	≤ 0.2	≤ 0.25	≤ 0.2
Free glycerin	wt. %	≤ 0.02	≤ 0.02	≤ 0.02	≤ 0.02	≤ 0.02
Total glycerin	wt. %	≤ 0.25	≤ 0.24	≤ 0.25	≤ 0.38	≤ 0.25
Group I metals (Na+K)	mg/kg	≤ 5.0	≤ 5.0	≤ 5.0	≤ 10	≤ 5.0
Group II metals (Ca+Mg)	mg/kg	≤ 5.0	≤ 5.0	≤ 5.0	report	≤ 5.0
Phosphorous	mg/kg	≤ 10.0	≤ 10.0	≤ 10.0	≤ 10.0	≤ 10.0
Cloud point	°C	-	report	-	-	report
Cold soak filtration	sec.	-	360	-	-	-
Cold filter Plugging Point (CFPP) Winter/Summer	°C	-	-	-4/+3 (max)	-	report
Distillation (90%)	°C	-	-	-	≤ 360	-
Aspect	-	-	-	-	Clear	-
Additives	-	-	-	-	-	report

The biodiesel standards (Table 1.13) are based on a variety of factors which vary from region to region, including characteristics of the existing diesel fuel standards, the emissions regulations, the development stage and the climatic properties of the region/country where it is produced and/or used, and not least, the purpose and motivation for the use of biodiesel.

The properties of biodiesel can be grouped by multiple criteria. The most important are those that influence the processes taking place in the engine (ignition qualities, ease of starting, formation and burning of the fuel-air mixture, exhaust gas formation and quality and the heating value, etc.), cold weather properties (cloud point, pour point and cold filter plugging point), transport and depositing (oxidative and hydrolytic stability, flash point, induction period, microbial contamination, filterability limit temperature, etc.), wear of engine parts (lubricity, cleaning effect, viscosity, compatibility with materials used to manufacture the fuel system, etc.).

1.3 Objective

- To determine suitable condition for methyl ester production by the batch processes: an acid catalyzed esterification of WVO and a base catalyzed transesterification of esterified oil.

- To design process for the continuous methyl esters production: CDR for esterification and CSTR for transesterification.

- To perform the optimum operating conditions for the continuous methyl ester production by CDR and CSTR.

- To improve the qualities of the methyl ester to meet the biodiesel standard (EN14214)

CHAPTER 2

RESEARCH METHODOLOGY

2.1 Materials

2.1.1 Raw materials

Waste vegetable oil (WVO), used cooking oil (UCO), refined palm oil (RPO), palm fatty acid distillate (PFAD), and methyl ester (ME) were all acquired from the Specialized R&D for Alternative Energy from Palm Oil and Oil Crops, Faculty of Engineering, Prince of Songkla University.

Undesirable components in the WVO were 13-17 wt.% free fatty acid (FFA) and 0.03-0.05 wt.% moisture contents. The UCO contained 0.25 wt.% FFA and 0.07 wt.% water. Mixed oil (MO) was obtained by mixing the RPO (0.10 wt.% FFA) with ME, and with PFAD (93 wt.% FFA). MO approx. compositions were 83 wt.% triglyceride (TG), 14 wt.% ME and 2.5 wt.% FFA.

Detailed in Section 2.3: Batch esterification process, WVO was used as feedstock for the first esterification stand-alone, two-step, and two-step with MeOH-rich phase recycling, whereas MO was used as feedstock for the second esterification stand-alone; and continuous esterification process, WVO was used as feedstock for the two-step, two-step with recycled the MeOH-rich phase, and three-step with recycled the MeOH-rich phase. Transesterification, UCO was blended with esterified vegetable oil (EWVO) to prepare a feedstock.

2.1.2 Chemicals

1) Methanol (CH_3OH) 99.8 wt.% commercial grade was obtained from P-General Co., Ltd. Thailand.

2) Sulfuric acid (H_2SO_4) 98 wt.% commercial grade was obtained from AGC Chemicals (Thailand) Co., Ltd.

3) Potassium methoxide (KOCH_3) 32 wt.% in methanol commercial grade was obtained from Jepsen & Jessen Chemicals (Thailand) Co., Ltd.

2.2 Equipment and instrument

1) A 1.0 L three-necked round bottom flask was used for batch experiments.

2) A 3.0 L continuous stirred-tank reactor (CSTR), 102 mm ID, 470 mm in length, a baffle tank equipped with 3-levels blade (6 blades) was used for continuous experiments.

3) A 3.0 L continuous dewater reactor (CDR), 102 mm ID, 470 mm in length, with 3-levels blade (6 blades) and phase separation tool was used for continuous experiments.

4) A 3.0 L settling tank, 102 mm ID, 470 mm in length, was used for phase separation in continuous experiments.

5) A 3.0 L packing tank, 102 mm ID, 470 mm in length, with wire screen was used for glycerol removal in continuous two-step transesterification experiments.

6) Digital dosing pumps, model DMS and DME, Grundfos, Germany was used for feeding feedstock and methanol-catalyst mixture.

7) A watt hour meter, type MF-63E, was used to monitor the power consumption.

8) A heater and temperature controller sets was used as the temperature controlling system.

2.3 Methodology

Methyl ester production from WVO with high FFA was studied in batch acid catalyzed esterification experiment to analyze the important variables affecting the production process and to find the suitable conditions for that production process.

The studied variable factors are H_2SO_4 -to-FFA molar ratio, MeOH-to-FFA molar ratio reaction, temperature, and reaction time.

The outcome from preliminary experiments was applied to design the continuous esterification and transesterification process experiments. An overview of the experiments is shown in Fig. 2.1. This thesis was studied in the following topics.

2.3.1 A study of batch acid catalyzed esterification of WVO

Four types of experiment were designed. The first esterification stand-alone, and the second esterification stand-alone using a freshly made yield resembling

the properties of those found in the first experiment. These two were one-step processes. The third was a combined continuous two-step esterification. The fourth involved the third experiment together with an alcohol-rich phase recycling obtained from its second esterification, introducing back to its first step.

2.3.1.1 The first esterification stand-alone

The purpose of this part is to investigate optimum conditions for the first esterification reaction. Variable factors in this step were: H_2SO_4 -to-FFA molar ratio (0.08:1 to 0.83:1), MeOH-to-FFA molar ratio (5:1 to 30:1), and reaction temperature (50, 60 and 70 °C). For an optimum yield, FFA in the WVO should drop down to approx 2.5 wt.% in this case.

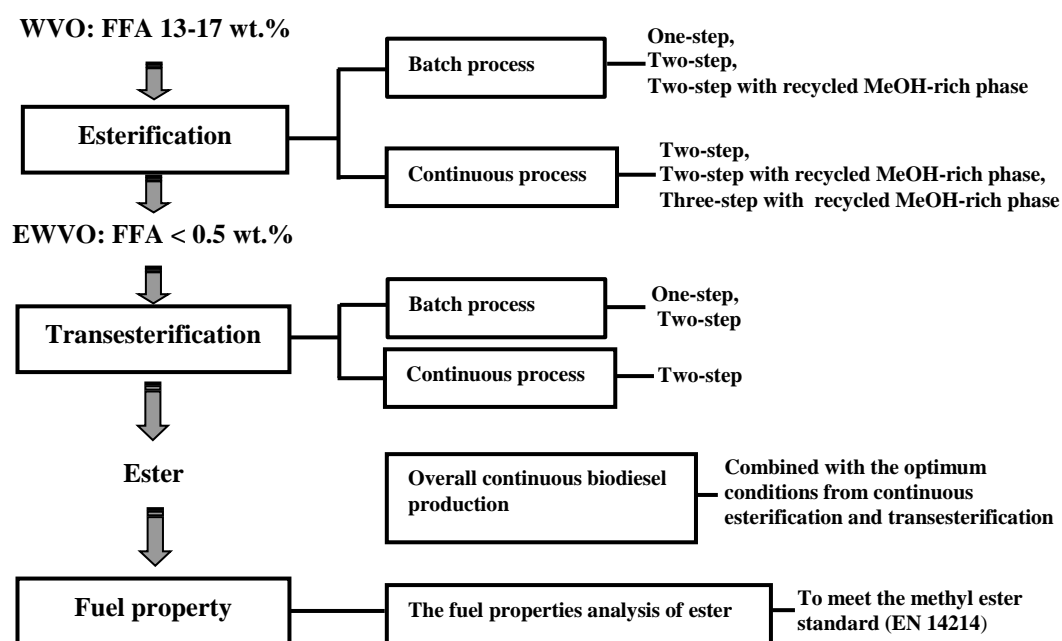


Fig. 2.1 Schematic of the experiments to produce biodiesel from WVO

2.3.1.2 The second esterification stand-alone

A larger quantity of MO with properties resembling those obtained in 2.3.1.1 was made and subjected to this experiment under the reaction temperature derived from the optimum yield in that first experiment. Variable parameters in this step were: MeOH-to-FFA molar ratio (20:1 to 80:1) and H_2SO_4 -to-FFA molar ratio

(0.83:1 to 1.93:1). An optimum yield with FFA content less than 0.5 wt.% should be achieved from this part.

2.3.1.3 The two-step esterification

This experiment was set up to investigate the effect of hydrolysis reaction occurring in the esterification, with practical optimum conditions in each step.

2.3.1.4 The two-step esterification combined with alcohol rich phase recycling

This fourth experiment was conducted identical to that done in 2.3.1.3. However, the alcohol-rich phase separated at the end of the second step would be recycled back to the beginning of the first step to esterify new WVO inputs. Nevertheless, new portions of MeOH and H₂SO₄ would be needed to add to that leftover from the second step to make up the required amount. This esterification investigation method is conducted in an effort to reduce the use of both chemicals detrimental to the environment.

2.3.1.5 General esterification procedure

FFA conversions via esterification reaction in WVO were studied in 1-L flask and connected with a sample taking, a condenser and a thermometer.

The reaction procedure started off as follows: 500 g WVO was poured into each flask, gradually heated up to a predetermined reaction temperature, a prepared MeOH/H₂SO₄ solution was then fed into reactor. The reaction mixture was stirred at a constant 1,200 rpm for all batch experiments. Samples were taken out at 0.25, 0.5, 1, 2, 3, and 4 h. FFA conversion was calculated from the FFA content in the reaction mixture by acid-base titration. After the four-hour reaction, the mixture product was settled overnight into two phases in a separation funnel.

Two settled phases could be identified as a 'MeOH-rich phase' consisting mainly of MeOH, H₂SO₄, H₂O and impurities; and a 'TG-rich phase' including mainly of TGs and esterified oils (Lotero et al., 2005). For the two-step esterification, the TG-rich phase obtained from the first step was used directly as feedstock for the second step.

The FFA conversion rate and FFA content are two indications of the efficiency of the esterification reaction. The goal of this study is to reduce FFA content of the second esterification to be less than 0.5 wt.% and to obtain MeOH-rich phase as a lower phase. At 80% of the FFA conversion was set as a cutoff point to present the reaction efficiency.

2.3.2 Process design and set up a continuous reactor

In the design, WVO was pumped to preheat and then flew into a continuous reactor 1. Solution of MeOH and H_2SO_4 was fed into the reactor for the first esterification step. From the reactor, the mixture would overflow into a settling tank 1. Here, TG-rich phase would overflow (light liquid) at a top position of the tank into a continuous reactor 2 and MeOH-rich phase (heavy liquid) would overflow at a bottom position of the tank.

Fresh solution of MeOH and H_2SO_4 was pumped into the reactor 2 which was controlled temperature at 60 °C for the second esterification process. The mixture would overflow into a settling tank 2. TG-rich phase and MeOH-rich phase would overflow as same as the first esterification. An overview of the continuous process is shown in Fig. 2.2.

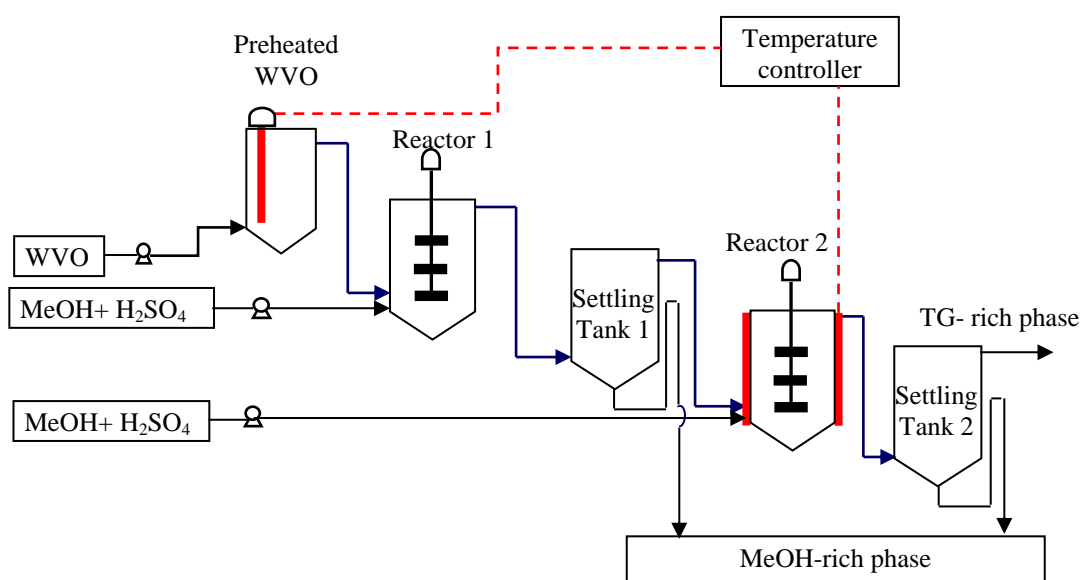


Fig. 2.2 Two-step continuous esterification process

2.3.2.1 Continuous dewater reactor (CDR)

Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops, Prince of Songkla University developed CD unit to run in transesterification process which could simultaneously separate glycerol. The conception of CD unit based on that the transesterification reaction is a reversible reaction and the reaction rate has severely slow since it reached equilibrium, subsequently glycerol (one of products) is eliminated out of reactor. Thus, the equilibrium can shift the reaction to the products side.

The esterification reaction is a reversible reaction similar to the transesterification thus the CDR unit was developed to remove water to drive the reaction for high yield. The CDR unit used in experiment and its details was shown in Fig. 2.3.

The 3.0 L CDR reactor was designed to have 2 virtual balance units inside a reactor by separating into 2.0 L mixing zone and 1.0 L calming zone in order to simultaneously separate MeOH-rich phase -a heavy liquid- down to its base. Outflow of TG-rich phase and MeOH-rich phase was designed by using pressure balance principle of immiscible liquid. The advantage of this technique is used simple equipment leading to economic and possible to develop to industrial scale.

2.3.2.2 Continuous stirred-tank reactor (CSTR)

The 3.0 L CSTR reactor was designed to have a baffle tank equipped with 3-levels blade (6 blades). Details of the reactor were shown in Fig. 2.4.

2.3.3 A Study of continuous acid catalyzed esterification of WVO using continuous dewater reactor (CDR) and continuous stirred-tank reactor (CSTR)

The commercial approach was aimed to conduct by a continuous process and assigned to run with CDR and CSTR. Experiment was set to compare performance of CDR and CSTR using the optimal condition based on the previous batch esterification experiment. The WVO was pumped into heating unit for heat up WVO to 70 °C. Chemicals, solution of methanol and H₂SO₄, are pumped to mix with heated WVO in the reactor which controlled temperature at 60 °C. Esterification reaction occurred simultaneously with phase separation between MeOH-rich phase and TG-rich phase. MeOH-rich phase, the heavy liquid, is settling and separated from reactor at its base. For TG-rich phase, light liquid, is separated overflow at the top line

of reactor. At interval time of reaction time until steady state, samples of 50 mL were taken out the reactor to analyze FFA.

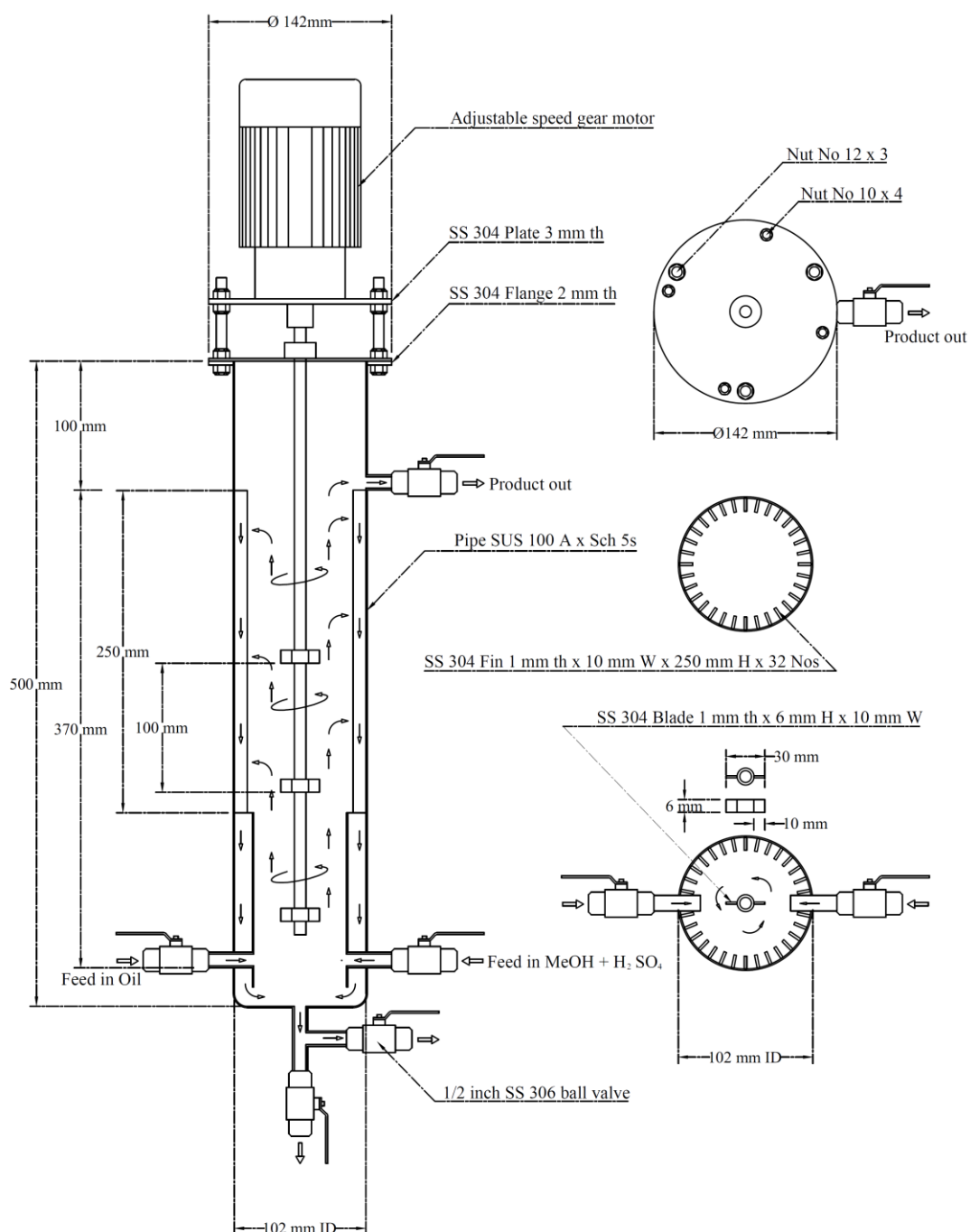


Fig. 2.3 The CDR unit for esterification process

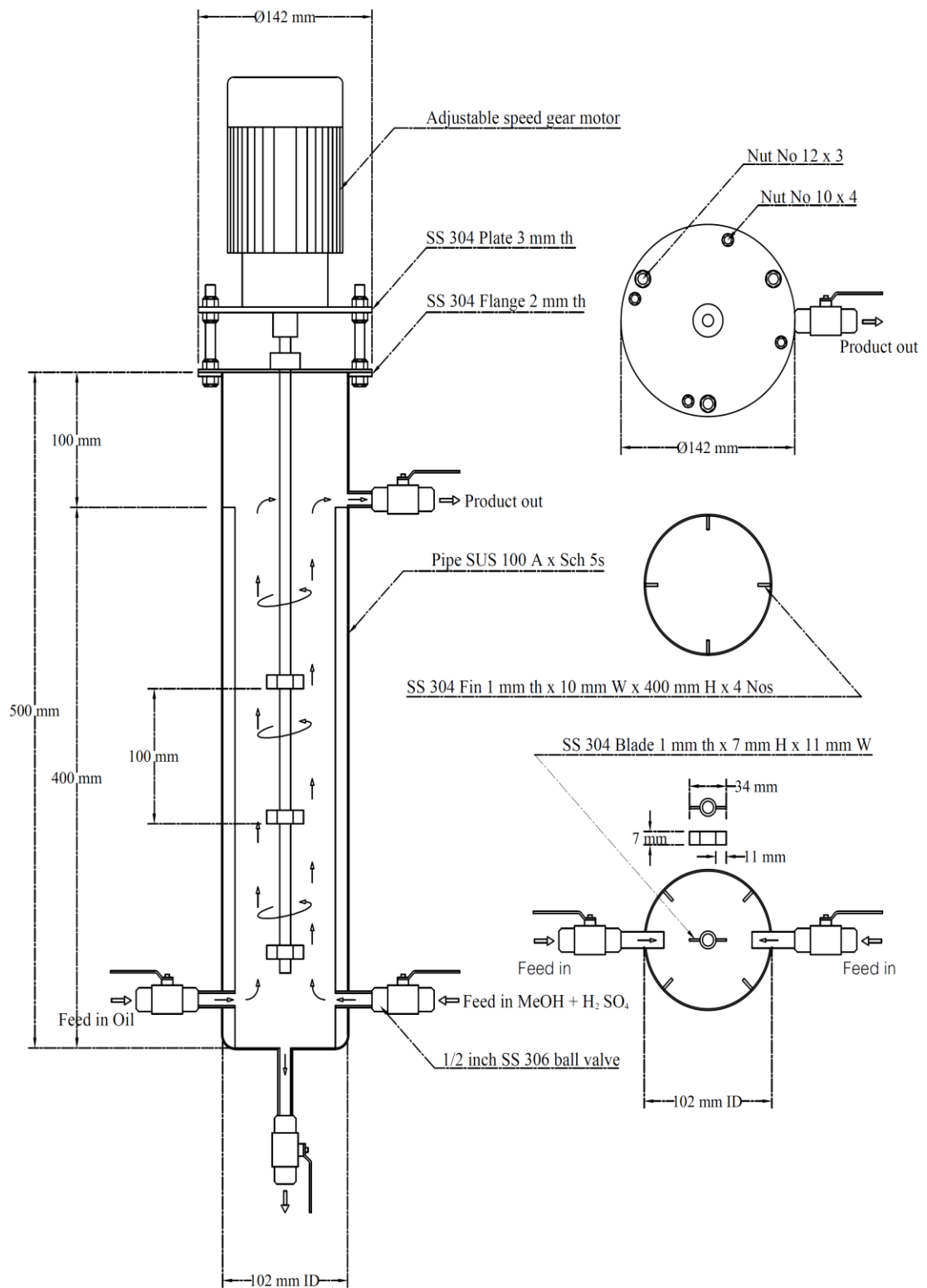


Fig. 2.4 The CSTR reactor

2.3.3.1 Effect of agitation speed on CDR and CSTR

The purpose of this part is to investigate optimum conditions of speed on the first esterification reaction. Variable factors in this experiment were: 0.41:1 H_2SO_4 -to-FFA molar ratio, 10: 1 MeOH-to-FFA molar ratio, 60°C reaction temperature, 1 h reaction time, and speed of agitator (100-800 rpm). The continuous esterification process is shown in Fig. 2.5 and Fig. 2.6.

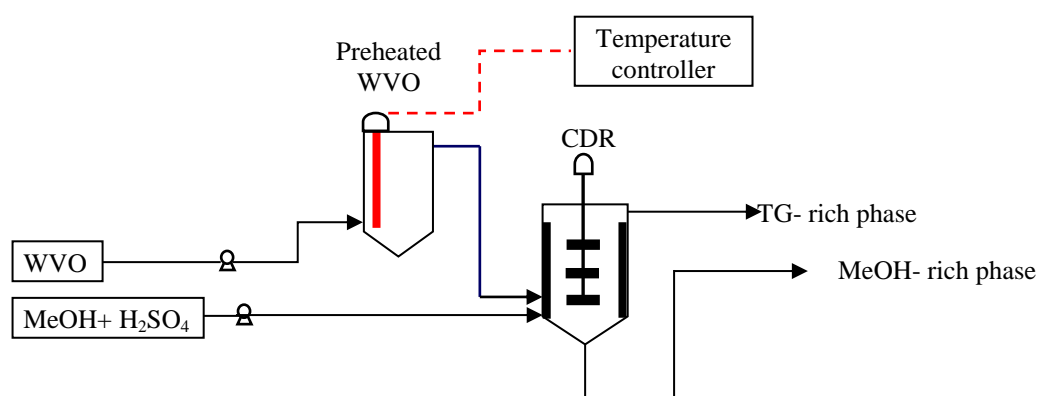


Fig. 2.5 CDR process for esterification

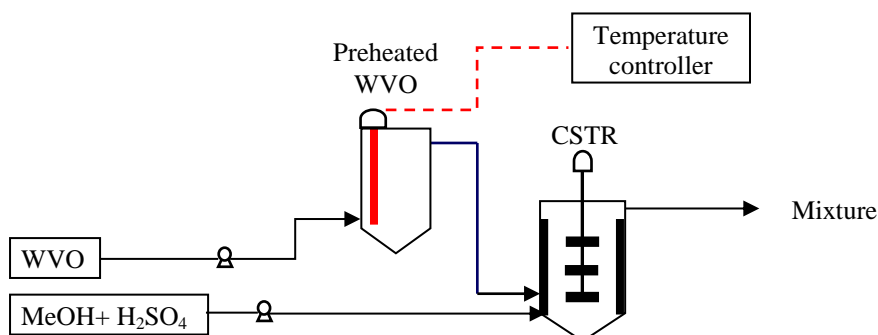


Fig. 2.6 CSTR process for esterification

2.3.3.2 Effect of type reactor on two-step esterification

This experiment was conducted to study the performance of reactor type on two-step esterification with practical optimum conditions in batch process. The two-step continuous esterification process is shown in Fig. 2.7 and Fig. 2.8.

2.3.3.3 Effect of MeOH-rich phase recycling

The suitable continuous process from section 2.3.3.3 was conducted identical to that done in 2.3.1.4. The MeOH-rich phase separated at the end of the second step would be recycled back to the beginning of the first step to esterify new WVO inputs. Nevertheless, new portions of MeOH and H_2SO_4 would be needed to add to that leftover from the second step to make up the required amount as shown in Fig. 2.9.

