Upgrading Biodiesel Derived from Palm Fatty Acid Distillate (PFAD) using 10% Ni/HZSM-5 as Catalyst

Metariya Ritsamak

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of
Master of Engineering in Chemical Engineering (International Program)
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Author	Miss Metariya Ritsamak
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I hereby certify that this work has not been accepted in substance for any degree, and is not being currently submitted in candidature for any degree.

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ชื่อวิทยานิพนธ์	การปรับปรุงคุณภาพไบโอดีเซลที่ใช้ส่วนกลั่นกรดไขมันเป็นวัตถุดิบโดยใช้ตัวเร่งปฏิกิริยา 10% นิกเกิลบน HZSM-5 ซีโอไลท์
ผู้เขียน	นางสาวเมธารียา ฤทธิ์สมัคร
สาขาวิชา	วิศวกรรมเคมี (หลักสูตรนานาชาติ)
ปีการศึกษา	2562

บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์เพื่อปรับปรุงคุณภาพไบโอดีเซลด้วยวิธีเอสเตอริฟิเคชั่นโดยใช้ส่วนกลั่นกรดไขมันเป็นวัตถุดิบด้วยวิธีการเติมไฮโดรเจนบางส่วนโดยใช้เอทานอลเป็นแหล่งของไฮโดรเจนและใช้ตัวเร่งปฏิกิริยา 10% นิกเกิลบน HZSM-5 จากนั้นองค์ประกอบของตัวเร่งปฏิกิริยา 10% นิกเกิลบน HZSM-5 จะถูกวิเคราะห์โดยใช้วิธีเอกซเรย์ฟลูออเรสเซนต์ การทดลองถูกออกแบบโดยใช้วิธีพื้นผิวตอบสนองและการทดลองทำในอุปกรณ์แบบกะที่สามารถทนแรงดันสูงปริมาตร 1000 มิลลิลิตร โดยใช้เวลาในการทำปฏิกิริยาระหว่าง 8 ถึง 12 ชั่วโมง ภายใต้อุณหภูมิระหว่าง 160 ถึง 250 องศาเซลเซียส ความดัน 10 ถึง 20 บาร์ และสัดส่วนโดยมวลของไบโอดีเซลและเอทานอลเป็น 0.56:1 ถึง 1.69:1 (สัดส่วนโดยปริมาตรของไบโอดีเซลและเอทานอลเป็น 0.5:1 ถึง 1.5:1) ปริมาณเอสเตอร์ของผลิตภัณฑ์ส่วนของเหลวที่ได้จากวิธีการเติมไฮโดรเจนบางส่วนจะวิเคราะห์ได้โดยใช้สารมาตรฐานภายในด้วยวิธีแก๊สโครมาโตกราฟฟีด้วยตัววัดสัญญาณชนิดเฟลมไอออไนเซชัน องค์ประกอบของผลิตภัณฑ์ส่วนแก๊สที่ได้จากวิธีการเติมไฮโดรเจนบางส่วนจะวิเคราะห์ด้วยวิธีแก๊สโครมาโตกราฟฟีด้วยตัววัดสัญญาณชนิดสภาพนำความร้อน จากผลการทดลองได้ปริมาณผลได้สูงสุดที่เพิ่มขึ้นของเอทิลเอสเตอร์เท่ากับ 52.77% โดยน้ำหนัก ที่สภาวะการทดลองโดยใช้เวลาในการทำปฏิกิริยา 12 ชั่วโมง ภายใต้อุณหภูมิ 250 องศาเซลเซียส ความดัน 10 บาร์ และสัดส่วนโดยมวลของไบโอดีเซลและเอทานอลเป็น 0.56:1 (สัดส่วนโดยปริมาตรของไบโอดีเซลและเอทานอลเป็น 0.5:1) ที่สภาวะที่มีผลได้สูงสุดนี้จะนำไปใช้ในการทดลองกับตัวเร่งปฏิกิริยา HZSM-5, Amberlyst 15 และไม่มีตัวเร่งปฏิกิริยาเพื่อศึกษาผลของการเพิ่มขึ้นเพิ่มขึ้นของเอทิลเอสเตอร์โดยการใช้ตัวเร่งปฏิกิริยาที่ต่างกัน นอกจากนี้วิธีพื้นผิวตอบสนองสามารถระบุได้ว่าสัดส่วนโดยมวลของไบโอดีเซลและเอทานอล อุณหภูมิและความดันมีผลกระทบอย่างมีนัยสำคัญในการเพิ่มขึ้นของเปอร์เซ็นต์ผลได้ของเอทิลเอสเตอร์ ซึ่งกระบวนการนี้ไม่เพียงแต่ทำให้การการเพิ่มขึ้นของผลได้ของเอทิลเอสเตอร์ แต่ยังสามารถลดปริมาณกรดไขมันอิสระได้ถึง 50% และทำให้เปอร์เซ็นต์ของเอสเตอร์เพิ่มเป็น 96.53% ซึ่งเป็นค่าที่ผ่านมาตรฐานสากล (EN14214)

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ABSTRACT

This research aimed to determine the influence of a high-pressure batch reactor for upgrading biodiesel derived from esterification of palm fatty acid distillate (PFAD) by partial hydrogenation using ethanol as hydrogen donor and 10% Ni/HZSM-5 as a catalyst. And then, the composition of the synthesized 10% Ni/HZSM-5 catalyst was characterized by x-ray fluorescence (XRF). The experiments were designed by using response surface methodology (RSM) and there were carried out in a 1000 mL high-pressure batch reactor for 8-12 hours over a temperature range 160-250˚C under pressure 10-20 bar and the biodiesel to ethanol mass ratio around 0.56:1-1.69:1 (the biodiesel to ethanol volumetric ratio around 0.5:1-1.5:1). The ester content from liquid phase product of partial hydrogenation was analyzed by gas chromatography-flame ionization detector (GC-FID) with an internal standard solution. The gas-phase product components of partial hydrogenation were analyzed by gas chromatography-thermal conductivity detector (GC-TCD). The maximum increasing yield of ethyl-ester 52.77 wt.% was achieved at reaction time 12 hours, under temperature 250˚C and pressure 10 bars at the biodiesel to ethanol mass ratio around 0.56:1 (the volumetric ratio of biodiesel to ethanol 0.5:1). The best condition was operated with HZSM-5, Amberlyst 15, and non-catalyst to studies of the effect on increasing yield of ethyl-ester using other catalysts. Also, the RSM model indicated that mass ratio of biodiesel to ethanol, temperature and pressure were significantly affected by the increasing %yield of ethyl-ester. The process was not only increasing yield of ethyl-esters but also reducing more than 50% of free fatty acid (FFA) content as well. And, the percent ester content up to 96.53% which met the requirements of the international standard (EN14214).

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CHAPTER 1

INTRODUCTION

1.1. Background and Rationale

Nowadays, the main energy in the transportation sector comes from fossil fuel sources. The increasing environmental impact of fuel combustion emissions is an important issue in the research, and development of alternative energy. Biodiesel is a petroleum diesel substitute one of the most promising renewable fuel (Rade et al. 2018; Borges, and Díaz 2012).

In general, biodiesel can be produced from renewable resources such as animal fats, and vegetable oils. This is a conventional feedstock for biodiesel production but the cost of operate is a major difficulty that prevents the growth of biodiesel industries. Palm fatty acid distillate (PFAD) is a by-product of palm oil production in the process of refining crude palm oil (CPO). Conversion of PFAD to biodiesel is more efficient way to add-value the large number of by-products, and solving the environmental problems (Lokman et al., 2014; Zero & Rainforest Foundation Norway, 2015).

Due to high free fatty acid (FFA) content, PFAD is not a suitable feedstock for transesterification reaction using bases as a catalyst. Since FFA reacts with the base catalyst to form soap by saponification reaction. So, the biodiesel production from PFAD need esterification reaction as shown in Equation (1.1) to reduce the amount of FFA by an acid catalyst such as sulfuric acid, which yields fatty acid alkyl ester, and water are product (Cho et al., 2012; Chongkhong et al., 2009; Encinar et al., 2011; Farag, El-Maghraby, & Taha, 2011; Photaworn et al., 2017; Ramadhas, Jayaraj, & Muraleedharan, 2005).

$$\underset{\text{FFA}}{\text{R-COO-H}} + \underset{\text{Alcohol}}{\text{R'OH}} \xleftrightarrow{\text{Acid}} \underset{\text{Ester}}{\text{R- COO-R'}} + \underset{\text{Water}}{H_2O} \tag{1.1}$$

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

Generally, biodiesel from esterification reaction of PFAD was unqualified of biodiesel properties. Then upgrading biodiesel is the next step for biodiesel production to achieve higher quality. There are many ways to improve biodiesel quality for improved usability, including; thermal or catalytic cracking, transesterification, deoxygenation under H_2, hydrodeoxygenation (HDO), and hydrodecarboxylation (HDC) (Bateni, Saraeian, & Able, 2017; Kanjaikaew et al., 2018; Thiruvengadaravi et al., 2012). The HDO proceeds by the removal of oxygen from oxygenated compounds. The HDC reaction is interlacing to remove carboxyl groups from compounds (Galadima, and Muraza 2015; Bateni, Saraeian, and Able 2017).