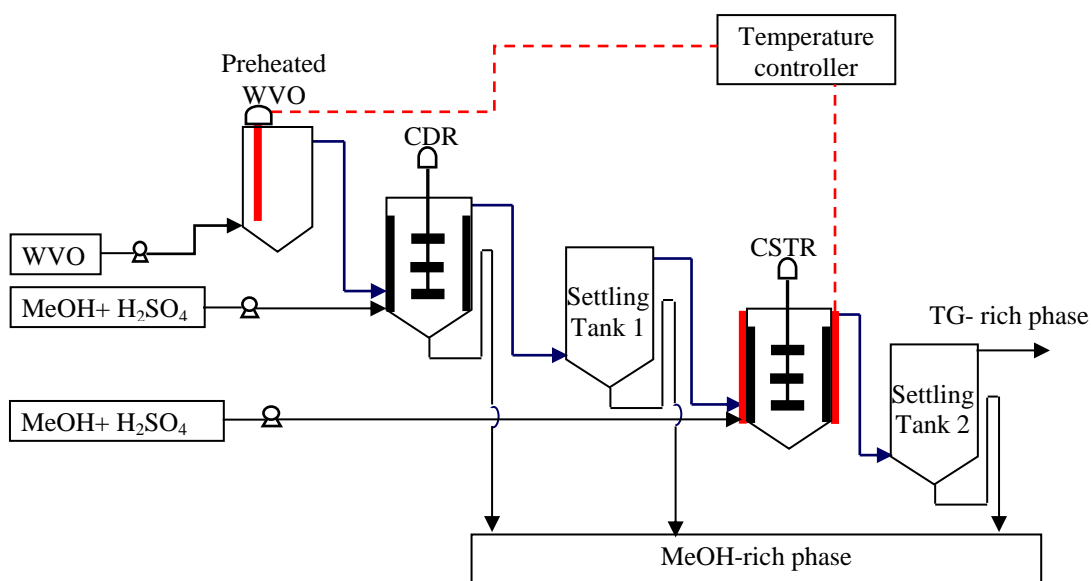


Fig. 2.7 Model 1: CDR and CSTR in the two-step esterification

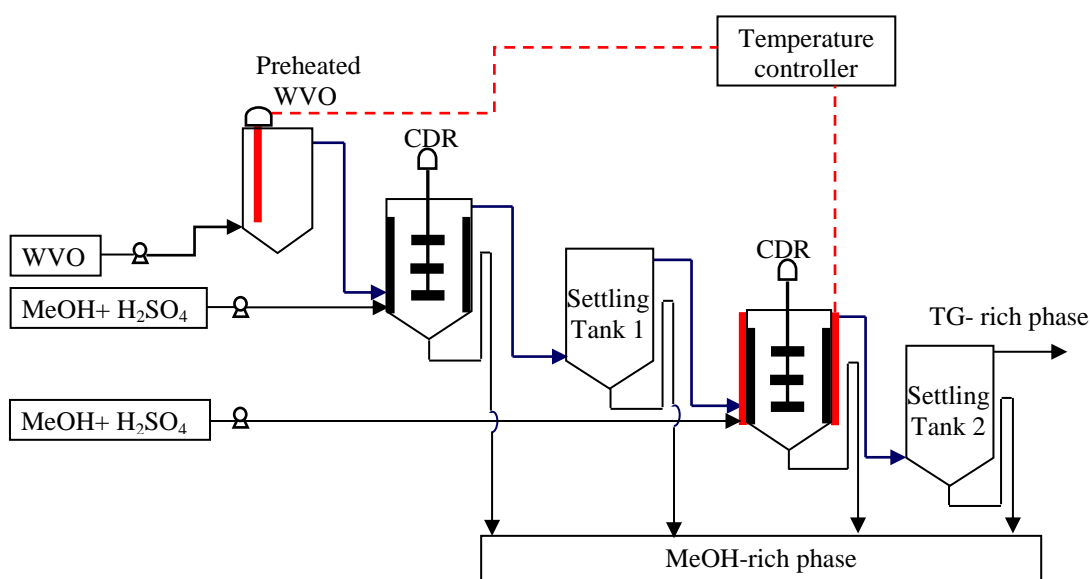


Fig. 2.8 Model 2: 2 CDRs in the two-step esterification

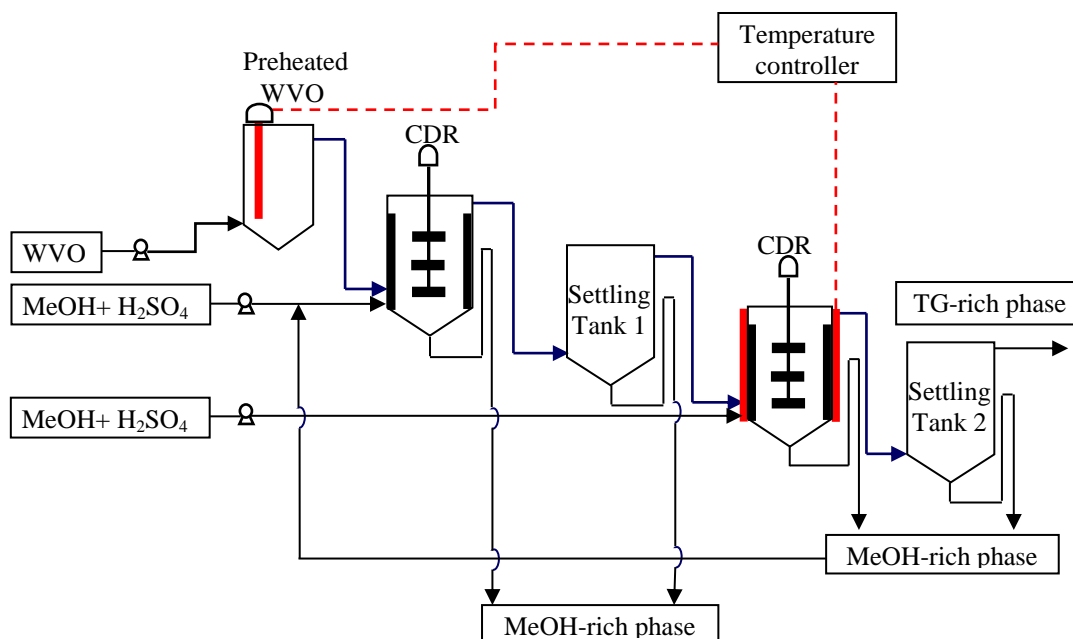


Fig. 2.9 The two-step continuous esterification process plus MeOH-rich phase recycling

2.3.4 A study of suitable condition for production methyl ester from esterified vegetable oil (EWVO) by batch transesterification

Transesterification of TG in EWVO was investigated in 1-L flask and connected with a sample taking, a condenser and a thermometer.

The reaction procedure started off as follows: 500 g EWVO was added into each flask, gradually heated up to a predetermined reaction temperature, a prepared MeOH/KOCH₃ solution was then fed into reactor. The reaction mixture was stirred at a constant 600 rpm for all batch experiments and kept reacting for 0.5 h.

After the end of the reaction, the mixture product was settled for 4 h into two phases in a separation funnel. Two settled phases could be identified as an ‘Ester-rich phase’ consisting of Ester, MeOH, Soap, KOCH₃, glycerol and impurities; and a ‘Glycerol-rich phase’ including of glycerol, MeOH, Soap and KOCH₃.

Samples of both phases were taken out from the reaction mixture to analyze soap and KOCH₃ by titration. Ester content in the ester-rich phase is an indication of the efficiency of the transesterification reaction.

For the two-step transesterification, the ester-rich phase obtained from the first step was used directly as feedstock for the second step.

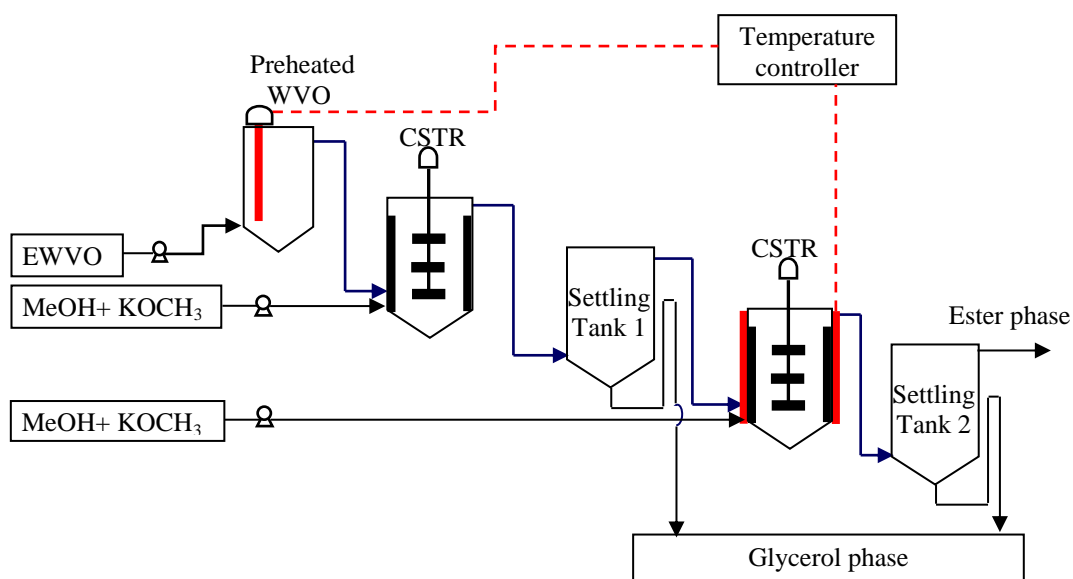
Table 2.1 presents the experimental factors for optimization in the transesterification reaction.

Table 2.1 Experimental factors of the batch transesterification

Experimental factor	Unit	
MeOH-to-TG molar ratio	mol/mol	6:1
Reaction time	h	0.5
Reaction temperature	°C	60
KOCH ₃	wt.% of TG	0.6, 0.8, 1.0, 1.2

2.3.5 A study of continuous transesterification of EWVO with methanol using continuous stirred-tank reactor (CSTR)

In this part, the experiment was aimed to conduct by a continuous process and assigned to run with CSTR using the optimal condition based on preliminary study in section 2.3.4. The EWVO was pumped into heating unit for heat up EWVO to 70 °C. Chemicals, solution of methanol and KOCH₃, are pumped to mix with heated EWVO in the reactor. Transesterification occurred in CSTR reactor which controlled temperature at 60 °C. From the CSTR, the mixture products were overflow into a settling tank. Glycerol-rich phase, a heavy liquid, is settling and separated from reactor at its base. For Ester-rich phase, a light liquid, is separated overflow at the top line of tank. At interval time of reaction time until steady state, samples of both phases were taken out from the settling tank to analyze soap and KOCH₃ content. The ester content was analyzed by GC. The continuous transesterification process is shown Fig. 2.10.

**Fig. 2.10** The continuous transesterification process

2.3.6 The fuel properties analysis

Table 2.2 presents the fuel properties of the final methyl ester product which was obtained from the optimum reaction condition. It was analyzed for fuel properties follow methyl ester standard which is specified by EN14214.

Table 2.2 The fuel property analysis

Item	Property	Unit	Test method	Specification (EN14214)
1	Ester content	wt. %	EN 14303	≥ 96.5
2	Density 15°C	kg/m ³	ASTM D1298	860-900
3	Viscosity 40°C	cSt	ASTM D445	3.5-5.0
4	Flash point	°C	ASTM D93	≥ 120
5	Sulfur content	mg/kg	ASTM D2622	≤ 10.0
6	Carbon residue	% wt	ASTM D5452	≤ 0.30
7	Cetane number	number	ASTM D613	≥ 51
8	Sulfated ash content	wt. %	ASTM D874	≤ 0.02
9	Water content	mg/kg	ASTM D2709	≤ 500
10	Total contamination	mg/kg	ASTM D5452	≤ 24
11	Copper strip corrosion	number	ASTM D130	≤ 1
12	Oxidation stability	h	EN 15751	> 10
13	Total acid number	mg KOH/g	ASTM D664	≤ 0.5
14	Iodine value	g Iodine/100g	EN 14111	≤ 120
15	Linolenic acid methyl ester	wt. %	EN 14103	≤ 12.0
16	Methanol content	wt. %	EN 14110	≤ 0.2
17	Monoglyceride	wt. %	EN 14105	≤ 0.8
18	Diglyceride	wt. %	EN 14105	≤ 0.2
19	Triglyceride	wt. %	EN 14105	≤ 0.2
20	Free glycerin	wt. %	EN 14105	≤ 0.02
21	Total glycerin	wt. %	EN 14105	≤ 0.25
22	Group I metals (Na+K)	mg/kg	EN 14538	≤ 5.0
	Group II metals (Ca+Mg)	mg/kg	EN 14538	≤ 5.0
23	Phosphorous	mg/kg	ASTM D 4951	≤ 10.0

2.3.7 Analytical methods for oil and biodiesel

2.3.7.1 FFA analyses

FFA content was determined by using the AOCS Ca-5a-40 method. FFA conversion was calculated using the following equation:

$$\text{FFA conversion, \%} = \frac{\text{FFA}_i - \text{FFA}_t}{\text{FFA}_i} \times 100 \quad (\text{Eq. 2.1})$$

where FFA_i is the initial FFA content, and the FFA_t is the FFA content at any time.

2.3.7.2 Soap and catalyst analyses

Soap and catalyst content in sample was determined using AOCS Cc17-79 method.

2.3.7.3 Glycerol analyses

Glycerol content in sample was measured follows BS 5711: part3: 1979 method.

2.3.7.4 Proximately analysis total glycerides and ester content (Thailand Patty Patent 5060)

Ester content in the sample was determined by the Thailand Patty Patent 5060.

2.3.7.5 Ester analyses

Ester content in biodiesel sample was determined by GC using EN 14103 method.

2.3.7.6 Physical properties

Density was determined according to ASTM D1298 and Water content in the sample was analyzed using Karl-Fischer method.

CHAPTER 3

RESULT and DISCUSSION

3.1 A study of batch acid catalyzed esterification of WVO

3.1.1 The first esterification stand-alone

As outlined earlier, the objective of this process is to reduce the FFA content of the WVO from its initial FFA content of approx. 13-17 wt.% down to 2.6-3.4 wt.%, or approx. 80% of the conversion; and to obtain the lower-layered MeOH-rich phase.

3.1.1.1 Effect of temperature and reaction time

The effect of reaction temperature on FFA conversion was studied under three temperatures (50, 60, and 70 °C). MeOH-to-FFA molar ratio of 10:1, H₂SO₄-to-FFA molar ratio of 0.25:1, and 4 h reaction time were investigated. From Fig. 3.1, the FFA conversion rate increased very rapidly in the first quarter hour directly and proportionately with the reaction time, almost regardless of temperature except at the lowest set temperature. After this period, the rate tapered and leveled off rapidly, and the effect from temperature stood out more clearly; that the two higher set temperatures reached the cutoff rate of 80% much quicker. The increasing temperature causes the decrease of oil viscosity, improving the contact between reactants (Diaz-Felix et al., 2009) and hence, in general, the higher temperature the better the performance. However, the end results after the first one or two hours seemed to coincide for the two higher temperatures. For economy, efficiency and effectiveness, 60 °C at 1 h can be considered a suitable condition, of which losses of MeOH due to temperature would also be lowered.

The results were in accordance with those obtained in several researches (e.g., Canakci and Gerpen, 2001; Encinar et al., 2011; Hassan and Vinjamur, 2014; Issariyakul et al., 2007).

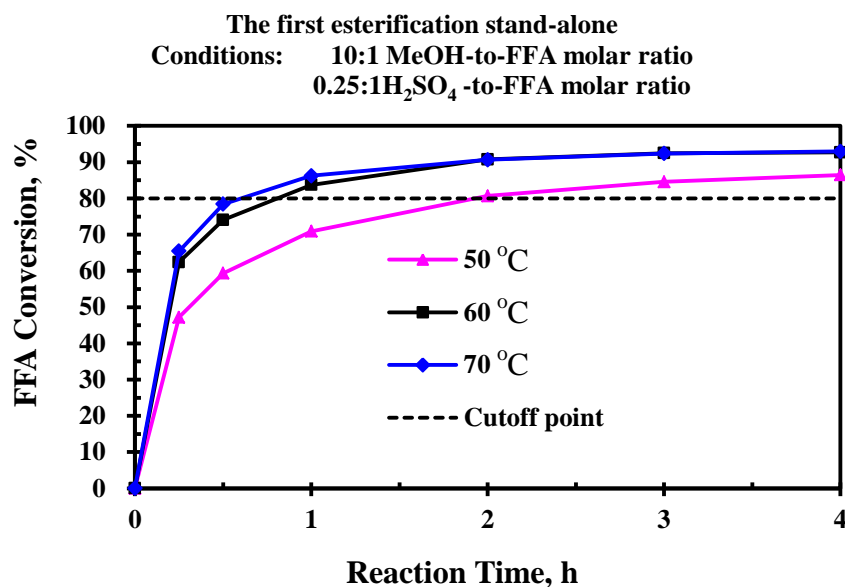


Fig. 3.1 Effect of temperature and reaction time on FFA conversion in the first esterification stand-alone

3.1.1.2 Effect of MeOH-to-FFA molar ratio and reaction time

The reaction was carried out at a constant temperature of 60 °C and H₂SO₄-to-FFA molar ratio of 0.25:1. MeOH-to-FFA molar ratios of the first esterification were varied in the range of 5:1 to 30:1.

Fig. 3.2 shows the change in FFA content of the WVO with respect to changes in molar ratio of MeOH-to-FFA since excess of MeOH amount promotes reaction completion, keeping the H₂SO₄ in the MeOH phase and the water produced is diluted to the level where it does not limit the reaction (Gerpen et al., 2004; Park et al., 2010). It should be noted here, that higher amounts of MeOH usage tended to move the MeOH-rich phase to the upper layer (above the oil) since their bulk density were decreased (Table 3.1), thus one disadvantage of this approach is that the more MeOH used, the more the process cost (Encinar et al., 2011). In Fig. 3.2 the reaction progressed rapidly during the first quarter hour, similar to the effect of temperature described earlier in 3.1.1.1, and continuously increased to the first hour, albeit with a declining rate. After the first hour, except the lowest MeOH-to-FFA ratio of 5:1, all others using higher ratios had reached the cutoff rate. After that, all reaction rates went up only slightly and soon stabilized, and even dropped down in the case of the highest ratio of 30:1. A reverse esterification reaction in this situation could be explained by the accumulation of water formed by the esterification of FFA (Diaz-Felix et al., 2009). The most economical MeOH-to-FFA molar ratio of this first

esterification stand-alone was found to be 10:1 at 1 h, having the MeOH -rich phase at the preferred lower layer.

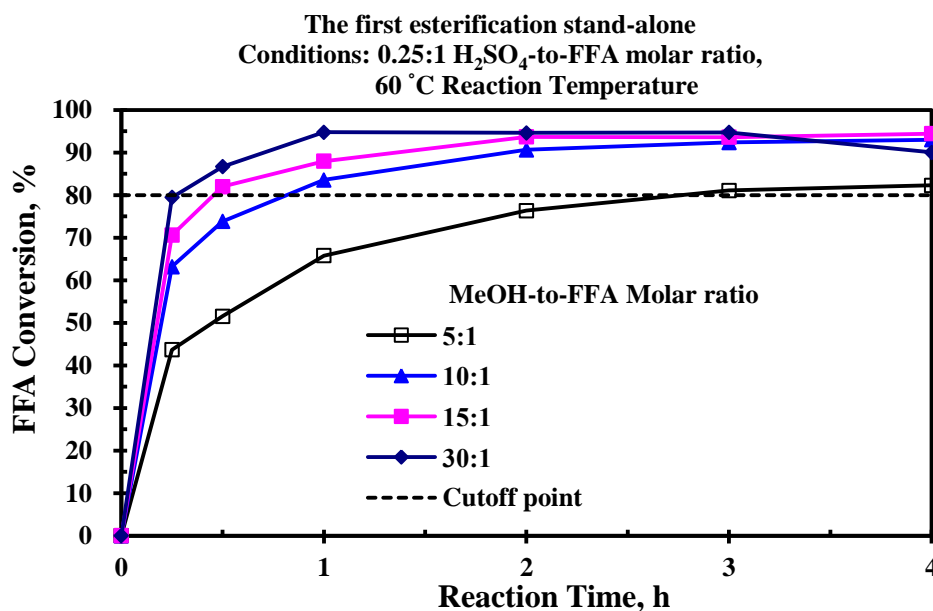


Fig. 3.2 Effect of MeOH-to-FFA molar ratio and reaction time on the FFA conversion in the first esterification stand-alone

Table 3.1 Weight distribution of TG- rich phase and MeOH-rich phase after 4 h of the first esterification stand-alone on MeOH-to-FFA molar ratio from 5:1 to 30:1 (at 0.25:1 H₂SO₄-to-FFA molar ratio, 60 °C reaction temperature)

MeOH-to-FFA molar ratio	TG-rich phase			MeOH-rich phase		
	Position	wt%	Density*, g/mL	Position	wt%	Density*, g/mL
5: 1	Upper	95.83	0.914	Lower	4.17	1.112
10: 1	Upper	92.55	0.908	Lower	7.45	0.960
15: 1	Upper	91.86	0.904	Lower	8.14	0.922
30: 1	Lower	73.61	0.898	Upper	26.39	0.856

Notes* Density at 20 °C

3.1.1.3 Effect of H₂SO₄-to-FFA molar ratio and reaction time

The esterification reaction was investigated at a constant temperature of 60 °C. MeOH-to-FFA molar ratio was 10:1, whereas H₂SO₄-to-FFA molar ratios were varied in the range of 0.08:1 to 0.83:1.

The results in Fig. 3.3 show that the FFA conversion rose sharply in the beginning of the reaction. After a quarter hour, reactions increased more slightly. The two higher amounts of H_2SO_4 reached the cutoff rate before the half hour and started to stabilize after 1 h. Except for the lowest amount of H_2SO_4 , all others almost leveled off at over 90 % conversion at 3 h. One reason that FFA conversion could not proceed much further was reported by some researchers that it is due to shortage of acid catalyst; H_2SO_4 might have migrated from MeOH to water (Diaz-Felix et al., 2009; Gerpen et al., 2004). Moreover, H_2SO_4 -to-FFA molar ratio of 0.33:1, or higher, produced dark esterified oils. The optimum H_2SO_4 -to-FFA molar ratio at 1 h was in the range 0.25:1-0.41:1. Considering performance is a more significant factor than color.

Thus, for the first esterification stand-alone, it could be summarized overall that the suitable conditions were: 60 °C reaction temperature, 1 h reaction time, 10:1 MeOH-to-FFA molar ratio and 0.25:1-0.41:1 H_2SO_4 -to-FFA molar ratios.

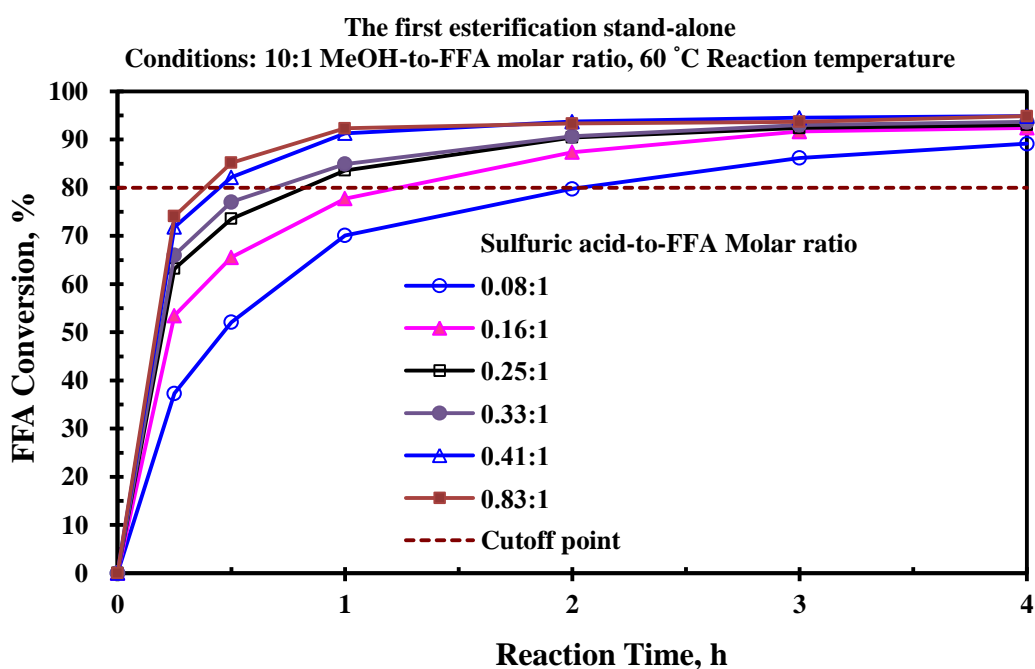


Fig. 3.3 Effect of H_2SO_4 -to-FFA molar ratio on FFA conversion in the first esterification stand-alone

3.1.2 The second esterification stand-alone

The goal of the second esterification stand-alone process is to reduce FFA of the MO from its initial 2.51 to below 0.5 wt.% or 80% of FFA conversion, and to obtain the MeOH rich phase at the lower layer.

The esterification reaction was studied at a constant temperature of 60 °C and reaction time 4 h. MeOH-to-FFA molar ratios of the second esterification stand-alone were varied from 20:1 to 80:1, whilst H₂SO₄-to-FFA molar ratio was fixed at 0.25:1.

Fig. 3.4 shows a clear trend that the second esterification required high amounts of MeOH in terms of molar ratio despite the fact that stoichiometry needs only 1:1. Because FFA content in the mixture was lower than that from the first esterification, MeOH was consumed at a much higher ratio to force reaction. Reaching a cutoff rate at reaction time 1 h, the suitable condition was MeOH-to-FFA molar ratio of 60:1.

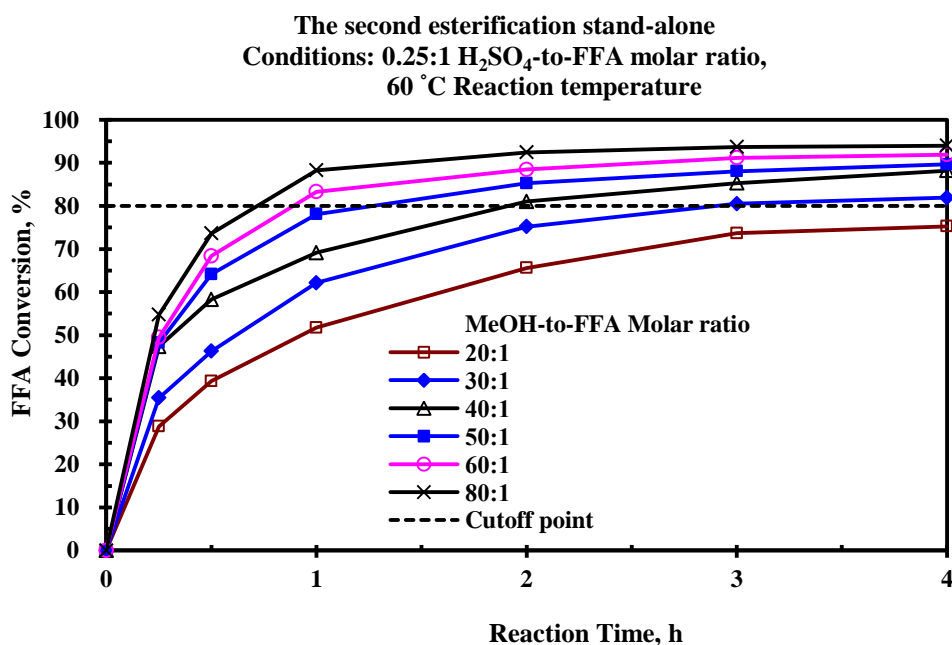


Fig. 3.4 Effect of MeOH-to-FFA molar ratio and reaction time on the FFA conversion of MO in the second esterification stand-alone

One disadvantage of using higher amount of MeOH is the higher production cost, and it tends to lead the MeOH rich phase to the upper layer, particularly when the MeOH-to-FFA molar ratio is 40:1, or more, as shown in Table 3.2.

The increase of H₂SO₄-to-FFA molar ratio from 0.83:1 to 1.93:1 was analyzed in an effort to increase the bulk density of the MeOH rich phase in order to lead the phase to the lower layer. Fig. 3.5 reveals that the progress of reactions rose steeply in the first quarter hour. After an hour, no significant differences were found on FFA conversion from the use of all molar ratios, and all had reached the cutoff rate. The suitable H₂SO₄-to-FFA molar ratio, having the MeOH rich phase settled on the lower layer, was found to be 1.93:1.

The optimum conditions for the second esterification were: 1 h reaction time, 60:1 MeOH-to-FFA molar ratio, 1.93:1 H₂SO₄-to-FFA molar ratio at 60 °C.

Table 3.2 Weight distribution of TG-rich phase and MeOH-rich phase after 4 h of the second esterification stand-alone on MeOH-to-FFA molar ratios from 20:1 to 80:1 (at 0.25:1 H₂SO₄-to-FFA molar ratio and 60 °C reaction temperature)

MeOH-to-FFA molar ratio	TG-rich phase			MeOH-rich phase		
	Position	wt%	Density*, g/mL	Position	wt%	Density*, g/mL
20:1	Upper	99.05	0.906	Lower	0.95	1.004
30:1	Upper	98.42	0.904	Lower	1.58	0.950
40:1	Lower	97.31	0.904	Upper	2.69	0.884
50:1	Lower	95.85	0.902	Upper	4.15	0.855
60:1	Lower	93.09	0.902	Upper	6.91	0.836
80:1	Lower	88.55	0.902	Upper	11.45	0.820

Notes* Density at 20 °C

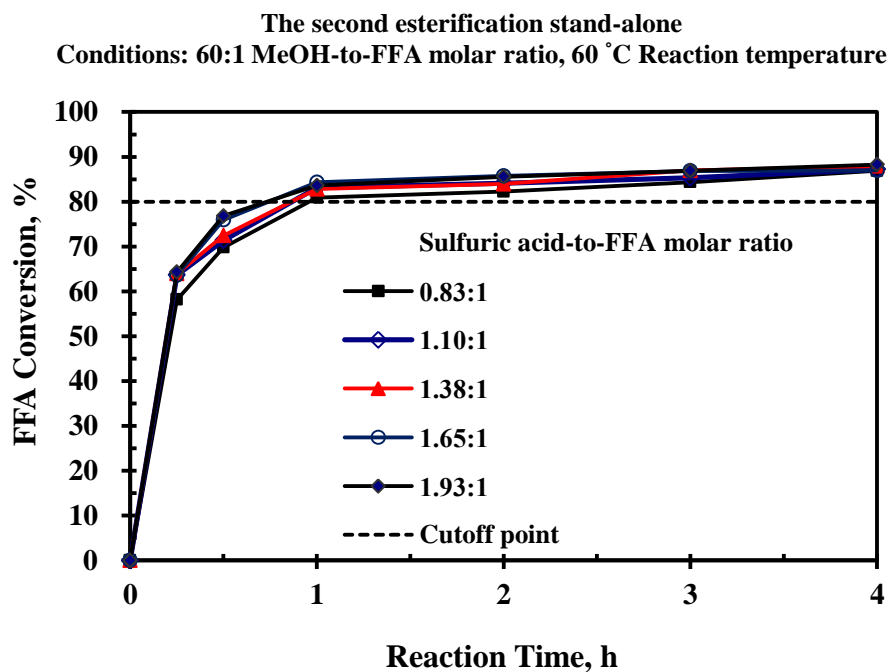


Fig. 3.5 Effect of H₂SO₄-to-FFA molar ratio and reaction time on the FFA conversion of MO in the second esterification stand-alone

3.1.3 Material balance of esterification

In this section, material balances of the first esterification stand-alone of WVO and the second esterification stand-alone of MO were analyzed according to FFA conversion at their corresponding optimum conditions. The results are as shown in Table 3.3.