Another way to upgrade biodiesel quality is partial hydrogenation, it is a process to transform polyunsaturated FAMEs (Fatty acid methyl esters) into monounsaturated FAMEs using hydrogen gas as hydrogen source which is effective. However high safety process must be recommended due to the explosive nature of hydrogen gas. As a result, hydrogen donors would be chosen. The commonly used hydrogen donors are cyclohexene, formic acid, ammonium formate, and alcohol. Due to the low cost, alcohols have been an appropriate hydrogen donor among them (Wei et al. 2018).

ZSM-5 zeolite is most commonly synthesized using the catalytic cracking, and hydrothermal process (HDO and HDC). In reason of its high thermal stability, exclusive structural network, ion exchangeability, solid acidity, and shape selectivity (Fawaz, Salam, and Daou 2019; Series, and Science 2017). Transition metals are suggested to effect of oxygen rejection by producing more carbon oxides, and less water. Nickel on HZSM-5 has been found to be active in the hydrocracking, isomerization of, and hydrocarbon hydrothermal stability of the catalyst (Yin, Zhao, and Liu 2005; Iliopoulou et al. 2012).

Ethanol is one of the most important resources for hydrogen production; high hydrogen content, storage, and handling safety, low price, no sulfur, no toxicity, ethanol can be produced renewable sources. The method that is the most interesting for hydrogen production from ethanol is the catalytic steam reforming of ethanol (SRE) (Fatsikostas, and Verykios 2004).

This research is focused on the upgrading biodiesel derived from PFAD using 10% Ni/HZSM-5 as catalyst, and ethanol as hydrogen source at high temperature, and high pressure in a batch high-pressure reactor, and schematic diagram of overall processes shown in Figure 1.1. The best operating parameters of mass ratio of biodiesel to ethanol, reaction temperature, reaction pressure, and reaction time on percent increasing yield of ethyl-ester were investigated by the response surface methodology.

1.2. Theoretical Background

1.2.1. Palm fatty acid distillate

Palm fatty acid distillate (PFAD) is a lower-value by-product from palm oil production. The free fatty acids (FFAs) must be removed from the process of refining crude palm oil (CPO) (K.Y. Cheah, T.S.Toh; Zero, and Rainforest Foundation Norway 2015). PFAD is mainly pale-yellow solid at room temperature with FFA content over 80% majorly include of palmitic acid, oleic acid, linoleic acid, myristic acid, stearic acid, and a little of squalene, sterols, and vitamin E. Nowadays, PFAD is used in the animal feed, laundry soap industries as raw material for cosmetics industry, and for pharmaceutical industry (Lokman et al. 2014; Gapor Md Top 2010). The amount of readily available PFAD is not insignificant, and it presents biodiesel producers with excellent access to a low-cost, non-food source of feedstock. PFAD is always traded at a discount to crude or refined, bleached, and deodorized (RBD) palm oil (K.Y. Cheah, T.S.Toh). Biodiesel production from PFAD as raw material, which both reduces cost of the biodiesel production and adds to value of PFAD. The fatty acid description of PFAD shown in Table 1.1.

Table 1.1. Fatty acid description of PFAD (Chongkhong et al. 2009).

Fatty acid	**Formula**	**Structure**	**wt.%**
Saturated fatty acids			
Myristic	$C_{14}H_{28}O_2$	14:0	1.0
Palmitic	$C_{16}H_{32}O_2$	16:0	45.6
Stearic	$C_{18}H_{36}O_2$	18:0	3.8
Arachidic	$C_{20}H_{40}O_2$	20:0	0.3
Monounsaturated fatty acids			
Palmitoleic	$C_{16}H_{30}O_2$	16:1	0.2
Oleic	$C_{18}H_{34}O_2$	18:1	33.3
Ecosenoic	$C_{20}H_{38}O_2$	20:1	0.2
Tetracosenoic	$C_{24}H_{46}O_2$	24:1	0.6
Poly Polyunsaturated fatty acids			
Linoleic	$C_{18}H_{32}O_2$	18:2	7.7
Linolenic	$C_{18}H_{30}O_2$	18:3	0.3

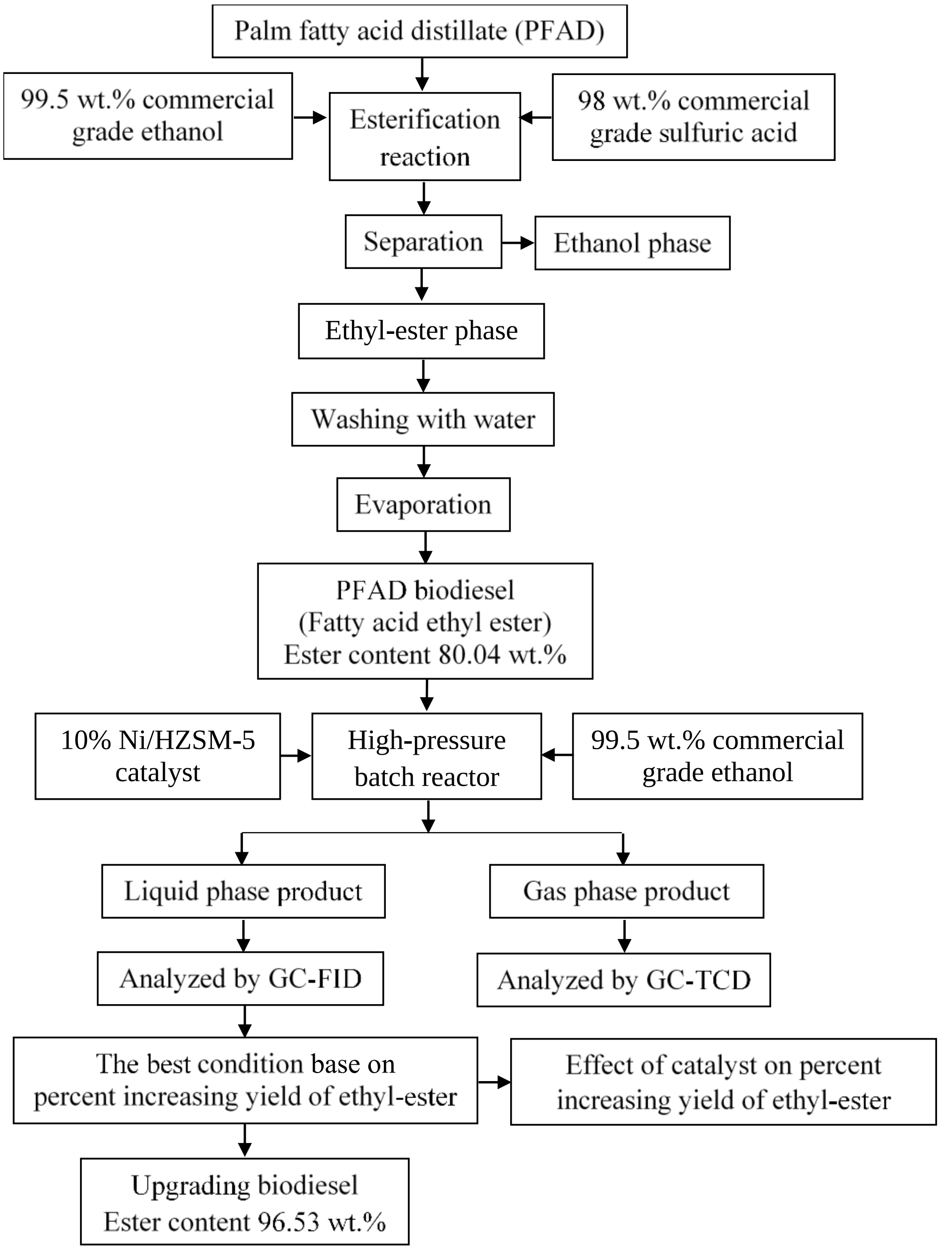


Figure 1.1. Arrangement flowchart of research methodology for experiments.