Table 3.3 Material balances of the first esterification stand-alone of WVO and the second esterification stand-alone of MO at suitable conditions* after 4 h (at 60 °C reaction temperature)

Component	The first esterification of WVO			The second esterification of MO		
	Initial amount	TG-rich phase	MeOH-rich phase	Initial amount	TG-rich phase	MeOH-rich phase
	g	g	g	g	g	g
TG	432.05	432.05	-	417.87	417.87	-
FFA	67.77	4.72	-	11.95	1.40	-
Ester	-	66.32	-	70.00	81.10	-
H ₂ O	0.56	1.83	2.93	0.62	0.94	0.38
MeOH	80.06	37.75	34.84	84.70	18.45	65.02
H ₂ SO ₄	5.98	2.77	3.21	8.20	2.56	5.64
total	586.42	545.44	40.98	593.34	522.31	71.03

Notes*

1. Conditions for the first esterification: 10:1 MeOH-to-FFA molar ratio, and 0.25:1 H₂SO₄-to-FFA molar ratio.
2. For the second esterification: 60:1 MeOH-to-FFA molar ratio, and 1.93:1 H₂SO₄-to-FFA molar ratio.

After esterification, each mixture is separated into two phases: a TG-rich phase, consisting mainly of non-polar compound TG; and a MeOH-rich phase, composing dominantly of polar compound MeOH. Water is the most undesirable component in the esterification system since it leads to hydrolysis reaction in the presence of H₂SO₄. Table 3.3 shows that in either reaction, total water from both rich phases increased from the initial amount. Water produced in the first esterification was over three times that of the second since the WVO contained much higher level of FFA compared with the MO; and it dispersed more in the MeOH-rich phase than in the TG-rich phase when compared in percentage of weight.

In the first reaction, moreover, the remaining high amount of MeOH in the TG-rich phase (6.92 wt.%) plus a designed fresh methanol added to the second step esterification could be a cause of an undesirable excess MeOH which would lift the MeOH-rich phase to the upper layer in the second step of a two-step esterification.

The lower amount of remaining MeOH in the second reaction (3.53 wt.%) could also be used to reduce MeOH consumption in a transesterification process.

3.1.4 Model analysis

Experimental data from the first esterification and the second esterification stand-alone were analyzed employing multiple regression model procedure of the data analysis function in the Excel program. Two types of model, one linear and one non-linear, were manipulated with the input variables: reaction time (h), MeOH-to-FFA molar ratio and H₂SO₄-to-FFA molar ratio.

Quadratic model, expressed as a second-order polynomial in Eq. 3.1, yielded a better fit to the data in both the first esterification and the second esterification stand-alone, thus:

$$Y = a_0 + a_1A + a_2B + a_3C + a_4A^2 + a_5B^2 + a_6C^2 + a_7AB + a_8AC + a_9BC \quad (\text{Eq. 3.1})$$

where Y is the FFA conversion (%); a_n , the coefficients ($n = 0, 1, 2, \dots, 9$); A , the reaction time (h); B , the MeOH-to-FFA molar ratio; and C , the H₂SO₄-to-FFA molar ratio.

The analysis of variance (ANOVA) results are summarized in Table 3.4. The results showed that the model at 1 h of the first esterification and the second esterification stand-alone had high F values, and very low p-values (<0.0001). In addition, the 1 h model fitted well to the experiment data, as evidenced by the high R². These indicated that the 1 h model is significant.

BC (multiplication of MeOH-to-FFA molar ratio to H₂SO₄-to-FFA molar ratio) was the highest coefficient impacting on FFA conversion in the 1 h model of the first esterification stand-alone, whereas C (H₂SO₄-to-FFA molar ratio) was the highest standardized coefficient in the second esterification stand-alone.

From these parametric analyses, it is thus verified that these two models are suitable and can be implemented to investigate further esterification processes.

3.1.5 The two-step esterification

The experiment was set up to verify the suitable conditions from the first esterification stand-alone and the second esterification stand-alone and to study the effect of hydrolysis reaction occurring in the esterification.

Table 3.4 Statistical analyses of non-linear regression model for the first esterification stand-alone and the second esterification stand-alone at 1 h

	The first esterification stand-alone			The second esterification stand-alone		
	Coefficient	Standardized Coefficient	p-value	Coefficient	Standardized Coefficient	p-value
a ₀	11.54		0.020	-49.65		<0.0001 ^a
a ₁	76.00	1.66	<0.0001 ^a	66.21	1.13	<0.0001 ^a
a ₂	1.45	0.65	0.012	1.872	1.66	<0.0001 ^a
a ₃	-	-	-	134.54	3.83	<0.0001 ^a
a ₄	-29.56	-0.84	0.002	-31.01	-0.68	0.003
a ₅	-0.10	-1.69	<0.0001 ^a	-0.01	-0.76	<0.0001 ^a
a ₆	-103.17	-1.37	<0.0001 ^a	-1.30	-0.07	0.657
a ₇	-0.49	-0.19	0.058	0.31	0.31	0.017
a ₈	-17.34	-0.19	0.043	-13.10	-0.28	0.002
a ₉	14.28	2.39	<0.0001 ^a	-1.98	-3.63	<0.0001 ^a
R ²	0.976			0.957		
Standard error	2.65			4.19		
F-value	106.71			110.24		

^aVery statistically significant.

In Fig. 3.6, the progress of reaction was continuously plotted from the first through to the second esterification. It was found that the continuous two-step esterification could reduce FFA to be less than 0.5 wt.%. However, the MeOH-rich phase was found to be in the upper layer since the TG-rich phase from the first esterification contained a significant amount of remaining MeOH, causing an excess in MeOH. This result confirmed the assumption earlier speculated in Section 3.1.3.

From Fig. 3.7, the MeOH-rich phase layer was studied by reducing MeOH-to-FFA molar ratio in the second esterification from 60:1 down to 50:1 ('Two-step1** line' in Fig. 3.7). Although, this 'succeeded' in settling the MeOH-rich phase to the lower layer, FFA was found to be higher than 0.5 wt.%. An increase of H₂SO₄-to-FFA molar ratio in the first esterification was thus investigated because in the second esterification high amounts of H₂SO₄ would be consumed due to the increased bulk density of the MeOH-rich phase

Since no significant differences between H₂SO₄-to-FFA molar ratio of 0.25:1 and 0.33:1 was found, as shown in Fig. 3.3, the highest end value in the H₂SO₄-to-FFA molar ratio optimal range, 0.41:1 in the first esterification, was thus selected. Fig. 3.7 shows that this new condition for the two-step esterification ('Two-step2*** line') could reduce the FFA to be less than 0.5 wt.% together with the MeOH-rich phase in the second esterification at the preferred lower layer.

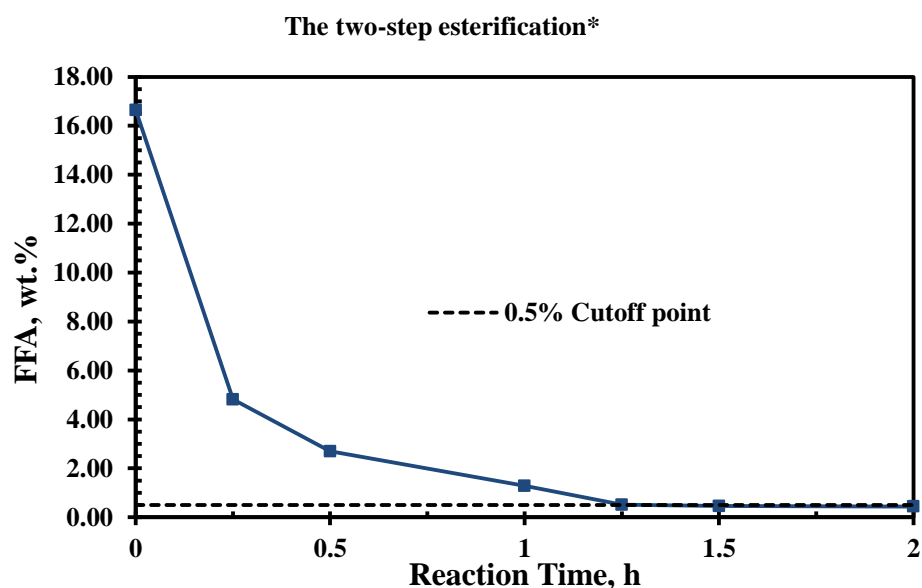


Fig. 3.6 FFA reduction of WVO from the two-step esterification (at 60 °C reaction temperature and 1 h reaction time)

Notes* Conditions for the two-step esterification: 1st esterification, 10:1 MeOH-to-FFA molar ratio, 0.25:1 H₂SO₄-to-FFA molar ratio; 2nd esterification, 60:1 MeOH-to-FFA molar ratio, 1.93:1 H₂SO₄-to-FFA molar ratio.

One advantage of the two-step esterification is the progression of reaction because the MeOH-rich phase consisting of high amount of H₂O would be separated and removed before the resulting TG-rich phase from the first esterification is fed into the second (Park et al., 2010). The presence of water interrupts the esterification process; Hydrolysis, a reversible reaction in the esterification, causes the reaction to approach equilibrium. Fig. 3.7 highlights that due to water accumulation, leading to hydrolysis reaction, the one-step esterification ('One-step* line') cannot attain high FFA conversion similar to the two-step esterification, even though it utilized the same amounts of MeOH and H₂SO₄.

From Fig. 3.7 and Table 3.5, it can be seen that FFA reduction in the one-step esterification was severely affected by water; it took a stronger condition (higher amounts of catalyst and MeOH; and longer reaction time) than the first step of the two-step esterification to obtain similar results in FFA reduction at 1 h reaction time.

Material balance of the two-step esterification was calculated according to FFA conversion and is shown in Table 3.5. Results reveal that the remaining water in the feedstock (0.37 wt.%) inputted into the second esterification had slightly inhibited progress of reaction in the second step, thus the total FFA reduction was found to be less than 0.5 wt.% ('Two-step2*** line' in Fig. 3.7).

As evident in Table 3.5, the MeOH-rich phase contained a low amount of water (3.84 wt.%) and hence it is possible to be recycled as catalyst solution.

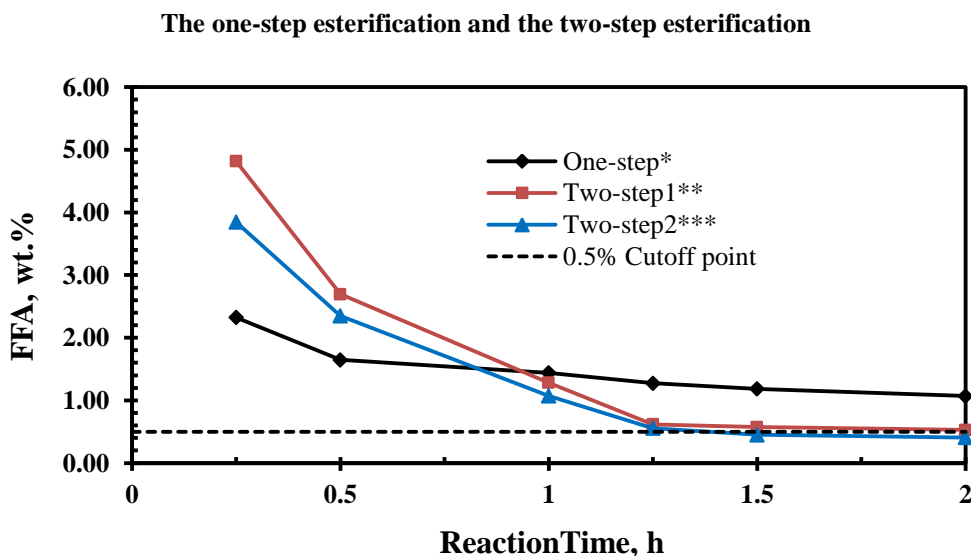


Fig. 3.7 FFA reduction of the one-step and two-step esterification at 60 °C reaction temperature

- Notes: 1. *Conditions for the one-step esterification: 13.55:1 MeOH-to-FFA molar ratio, 0.55:1 H₂SO₄-to-FFA molar ratio, and 2 h reaction time.
2. **For the two-step1: 1st esterification 10:1 MeOH-to-FFA molar ratio, 0.25:1 H₂SO₄-to-FFA molar ratio, and 1 h reaction time; 2nd esterification, 50:1 MeOH-to-FFA molar ratio, 1.93:1 H₂SO₄-to-FFA molar ratio, and 1 h reaction time.
3. ***For the two-step2: 1st esterification, 10:1 MeOH-to-FFA molar ratio, 0.41:1 H₂SO₄-to-FFA molar ratio, and 1 h reaction time; 2nd esterification, 50:1 MeOH-to-FFA molar ratio, 1.93:1 H₂SO₄-to-FFA molar ratio, and 1 h reaction time.

3.1.6 Recycling study of MeOH-rich phase

According to material balance of the two-step esterification in Table 3.5, MeOH-rich phase of the second esterification contained nearly five times less water than the first esterification. It is possible to recycle this MeOH-rich phase. In this study, The MeOH-rich phase of the second esterification was recycled by blending with fresh catalyst solution to be reused for the first esterification, as shown in Fig. 3.8, and its activity was investigated.

Table 3.5 Material balance of the one-step and two-step esterification at 60 °C reaction temperature

Condition	One-step esterification			Two-step esterification					
				The first esterification			The second esterification		
MeOH-to-FFA molar ratio	13.55:1			10:1			50:1		
H ₂ SO ₄ -to-FFA molar ratio	0.55:1			0.41:1			1.93:1		
Reaction time	2 h			1 h			1 h		
Component	Initial amount	TG-rich phase	MeOH-rich phase	Initial amount	TG-rich phase	MeOH-rich phase	Initial amount	TG-rich phase	MeOH-rich phase
	g	g	g	g	g	g	g	g	g
TG	424.18	424.18	-	424.18	424.18	-	424.18	424.18	-
FFA	75.55	8.24	-	75.55	5.37	-	5.37	2.23	-
Ester	-	70.80	-	-	73.82	-	73.82	77.12	-
H ₂ O	0.69	1.24	3.94	0.69	2.02	3.35	2.17	1.64	0.74
MeOH	121.22	57.74	55.50	89.34	37.21	43.81	68.93	52.20	16.36
H ₂ SO ₄	14.78	1.09	13.69	11.11	5.01	6.10	8.69	6.52	2.17
Total	636.42	563.29	73.13	600.87	547.61	53.26	583.16	563.89	19.27

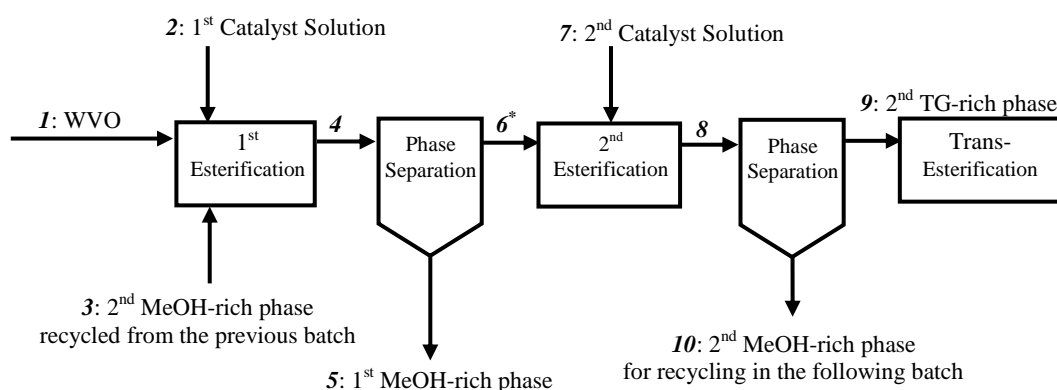


Fig. 3.8 Flow diagram of the two-step esterification with MeOH-rich phase solution recycling in batch process

Note: Numbers in *Italic* are *Mass Flow Nos*, and their associated compositions are detailed in Table 3.6

Fig. 3.9 reveals that the use of fresh catalyst solution could reduce FFA content of the second esterification to be less than the 0.5 wt.% cutoff point while recycling of the MeOH-rich phase solution was nearly able to achieve the goal. The remaining water in the recycled MeOH-rich phase (*Mass Flow No 3*) caused an increase of initial water in the first step (see Table 3.7) and accelerated the hydrolysis

reaction to rapidly reach esterification equilibrium. This, however, was only slightly more than the target cutoff level. However, whether FFA content of the second esterification was over 0.5 wt.% or not, it was definitely less than 1 wt.%, which is within the recommended limit for base-catalyzed transesterification reactions (Canakci and Gerpen, 2001).

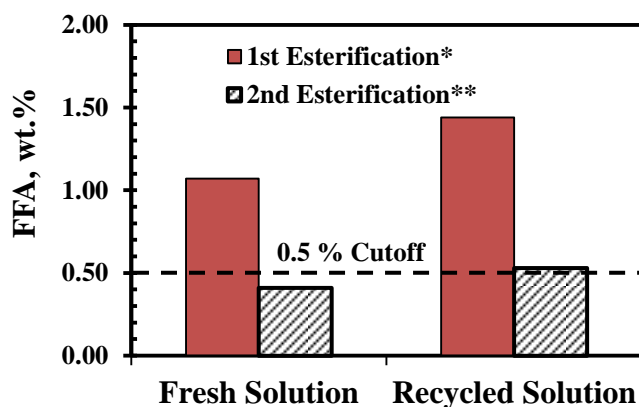


Fig. 3.9 Comparison of FFA reduction between fresh solution and repeated recycle solution of the MeOH-rich phase at steady state in the two-step esterification (at 60 °C reaction temperature and 1 h reaction time)

- Notes: 1. *Conditions for the first esterification: 10:1 MeOH-to-FFA molar ratio, and 0.41:1 H₂SO₄-to-FFA molar ratio.
2. **For the second esterification: 50:1 MeOH-to-FFA molar ratio, and 1.93:1 H₂SO₄-to-FFA molar ratio.

Table 3.6 tabulates the material balances of the two-step esterification with recycling of MeOH-rich phase solution at steady state, and Table 3.7, derived from results in Table 3.5 and Table 3.6, highlights the inputs and the outcomes of FFA and H₂O. From Table 3.7, it is noted that 1) The first step of the novel two-step esterification was a little less effective in FFA conversion than the conventional process, and 2) Although the amount of initial water in the esterification was 0.42 wt.% higher than the another, it affected lesser the FFA reduction, thus it was considered acceptable.

In our conventional two-step esterification experiment with fresh solution the overall total chemicals consumed were 14.11:1 MeOH-to-FFA molar ratio, and 0.57:1 for H₂SO₄-to-FFA. The use of recycled MeOH-rich phase solutions reduced the MeOH-to-FFA molar ratio to 10.26:1 (a 27% reduction) and the H₂SO₄-to-FFA molar ratio down to 0.44:1 (a 23% reduction), as can be derived from Table 3.6. With the use of MeOH-rich phase recycling, the amounts of these chemicals were found to be less than that reported in several papers employing similar two-step esterification (e.g., Canakci and Gerpen, 2001; Ghadge and Raheman, 2005; Lin et

al., 2009). Recycling of the MeOH-rich phase is thus proposed to economically treat WVO to yield satisfactory esterified oils with FFA below 1 wt.% suitable for further transesterification.

Table 3.6 Material balance of the two-step esterification with recycling of MeOH rich phase solution at the steady state

Mass Flow No	Name	Component (g)						
		TG	Ester	FFA	MeOH	H ₂ SO ₄	H ₂ O	Total
1	WVO	417.60	-	81.70	-	-	0.70	500.00
2	1 st catalyst solution	-	-	-	56.14	7.92	0.21	64.27
3*	2 nd MeOH-rich phase	-	-	-	40.60	4.09	1.68	46.37
4	Mixture 1	417.60	78.27	7.29	87.92	12.01	7.55	610.64
5	1 st MeOH-rich phase	-	-	-	50.84	6.48	5.61	62.93
6	1 st TG-rich phase	417.60	78.27	7.29	37.08	5.53	1.94	547.71
7	2 nd catalyst solution	-	-	-	43.16	5.00	0.14	48.30
8	Mixture 2	417.60	83.12	2.68	79.70	10.53	2.39	596.02
9	2 nd TG-rich phase	417.60	83.12	2.68	39.10	6.44	0.71	549.65
10†	2 nd MeOH-rich phase	-	-	-	40.60	4.09	1.68	46.37

Note: * recycled from the previous batch

† for recycling in the subsequent batch

Table 3.7 Amount of FFA and water in the two-step esterification*

Component	Unit	Conventional two-step esterification		<i>Novel</i> *** two-step esterification	
		The 1 st step	The 2 nd step	The 1 st step	The 2 nd step
		Initial FFA	wt.%	15.11	1.07
Final FFA	wt.%	1.07	0.41	1.44	0.53
Initial H ₂ O	wt.%	0.11	0.37	0.42	0.35
H ₂ O Produced **	wt.%	0.78	0.04	0.81	0.05

Note: 1. * Conditions for the two-step: 1st esterification 10:1 MeOH-to-FFA molar ratio, 0.41:1 H₂SO₄-to-FFA molar ratio, and 1 h reaction time; and, respectively for the 2nd esterification: 50:1, 1.93:1, and 1 h.

2. ** H₂O Produced: the total amount of water produced during the reaction.

3. *** '*Novel*' infers two-step esterification with MeOH-rich phase recycling.

3.2 Process Design and set up the continuous experiments

A set of apparatus used in the two-step esterification process is shown in Fig. 3.10.



Fig. 3.10 A set of apparatus used in the esterification process

3.3 A study of continuous acid catalyzed esterification of WVO using continuous dewater reactor (CDR) and continuous stirred-tank reactor (CSTR)

3.3.1 Effect of agitation speed on CDR and CSTR

The effect of speed of agitation on FFA conversion was carried at a constant temperature of 60°C , MeOH-to-FFA molar ratio of 10:1, H_2SO_4 -to-FFA molar ratio of 0.41:1, and 1 h reaction time. Agitation speeds ranging from 100 to 800 rpm were studied with two types of reactor (CDR and CSTR).

From Fig. 3.11, the results revealed that FFA conversion is dependent on agitation speed. A much lower FFA conversion at 100 rpm on CDR or 200 rpm on CSTR was observed. Increase of agitation speed provided a higher reaction rate.

Because esterification is a biphasic liquid system consisting of a dispersed phase (catalyst in alcohol droplets) and a continuous phase (TG phase) which resembles the base-catalyzed transesterification system (Stamenkovic et al., 2007; Waisuwan and Tongurai, 2014). Thus, at low speed agitation, dispersion of MeOH is not fully established at the beginning of the reaction, the mass transfer limitation between two immiscible phases results in slow reaction rate (Noureddini and Zhu, 1997; Stamenkovic et al., 2007).

One advantage of CDR is the progress of reaction, because the MeOH-rich phase consisting of high amount of H_2O would be separated and removed out of

reactor. Fig. 3.11 highlights that CDR provides a higher FFA conversion than CSTR approx. 10% at the same agitation speed.

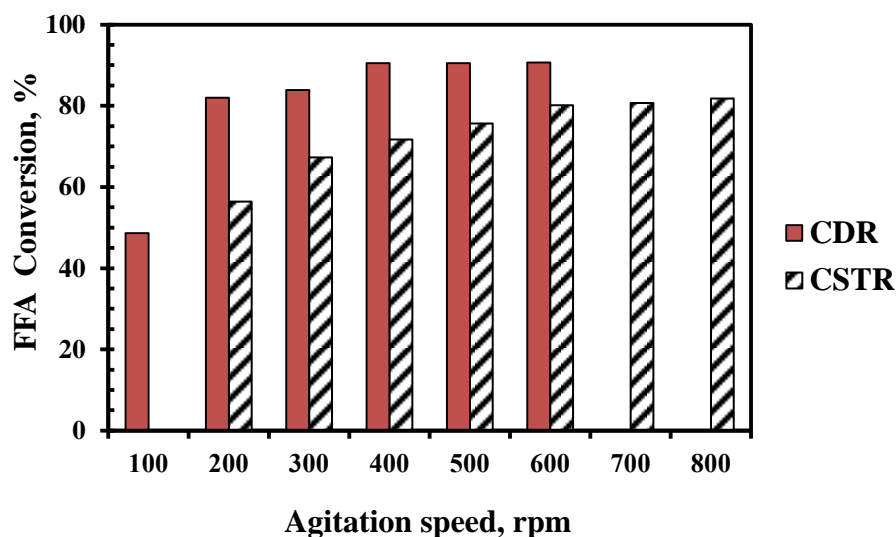


Fig. 3.11 Effect of agitation intensity during continuous esterification on FFA conversion (%) of WVO (Conditions: 10:1 MeOH-to-FFA molar ratio, 0.41:1 H₂SO₄-to-FFA molar ratio, 1 h reaction time, and 60 °C reaction temperature)

3.3.2 Effect of reactor type on the continuous two-step esterification

The effect of type reactor on FFA conversion at the second esterification was carried at a constant temperature of 60 °C. Conditions for the continuous two-step: the first esterification, 10:1 MeOH-to-FFA molar ratio, 0.41:1 H₂SO₄-to-FFA molar ratio, and 1 h reaction time; the second esterification, 50:1 MeOH-to-FFA molar ratio, 1.93:1 H₂SO₄-to-FFA molar ratio, and 1 h reaction time were investigated with two types of reactor (CDR and CSTR).

Fig.3.12, FFA reduction of the first esterification with CDR decreased very rapidly in the first half-hour. After that, all reaction rates went down only slightly similar to the rate of the second esterification with CDR. Whereas the rate of the second esterification with CSTR continuously decreased with a declining rate to the two hours. It was clear that FFA reduction of the second esterification with CDR was better than the second esterification with CSTR because the results of CDR were down to less than 1.0 wt.% since the half-hour and less than 0.5 wt.% at the two hours. Whereas FFA content of CSTR was to be lower 1.0 wt.% at the two hour.

One benefit of esterification reaction with CDR is the progress of reaction because the MeOH-rich phase consisting of high amount of H₂O would be separated and removed out of reactor during process.

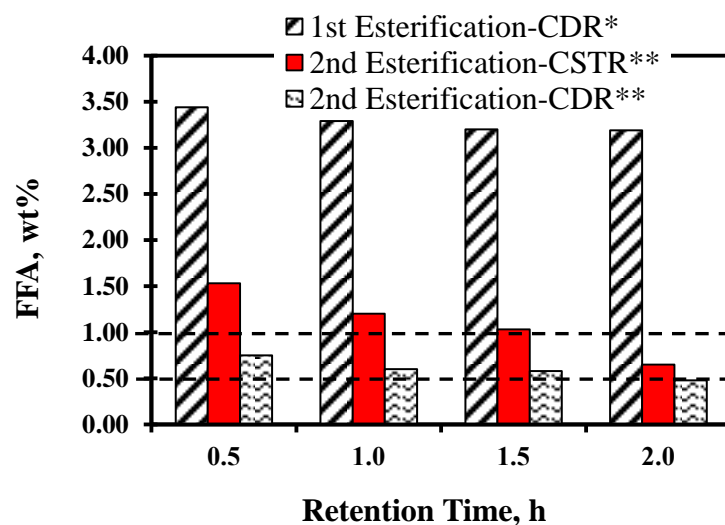


Fig. 3.12 Effect of reactor type on FFA reduction on continuous esterification (initial FFA, 16.34 wt.%)

- Notes: 1. *Conditions for the 1st esterification: 10:1 MeOH-to-FFA molar ratio, 0.41:1 H₂SO₄-to-FFA molar ratio, and 60 °C reaction temperature.
 2. **For the 2nd esterification: 50:1 MeOH-to-FFA molar ratio, 1.93:1 H₂SO₄-to-FFA molar ratio, and 60 °C reaction temperature.

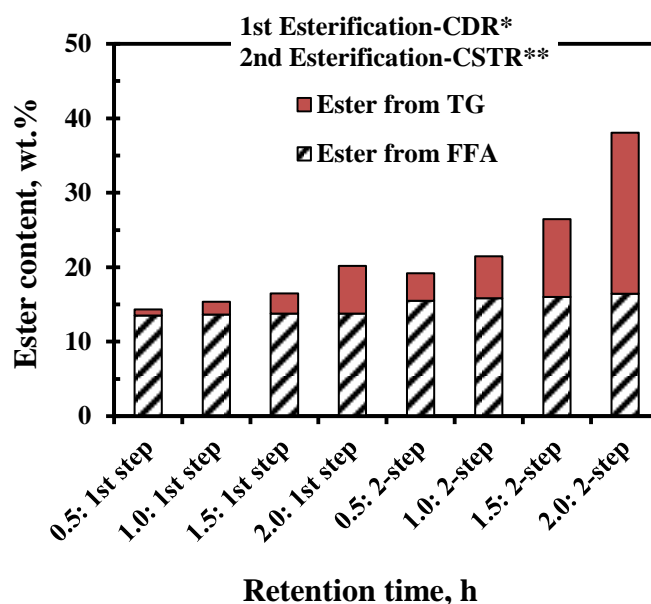


Fig. 3.13 Ester content in esterified oil from Model 1

- Notes: 1. *Conditions for the 1st esterification: 10:1 MeOH-to-FFA molar ratio, 0.41:1 H₂SO₄-to-FFA molar ratio, and 60 °C reaction temperature.
 2. **For the 2nd esterification: 50:1 MeOH-to-FFA molar ratio, 1.93:1 H₂SO₄-to-FFA molar ratio, and 60 °C reaction temperature.

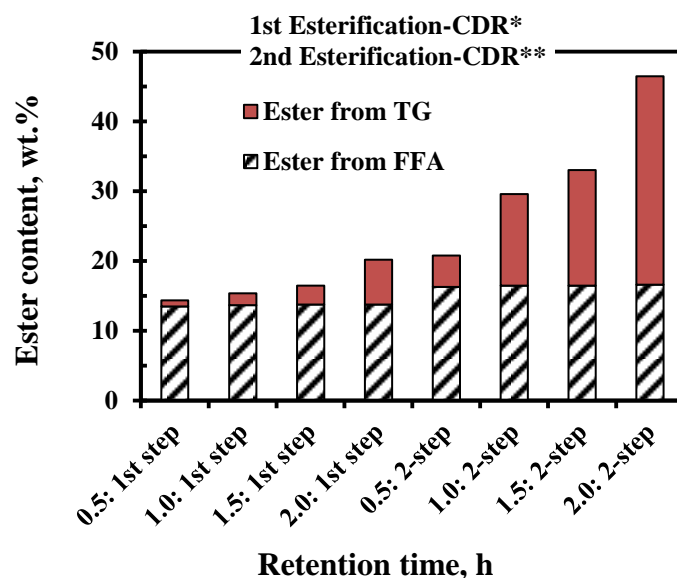


Fig. 3.14 Ester content in esterified oil from Model 2

- Notes: 1. *Conditions for the 1st esterification: 10:1 MeOH-to-FFA molar ratio, 0.41:1 H₂SO₄-to-FFA molar ratio, and 60 °C reaction temperature.
 2. **For the 2nd esterification: 50:1 MeOH-to-FFA molar ratio, 1.93:1 H₂SO₄-to-FFA molar ratio, and 60 °C reaction temperature.

From Fig. 3.13 and Fig. 3.14, the results shown that ester content in esterified oil was derived from two sources: FFA by acid esterification and TG via acid transesterification which is the advantage of the homogeneous acid-catalyzed. In the first step, almost FFA was converted from esterification reaction with CDR because the acid transesterification was slowly reaction (Lotero et al., 2005), whereas TG was converted by the acid transesterification in the second step because of low amount of FFA (Table 3.8)

The increase of reaction time from 0.5 to 2 h was studied in an effort to increase ester content. The results show that no significant differences were found on the FFA conversion in the first step from the use of all reaction time. Whilst the ester content from the acid transesterification were increased with the time because of slowly reaction. As it can be observed from the data, the ester content in the second step from CDR was higher than CSTR because water and glycerol were continuously removed from reactor.

From Fig. 3.15 shows that the remaining catalyst solutions in TG-rich phase from the two step esterification went down sharply in 1 h of the reaction. After 1.5 h, the remaining catalyst solutions were not found in TG-rich phase. Thus, for the continuous two-step esterification, reaction time at 1 h and CDR can be considered suitable conditions.

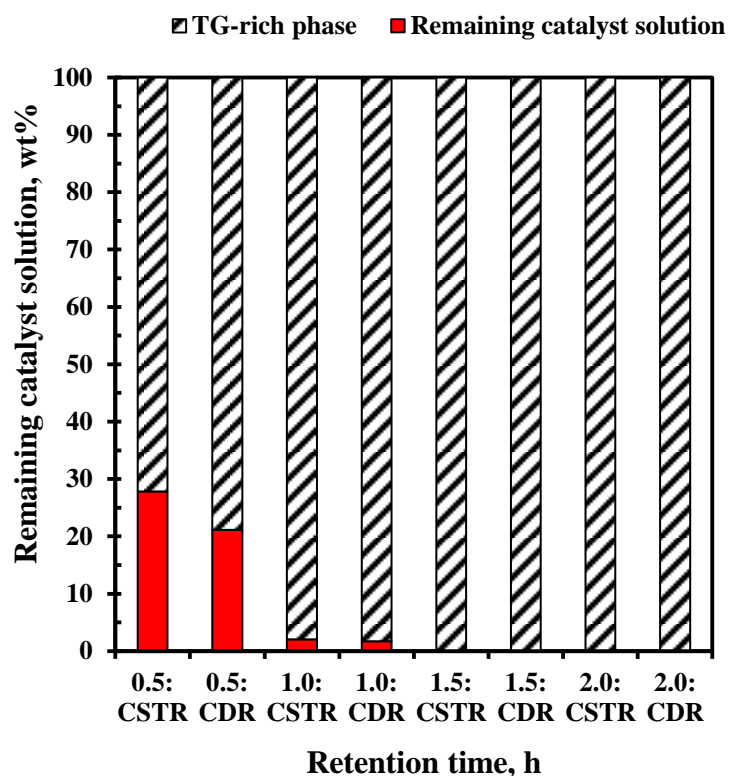


Fig. 3.15 Remaining catalyst solution in TG-rich phase of the two-step after settling for 4 h (take sample at settling tank No.2)

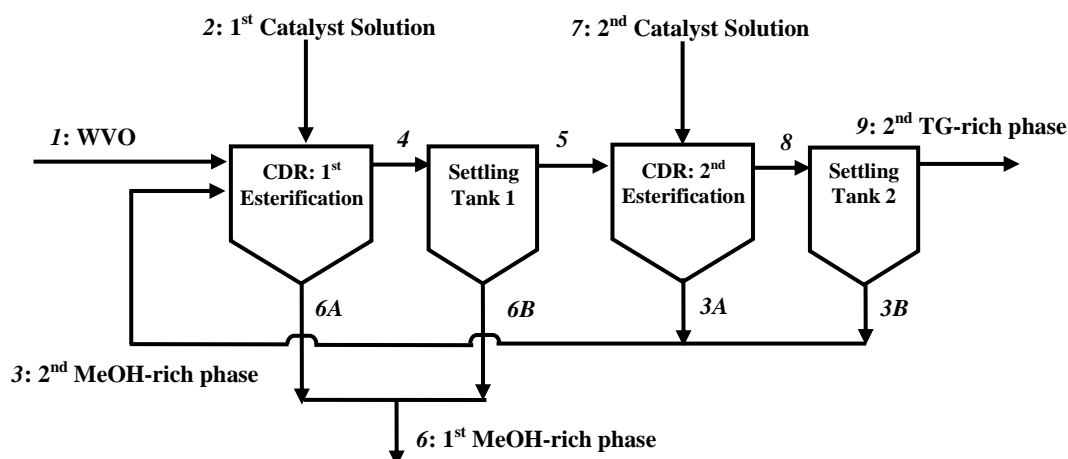
Table 3.8 shows material balance at the optimum conditions of the continuous two-step esterification. Three high amount components were TG (61.84 wt.%), Ester (26.00 wt.%), and MeOH (8.79 wt.%). The final FFA content was 0.53 wt.%, it was less than the recommended limit of 1 wt.%.

3.3.3 Effect of MeOH-rich phase recycling

In this study, The MeOH-rich phase was recycled by blending with fresh catalyst solution to be reuse in two-step and three-step esterification, as shown in Fig. 3.16 and Fig. 3.17, and its activity was investigated.

Table 3.8 Material balance of the continuous two-step esterification at 60 °C and 1h

Condition	The continuous two-step esterification					
	The first esterification with CDR			The second esterification with CDR		
MeOH-to-FFA molar ratio	10:1			50:1		
H ₂ SO ₄ -to-FFA molar ratio	0.41:1			1.93:1		
Component	Initial amount kg	TG-rich phase kg	MeOH-rich phase kg	Initial amount kg	TG-rich phase kg	MeOH-rich phase kg
TG	83.59	81.96	-	81.96	70.54	-
FFA	16.34	3.29	-	3.29	0.60	-
MeOH	19.34	9.51	8.10	28.98	10.03	17.34
H ₂ SO ₄	2.40	1.58	0.82	3.84	2.18	1.66
Ester	-	15.36	-	15.36	29.66	-
H ₂ O	0.13	0.31	0.69	0.37	0.17	0.38
Glycerol	-	0.13	0.05	0.13	0.89	0.48
Total	121.80	112.14	9.66	133.93	114.07	19.86

**Fig. 3.16** Flow diagram of the continuous two-step esterification with MeOH-rich phase solution recycling

Note: Numbers in *Italic* are *Mass Flow Nos*, and their associated compositions are detailed in Table 3.9.

Table 3.9 Material balance of the continuous two-step esterification with recycling of MeOH rich phase solution at the steady state

<i>Mass Flow No.</i>	Name	Component (kg)							
		TG	Ester	FFA	MeOH	H ₂ SO ₄	H ₂ O	Glycerol	Total
<i>1</i>	WVO	84.09	-	15.84	-	-	0.07	-	100.00
<i>2</i>	1 st catalyst solution				2.60	0.91	0.02	-	3.53
<i>3</i>	2 nd MeOH-rich phase				16.16	1.42	0.35	0.14	18.07
<i>3A</i>	CDR: 2nd MeOH-rich phase				2.08	0.13	0.16	0.05	2.42
<i>3B</i>	Settling tank: 2nd MeOH-rich phase				14.08	1.29	0.19	0.09	15.65
<i>4</i>	Mixture 1	80.88	12.77	6.76	7.96	1.45	0.77	0.38	110.97
<i>5</i>	1 st TG-rich phase	80.88	12.77	6.76	2.63	0.65	0.37	0.34	104.40
<i>6</i>	1 st MeOH-rich phase				14.69	1.68	0.68	0.15	17.20
<i>6A</i>	CDR: 1 st MeOH-rich phase				9.36	0.88	0.28	0.11	10.63
<i>6B</i>	Settling tank: 1st MeOH-rich phase				5.33	0.80	0.40	0.04	6.57
<i>7</i>	2 nd catalyst solution				40.04	4.64	0.11	-	44.79
<i>8</i>	Mixture 2	79.65	18.80	2.21	39.91	5.16	0.62	0.42	146.77
<i>9</i>	2 nd TG-rich phase	79.65	18.80	2.21	25.83	3.87	0.43	0.33	131.12

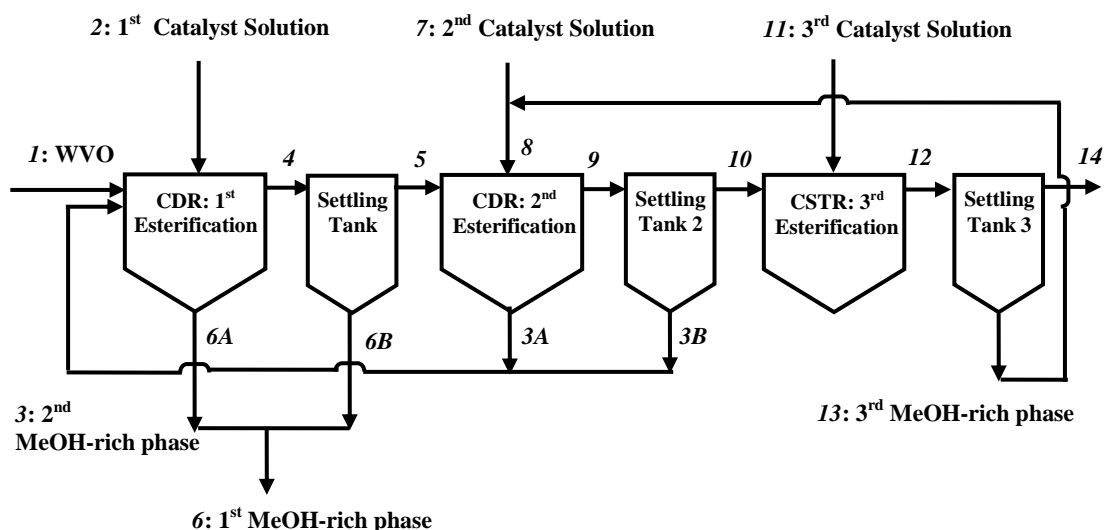


Fig. 3.17 Flow diagram of the continuous three-step esterification with MeOH-rich phase solution recycling

Note: Numbers in *Italic* are *Mass Flow Nos.*, and their associated compositions are detailed in Table 3.10.

Table 3.10 Material balance of the continuous three-step esterification with recycling of MeOH rich phase solution at the steady state

<i>Mass Flow No.</i>	Name	Component (kg)							
		TG	Ester	FFA	MeOH	H ₂ SO ₄	H ₂ O	Glycerol	Total
1	WVO	84.09	-	15.84	-	-	0.07	-	100.00
2	1 st catalyst solution				3.24	0.88	0.02	-	4.14
3	2 nd MeOH-rich phase				15.52	1.45	0.82	0.58	18.37
3A	CDR: 2nd MeOH-rich phase				2.00	0.13	0.38	0.20	2.71
3B	Settling tank: 2nd MeOH-rich phase				13.52	1.32	0.44	0.38	15.66
4	Mixture 1	82.32	11.20	6.88	7.91	1.40	1.04	0.66	111.41
5	1 st TG-rich phase	82.32	11.20	6.88	2.45	0.57	0.37	0.62	104.41
6	1 st MeOH-rich phase				15.05	1.76	1.14	0.15	18.10
6A	CDR: 1 st MeOH-rich phase				9.59	0.93	0.47	0.11	11.10
6B	Settling tank: 1st MeOH-rich phase				5.46	0.83	0.67	0.04	7.00
7	2 nd catalyst solution				29.01	3.19	0.08	-	32.28
8	Mixed catalyst solution				40.75	4.72	0.58	1.25	47.30
9	Mixture 2	81.81	16.56	2.27	40.59	5.16	0.88	1.73	149.00
10	2 nd TG-rich phase	81.81	16.56	2.27	27.07	3.84	0.44	1.35	133.34
11	3 rd catalyst solution				13.44	1.56	0.04	-	15.04
12	Mixture 3	73.36	27.18	0.25	39.31	5.40	0.61	2.27	148.38
13	3 rd MeOH-rich phase				11.74	1.53	0.50	1.25	15.02
14	3 rd TG-rich phase	73.36	27.18	0.25	27.57	3.87	0.11	1.02	133.36

Fig. 3.18 reveals that the use of fresh catalyst solution could reduce FFA content of the second esterification to be less than the 1.0 wt.% , but recycling of the MeOH-rich phase solution could not. Table 3.9 and Table 3.10 show that the remaining water in the recycled MeOH-rich phase caused an increase of water in the system and accelerated hydrolysis reaction to rapidly reach esterification equilibrium. However FFA content of the third esterification was less than 0.5 wt.% which is

within the recommended limit for alkaline-catalyzed transesterification reactions (Canakci and Gerpen, 2001).

Fig. 3.19, the results show that the use of fresh catalyst solution could be obtained ester content higher than the use of recycling catalyst solution.

Table 3.11 shows that the overall total chemicals consumed in the continuous two-step esterification with fresh catalyst solution were 20.04:1 MeOH-to-FFA molar ratio and 0.79:1 H₂SO₄-to-FFA molar ratio. It was higher than batch process about 42.03% in MeOH-to-FFA molar ratio and 38.59% in H₂SO₄-to-FFA molar ratio. Moreover, the overall total chemicals consumed in the continuous esterification with recycling catalyst solution were higher than the continuous two-step esterification with fresh catalyst solution about 14.33% in two-step and 21.76% in three-step.

The three-step esterification with recycling of the MeOH-rich phase could thus be used to effectively treat WVO to yield esterified oil with FFA below 0.5 wt.% suitable for further transesterification to produce biodiesel.

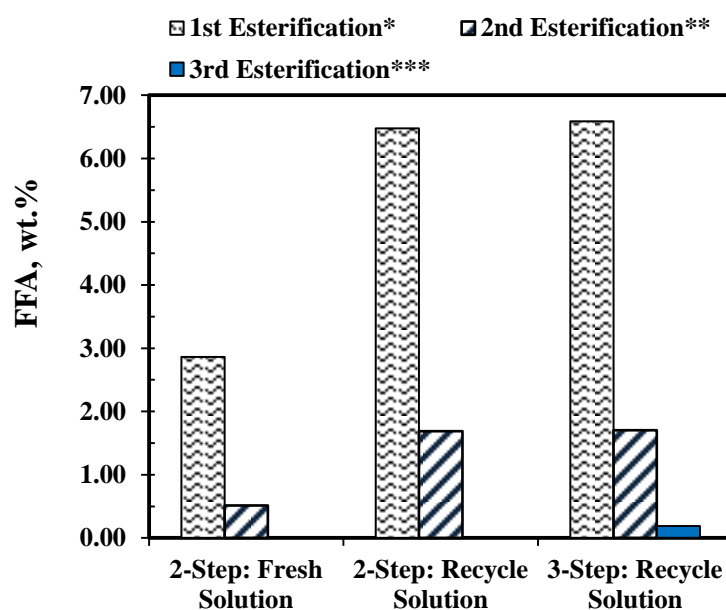


Fig. 3.18 Comparison of FFA reduction between fresh solution and repeated recycle solution of the MeOH-rich phase at steady state (at 60 °C reaction temperature and 1 h reaction time)

- Notes: 1. *Conditions for the first esterification: 10:1 MeOH-to-FFA molar ratio, and 0.41:1 H₂SO₄-to-FFA molar ratio.
 2. **For the second esterification: 50:1 MeOH-to-FFA molar ratio, and 1.93:1 H₂SO₄-to-FFA molar ratio.
 3. ***For the third esterification: 50:1 MeOH-to-FFA molar ratio, and 1.93:1 H₂SO₄-to-FFA molar ratio.

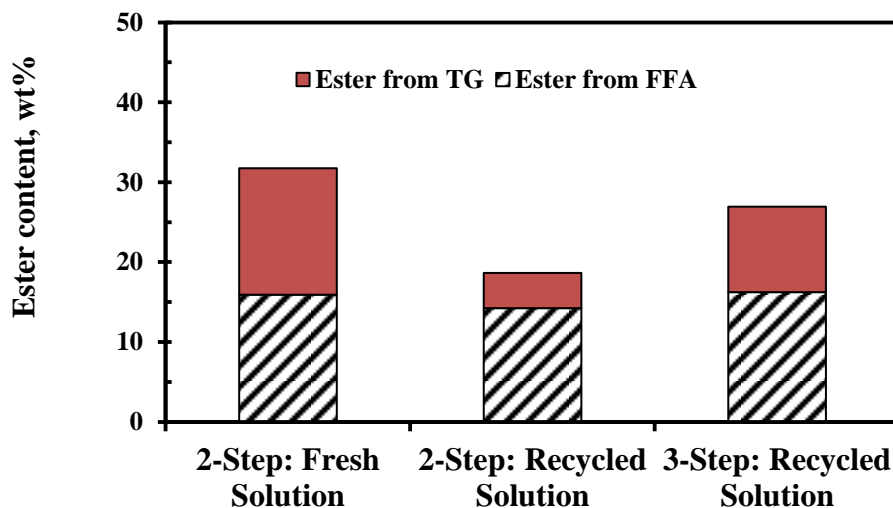


Fig. 3.19 Ester content in esterified oil (Conditions for the 1st esterification 10:1 MeOH-to-FFA molar ratio, 0.41:1 H₂SO₄-to-FFA molar ratio, 60 °C reaction temperature and 1 h reaction time; and, respectively for the 2nd esterification and the 3rd esterification: 50:1, 1.93:1, 60 °C and 1 h)

Table 3.11 Chemical consumption in the continuous esterification with recycling of MeOH rich phase

Chemical consumption	Unit	2-Step: Fresh Solution	2-Step: Recycled Solution	3-Step: Recycled Solution
MeOH	kg	37.63	42.64	45.69
H ₂ SO ₄	kg	4.52	5.55	5.63
Total	kg	42.15	48.19	51.32

3.4 A study of suitable condition for production methyl ester from esterified waste vegetable oil (EWVO) by batch transesterification

3.4.1 One-step Transesterification

A study case of alkaline-catalyzed transesterification was run using EWVO from the continuous 2-step esterification process. A composition of EWVO is shown in Table 3.12 and EWVO contains some of undesirable components.

Table 3.12 The composition of EWVO

Desirable Component	wt.%	Undesirable component	wt.%
TG	42.93		
FFA	0.88		
Ester	48.17		
MeOH	6.82		
		H ₂ SO ₄	0.05
		H ₂ O	0.20
		Glycerol	0.95
Total	98.80		1.20

Table 3.13 One-step transesterification experiment

Condition	Unit	
MeOH-to-TG	mol/mol	6:1
KOCH ₃	wt.% of TG	0.80
KOCH ₃ for neutralization H ₂ SO ₄	wt.% of TG	0.19
Temperature	°C	60
Time	h	0.5
		EWVO
Result	Unit	
Soap content	wt.% of TG	1.00
	(ppm)	(14,540)
Ester content*	wt.%	80.12
Yield	wt.%	81.55

Notes* Ester content was determined by proximately analysis total glycerides and ester content (Thailand Patty Patent 5060).

From Table 3.13, the results found that the ester content could not reach a standard of methyl ester (96.5 wt.%) because soap formation from ester in EWVO occurred and inhibited the progress of reaction (Mendow et al., 2011; Rashid and Anwar, 2008). Moreover, glycerol could not separate from biodiesel and led to loss production yield due to emulsion effect during washing process.

In Table 3.14, the improvement of one-step transesterification was studied by adding UCO (0.33 wt.% FFA) into EWVO from 10 to 90 wt.% of oil. An increase of UCO into EWVO was reduced amount of components by dilution affect except TG component.

From Fig.3.20 and Table 3.14, the results shown that the higher amount of ester in feedstock (> 33.64 wt.%) limited the progress of reaction. In addition, H₂SO₄ neutralization in EWVO from base catalyst (Fig. 3.21) was caused

water in the system which led to interrupt the progress of transesterification by saponification reaction (Pisarello and Querini, 2013).

Table 3.14 The composition of mixed EWVO

Component	EWVO/UCO, wt./wt				
	90/10	80/20	70/30	60/40	50/50
	wt.%	wt.%	wt.%	wt.%	wt.%
TG	48.56	54.23	59.96	65.54	71.21
FFA	0.85	0.82	0.78	0.75	0.71
Ester	43.36	38.53	33.64	28.89	24.05
MeOH	6.15	5.46	4.77	4.09	3.41
H ₂ SO ₄	0.04	0.04	0.04	0.03	0.03
H ₂ O	0.18	0.16	0.15	0.13	0.12
Glycerol	0.86	0.76	0.66	0.57	0.47
Total	100.00	100.00	100.00	100.00	100.00

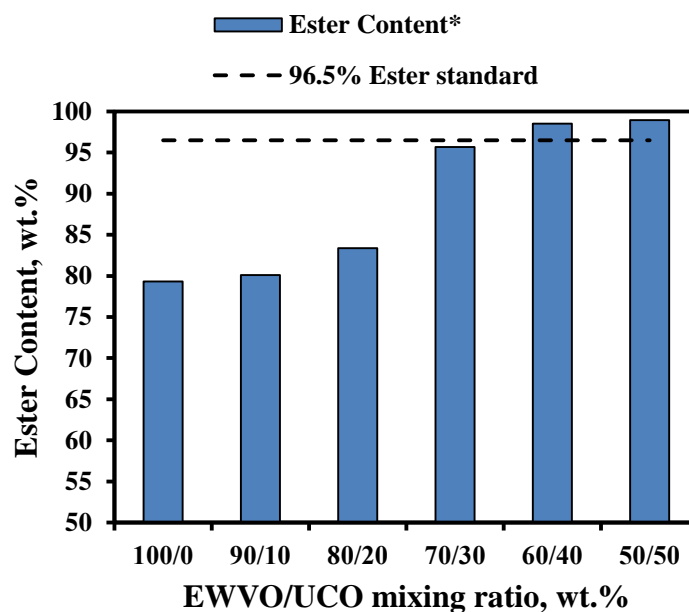


Fig. 3.20 Effect of EWVO/UCO mixing ratio on ester content (Condition: 1 wt.% KOCH₃ of TG, 6:1 MeOH-to-TG molar ratio, 60 °C reaction temperature and 0.5 h reaction time)

Notes* Ester content was determined by proximately analysis total glycerides and ester content (Thailand Patty Patent 5060).

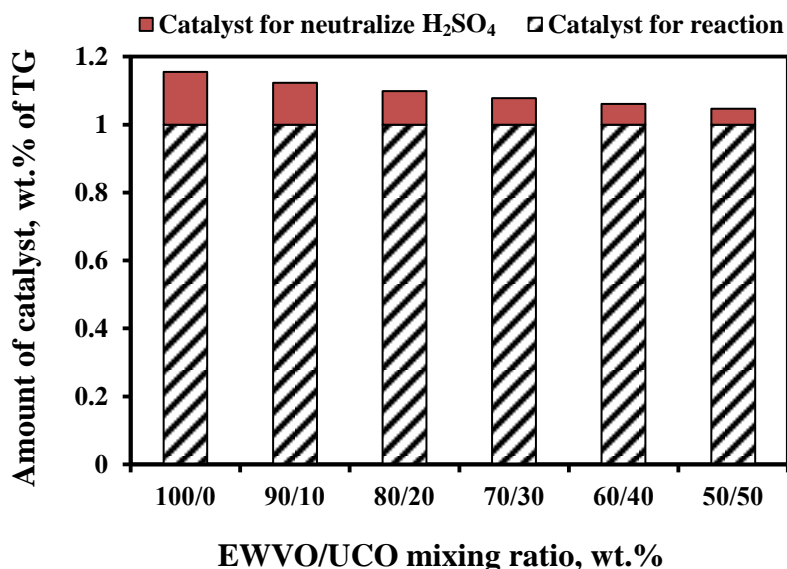


Fig. 3.21 Total amount of catalyst (KOCH_3) added in the reactor for different EWVO/UCO mixing ratios

The results from Fig. 3.22 and Fig. 3.23 clearly indicated that the remaining catalyst after reaction which activated for reaction was depended on EWVO/UCO mixing ratio. In the case of EWVO/UCO mixing ratio 50/50 presented in the highest in remaining catalyst and the lowest in an amount of soap in the ester-rich phase. Thus, EWVO/UCO mixing ratio 50/50 was selected as an optimum raw material for two-step transesterification.

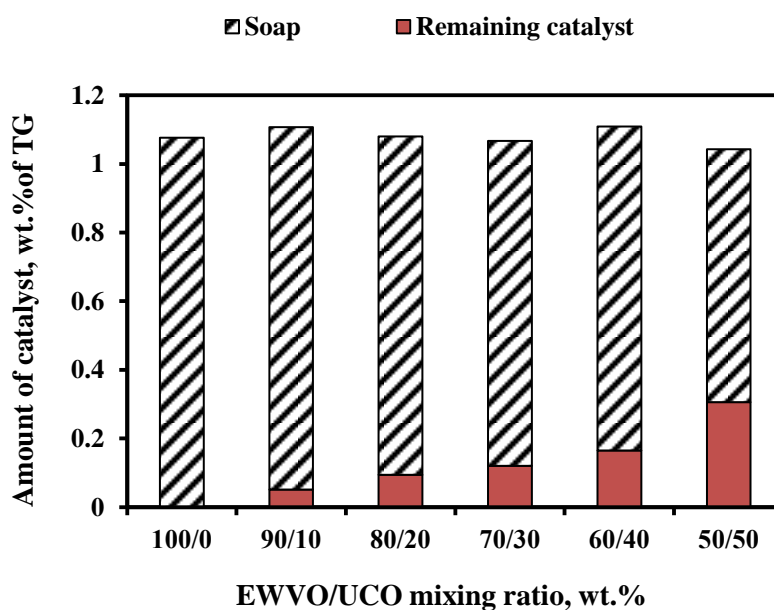


Fig. 3.22 Total amount of soap and catalyst after reaction (Condition: 1 wt.% KOCH_3 of TG, 6:1 MeOH-to-TG molar ratio, 60 °C reaction temperature and 0.5 h reaction time)

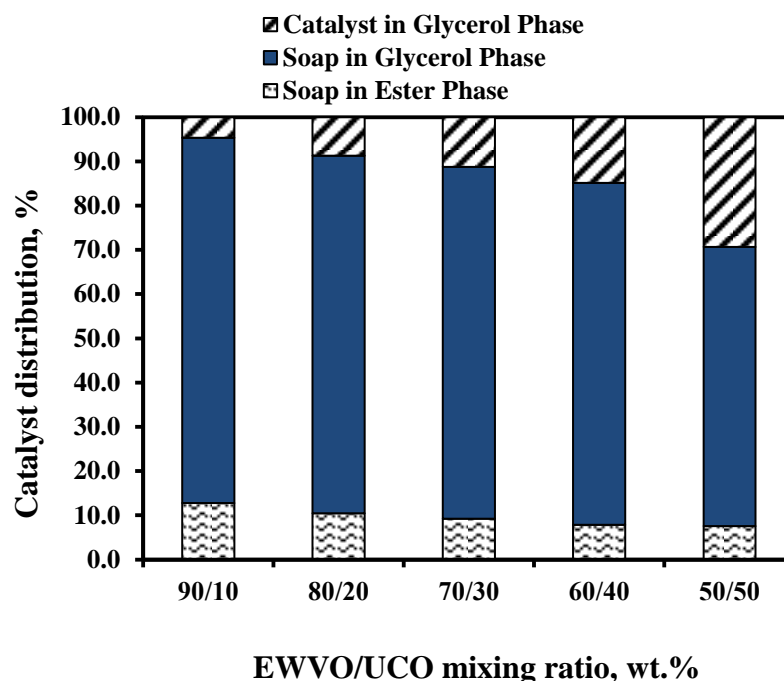


Fig. 3.23 Catalyst distribution after reaction in the ester-rich phase and the glycerol-rich phase (Condition: 1 wt.% KOCH₃ of TG, 6:1 MeOH-to-TG molar ratio, 60 °C reaction temperature and 0.5 h reaction time)

3.4.2 Two-step Transesterification

The experiment was set up to investigate and improve the conversion of methyl ester because of the reverse transesterification reaction. In this study, a catalyst solution was divided into separate parts. The first step, 80 wt.% of the total amount of catalyst solution plus the amount of catalyst which needed to neutralize H₂SO₄ were added and the remaining catalyst solution was added in the second step.

The experiment conditions were shown in Table 3.15. In both steps, reaction temperature and reaction time were 60 °C and 0.5 h, respectively.

Table 3.15 Batch two-step transesterification experiment

Condition	Unit	6:1	6:1	6:1	6:1
MeOH-to-TG	mol/mol	6:1	6:1	6:1	6:1
KOCH ₃	wt.% of TG	0.60	0.80	1.00	1.20
KOCH ₃ for neutralization H ₂ SO ₄	wt.% of TG	0.05	0.05	0.05	0.05

From Fig. 3.24, it was observed that the increase of an amount of KOCH_3 was increased the conversion of ester. At 0.80 wt.% amount of KOCH_3 , the ester content reached the ester standard level (96.5 wt.%). After that, reaction rates went up only slightly and soon stabilized. However, using a high amount of catalyst caused a loss of yield due to soap formation (Keera et al., 2011). For economy, an amount of KOCH_3 at 1.0 wt.% can be considered a suitable condition.

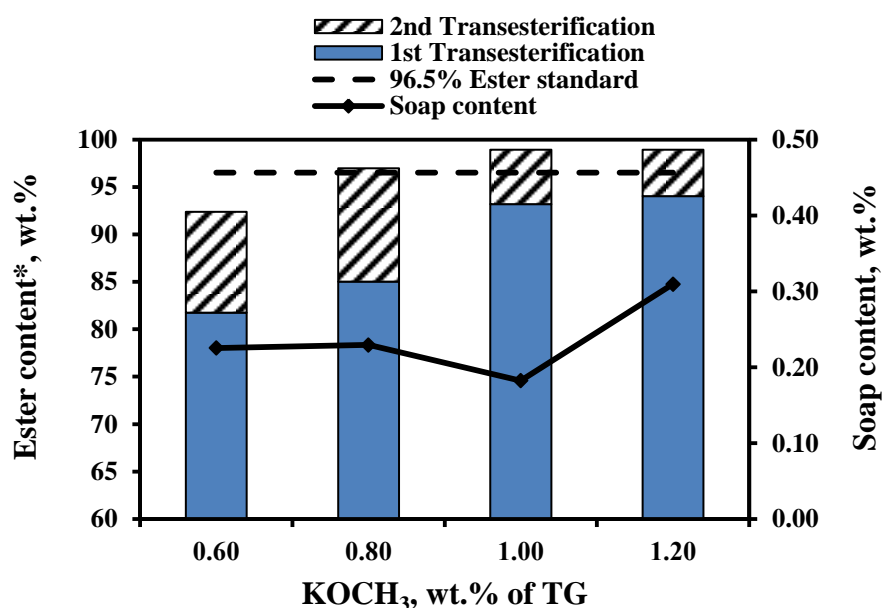


Fig. 3.24 Effect of amount of catalyst on ester content in batch two-step transesterification (Conditions for the 1st transesterification 4.8:1 MeOH-to-TG molar ratio, 80 wt.% catalyst solution, 60 °C reaction temperature and 0.5 h reaction time; and, respectively for the 2nd transesterification: 1.2, 20, 60 and 0.5)

Notes* Ester content was determined by proximately analysis total glycerides and ester content (Thailand Patty Patent 5060).

In Fig. 3.25, an amount of catalyst solution ratio in the first and second transesterification on ester content was studied in the range of 70/30, 80/20, and 90/10. The results shown that the ester content in the first esterification was increased significantly when increase an amount of catalyst solution. The use of all ratios had reached the ester content standard. However, the total ester content of 80/20 ratio was higher than 70/30 ratio and soap content in the ester-rich phase of 80/20 ratio was less than 90/10 ratio. It can be considered that a suitable condition was 80/20 in an amount of catalyst solution ratio.

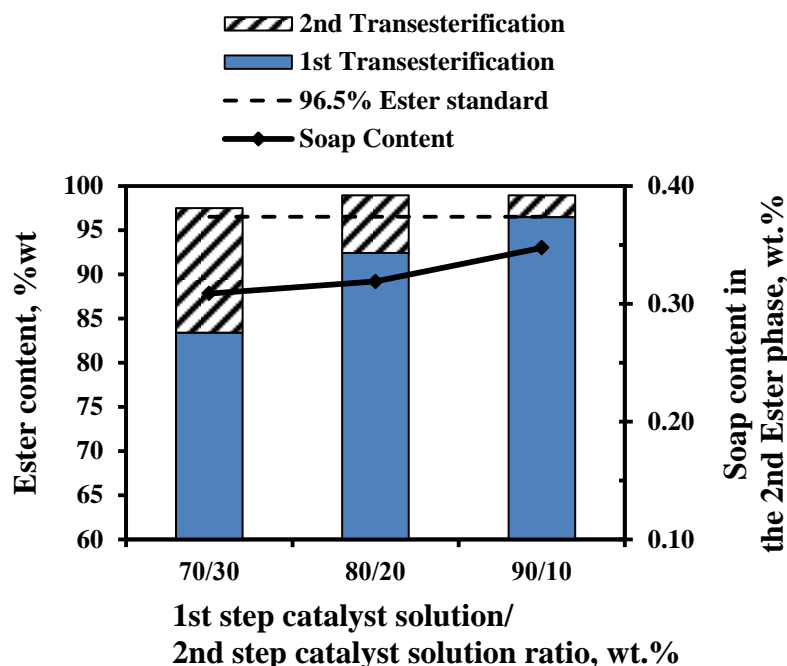


Fig. 3.25 Effect of amount of catalyst solution ratio on ester content in batch two-step transesterification (Conditions for the 1st transesterification 4.8:1 MeOH-to-TG molar ratio, 0.8 wt.% KOCH₃ of TG, 60 °C reaction temperature and 0.5 h reaction time; and, respectively for the 2nd transesterification: 1.2, 0.2, 60 and 0.5)
 Notes* Ester content was determined by proximately analysis total glycerides and ester content (Thailand Patty Patent 5060).

3.5 A study of continuous transesterification of mixed EWVO with methanol using continuous stirred-tank reactor (CSTR)

3.5.1 Continuous two-step transesterification

The experiment was set up to investigate the suitable conditions for continuous two-step transesterification. The experiments were run using mixed EWVO and the conditions were shown in Table 3.16. The amount of catalyst was varied in the range of 0.9, 1.0, 1.2 and 1.4 wt.% of TG. The amount of catalyst solution ratio in the first and second transesterification was 80/20. In both steps, reaction temperature and reaction time were 60 °C and 0.5 h, respectively.

CSTR was selected for the continuous two-step transesterification process. Because the remaining ester in the mixed EWVO could be act as co-solvent

to decrease mass transfer resistance between oil and methanol (Casas et al., 2010). Thus, the utilization of co-solvent and CSTR led to acquire a higher reaction.

The effect of the amount of catalyst on the ester content was shown in Fig. 3.26. The results show that the ester content rose slightly when the amount of catalyst was increased from 0.9-1.0 wt.%. The two higher amounts of KOCH₃ reached the ester content standard. However, the addition of excess amount of catalyst led to form soap and decreased a yield of methyl ester. The optimum of the catalyst concentration for continuous two-step transesterification was 1.20 wt.% of TG. The obtained result was higher than the batch result (1.00 wt.% of TG) because the flow of oil could be have some of shortcut flow in the first step transesterification and a remaining glycerol in the first ester-rich phase.

Table 3.16 Condition of continuous two-step transesterification experiment

Condition	Unit	Total	The first step	The second step
Reactor			CSTR	CSTR
Speed	rpm		600	600
Catalyst solution ratio	wt.%		80	20
MeOH-to-TG	mol/mol		4.8:1	1.2:1
KOCH ₃	wt.% of TG	0.90	0.72	0.18
		1.00	0.80	0.20
		1.20	0.96	0.24
		1.40	1.12	0.28
KOCH ₃ for neutralization H ₂ SO ₄	wt.% of TG		0.05	-

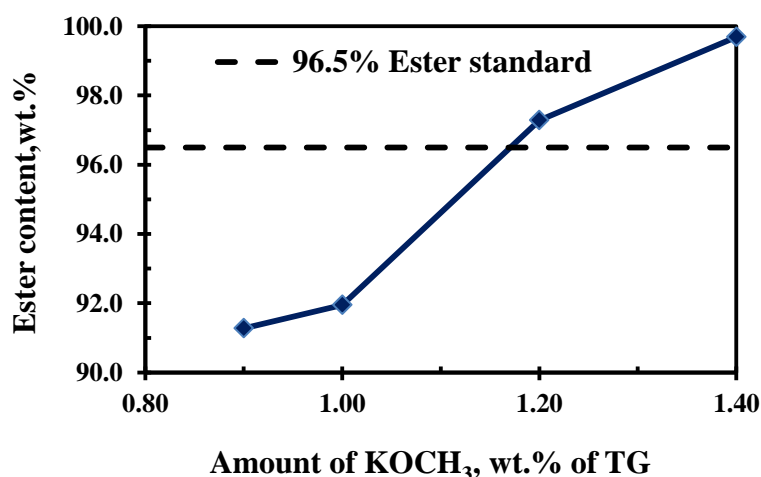


Fig. 3.26 Effect of the amount of KOCH₃ on the ester content with continuous two-step transesterification (Conditions for the 1st transesterification 4.8:1 MeOH-to-TG molar ratio, 80 wt.% catalyst solution, 60 °C reaction temperature and 0.5 h reaction time; and, respectively for the 2nd transesterification: 1.2, 20, 60 and 0.5)

Notes* Ester content was determined by GC.

It should be noted that a settling time of continuous two-step transesterification was shorter than batch transesterification (2 h) then glycerol from continuous process could be remain in the ester-rich phase higher than the batch. The reaction was inhibited from the remaining glycerol by reducing the mass transfer of TGs into the methanol region and decreasing the solubility of triglyceride in methanol (Csernica and Hsu, 2013).

Glycerol removal in the first ester-rich phase was studied by adding packing tank between settling tank 1 and CSTR 2. Packing tank was set up in a 3.0 L tank same as settling tank. Wire screen, 100 mm in width, 360 mm in length (4 holes/mm²) was packed in tank for 6 pieces. The packing tank used in experiment and its details was shown in Fig. 3.27.

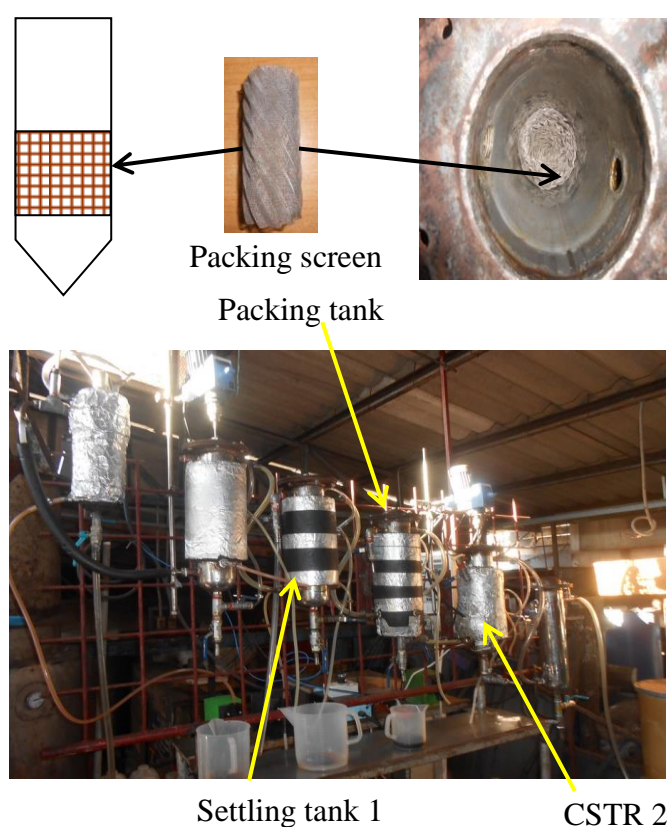


Fig. 3.27 Packing tank and wire screen

Fig. 3.28 shown that the glycerol removal was decreased significantly when the amount of catalyst was increased in range of 0.9 to 1.4 wt.% of TG. At the low amount of catalyst in the first step transesterification, the reaction was incomplete then glycerol could not settle down enough in the glycerol-rich phase because of low amount of glycerol. A Soap removal was similar to the glycerol removal. An advantage of glycerol and soap removal in the packing tank was that the reaction got a

high conversion because an amount of TGs increased in the methanol region. The ester content of continuous two-step transesterification with a packing tank was shown in Fig. 3.29. The ester content could be increase approx. 2 wt.% when compared with two-step transesterification without a packing tank. At 1.40 wt.% of catalyst was obtained a high value of the ester content (99.74 wt.%) but the ester content at 1.00 wt.% of catalyst could not reach the ester content standard. Thus, the optimum an amount of catalyst was 1.20 wt.% KOCH_3 of TG.

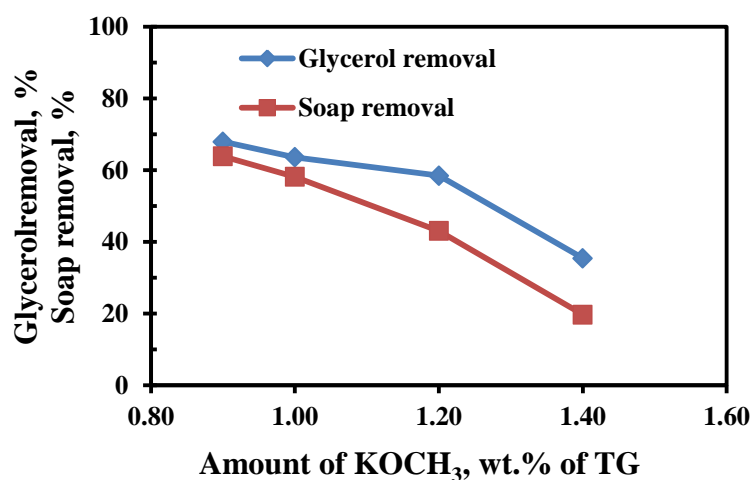


Fig. 3.28 Percentage of glycerol and soap removal in packing tank

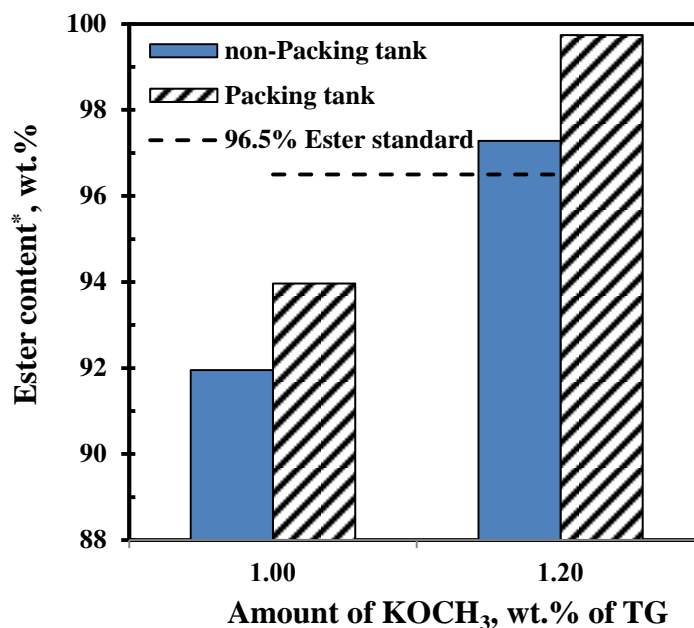


Fig. 3.29 Effect of the glycerol and soap removal in packing tank on the ester content with continuous two-step transesterification

Notes* Ester content was determined by GC.

3.5.2 Material balance of continuous two-step transesterification

In this section, material balances of continuous two-step transesterification were analyzed according to ester conversion at their corresponding optimum conditions. Flow diagram of this experiment was shown in Fig. 3.30.

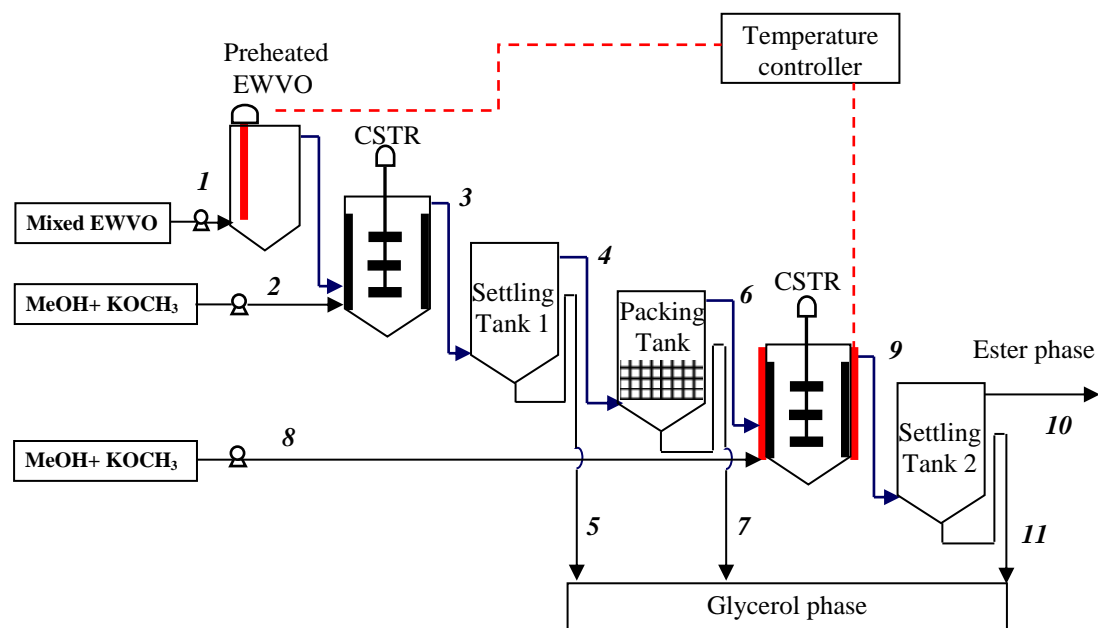


Fig. 3.30 Flow diagram of the continuous two-step transesterification with a packing tank

Note: Numbers in *Italic* are *Mass Flow Nos*, and their associated compositions are detailed in Table 3.17

Table 3.17 shows that the mixed EWVO approx. compositions were 75 wt.% triglyceride (TG), 20 wt.% ME, 0.4 wt.% FFA, and some of undesirable components such as glycerol, water, and sulfuric acid. After the first transesterification, the results show that the TG conversion was 84% and the ester content was 87 wt.%. The settling tank 1 and packing tank could remove glycerol, soap, and water from the first ester-rich phase (Mass Flow No. 3) approx. 90%, 66%, and 70%, respectively. The undesirable components removal led a progress of reaction, thus the ester content of the second transesterification could reach a high level at 99 wt.%. The yield of transesterification process before washing step was approx. 98%.

Table 3.17 Material balance of the continuous two-step esterification with a packing tank at 1.2 wt.% KOCH₃ of TG

Mass Flow No.	Name	Component (kg)										
		TG	FFA	Ester	Glycerol	MeOH	H ₂ SO ₄	H ₂ O	KOCH ₃	Soap	K ₂ SO ₄	Total
1	Mixed EWVO	75.78	0.40	21.26	0.13	1.98	0.35	0.10	-	-	-	100.00
2	1 st catalyst solution	-	-	-	-	11.73	-	0.00	1.23	-	-	12.96
3	Mixture 1	11.83	0.20	84.45	7.06	6.90	-	0.10	0.41	1.35	0.66	112.96
4	1 st Ester-rich phase: Settling tank	11.83	0.20	84.45	1.13	6.10	-	0.05	0.03	0.65	0.33	104.77
5	1 st Glycerol-rich phase: Settling tank	-	-	-	5.93	0.80	-	0.05	0.38	0.70	0.33	8.19
6	1 st Ester-rich phase: Packing tank	11.83	0.20	84.45	0.68	5.98	-	0.03	0.00	0.45	0.30	103.92
7	1 st Glycerol-rich phase: Packing tank	-	-	-	0.45	0.11	-	0.03	0.03	0.20	0.03	0.85
8	2 nd catalyst solution	-	-	-	-	3.40	-	0.00	0.20	-	-	3.60
9	Mixture 2	0.18	0.10	95.73	1.93	8.21	-	0.03	0.08	0.96	0.30	107.52
10	2 nd Ester-rich phase	0.18	0.10	95.73	0.55	7.96	-	0.03	0.00	0.78	0.15	105.48
11	2 nd Glycerol-rich phase	-	-	-	1.38	0.25	-	0.00	0.08	0.18	0.15	2.04

3.5.3 Overall continuous biodiesel production from WVO

Experimental data from the three-step esterification and the two-step transesterification were analyzed into material balance for overall continuous biodiesel production. Flow diagram was shown in Fig. 3.31 and material balance was shown in Table 3.18.

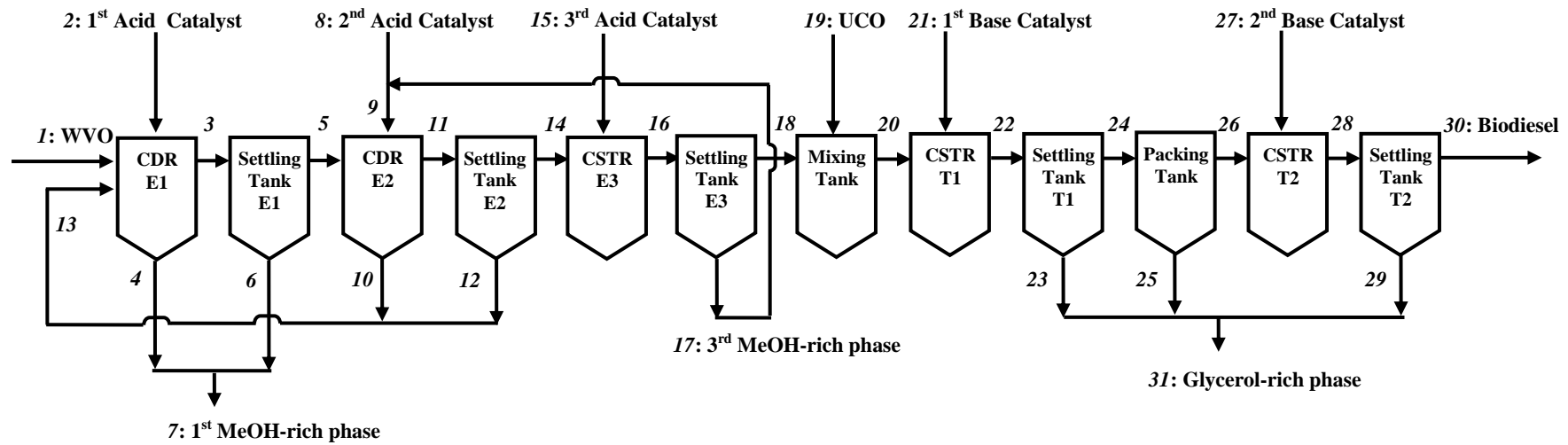


Fig. 3.31 Continuous flow diagram of the three-step esterification with MeOH-rich phase solution recycling and the two-step transesterification with packing tank

Note: Numbers in *Italic* are *Mass Flow Nos*, and their associated compositions are detailed in Table 3.18.

Table 3.18 Material balance of the continuous process of the three-step esterification and the two-step transesterification

Mass Flow No.	Name	Component (kg)										Total
		TG	Ester	FFA	MeOH	H ₂ SO ₄	H ₂ O	Glycerol	KOCH ₃	Soap	K ₂ SO ₄	
1	WVO	84.09	-	15.84	-	-	0.07	-	-	-	-	100.00
2	1 st Acid Catalyst	-	-	-	3.24	0.88	0.02	-	-	-	-	4.14
3	Mixture E1	82.32	11.20	6.88	7.91	1.40	1.04	0.66	-	-	-	111.41
4	CDR: 1 st MeOH-rich phase	-	-	-	9.59	0.93	0.47	0.11	-	-	-	11.10
5	1 st TG-rich phase	82.32	11.20	6.88	2.45	0.57	0.37	0.62	-	-	-	104.41
6	Settling tank: 1 st MeOH-rich phase	-	-	-	5.46	0.83	0.67	0.04	-	-	-	7.00
7	1 st MeOH-rich phase	-	-	-	15.05	1.76	1.14	0.15	-	-	-	18.10
8	2 nd Acid Catalyst	-	-	-	29.01	3.19	0.08	-	-	-	-	32.28
9	Mix catalyst solution	-	-	-	40.75	4.72	0.58	1.25	-	-	-	47.30
10	CDR: 2 nd MeOH-rich phase	-	-	-	2.00	0.13	0.38	0.20	-	-	-	2.71
11	Mixture E2	81.81	16.56	2.27	40.59	5.16	0.88	1.73	-	-	-	149.00
12	Settling tank: 2 nd MeOH-rich phase	-	-	-	13.52	1.32	0.44	0.38	-	-	-	15.66
13	2 nd MeOH-rich phase	-	-	-	15.52	1.45	0.82	0.58	-	-	-	18.37
14	2 nd TG-rich phase	81.81	16.56	2.27	27.07	3.84	0.44	1.35	-	-	-	133.34
15	3 rd Acid Catalyst	-	-	-	13.44	1.56	0.04	-	-	-	-	15.04
16	Mixture E3	73.36	27.18	0.25	39.31	5.40	0.61	2.27	-	-	-	148.38
17	3 rd MeOH-rich phase	-	-	-	11.74	1.53	0.50	1.25	-	-	-	15.02

Table 3.18 Material balance of the continuous process of the three-step esterification and the two-step transesterification (Continued)

Mass Flow No.	Name	Component (kg)										Total
		TG	Ester	FFA	MeOH	H ₂ SO ₄	H ₂ O	Glycerol	KOCH ₃	Soap	K ₂ SO ₄	
18	3 rd TG-rich phase	73.36	27.18	0.25	27.57	3.87	0.11	1.02	-	-	-	133.36
19	UCO	132.94	-	0.33	-	-	0.09	-	-	-	-	133.36
20	Mixed EWVO	206.30	27.18	0.58	27.57	3.87	0.20	1.02	-	-	-	266.72
21	1 st Base Catalyst				37.35		0.00		7.54			44.89
22	Mixture T1	39.52	191.09	0.66	49.01	-	0.20	19.10	1.12	3.97	6.94	311.61
23	Settling tank: 1st Glycerol-rich phase	-	-	-	1.51	-	0.07	16.68	1.05	2.20	3.47	24.98
24	Settling tank: 1st Ester-rich phase	39.52	191.09	0.66	47.50	-	0.13	2.42	0.07	1.77	3.47	286.63
25	Packing tank: 1st Glycerol-rich phase	-	-	-	0.32	-	0.06	0.72	0.07	0.52	0.32	2.01
26	Packing tank: 1st Ester-rich phase	39.52	191.09	0.66	47.18	-	0.07	1.70	0.00	1.25	3.15	284.62
27	2 nd Base Catalyst	-	-	-	9.34	-	-	-	0.50	-	-	9.84
28	Mixture T2	0.52	228.71	0.26	52.72	-	0.07	5.94	0.10	3.00	3.14	294.46
29	Settling tank: 2 nd Glycerol-rich phase	-	-	-	2.00	-	0.00	5.24	0.10	0.90	1.57	9.81
30	Settling tank: 2 nd Ester-rich phase	0.52	228.71	0.26	50.72	-	0.07	0.70	0.00	2.10	1.57	284.65
31	Glycerol-rich phase	-	-	-	3.83	-	0.13	22.64	1.22	3.62	5.36	36.80

Table 3.18 shows that the three-step esterification could be reduce FFA content to be less than the recommended standard of 0.5 wt.%. However the TG-rich phase (Mass Flow No.18) from the three-step esterification contained a high amount of MeOH (21 wt.%) similar to TG-rich phase (Mass Flow No.14) from the two-step

esterification (20 wt.%) because of using an high amount of MeOH (70:1 MeOH-to-FFA Molar ratio). The remaining MeOH in the TG-rich phase (Mass Flow No.18) was too close to an optimum condition (22 wt.% or 6:1 MeOH-to-Oil Molar ratio) of transesterification. Thus, the benefits of mixing the TG-rich phase (Mass Flow No.18) with UCO in 50/50 weight ratio were a decrease amount of MeOH, ester and undesirable components (FFA, H_2SO_4 , and H_2O) and a increase amount of TG in Mass Flow No.20.

The ester-rich phase (Mass Flow No.30) approx. compositions were 80 wt.% ME, 18 wt.% MeOH, and some of undesirable components such as TG, FFA, glycerol, water, and soap. The yield of biodiesel from continuous process before washing step was approx. 98%.

The overall total MeOH was consumed in the continuous process approx. 40 wt.% of oils (WVO and UCO) or 11:1 MeOH-to-Oil molar ratio. Thus, MeOH form the ester-rich phase (Mass Flow No.30), the glycerol-rich phase (Mass Flow No.31), and the MeOH-rich phase (Mass Flow No.7) could be recover for a economical process.

Normally, The recovery MeOH process from the ester-rich phase and the glycerol-rich phase was distillation unit or flash evaporation (Gerpen et al., 2004). The MeOH-rich phase (Mass Flow No.7) contained a corrosive component, H_2SO_4 , in high level (83 wt.%) which caused a corrosion in equipment.

The suggestion of the MeOH-rich phase (Mass Flow No.7) is a neutralization step between H_2SO_4 in the MeOH-rich phase and $KOCH_3$ in the glycerol-rich phase (Mass Flow No.31).

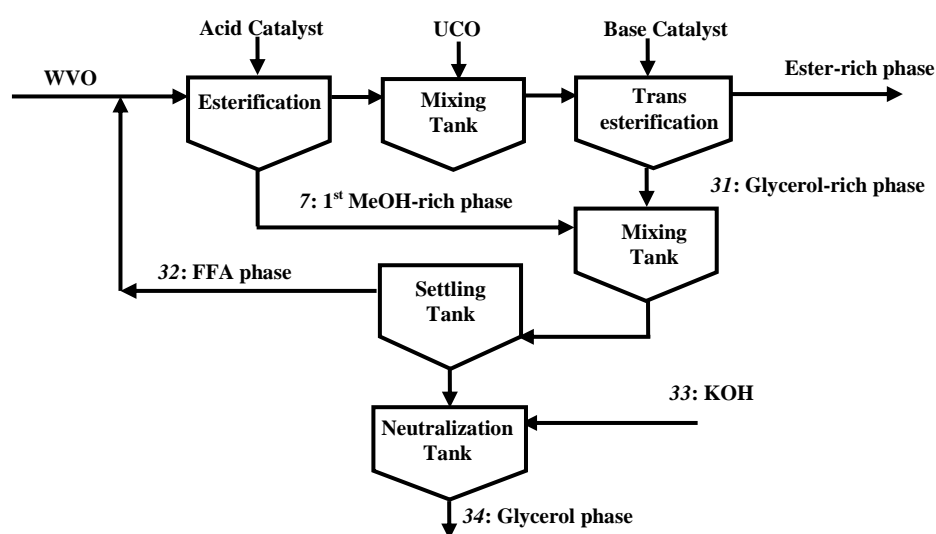


Fig. 3.32 Neutralization process for the continuous process of the three-step esterification and the two-step transesterification

Note: Numbers in *Italic* are *Mass Flow Nos.*, and their associated compositions are detailed in Table 3.19

Table 3.19 Material balance of neutralization process the continuous process of the three-step esterification and the two-step transesterification

<i>Mass Flow No.</i>	Name	Component (kg)									Total
		FFA	MeOH	H ₂ SO ₄	H ₂ O	Glycerol	KOH	KOCH ₃	Soap	K ₂ SO ₄	
7	1 st MeOH- rich phase	-	15.05	1.76	1.14	0.15		-	-	-	18.10
31	Glycerol- rich phase	-	3.83	-	0.13	22.64		1.22	3.62	5.36	36.80
32	FFA phase	3.16									3.16
33	KOH						0.39				0.39
34	Glycerol phase	-	19.44	-	1.40	22.79	-	-	-	8.50	52.13

From Fig. 3.32 and Table 3.19, the neutralization step needed more an amount of base (KOH) to the neutralize H₂SO₄ after it react with KOCH₃ and soap in the glycerol-rich phase. KOH was selected to react with H₂SO₄ because precipitate salt (K₂SO₄) which obtained from a purified glycerol process was friendly to environment more than Na-form. The benefit of the neutralization step was FFA which can be recycled to the esterification for increasing yield.

3.6 The fuel properties analysis of the product

The ester content in final methyl ester product at optimum conditions was measured using GC. Fatty acid components in methyl esters are shown in Table 3.20. It can be observed from the data, an amount of saturated fatty acid was quite high because WVO and UCO which acquired from the Specialized R&D for Alternative Energy from Palm Oil and Oil Crops were almost frying oil. The methyl ester from WVO is suitable for hot countries because of high saturated fatty acids.

The fuel properties of methyl ester are shown in Table 3.21. The most of fuel properties met the limits according to the EN14214 standards except the oxidation stability. It can be improved by adding oxidants approx. 500 ppm into the final methyl esters product to increase the oxidation stability to 13 h.

The produced biodiesel from WVO showed the high purity of methyl ester and the effectiveness of the continuous process using three-step esterification and two-step transesterification.

Table 3.20 Fatty acid components in methyl esters from WVO

Fatty acid name	Carbon chains	Composition, wt.%	
		Saturated	Unsaturated
Lauric acid	C12:0	0.19	
Myristic acid	C14:0	0.89	
Pentadecylic acid	C15:0	0.05	
Palmitic acid	C16:0	39.14	
Palmitoleic acid	C16:1		0.22
Stearic acid	C18:0	4.30	
Oleic acid	C18:1		44.50
Linoleic acid	C18:2		10.00
Linolenic acid	C18:3		0.17
Arachidic acid	C20:0	0.38	
Paullinic acid	C20:1		0.16
Total		44.95	55.05

Table 3.21 Property of final methyl ester comparison with EN14214 standard

Item	Property, unit	Unit	Test Method	Specification (EN14214)	Result
1	Ester content	wt.%	EN 14103	96.5 min	99.69
2	Density at 15 °C	kg/m ³	ASTM D4052	860-900	875.1
3	Viscosity at 40 °C	cSt	ASTM D445	3.5-5.0	4.6
4	Flash point	°C	ASTM D93	120 min	161
5	Sulfur	wt.%	ASTM D5453	0.001 max	<0.0001
6	Carbon residue	wt.%	ASTM D4530	0.3 max	0.021
7	Sulfated ash	wt.%	ASTM D874	0.02 max	<0.005
8	Water content	wt.%	ASTM D2709	0.05 max	0.034
9	Total acid number	mgKOH/g	ASTM D664	0.50 max	0.35
10	Iodine value	gI/100g	EN 14111	120 max	54.2

Table 3.21 Property of final methyl ester comparison with EN14214 standard (Continued)

Item	Property, unit	Unit	Test Method	Specification (EN14214)	Result
11	Linoleic acid methyl ester	wt.%	EN 14103	12 max	0.280
12	Total contamination	wt.%	EN 12662	0.0024 max	0.0003
13	Copper strip corrosion	No.	ASTM D130	1 max	1a
14	Oxidation stability at 110 °C	h	EN 14112	10.0 min	1.38
15	Monoglyceride	wt.%	EN 14105	0.80 max	0.2
16	Diglyceride	wt.%	EN 14105	0.20 max	0.04
17	Triglyceride	wt.%	EN 14105	0.20 max	0.0
18	Free glycerol	wt.%	EN 14105	0.02 max	0.0
19	Total glycerol	wt.%	EN 14105	0.25 max	0.06
20	Group II metals (Calcium)	mg/kg	ASTM D5185	5 max	<0.023
	Group II metals (Magnesium)	mg/kg		5 max	<0.023
21	Phosphorus	wt.%	ASTM D4951	0.001 max	<0.0007385

CHAPTER 4

CONCLUSIONS and SUGGESTIONS

The objective of this research was to produce biodiesel from a low-cost WVO which has high FFA. For this aim, an esterification process was effective to reduce the FFA level of feedstock to be less than the recommended standard of 1 wt.%. The following process was transesterification with alkaline catalyst to convert TG.

4.1 Batch Esterification

In esterification process, the FFA conversion increased considerably with increasing H_2SO_4 -to-FFA molar ratio, MeOH-to-FFA molar ratio, reaction temperature, and reaction time. The presence of water in the system inhibited the progress of reaction by hydrolysis reaction. Thus, the two-step esterification was suitable for the FFA conversion due to water removal.

The batched two-step esterification process with recycling studied had succeeded in reducing FFA content in WVO with high FFA content (approx. 13-17 wt.%) to be less than 1 wt.%. The use of recycled MeOH-rich phase solutions was a 27% reduction in methanol consumption and a 23% reduction of sulfuric acid.

The optimum conditions found were: 0.41:1 H_2SO_4 -to-FFA molar ratio, 10:1 MeOH-to-FFA molar ratio in the first step; and 1.93:1 H_2SO_4 -to-FFA molar ratio, 50:1 MeOH-to-FFA molar ratio in the second step. In both steps, the appropriate reaction temperature was found to be 60 °C, and the reaction time 1 h; and material balance to predict the progress of reaction was calculated. Non-linear model yielded high F-value, high R^2 and low p-value, and thus is most applicable.

4.2 Continuous esterification

The CDR was selected for the continuous esterification process in the first and second esterification but The CSTR was operated in the third esterification. Since the feedstock or EWVO for the first and the second step had a FFA level higher than the third step. The CDR could drive the reaction for high yield by removing water from reactor, whereas the CSTR needed a high of agitation speed to obtain a higher reaction rate.

The benefit of esterification process was acid transesterification which increased an amount of ester in EWVO. The results show that the ester content was significantly higher than an amount of FFA in the third step.

The optimum conditions for the continuous three-step esterification with recycling were: 10:1 MeOH-to-FFA molar ratio, 0.41:1 H₂SO₄-to-FFA molar ratio in the first step; 50:1 MeOH-to-FFA molar ratio, 1.93:1 H₂SO₄-to-FFA molar ratio in the second step; and 50:1 MeOH-to-FFA molar ratio, 1.93:1 H₂SO₄-to-FFA molar ratio in the third step. The reaction temperature and time in each step was similar to the batch process.

The highlight of this study was that recycling of the MeOH-rich phase from the second esterification back to the beginning of the first esterification and recycling of the MeOH-rich phase from the third esterification as catalyst solution back to the second esterification to reduce the FFA level was from 15.84 to 0.25 wt.% in the 3.0 L reactor.

4.3 Batch transesterification

The mixed EWVO which consisted of the TG-rich phase and UCO in ratio 50/50 by weight was suitable for feedstock for transesterification because of low amount undesirable components and ester content.

An amount of catalyst was a strong effect on the ester conversion because the mixed EWVO needed some of catalyst to neutralize a remaining acid.

The two-step transesterification was selected to improve the ester conversion due to glycerol removal.

The optimum conditions for the batch two-step esterification were: 4.8:1 MeOH-to-TG molar ratio, 0.80 wt.% of KOCH₃ to TG plus KOCH₃ for neutralization in the first step; and 1.2:1 MeOH-to-TG molar ratio, 0.20 wt.% of KOCH₃ to TG in the second step. In both steps, the reaction temperature was 60 °C, and the reaction time was 0.5 h.

4.4 Continuous transesterification

The optimum conditions for the continuous two-step esterification with CSTR process were: 4.8:1 MeOH-to-TG molar ratio, 0.96 wt.% of KOCH₃ to TG plus KOCH₃ for neutralization in the first step; and 1.2:1 MeOH-to-TG molar ratio, 0.24 wt.% of KOCH₃ to TG in the second step. In both steps, the reaction temperature was 60 °C, and the reaction time was 0.5 h.

Glycerol and soap removal of the first TG-rich phase in packing tank was caused a high yield in the second transesterification.

Following the above conditions, 99.69 wt.% of methyl ester purity and 98 wt.% of methyl ester yield (before washing) were obtained. The fuel properties of methyl ester almost fall within the specifications prescribed by EN 14214 standards.

4.5 Suggestions for future work

1) Methanol recovery in biodiesel production should be studied to reduce the consumption of chemicals.

2) To increase the biodiesel yield, the MeOH-rich phase from esterification process should be neutralized with the glycerol-rich phase from transesterification process. After that, FFA phase was recycled to blend with WVO.

3) The cost of biodiesel production should be evaluated to compare with conventional method. Thus, a more efficient and more economical process to produce biodiesel from waste vegetable oil with high FFA could be succeeded.

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APPENDIX

APPENDIX A

CALCULATIONS

Mass balance for continuous two-step esterification process

1.1. Molecular weight

WVO = 848.09 g/mol	FFA = 270 g/mol
Methanol = 32.04 g/mol	KOCH ₃ = 70.13 g/mol
Methyl ester = 284.04 g/mol	Glycerol = 92.09 g/mol
K soap = 320.56 g/mol	Water = 18.01 g/mol
H ₂ SO ₄ = 98.08 g/mol	

1.2. Density

WVO = 0.900 g/cm ³	Methyl ester = 0.860 g/cm ³
Glycerol = 1.000 g/cm ³	Methanol = 0.790 g/cm ³
H ₂ SO ₄ = 1.840 g/cm ³	

1.3. Esterification

Basis: WVO = 100 kg

Table A.1 Conditions for the continuous two-step esterification

Condition	The continuous two-step esterification	
	The first esterification with CDR	The second esterification with CDR
MeOH-to-FFA molar ratio	10:1	50:1
H ₂ SO ₄ -to-FFA molar ratio	0.41:1	1.93:1
Temperature, °C	60	60
Time, h	1	1

Table A.2 Property of feedstock and chemicals

Name	Composition, wt.%	
	FFA	Water
WVO	16.34	0.069
MeOH	-	0.079
H ₂ SO ₄	-	2.0

1.4. The first-step esterification

Step 1: Calculation in feed

From Table A.1 and A.2,

$$\text{FFA} = 16.34 \text{ kg} = 16.34/270 = 0.0605 \text{ kmol}$$

$$\text{Thus, MeOH include water} = 10 \times 0.0605 = 0.6050 = 19.36 \text{ kg}$$

$$\text{H}_2\text{SO}_4 \text{ include water} = 0.41 \times 0.0605 = 0.0250 = 2.45 \text{ kg}$$

$$\text{MeOH exclude water} = 19.36 - (19.36 \times 0.079/100) = 19.36 - 0.02 = 19.34 \text{ kg}$$

$$\text{H}_2\text{SO}_4 \text{ exclude water} = 2.45 - (2.45 \times 2/100) = 2.45 - 0.05 = 2.40 \text{ kg}$$

Table A.3 Composition of feed in the first-step

Composition	kg	kmol	wt.%
TG	83.59	0.0985	68.63
FFA	16.34	0.0605	13.42
MeOH	19.34	0.6044	15.88
H ₂ SO ₄	2.40	0.0245	1.97
Ester	0.00	0.000	
Total H ₂ O	0.13	0.0072	0.11
Total	121.80	0.795	100.00

Step 2A: Calculation in esterification reaction

Measurement data after reaction show in Table A.4

Table A.4 Measurement data of the first-step esterification

Parameter	Unit	TG-rich phase	MeOH-rich phase	Method
FFA	wt.%	3.29	-	Titration
H ₂ O	wt.%	0.274	-	Karl-Fischer
MeOH	wt.%	8.48	83.83	Evaporation
Acid (as H ₂ SO ₄)	wt.%	1.41	8.51	Titration
Ester content	wt.%	15.27	-	Titration
Glycerol content	wt.%	0.148	-	Titration



FFA conversion = 79.88%

Calculation in this step based on FFA conversion.

Composition	Feed			Reaction		Product	
	kg	kmol		kg	kmol	kg	kmol
TG	83.59	0.0985				83.59	0.0985
FFA	16.34	0.0605	consume	13.05	0.0483	3.29	0.0122
MeOH	19.34	0.6044	consume	1.55	0.0483	17.79	0.5561
H ₂ SO ₄	2.40	0.0245				2.40	0.0245
Ester	0.00	0.0000	form	13.73	0.0483	13.73	0.0483
Total H ₂ O	0.13	0.0072	form	0.87	0.0483	1.00	0.0556
Total	121.80	0.7951				121.80	0.7951

Step 2B: Calculation in acid transesterification reaction



Amount of TG convert to ester (mol) = mol of glycerol = $(0.148 \times 121.80 / 100 / 92.09)$
= 0.002

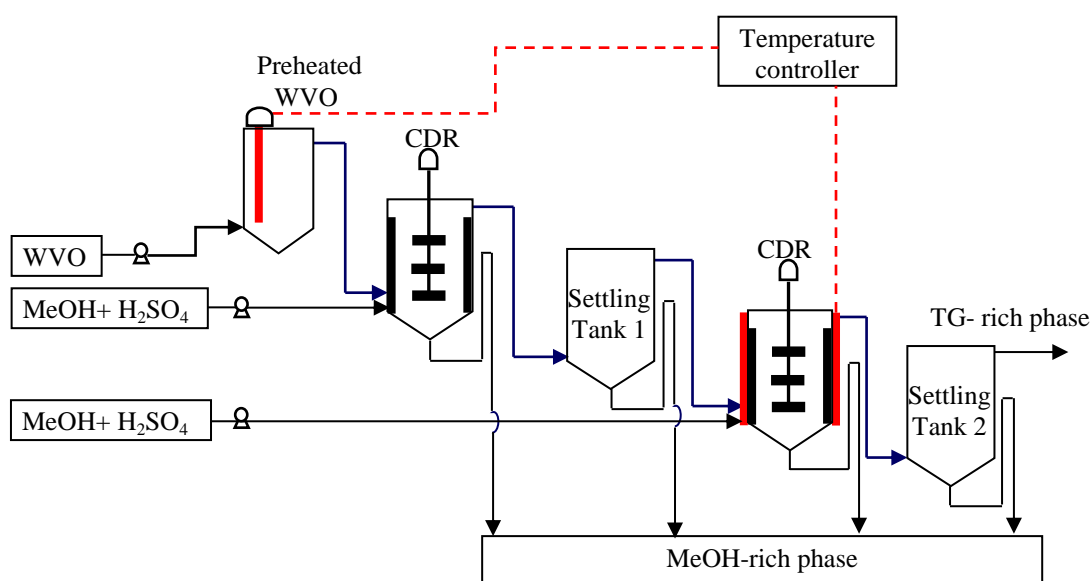
Calculate in this step based on amount of TG convert to ester.

Composition	Feed			Reaction		Product	
	kg	kmol		kg	kmol	kg	kmol
TG	83.59	0.0985	consume	1.63	0.002	81.96	0.0966
FFA	3.29	0.0122				3.29	0.0122
MeOH	17.79	0.5561	consume	0.18	0.006	17.61	0.5503
H ₂ SO ₄	2.40	0.0245				2.40	0.0245
Ester	13.73	0.0483	form	1.64	0.006	15.36	0.0541
Total H ₂ O	1.00	0.0556				1.00	0.0556
Glycerol			form	0.18	0.002	0.18	0.0019
total	121.80	0.7951				121.80	0.7951

After reaction, the mixture was separated into three streams (Fig. A.1): TG-rich phase, MeOH-rich phase from CDR, and MeOH-rich phase from settling tank. The results were shown in Table A.5.

Table A.5 Composition of TG-rich phase and MeOH-rich phase in the first-step esterification

Composition	TG-rich phase			MeOH-rich phase				Total kg
	kg	wt. %	kmol	CDR		Settling tank		
				kg	wt. %	kg	wt. %	
TG	81.96	73.09	0.0966					81.96
FFA	3.29	2.93	0.0122					3.29
MeOH	9.51	8.48	0.2972	4.01	84.07	4.09	83.64	17.61
H ₂ SO ₄	1.58	1.41	0.0161	0.42	8.81	0.40	8.18	2.40
Ester	15.36	13.70	0.0541					15.36
Total H ₂ O	0.31	0.28	0.0172	0.34	7.13	0.35	7.16	1.00
Glycerol	0.13	0.12	0.0019			0.05	1.02	0.18
Total	112.14	100.00	0.4953	4.77	100.00	4.89	100.00	121.80

**Fig. A.1** Two-CDRs in the two-step esterification

1.5. The second-step esterification

Calculation in this step was similar to the first-step. TG-rich phase from the first-step esterification was used as feedstock in this step.

Step 3: Calculation in feed

From Table A.1 and A.2,

$$\begin{aligned} \text{FFA} &= 3.29 \text{ kg} = 3.29/270 = 0.0122 \text{ kmol} \\ \text{Thus, MeOH include water} &= 50 \times 0.0122 = 0.6050 = 19.49 \text{ kg} \\ \text{H}_2\text{SO}_4 \text{ include water} &= 1.93 \times 0.0122 = 0.0250 = 2.30 \text{ kg} \end{aligned}$$

$$\begin{aligned} \text{MeOH exclude water} &= 19.49 - 7(19.49 \times 0.079/100) = 19.47 \text{ kg} \\ \text{H}_2\text{SO}_4 \text{ exclude water} &= 2.30 - (2.30 \times 2/100) = 2.26 \text{ kg} \end{aligned}$$

Table A.5 Composition of feed in the second-step

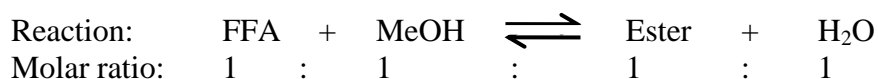
Composition	kg	kmol	wt. %
TG	81.96	0.0966	61.20
FFA	3.29	0.0122	2.46
MeOH	28.98	0.9056	21.64
H ₂ SO ₄	3.84	0.0392	2.87
Ester	15.36	0.0541	11.47
totalH ₂ O	0.37	0.0206	0.28
Glycerol	0.13	0.0014	0.10
total	133.93	1.1296	100.00

Step 4A: Calculation in esterification reaction

Measurement data after reaction show in Table A.6

Table A.6 Measurement data of the second-step esterification

Parameter	Unit	TG-rich phase	MeOH-rich phase	Method
FFA	wt. %	0.60	-	Titration
H ₂ O	wt. %	0.145	-	Karl-Fischer
MeOH	wt. %	8.80	87.31	Evaporation
Acid (as H ₂ SO ₄)	wt. %	1.91	8.36	Titration
Ester content	wt. %	29.42	-	Titration
Glycerol content	wt. %	1.023	-	Titration



FFA conversion = 81.78%

Calculation in this step based on FFA conversion.

Composition	Feed		Reaction			Product	
	kg	kmol		kg	kmol	kg	kmol
TG	81.96	0.0966				81.96	0.0966
FFA	3.29	0.0122	consume	2.690	0.0100	0.60	0.0022
MeOH	28.98	0.9056	consume	0.320	0.0100	28.66	0.8957
H ₂ SO ₄	3.84	0.0392				3.84	0.0392
Ester	15.36	0.0541	form	2.8300	0.0100	18.19	0.0640
Total H ₂ O	0.37	0.0206	form	0.1800	0.0100	0.55	0.0306
Glycerol	0.13	0.0014				0.13	0.0014
Total	133.93	1.1296				133.93	1.1296

Step 4B: Calculation in acid transesterification reaction



Amount of TG convert to ester (mol)

$$\begin{aligned} &= \text{mol of glycerol} = (1.023 \times 133.93 / 100 / 92.09) - (0.13 / 92.09) \\ &= 0.013 \text{ kmol} \end{aligned}$$

Calculate in this step based on amount of TG convert to ester.

Composition	Feed		Reaction			Product	
	kg	kmol		kg	kmol	kg	kmol
TG	81.96	0.0966	consume	11.420	0.013	70.54	0.0832
FFA	0.60	0.0022				0.60	0.0022
MeOH	28.66	0.8957	consume	1.290	0.040	27.37	0.8553
H ₂ SO ₄	3.84	0.0392				3.84	0.0392
Ester	18.19	0.0640	form	11.470	0.040	29.66	0.1044
Total H ₂ O	0.55	0.0306				0.55	0.0306
Glycerol	0.13	0.0014	form	1.240	0.013	1.37	0.0149
total	133.93	1.1296				133.93	1.1296

After reaction, the mixture was separated into three streams (Fig. A.1): TG-rich phase, MeOH-rich phase from CDR, and MeOH-rich phase from settling tank. The results were shown in Table A.7.

Table A.7 Composition of TG-rich phase and MeOH-rich phase in the second-step esterification

Composition	TG-rich phase			MeOH-rich phase				Total kg
	kg	wt. %	kmol	CDR		Settling tank		
	kg	wt. %	kmol	kg	wt. %	kg	wt. %	kg
TG	70.54	61.84	0.0832					70.54
FFA	0.60	0.53	0.0022					0.6
MeOH	10.03	8.79	0.3134	2.31	88.85	15.03	87.08	27.37

Table A.7 Composition of TG-rich phase and MeOH-rich phase in the second-step esterification (Continued)

Composition	TG-rich phase			MeOH-rich phase				Total kg
	kg	wt. %	kmol	CDR		Settling tank		
				kg	wt. %	kg	wt. %	
H ₂ SO ₄	2.18	1.91	0.0222	0.24	9.23	1.42	8.23	3.84
Ester	29.66	26.00	0.1044				0.00	29.66
Total H ₂ O	0.17	0.15	0.0094	0.05	1.92	0.33	1.91	0.55
Glycerol	0.89	0.78	0.0097			0.48	2.78	1.37
Total	114.07	100.00	0.5445	2.60	100.00	17.26	100.00	133.93

APPENDIX B

ANALYTICAL METHODS

1. Free Fatty Acids (FFAs) analysis

This method determines the FFAs existing in the sample by acid-base titration method (AOCS Ca 5a-40). Each sample (between 1-10 g) was dissolved in 50 mL of ethanol, and titrated with 0.1 M NaOH solution, using Phenolphthalein as an indicator to determine the FFAs content.

FFA content was calculated using Eq. B-1.

$$\text{FFA content as palmitic, wt.\%} = \frac{\text{mL of alkali} \times C \times 25.6}{\text{mass, g of test sample}} \quad (\text{Eq. B-1})$$

Where C is the concentration of NaOH solution.

2. Catalyst and soap analysis

This method determines the catalyst and soap contents in the sample by an acid-base titration method (AOCS Cc17-79). Small samples of the reacting mixture were taken at time intervals. Each sample was dissolved in 50 mL of ethanol, and titrated with 0.1 M HCl solution. Firstly, Phenolphthalein was employed as an indicator to determine the catalyst concentration after that Bromophenol blue was used to determine the soap concentration.

Catalyst content was calculated using the following equation:

$$\text{Catalyst content (g of catalyst/g of sample)} = \frac{\text{mL of acid solution} \times C \times MW_1}{\text{mass, g of test sample} \times 1000} \quad (\text{Eq. B-2})$$

where C is the concentration of HCl solution and MW_1 is molecular weight of catalyst such as NaOH = 40.0, KOH = 56.1, NaOCH₃ = 54.0, and KOCH₃ = 70.1.

Soap content was calculated using the following equation:

$$\text{Soap content (g of soap/g of sample)} = \frac{\text{mL of acid solution} \times C \times MW_2}{\text{mass, g of test sample} \times 1000} \quad (\text{Eq. B-3})$$

where C is the concentration of HCl solution and MW_2 is molecular weight of soap such as potassium oleate = 320.56 and sodium oleate = 304.4.

3. Proximate analysis of total glyceride and ester content

Following the Thailand patty patent 5060, total glycerides content in biodiesel was obtained by transesterification again using microwave irradiation. The remaining glycerides in biodiesel sample and methanol should be reacted with a base catalyst to obtain methyl ester and glycerol. An amount of glycerol can be pointed out to glycerides content with the relationship curve between an amount of glycerol and an amount of total glycerides from GC analysis. The ester content in biodiesel sample can be proximately converted by minus from 100 wt.% with the total glycerides content in the unit of wt.%.

4. Determination of the glycerol content in oil

This method determines the glycerol content in the sample by titration method (BS 5711: part3: 1979). The glycerol reacts with sodium periodate in an acid solution, forming aldehydes and formic acid. The formic acid, produced from the reaction, was titrated with a standard solution of sodium hydroxide, using Bromothymol blue as an indicator.

The glycerol content was calculated by the formula:

$$\text{Glycerol content, wt.\%} = \frac{(V_1 - V_2) \times C \times 0.0921 \times 100}{\text{mass, g of test sample}} \quad (\text{Eq. B-4})$$

Where V_1 = volume of NaOH solution used for the determination (mL)
 V_2 = volume of NaOH solution used for the blank test (mL)
 C = concentration of NaOH solution (M)

APPENDIX C

LIST OF PUBLICATION AND PROCEEDING

Chemical Engineering & Processing: Process Intensification 118 (2017) 1–8



Contents lists available at ScienceDirect

Chemical Engineering & Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep

Process development of two-step esterification plus catalyst solution recycling on waste vegetable oil possessing high free fatty acid



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ARTICLE INFO

Keywords:
Esterification
Catalyst solution recycling
Waste vegetable oil
Free fatty acid
Biodiesel production

ABSTRACT

In biodiesel production, cost of chemicals is usually of concern and any amount of reduction would be welcomed. Inferior inputs, such as waste vegetable oils (WVOs), if can be upgraded through a suitable process would bring about additional benefits. In this research, a 'novel' two-step esterification process plus catalyst solution recycling on WVO having high free fatty acid (FFA) content was developed in an effort to reduce usage of chemicals. In the first step esterification, FFA was esterified by methanol (MeOH) employing sulfuric acid (H₂SO₄) catalyst. In the second step, the MeOH-rich phase was recycled back as catalyst solution to the first step esterification. The final FFA concentration was 0.53 wt.% which is within the recommended standard of 1 wt.%. The optimum condition used in the final methanol-and-acid-recycle experiment was investigated from a three-set experiment: first esterification stand-alone; second esterification stand-alone; and conventional two-step esterification, and material balances. The advantage of this novel two-step esterification process plus catalyst solution recycling over a normal conventional two-step method is a 27% reduction in methanol consumption and a 23% reduction of sulfuric acid. Inferior quality WVOs can thus be potential low-cost feedstocks in biodiesel production using this process.

1. Introduction

Biodiesel, a liquid biofuel, is derived from renewable feedstocks such as vegetable oils and animal fats via a transesterification reaction. Biodiesel has become increasingly of interest in comparison with petroleum diesels due to its many merits such as non-toxicity, biodegradability and renewability [1–3]. The main problem of commercial biodiesel is high cost from premium feedstocks that reaches 60–80% of the total production cost [4–8]. Low-cost Waste vegetable oils (WVOs) or non-edible oils are alternative sources for biodiesel production [9,10].

Disadvantages of low-cost feedstocks are inherent undesirable high free fatty acid (FFA) and moisture. Presence of water in the raw materials further hydrolyzes triglyceride (TG) to form FFA via hydrolysis reaction. FFA poses a major problem in a base-catalyst transesterification process due to soap formation and leads to high catalyst consumption and lowering of ester product, and also causes complication to production process [11].

To tackle the problem pretreatment processes have been employed to reduce FFA of low-cost oils to be less than 1.0 wt.% suitable for subsequent transesterification [12–14]. One effective pretreatment method is a direct esterification of FFA with an alcohol, having sulfuric

acid (H₂SO₄) acting as catalyst [15,16], as shown in Eq. (1).



Where R is long-chain hydrocarbons; and R' is alkyl group of alcohol.

One-step esterification process usually requires a large amount of chemicals (commonly methanol: MeOH and H₂SO₄) plus a lengthy reaction time in order to obtain a high yield reaction. For example, a one-step esterification of mixed oil involving crude palm oil and crude rubber seed oil observed 0.54% FFA after 5 h at 65 °C with 15:1 MeOH/FFA molar ratio and 0.09:1 H₂SO₄/FFA molar ratio (3.14 wt.% of FFA) [17]; and another one using used cooking oil achieved 0.25% FFA after 2 h at 60 °C with 40:1 MeOH/FFA molar ratio and 0.28:1 H₂SO₄/FFA molar ratio (10 wt.% of FFA) [18]. Moreover, utilization of excess MeOH and H₂SO₄ requires complicate processes to recover and/or discharge and leads to increased production costs.

Two-step esterification, having water removed from the first esterification before subjected to the second, has sometimes replaced the one-step process. For instance, a two-step esterification of mahua oil acquired 2.42% FFA after the first esterification at 1 h, 60 °C, 14:1 MeOH/FFA molar ratio and 0.30:1 H₂SO₄/FFA molar ratio (10.53 wt.% of FFA); and 0.80% FFA after the second esterification at 1 h, 60 °C,

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Received 2 December 2016; Received in revised form 20 April 2017; Accepted 23 April 2017

Available online 27 April 2017

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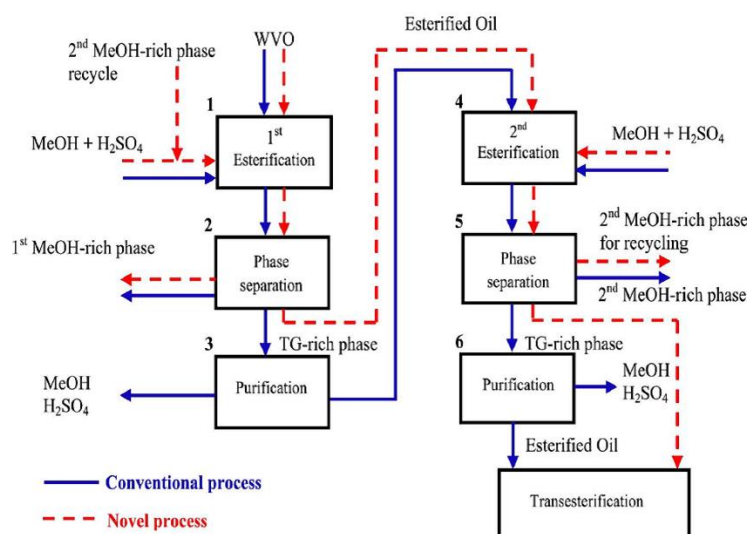


Fig. 1. Flowchart of a conventional and novel two-step acid esterification.

47:1 MeOH/FFA molar ratio and 1.17:1 H_2SO_4 /FFA molar ratio (41.32 wt.% of FFA) [19].

Normally, conventional two-step acid esterification (Fig. 1) needs multiple steps to purify the TG-rich phase, such as adding hexane to absorb and dissolve the oil product, evaporation the oil to remove MeOH, washing the oil with water, and removing water by sodium sulfate anhydrous [13,17,20,21]. To eliminate the purification problem, in this study a novel two-step acid esterification process is attempted: Stage 3 and 6 in the Figure are dispensed with, and output Stage 5 is recycled straight back to Stage 1 (Generally recycling is practiced on solid heterogeneous catalyst, but not on recycling of catalyst solution, if any.) The process development, presented partially in a conference only on stand-alone experiments [22], focuses now on recycling of the MeOH-rich phase as catalyst solution. The aim of this attempt is to seek a suitable and cost-effective process for two-step esterification of high-FFA WVO. In this research, material balance was used to describe the amount of components after a reaction was complete.

2. Materials and methods

2.1. Materials

Waste vegetable oil (WVO), palm fatty acid distillate (PFAD), refined palm oil (RPO), and methyl ester (ME) were all acquired from the Specialized R&D for Alternative Energy from Palm Oil and Oil Crops, Faculty of Engineering, Prince of Songkla University, Thailand. Two other reagents: methanol (MeOH, purity > 99.8 wt.%) and sulfuric acid (H_2SO_4 , purity > 98 wt.%) are of commercial grade.

The WVO with free fatty acid (FFA) and moisture contents were found to be 13–17 wt.% and 0.03–0.05%, respectively. Mixed oil (MO) was obtained by mixing the RPO (0.10 wt.% FFA) with ME and PFAD (93 wt.% FFA). Detailed in Section 2.2, WVO was used as feedstock for the first, the third, and the fourth set of experiment, whereas MO was used as feedstock for the second esterification.

2.2. Methodology

Four sets of experiment were designed. The first esterification stand-alone and the second esterification stand-alone were both a one-step process which employed fractional factorial design to search for optimum conditions on FFA conversion in each step. The third was a

conventional two-step esterification to investigate the effect of water on FFA conversion using the optimum conditions from results of the two one-step processes. The fourth involved the third experiment together with an alcohol-rich phase recycling obtained from its second, feeding back to its first step. This fourth experiment was conjured up with an aim to reduce the usage of chemicals in the two-step esterification.

2.2.1. The first esterification stand-alone

The purpose of this part is to investigate optimum conditions on the first esterification reaction. Variable factors in this step were: reaction temperature, MeOH/FFA molar ratio, and H_2SO_4 /FFA molar ratio. The studied temperatures were 50, 60, and 70 °C. MeOH/FFA molar ratio and H_2SO_4 /FFA molar ratio were varied from 5:1 to 30:1 and 0.08:1 to 0.83:1, respectively.

2.2.2. The second esterification stand-alone

A larger quantity of MO with compositions resembling those obtained in 2.2.1 was made and subjected to this experiment under the reaction temperature derived from the optimum yield conditions in that first experiment. Variable parameters in this step were: MeOH/FFA molar ratios (20:1 to 80:1) and H_2SO_4 /FFA molar ratios (0.83:1 to 1.93:1).

2.2.3. The two-step esterification

This experiment was set up with practical optimum conditions in the previous each step to demonstrate the FFA conversion.

2.2.4. The two-step esterification together with alcohol-rich phase recycling

This fourth experiment was conducted identically to that done in 2.2.3. However, the alcohol-rich phase separated at the end of the second step was recycled to the beginning of the first step to esterify new WVO inputs. Nevertheless, additional portions of MeOH and H_2SO_4 were needed to that leftover from the second step to make up the required amount. This esterification investigation method was conducted in an effort to reduce the use of both chemicals detrimental to the environment.

2.2.5. General esterification procedure

The esterification reaction was performed in 1-L three-necked round bottom flask which was immersed in a controlled temperature oil bath. The reactor was equipped with a magnetic stirrer, a thermometer, a reflux condenser, and one spout for chemical addition and/or sample

taking.

The reaction procedure started off as follows. Five hundred grams of WVO, or MO as the case maybe, was added into the reactor and heated up to a predetermined temperature. A MeOH/H₂SO₄ mixture was prepared and then poured into the oil under a constant 1200 rpm mixing speed, considering this moment as time zero of the reaction. The mixture was kept reacting for 4 h. Samples of 10 mL were withdrawn from the reactor at 0.25, 0.5, 1, 2, 3, and 4 h. The reaction in each sample was halted by washing with water to separate the oil phase from impurities such as MeOH and H₂SO₄. To determine FFA content of the reaction mixture, the AOCS Ca-5a-40 method was used.

After the four-hour reaction, the reactor contents were transferred to a decantation funnel and let stand overnight. The MeOH-rich phase – the minor phase – was separated from the TG-rich phase. For the two-step esterification, the TG-rich phase obtained from the first step was used directly as feedstock for the second step.

The FFA conversion and FFA content are two indications of efficiency of the esterification reaction. The goal of this study is to reduce FFA content of the second esterification to be less than 0.5 wt.%. The FFA conversion was set at 80% for the reaction efficiency cutoff point before the reaction shifts to equilibrium state.

2.3. Analytical methods

Conversion of FFA was determined using Eq. (2)

$$\text{FFA conversion, \%} = \frac{\text{FFA}_i - \text{FFA}_f}{\text{FFA}_i} \times 100 \quad (2)$$

where FFA_i is the initial FFA content, and the FFA_f is the FFA content at any time.

FFA content by titration, and density according to ASTM D1298, were determined for the two settled phases. Water content in the TG-rich phase was analyzed using Karl-Fischer method (ISO 12937). Material balance was used to calculate compositions in both phases based on FFA conversion.

3. Results and discussion

3.1. The first esterification stand-alone

As earlier outlined, the objective of this process is to reduce FFA content of the WVO from its initial FFA content of approx. 13–17 wt.% down to 2.6–3.4 wt.%, or approx. 80% of the conversion; and to obtain a lower-layered MeOH-rich phase.

3.1.1. Effect of temperature

The effect of reaction temperature on FFA conversion was studied at three temperatures (50, 60, and 70 °C). Conditions in this experiment were: 10:1 MeOH/FFA molar ratio, 0.25:1 H₂SO₄/FFA molar ratio, and 4 h reaction time. From Fig. 2a, the FFA conversion rate increased very rapidly in the first quarter hour directly and proportionately with the reaction time, almost regardless of temperature except at the lowest set temperature. After this period, the rate tapered and leveled off rapidly, and the effect of temperature stood out more clearly; that the two higher set temperatures reached the cutoff rate of 80% much quicker. The temperature increase causes the decrease of oil viscosity, improving the contact between reactants [8] and hence, in general, the higher temperature the better the performance. However, the end results after the first one or two hours seemed to coincide for the two higher temperatures. For economy, efficiency and effectiveness, 60 °C at 1 h can be considered a suitable condition, of which losses of MeOH due to temperature would also be lowered.

The results were in accordance with those obtained in several researches, for example, [7,11,13,14].

3.1.2. Effect of MeOH/FFA molar ratio

The experiment was investigated at 60 °C reaction temperature and 0.25:1 H₂SO₄/FFA molar ratio. MeOH/FFA molar ratios were varied in the range of 5:1 to 30:1.

Fig. 2b shows that the change in FFA content of the WVO was influenced by the MeOH/FFA molar ratio since an excess of MeOH promoted reaction completion, keeping H₂SO₄ in the MeOH phase and the water produced was diluted to the level where it did not disturb the esterification reaction [23,24]. It should be noted here, that higher amounts of MeOH usage tended to move the MeOH-rich phase to the upper layer (above the oil) since their bulk density was decreased (Table 1), thus one disadvantage of this approach is that the more the MeOH used the more the production cost [11]. Also in Fig. 2b the reaction progressed rapidly during the first quarter hour and continuously increased to the first hour, albeit with a declining rate. After the first hour, except the lowest MeOH/FFA ratio of 5:1, all others using higher ratios had reached the cutoff rate. After that, all reaction rates went up only slightly and soon stabilized, and even dropped down in the case of the highest ratio of 30:1. A reverse esterification reaction in this situation could be explained by the accumulation of water formed by esterification of FFA [8]. The most economical MeOH/FFA molar ratio of this first esterification stand-alone was found to be 10:1 at 1 h, having the MeOH-rich phase siting at the preferred lower layer.

3.1.3. Effect of H₂SO₄/FFA molar ratio

The experiment was investigated at 60 °C reaction temperature and 10:1 MeOH/FFA molar ratio, whereas H₂SO₄/FFA molar ratios were varied in the range of 0.08:1 to 0.83:1.

The results in Fig. 2c show that the FFA conversion rose sharply in the beginning of the reaction. After a quarter hour, reactions increased more slightly. The two higher amounts of H₂SO₄ reached the cutoff rate before the half hour and started to stabilize after 1 h. Except for the lowest amount of H₂SO₄, all others almost leveled off at over 90% conversion at 3 h. One reason that FFA conversion could not proceed much further was reported by some researchers that it was due to shortage of acid catalyst; H₂SO₄ might have migrated from MeOH to water [8,24]. Moreover, H₂SO₄/FFA molar ratio of 0.33:1, or higher, produced less-preferred dark esterified oils. The optimum H₂SO₄/FFA molar ratio at 1 h was in the range 0.25:1–0.41:1. Performance is considered a more significant factor than color.

Thus, for the first esterification stand-alone, it could be summarized in overall that the suitable conditions were: 60 °C reaction temperature, 1 h reaction time, 10:1 MeOH/FFA molar ratio, and 0.25:1 to 0.41:1 H₂SO₄/FFA molar ratios.

3.2. The second esterification stand-alone

The goal of the second esterification stand-alone process is to reduce FFA of the MO from its initial 2.51 wt.% to below 0.5 wt.%, or 80% of FFA conversion, and to obtain the MeOH-rich phase at the lower layer.

The experiment was studied at 60 °C reaction temperature, 4 h reaction time, and 0.25:1 H₂SO₄/FFA molar ratio, whilst MeOH/FFA molar ratios were varied from 20:1 to 80:1.

Fig. 3a shows a clear trend that the second esterification required high amounts of MeOH in terms of molar ratio despite the fact that stoichiometry needs only 1:1. Because FFA content in the mixture was lower than that from the first esterification, MeOH was consumed at a much higher ratio to force a reaction. Reaching a cutoff rate at reaction time 1 h, the suitable condition was MeOH/FFA molar ratio of 60:1.

One disadvantage of using a higher amount of MeOH is the higher production cost, and it tends to lead the MeOH-rich phase to the upper layer, particularly when the MeOH/FFA molar ratio is 40:1 or more, as shown in Table 2.

The increase of H₂SO₄/FFA molar ratio from 0.83:1 to 1.93:1 was analyzed in an effort to increase the bulk density of the MeOH-rich phase in order to lead the phase to the lower layer. Fig. 3b reveals that

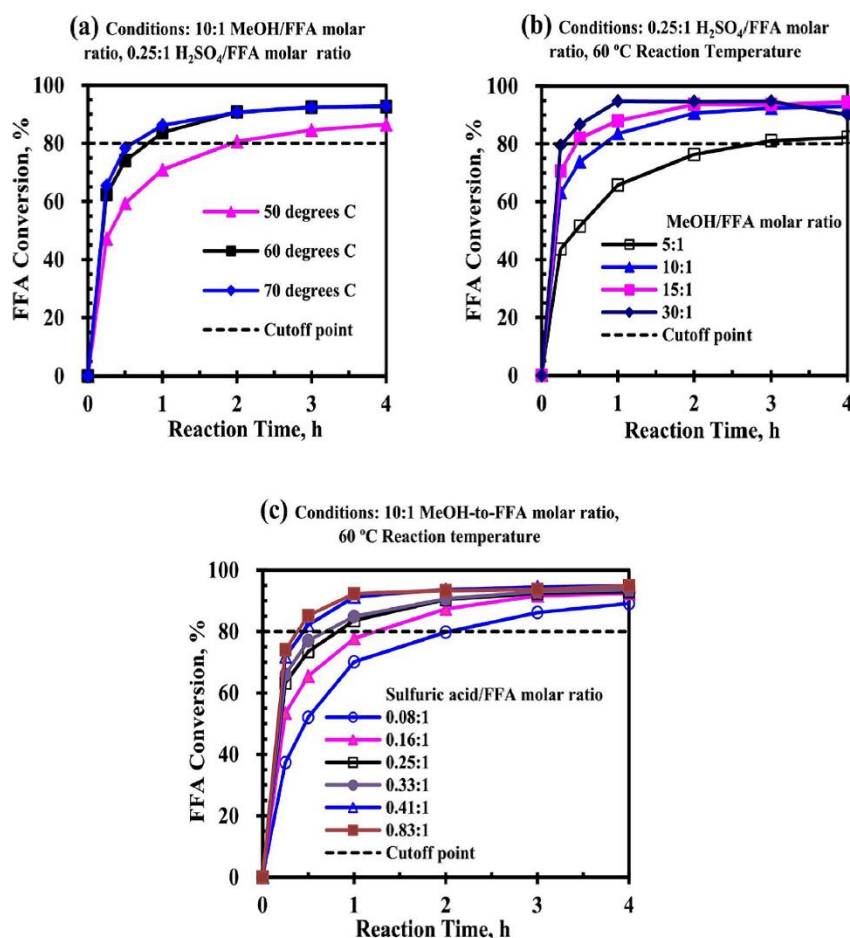


Fig. 2. FFA conversion of WVO in the first esterification stand-alone, as a function of temperature (a), of MeOH/FFA molar ratio (b), and of H₂SO₄/FFA molar ratio (c).

Table 1

Weight distribution and density of TG-rich phase and MeOH-rich phase after 4 h of the first esterification stand-alone on MeOH/FFA molar ratio from 5:1 to 30:1 (at 0.25:1 H₂SO₄/FFA molar ratio, 60 °C reaction temperature).

MeOH/FFA molar ratio	TG-rich phase			MeOH-rich phase		
	Position	wt.%	Density* g/mL	Position	wt.%	Density* g/mL
5: 1	Upper	95.83	0.914	Lower	4.17	1.112
10: 1	Upper	92.55	0.908	Lower	7.45	0.960
15: 1	Upper	91.86	0.904	Lower	8.14	0.922
30: 1	Lower	73.61	0.898	Upper	26.39	0.856

Note: * Density at 20 °C.

the reactions progress steeply in the first quarter hour. After an hour, no significant differences were found on FFA conversion from the use of any molar ratio, and all had reached the cutoff rate. The suitable H₂SO₄/FFA molar ratio, having the MeOH rich phase settled on the lower layer, was found to be 1.93:1.

The optimum conditions for the second esterification were: 1 h reaction time, 60:1 MeOH/FFA molar ratio, and 1.93:1 H₂SO₄/FFA molar ratio at 60 °C.

3.3. Material balance of esterification

In this section, material balances of the first esterification stand-alone of WVO and the second esterification stand-alone of MO were analyzed according to FFA conversion at their corresponding optimum conditions. Results are presented in Table 3. After esterification, each mixture is separated into two phases: a TG-rich phase, consisting mainly of non-polar compound TG; and a MeOH-rich phase, composing dominantly of polar compound MeOH. Water is the most undesirable component in the esterification system since it leads to hydrolysis reaction in the presence of H₂SO₄. Table 3 shows that in either reaction, total water from both rich phases increased from the initial amount. Water produced in the first esterification was over three times that of the second since the WVO contained much higher level of FFA compared with the MO; and it dispersed more in the MeOH-rich phase than in the TG-rich phase when compared in percentage of weight.

In the first reaction, moreover, the remaining high amount of MeOH in the TG-rich phase (6.92 wt.%) plus a designed fresh methanol added to the second step esterification could be a cause of an undesirable excess MeOH which would lift the MeOH-rich phase to the upper layer in the second step of a two-step esterification. The lower amount of remaining MeOH in the second reaction (3.53 wt.%) could also be used to reduce MeOH consumption in a transesterification process. This, however, is beyond the scope of this paper.

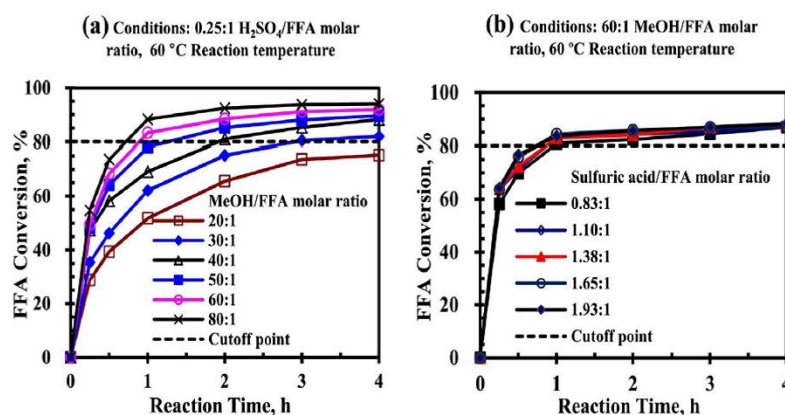


Fig. 3. FFA conversion of MO in the second esterification stand-alone as a function of MeOH/FFA molar ratio (a), and of H₂SO₄/FFA molar ratio (b).

Table 2

Weight distribution and density of TG-rich phase and MeOH-rich phase after 4 h of the second esterification stand-alone on MeOH/FFA molar ratios from 20:1 to 80:1 (at 0.25:1 H₂SO₄/FFA molar ratio and 60 °C reaction temperature).

MeOH/FFA molar ratio	TG-rich phase			MeOH-rich phase		
	Position	wt.%	Density*g/mL	Position	wt.%	Density*g/mL
20:1	Upper	99.05	0.906	Lower	0.95	1.004
30:1	Upper	98.42	0.904	Lower	1.58	0.950
40:1	Lower	97.31	0.904	Upper	2.69	0.884
50:1	Lower	95.85	0.902	Upper	4.15	0.855
60:1	Lower	93.09	0.902	Upper	6.91	0.836
80:1	Lower	88.55	0.902	Upper	11.45	0.820

Note: * Density at 20 °C.

Table 3

Material balance of the first esterification stand-alone of WVO and the second esterification stand-alone of MO at suitable conditions* after 4 h (at 60 °C reaction temperature).

Component	The first esterification of WVO			The second esterification of MO		
	Initial amount	TG-rich phase	MeOH-rich phase	Initial amount	TG-rich phase	MeOH-rich phase
	g	g	g	g	g	g
TG	432.05	432.05	–	417.87	417.87	–
FFA	67.77	4.72	–	11.95	1.40	–
Ester	–	66.32	–	70.00	81.10	–
H ₂ O	0.56	1.83	2.93	0.62	0.94	0.38
MeOH	80.06	37.75	34.84	84.70	18.45	65.02
H ₂ SO ₄	5.98	2.77	3.21	8.20	2.56	5.64
Total	586.42	545.44	40.98	593.34	522.31	71.03

Note: * Conditions for the first esterification: 10:1 MeOH/FFA molar ratio, and 0.25:1 H₂SO₄/FFA molar ratio; and, respectively for the second, 60:1 and 1.93:1.

3.4. The two-step esterification

The experiment was set up to verify the suitable conditions from the first esterification stand-alone and the second esterification stand-alone, and to investigate the effect of hydrolysis reaction occurring in the process.

In Fig. 4 the progress of reaction was continuously plotted from the first through to the second esterification. It was found that the two-step esterification could reduce FFA to be less than 0.5 wt.%. However, the MeOH-rich phase was found to be in the upper layer since the TG-rich phase from the first esterification contained a significant amount of remaining MeOH, causing an excess in MeOH. This result confirmed the assumption earlier speculated in Section 3.3.

In Fig. 5, the MeOH-rich phase layer was studied by reducing

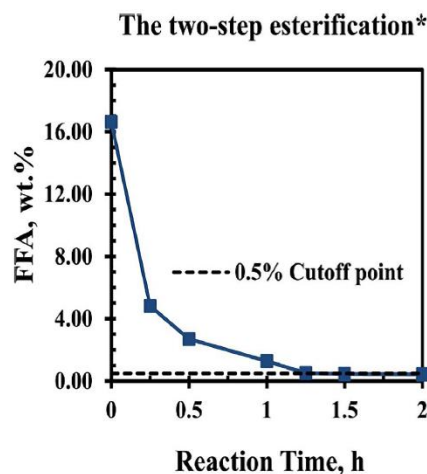


Fig. 4. FFA reduction in WVO from the two-step esterification (at 60 °C reaction temperature and 1 h reaction time). Note: * Conditions for the two-step esterification: For the 1st step, 10:1 MeOH/FFA molar ratio, 0.25:1 H₂SO₄/FFA molar ratio; and, respectively for the 2nd step: 60:1 and 1.93:1.

MeOH/FFA molar ratio in the second esterification from 60:1 down to 50:1 ('Two-step1** line' in Fig. 5). Although, this 'succeeded' in settling the MeOH-rich phase to the lower layer, FFA was found to be higher than 0.5 wt.%. An increase of H₂SO₄/FFA molar ratio in the first esterification was thus investigated because in the second esterification high amounts of H₂SO₄ would be consumed due to the increased bulk density of the MeOH-rich phase.

Since no significant difference between H₂SO₄/FFA molar ratio of

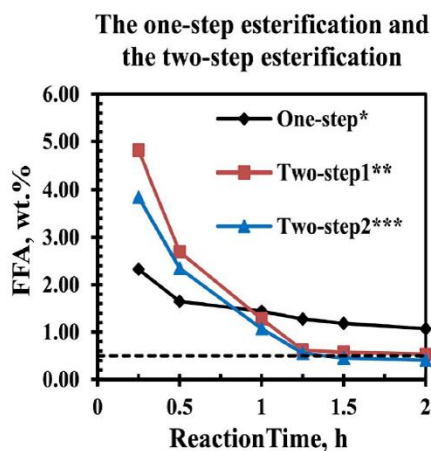


Fig. 5. FFA reduction in WVO from the one-step and the two-step esterification at 60 °C reaction temperature. Note: 1. *Conditions for the one-step esterification: 13.55:1 MeOH/FFA molar ratio, 0.55:1 H₂SO₄/FFA molar ratio, and 2 h reaction time. 2. **For the two-step: 1st esterification 10:1 MeOH/FFA molar ratio, 0.25:1 H₂SO₄/FFA molar ratio, and 1 h reaction time; and, respectively for the 2nd esterification: 50:1, 1.93:1, and 1 h. 3. ***For the two-step: 1st esterification, 10:1 MeOH/FFA molar ratio, 0.41:1 H₂SO₄/FFA molar ratio, and 1 h reaction time; and, respectively for the 2nd esterification: 50:1, 1.93:1, and 1 h.

0.25:1 and 0.33:1 was found, as shown in Fig. 2c, the highest end value in the H₂SO₄/FFA molar ratio optimal range, 0.41:1 in the first esterification, was thus selected. Fig. 5 shows that this new condition for the two-step esterification ('Two-step2*** line') could reduce FFA to be less than 0.5 wt.% together with the MeOH-rich phase in the second esterification at the preferred lower layer. These conditions were employed in the two-step esterification plus catalyst solution recycling, in Section 3.5.

One advantage of the two-step esterification is the progression of reaction because the MeOH-rich phase consisting of high amount of water would be separated and removed before the resulting TG-rich phase from the first esterification is fed into the second [23]. The presence of water interrupts the esterification process; Hydrolysis, a

reversible reaction in esterification, causes the reaction to approach equilibrium. Fig. 5 highlights that due to water accumulation the deployment of one-step esterification ('One-step* line') cannot attain high FFA reduction in contrast to the two-step esterification, even though it utilized the same amounts of MeOH and H₂SO₄. From Fig. 5 and Table 4, it can be seen that FFA reduction in the one-step esterification was severely affected by water; it took a stronger condition (higher amounts of catalyst and MeOH; and longer reaction time) than the first step of the two-step esterification to obtain similar results in FFA reduction at 1 h reaction time.

Material balance of the two-step esterification was calculated according to FFA conversion and is shown in Table 4. Results reveal that the remaining water in the feedstock (0.37 wt.%) inputted into the second esterification had slightly inhibited progress of reaction in the second step, thus the total FFA reduction was found to be less than 0.5 wt.% ('Two-step2*** line' in Fig. 5).

As evident in Table 4, the second step MeOH-rich phase contained a low amount of water (0.74 g, in a total of 19.27 g) and hence it is possible to be recycled as catalyst solution.

3.5. Recycling study of the MeOH-rich phase

In this study, a two-step esterification was developed, as illustrated in Fig. 6, using the MeOH-rich phase of the second esterification (10) as catalyst solution to be reused for the first esterification (3) by blending it with fresh catalyst solution (2), and its activities were investigated.

Fig. 7 reveals that the use of fresh catalyst solution could reduce FFA content of the second esterification to be less than the 0.5 wt.% cutoff point while recycling of the MeOH-rich phase solution was nearly able to achieve the goal. The remaining water in the recycled MeOH-rich phase (Mass Flow No 3) caused an increase of initial water in the first step (see Table 6) and accelerated the hydrolysis reaction to rapidly reach esterification equilibrium. This, however, was only slightly more than the target cutoff level. However, whether FFA content of the second esterification was over 0.5 wt.% or not, it was definitely less than 1 wt.%, which is within the recommended limit for base-catalyzed transesterification reactions [13].

Table 5 tabulates the material balances of the two-step esterification with recycling of MeOH-rich phase solution at steady state, and Table 6, derived from results in Tables 4 and 5, highlights the inputs and the

Table 4
Material balance of the one-step and the two-step esterification at 60 °C reaction temperature.

Condition	One-step esterification				Two-step esterification				
					The first esterification		The second esterification		
MeOH/FFA molar ratio	13.55:1				10:1		50:1		
H ₂ SO ₄ /FFA molar ratio	0.55:1				0.41:1		1.93:1		
Reaction time	2 h				1 h		1 h		
Component	Initial amount	TG-rich phase	MeOH-rich phase	Initial amount	TG-rich phase	MeOH-rich phase	Initial amount	TG-rich phase	MeOH-rich phase
	g	g	g	g	g	g	g	g	g
TG	424.18	424.18	–	424.18	424.18	–	424.18	424.18	–
FFA	75.55	8.24	–	75.55	5.37	–	5.37	2.07	–
Ester	–	70.80	–	–	73.82	–	73.82	77.29	–
H ₂ O	0.69	1.24	3.94	0.69	2.02	3.35	2.17	1.64	0.74
MeOH	121.22	57.74	55.50	89.34	37.21	43.81	68.93	52.19	16.36
H ₂ SO ₄	14.78	1.09	13.69	11.11	5.01	6.10	8.69	6.52	2.17
Total	636.42	563.29	73.13	600.87	547.61	53.26	583.16	563.89	19.27

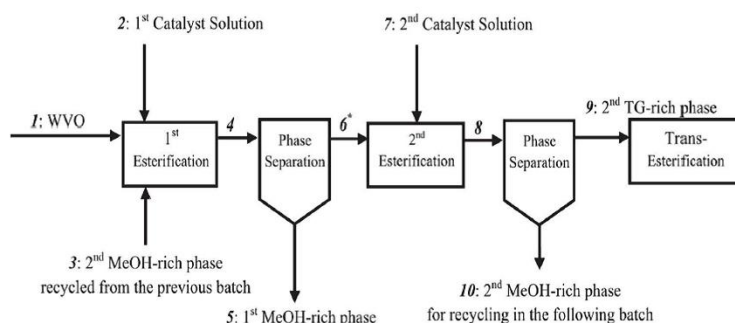


Fig. 6. Flow diagram of the two-step esterification with MeOH-rich phase recycling in batch process. Note: Numbers in *Italic* are Mass Flow Nos.; their associated compositions are detailed in Table 5. * Mass Flow No 6 signifies the 1st TG-rich phase

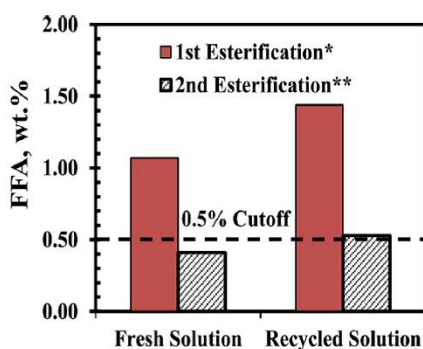


Fig. 7. Comparison of FFA reduction between fresh solution and repeated recycled solution of the MeOH-rich phase at steady state in the two-step esterification (at 60 °C reaction temperature and 1 h reaction time). Note: 1. * Conditions for the first esterification: 10:1 MeOH/FFA molar ratio, and 0.41:1 H₂SO₄/FFA molar ratio. ** For the second esterification: 50:1 MeOH/FFA molar ratio, and 1.93:1 H₂SO₄/FFA molar ratio.

Table 5
Material balance of the two-step esterification with recycling of MeOH-rich phase solution at steady state.

Mass Flow No	Name	Component						
		TG	Ester	FFA	MeOH	H ₂ SO ₄	H ₂ O	Total
		g	g	g	g	g	g	g
1	WVO	417.60	–	81.70	–	–	0.70	500.00
2	1st catalyst solution	–	–	–	56.14	7.92	0.21	64.27
3*	2nd MeOH-rich phase	–	–	–	40.60	4.09	1.68	46.37
4	Mixture 1	417.60	78.27	7.29	87.92	12.01	7.55	610.64
5	1st MeOH-rich phase	–	–	–	50.84	6.48	5.61	62.93
6	1st TG-rich phase	417.60	78.27	7.29	37.08	5.53	1.94	547.71
7	2nd catalyst solution	–	–	–	43.16	5.00	0.14	48.30
8	Mixture 2	417.60	83.12	2.68	79.70	10.53	2.39	596.02
9	2nd TG-rich phase	417.60	83.12	2.68	39.10	6.44	0.71	549.65
10†	2nd MeOH-rich phase	–	–	–	40.60	4.09	1.68	46.37

Note: * recycled from the previous batch.

† for recycling in the subsequent batch.

outcomes of FFA and H₂O. From Table 6, it is noted that 1) The first step of the novel two-step esterification was a little less effective in FFA conversion than the conventional process, and 2) Although the amount of initial water in the esterification was 0.42 wt.% higher than the

Table 6
Amount of FFA and water in the two-step esterification*.

Component	Unit	Conventional two-step esterification		Novel*** two-step esterification	
		The 1st step	The 2nd step	The 1st step	The 2nd step
Initial FFA	wt.%	15.11	1.07	16.34	1.44
Final FFA	wt.%	1.07	0.41	1.44	0.53
Initial H ₂ O	wt.%	0.11	0.37	0.42	0.35
H ₂ O Produced **	wt.%	0.78	0.04	0.81	0.05

Note: 1. * Conditions for the two-step: 1st esterification 10:1 MeOH/FFA molar ratio, 0.41:1 H₂SO₄/FFA molar ratio, and 1 h reaction time; and, respectively for the 2nd esterification: 50:1, 1.93:1, and 1 h.

2. ** H₂O Produced: the total amount of water produced during the reaction.

3. *** 'Novel' infers two-step esterification with MeOH-rich phase recycling.

another, it affected lesser the FFA reduction, thus it was considered acceptable.

In our conventional two-step esterification experiment with fresh solution the overall total chemicals consumed were 14.11:1 MeOH/FFA molar ratio, and 0.57:1 for H₂SO₄/FFA. The use of recycled MeOH-rich phase solutions reduced the MeOH/FFA molar ratio to 10.26:1 (a 27% reduction) and the H₂SO₄/FFA molar ratio down to 0.44:1 (a 23% reduction), as can be derived from Table 5. With the use of MeOH-rich phase recycling, the amounts of these chemicals were found to be less than that reported in several papers employing similar two-step esterification, e.g., [13], [19], and [20]. Recycling of the MeOH-rich phase is thus proposed to economically treat WVO to yield satisfactory esterified oils with FFA below 1 wt.% suitable for further transesterification.

Finally, in addition to this subject of transesterification, our second TG-rich phase esterified oil product (Mass Flow No 9 in Table 5) was found to contain two undesirable components: water (0.13 wt.%) and H₂SO₄ (1.17 wt.%). To counter acidity, alkali catalyst for neutralization is needed more when the esterified oil product is to be fed to a base-catalyst transesterification process. The remaining MeOH in the TG-rich phase is useful because it would reduce the amount of MeOH in its next step.

4. Conclusions

This research investigated four individual experiments: First esterification stand-alone, Second esterification stand-alone, Two-step esterification, and Two-step esterification with MeOH-rich phase recycling. The last attempt was to seek a more efficient and more economical process to produce suitable esterified WVO appropriate for further transesterification. The first three experiments were conducted to evaluate workable criteria to bring the MeOH-rich phase – the minor

phase – down to the bottom layer such that it could be drained out to be reused. The batched two-step esterification process with recycling studied had succeeded in reducing FFA content in WVO with high FFA content (approx. 13–17 wt.%) to be less than the recommended standard of 1 wt.%. The optimum conditions found were: 10:1 MeOH/FFA molar ratio, 0.41:1 H₂SO₄/FFA molar ratio in the first step; and 50:1 MeOH/FFA molar ratio, 1.93:1 H₂SO₄/FFA molar ratio in the second step. In both steps, the appropriate reaction temperature was found to be 60 °C, and the reaction time 1 h; and the material balance to predict the progress of reaction was calculated.

The highlight of this study is that recycling of the MeOH-rich phase from the second esterification as catalyst solution back to the beginning of the first esterification of the next batch in order to reduce the amount of MeOH and H₂SO₄ could be successfully employed. Our future work shall focus on continuous two-step esterification process using WVO as feedstock.

Acknowledgments

Financial supports on this research from the Graduate Studies Grant and the Graduate School of Prince of Songkla University (PSU) are gratefully acknowledged. The authors are grateful to the Department of Chemical Engineering and the Specialized R & D Center for Alternative Energy from Palm Oil and Oil Crops, and the PSU Faculty of Engineering. Finally, the authors would like to express a special thank to Mr. Wiwat Sutiwipakorn for reviewing the English of this paper.

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Process Development for 2-Step Acid Esterification from Waste Vegetable Oil with High Free Fatty Acids Content

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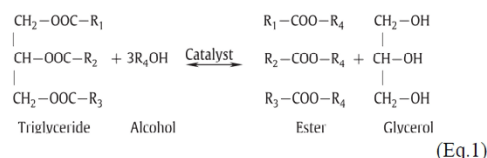
Abstract Biodiesel is an alternative diesel fuel composed of the monoalkyl esters of long chain fatty acids from vegetable oils or animal fats. Currently, most biodiesel is produced from edible oils with a low content of free fatty acid (FFA), then the cost of biodiesel is higher than diesel oil. However, the cost of biodiesel can be reduced by using low-cost feedstock such as animal fat and waste vegetable oil (WVO). An acid esterification is necessary to reduce FFA to the desirable level before alkaline transesterification to avoid soap formation by alkaline catalyst in transesterification. The aim of this study was to investigate the suitable conditions of 2-step acid esterification of FFA in WVO. The variable parameters involved in the process were methanol-to-FFA molar ratio; sulfuric acid-to-FFA molar ratio; temperature and reaction time. The results show that the 2-step acid esterification could obtained 97% conversion, from FFA 14% to 0.43%. The suitable conditions were: temperature of 60 °C; reaction time of 1hr in both steps; the MeOH-to-FFA molar ratio of 10:1 in the 1st step and 50:1 in the 2nd step and the H₂SO₄-to-FFA molar ratio of 0.25:1 in the 1st step and 0.55:1 in the 2nd step. Finally, it can be concluded that WVO with a high content of FFA is a viable and valuable feedstock for biodiesel production with low cost by an acid esterification process as a pretreatment step.

Keywords: Alternative diesel, biodiesel, esterification, free fatty acid.

I. Introduction

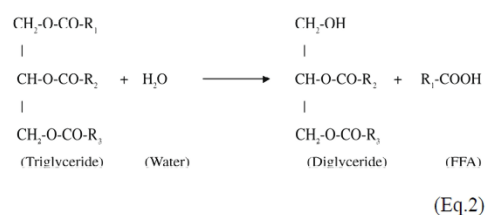
Biodiesel, an alternative petroleum diesel, is derived from renewable sources such as vegetable oil, animal fat,

and WVO. Chemically, biodiesel is a mixture of fatty acid alkyl esters which produced by transesterification process (Eq.1). It is biodegradable, non-toxic, and environmentally-friendly when compares with petroleum diesel [1,2].

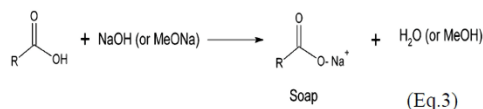


The commercial biodiesel is limited by the high production cost due to the high cost of premium feedstock such as edible oil that costs 70-95% of the overall production expense. So the use of low-cost sources such as WVO or non-edible oils for biodiesel production are an effective way to reduce production costs, therefore, increasing its economic competition [3,4].

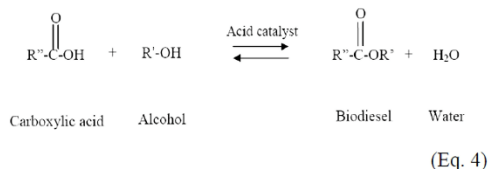
The most of low-cost feedstocks contain high moisture and free fatty acids contents. The presence of water in the oil sample can hydrolyze the triglyceride to form FFA by the hydrolysis reaction (Eq.2). The FFAs present major problem when using a base-catalyzed transesterification process since the FFAs react with a base catalyst to form soaps by saponification (Eq.3). Both reactions lead to loss of catalyst and ester product and increase production processing steps and costs [5, 6].



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Therefore, the low-cost feedstocks require the additional processes as a pretreatment step to reduce the FFAs level of the feedstock less than 1% within the recommendable amount before using alkaline transesterification [7,8,9]. The common pretreatment is esterification (Eq. 4) of the FFAs with alcohol in the presence sulfuric acid as catalyst [6]. The direct esterification of the FFAs is important due to increasing of biodiesel production [10].



The objectives of this study was: (a) to investigate the potential of WVO as a low-cost feedstock for biodiesel production; (b) to study the 2-step acid-catalyzed esterification reaction as possible pretreatment step; and (c) to study the effect of operating parameters such as molar ratio, reaction temperature and reaction time on the pretreatment of WVO.

II. Materials and Methods

1. Materials

Waste vegetable oil (WVO) was obtained from the Specialized R&D for Alternative Energy from Palm Oil and Oil Crops, Prince of Songkla University, Thailand. Free fatty acid (FFA) and the moisture content were 14 wt% and 0.03 wt%, respectively.

Mixed oil (MO) was a synthetic raw material for the second esterification which consisted of 83.5 wt% triglyceride (TG), 14 wt% methyl ester and 2.5 wt% FFA. The MO obtained by mixing refined palm oil (RPO) with 0.10 wt% FFA, pure methyl ester (ME) and palm fatty acid distillate (PFAD) with 93 wt% FFA.

Two other acquired chemicals are methanol, (P General Group, Thailand, purity > 99.8 wt%) and sulfuric acid (S.T. Chemicals, Thailand, purity > 98 wt%).

2. Esterification Procedure

The WVO and MO were esterified with MeOH and H₂SO₄ as catalyst in the first step and second step, respectively.

The esterification of FFA in TG was performed in 1-litre three-necked round bottom flasks, each attached to a thermometer, a reflux condenser and chemical addition or taking samples.

The esterification reaction was carried out with 500 g WVO fed into a reactor was gradually heated up to reaction temperature (50, 60 and 70°C). A prepared MeOH/H₂SO₄ mixture was then added under a constant mixing speed of 1,200 rpm by magnetic stirrer, taking this moment as zero time.

Keeping the flasks immersed in constant temperature oil baths, reactions were carried out for 4 hr. At 0.25, 0.5, 1, 2, 3, and 4 hr, samples of 10 ml were taken out from each reaction mixture and washed with water to stop the reaction and to remove the catalyst and the alcohol from its oil phase. The acid value of the reaction mixture was determined by titration. At the end of the reaction, the mixture product was poured into a separation funnel and allowed to stand overnight (or approximately 16 hr). Two settled phases could be identified as an 'alcohol rich phase' consisting of MeOH, H₂SO₄, H₂O and impurities; and a 'triglyceride rich phase' consisting mainly of fats and esterified fatty acids[11].

The experimental parameters of the first step were: MeOH-to-FFA molar ratios in the range of 5:1 to 30:1 and H₂SO₄-to-FFA molar ratios of 0.08:1 to 0.41:1 and the second reaction were: MeOH-to-FFA molar ratios in the range of 20:1 to 60:1 and H₂SO₄-to-FFA molar ratios of 0.25:1 to 0.83:1.

The FFA conversion rate indicated the efficiency of esterification reaction. The reaction efficiency was set at 80% of the FFA conversion as a cutoff point.

3. Analytical methods

The acid value of the reaction mixture was determined by the acid-base titration using the AOCS Cd-3a-63 method. Conversion of FFA was calculated using the following equation:

$$\text{FFA conversion, \%} = \frac{A_i - A_t}{A_i} \times 100 \quad (\text{Eq.5})$$

where A_i is the initial acidity, and the A_t is acidity at any time.

All experiments were carried out in triplicate in order to assess random errors.



III. Results and discussion

1. Effect of the temperature and reaction time

The reaction temperature was varied in the range 50 to 70 °C. The MeOH-to-FFA molar ratio and the H₂SO₄-to-FFA molar ratio of were 10:1 and 0.25:1, respectively. Figure 1, it can be seen that as the temperature increased the final conversion increased. The result was in accordance with the results obtained in previous reports [4,10,11,12]. The higher percentage conversion was for higher temperature. After two hr, there was no significant reduction in the acid value for 60 and 70°C. Hence, it can be concluded that temperature 60°C and reaction time at 1 hr can consider as the suitable economic conditions and reduce the chance of loss of MeOH.

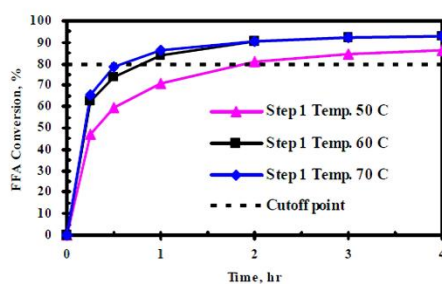


Figure 1 Effect of temperature and reaction time on the FFA conversion of WVO (MeOH -to-FFA molar ratio of 10: 1, H₂SO₄-to-FFA molar ratio of 0.25: 1).

2. Effect of MeOH-to-FFA molar ratio and reaction time

The reaction was carried out at a constant temperature of 60°C and H₂SO₄-to-FFA molar ratio of 0.25: 1. The MeOH-to-FFA molar ratio of first esterification and second esterification was varied between 5: 1 to 30: 1 and 20: 1 to 60: 1, respectively. Figure 2 and 3 showed the change in acid value of WVO with respect to change in molar ratio of MeOH-to-FFA. The reaction progressed rapidly during the first hour in both of step 1 and 2. After two hr, the reaction rate was slowly. The reverse esterification reaction could explain this situation [13]. Excess of MeOH promotes reaction completion keeping the sulfuric acid in MeOH phase and changes MeOH rich phase to upper phase due to decreasing of bulk density as shown in table 1. The disadvantage of this approach is that the more MeOH is used, the more process costs will increase [11]. Therefore, the suitable MeOH-to-FFA molar ratio of first esterification and second esterification were 10: 1 and 50: 1, respectively.

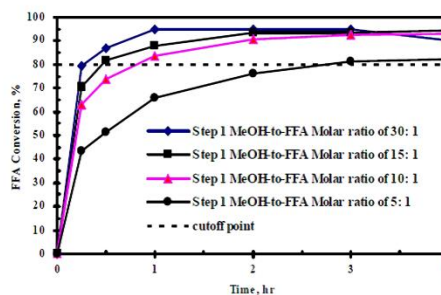


Figure 2 Effect of MeOH-to-FFA molar ratio and reaction time on the FFA conversion of WVO (H₂SO₄-to-FFA molar ratio of 0.25:1, reaction temperature of 60°C).

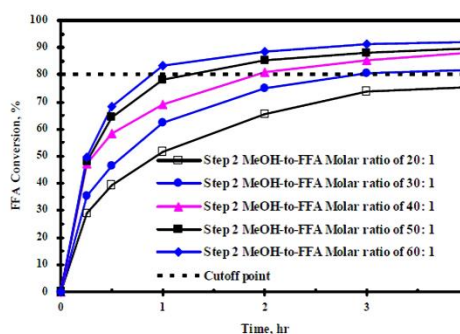


Figure 3 Effect of MeOH-to-FFA molar ratio and reaction time on the FFA conversion of MO (H₂SO₄-to-FFA molar ratio of 0.25: 1, reaction temperature of 60°C).

3. Effect of H₂SO₄-to-FFA molar ratio and reaction time

The esterification reaction was carried out at a constant temperature of 60°C. The MeOH-to-FFA molar ratio of first esterification and second esterification were 10: 1 and 60: 1, respectively. The H₂SO₄-to-FFA molar ratio of first esterification was varied between 0.08: 1 to 0.41: 1 and second esterification was varied between 0.25: 1 to 0.83: 1.

The results in Figure 4 and 5 showed that FFA conversion rate of both step 1 and step 2 increased with increasing molar ratio of H₂SO₄-to-FFA. For the lower H₂SO₄-to-FFA molar ratio, the FFA conversion was increased by increasing reaction time while at high H₂SO₄-to-FFA molar ratio the conversion was higher than lower amount in the beginning of the reaction and nearly constant after 2 hr of reaction to reach the higher conversion value about 94% (step 1). Moreover, the

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addition of excess H₂SO₄-to-FFA molar ratio could produce a dark esterified oil [14] and change MeOH rich phase to lower phase due to increasing of bulk density. Then it can be concluded that the suitable condition of H₂SO₄-to-FFA molar ratio for first esterification and second esterification were 0.25:1 and 0.55: 1, respectively.

Table 1 Weight distribution of TG- rich phase and MeOH-rich phase of 1st esterification on MeOH-to-FFA molar ratio from 5: 1 to 30:1 (H₂SO₄-to-FFA molar ratio of 0.25: 1, reaction temperature of 60°C).

MeOH-to-FFA molar ratio	TG-rich phase			MeOH-rich phase		
	Position	%wt	Density, g/mL	Position	%wt	Density, g/mL
5: 1	Upper	96.88	0.797	Lower	3.12	1.017
10: 1	Upper	93.88	0.783	Lower	6.12	0.888
15: 1	Lower	90.08	0.781	Upper	9.92	0.775
30: 1	Lower	78.05	0.774	Upper	21.95	0.747

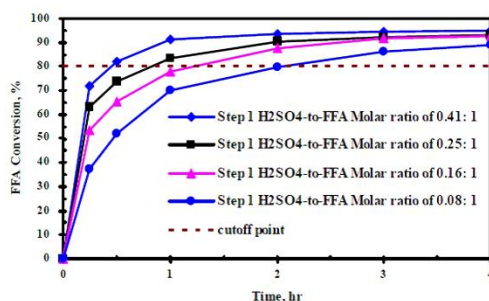


Figure 4 Effect of H₂SO₄-to-FFA molar ratio and reaction time on the FFA conversion of WVO (MeOH-to-FFA molar ratio of 10: 1, reaction temperature of 60 °C).

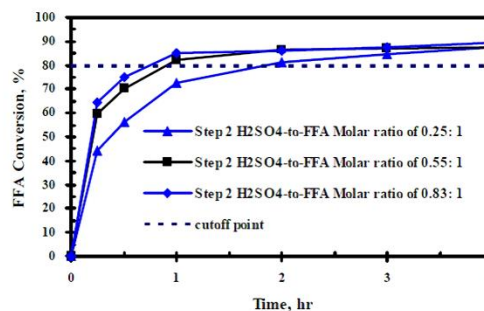


Figure 5 Effect of H₂SO₄-to-FFA molar ratio and reaction time on the FFA conversion of MO (MeOH-to-FFA molar ratio of 50: 1, reaction temperature of 60 °C).

IV. Conclusion

2-step acid-catalyzed esterification from WVO with high free fatty acid content was studied using H₂SO₄ as a catalyst and MeOH as alcohol to reduce the amount of FFA from 14 wt% to 0.43 wt%, 97% FFA conversion, within the recommendable amount for biodiesel production. Effect of operating parameters related to the acid-catalyzed esterification was studied and optimized, including reaction temperature, MeOH-to-FFA molar ratio, H₂SO₄-to-FFA molar ratio and reaction time. Finally, it can be concluded that WVO with high FFA content is an alternative and economic feedstock for biodiesel production.

Acknowledgments

The author gratefully acknowledges financial support from a Graduate Studies Grant and the Graduate School of Prince of Songkla University, and the provision of equipment by the Specialized R&D Center for Alternative Energy from Palm Oil Crops (Thailand).

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Publication

Photaworn, S., Tongurai, C., Kungsanunt, S., 2017. Process development of two-step esterification plus catalyst solution recycling on waste vegetable oil possessing high free fatty acid. *Chem. Eng. Process. Process Intensif.* 118, 1–8.

Proceeding

Photaworn, S., Kungsanunt, S., Tongurai, C., 2014. Process development for 2-step acid esterification from waste vegetable oil with high free fatty acids content, in: *The 4th TIChE International Conference 2014*. Chiangmai, Thailand, 18-19 December 2014, pp. 313–317.