1.2.2. Biodiesel production

Biodiesel, a liquid fuel produced from new or used vegetable oils, and animal fats, is a cleaner-burning replacement for diesel fuel from petroleum-based. It is biodegradable and nontoxic. Like diesel from petroleum, biodiesel is used to fuel compression-ignition (diesel) engines. Generally, biodiesel production from raw materials with FFA less than 1 wt.% can be used to produce biodiesel single step with transesterification reaction. However, biodiesel production from these raw materials with very high FFA has required a two-step process. The first step is to use esterification to reduce FFA content less than 1 wt.% because FFA reacts with alkali in transesterification process, and convert into soaps, so alkyl esters are difficult to obtain. The second step when FFA was less than 1 wt.%, then transesterification convert the glyceride to ester (Trejo-calzada, and Pedroza-sandoval 2015; Lanna, and Reserved 2017).

Esterification is not only the reaction used to reduce high FFA in raw materials before transesterification in the next step but also biodiesel can be produced from this reaction (Kanjaikaew et al. 2018). Esterification can produce ester by reaction between carboxylic acids or FFA, and alcohol using acid, and heat as a catalyst. In a mechanism, the hydroxyl (-OH) groups of carboxylic acids, and the hydrogen (H) from alcohol are eliminated (Rade et al. 2018).

Alcohols used in biodiesel production are those with short chains, and the most widely used alcohols are methanol (CH_3OH), and ethanol (C_2H_5OH). Methanol is commercially used more than ethanol because higher reaction speeds are reached, and excess alcohol can be recovered using a low cost. But methanol is highly toxic than ethanol (Romano, and Sorichetti 2011). Ethanol is an alternative to the interest in the production of biodiesel as fatty acid ethyl ester (FAEE). In addition, ethanol is less toxic than methanol, and also can be obtained from the fermentation of crops with high sugar or carbohydrate. Therefore, the production of biodiesel with ethanol is a renewable energy that is environmentally friendly, and sustainable resource (Kanjaikaew et al. 2018; Brunschwig, Moussavou, and Blin 2012).

1.2.3. Fuel properties of biodiesel

Biodiesel is generally manufactured for use with diesel engines. Before the biodiesel goes to the engine, it must be inspected properties of biodiesel in the same standard diesel engine general can accommodate. Promoting the use of biodiesel widely must define the standards for the quality of biodiesel. European Committee for Standardization that describes the requirements and test methods for fatty acid methyl ester (FAME) as shown in Table 1.2.

Table 1.2. International standard (EN14214).

List	Properties	Unit	Specification	Test method
1	Ester content	wt.%	96.5 min	EN 14103
2	Density at 15 °C	kg/m^3	860-900	EN 12185, ASTM D1298
3	Viscosity at 40 °C	cSt	3.5-5.0	EN 14105, ASTM D445
4	Flash Point	°C	101 min	EN ISO 2719, ASTM D93
5	Sulphur content	mg/kg	10 min	EN ISO 20846, ASTM D2622
6	Cetane Number	-	51 min	EN ISO 5165, ASTM D613
7	Sulphated Ash	wt.%	0.02 max	ASTM D874
8	Water content	mg/kg	500 max	EN ISO 12937
9	Total Contamination	mg/kg	24 max	EN 12662
10	Copper Strip Corrosion	-	Class 1 max	EN ISO 2160, ASTM D130
11	Oxidation Stability at 110 °C	hr.	8 min	EN 14112

List	Properties	Unit	Specification	Test method
12	Acid Value	mg KOH/g	0.50 max	EN 14104, ASTM D664
13	Iodine Value	-	120 max	EN 14111
14	Linolenic Acid Methyl Ester	wt.%	12 max	EN 14103
15	Methanol	wt.%	0.2 max	EN 14110
16	Monoglyceride	wt.%	0.7 max	EN 14105
17	Diglyceride	wt.%	0.2 max	EN 14105
18	Triglyceride	wt.%	0.2 max	EN 14105
19	Free glycerin	wt.%	0.02 max	EN 14105
20	Total glycerin	wt.%	0.25 max	EN 14105
21	Group I metals (Na +K)	mg/kg	5.0 max	EN 14538
22	Group II metals (Ca + Mg)	mg/kg	5.0 max	EN 14538

1.2.4. The reaction for biodiesel upgrading

1.2.4.1. Reforming of ethanol for hydrogen production

Hydrogen is a clean alternative to current fuels. Reforming alcohol for hydrogen production has a current interest because this technique is based on renewable sources, such as bioethanol, which produced, and distributed biofuel popularly. The method that is the most interesting for hydrogen production from ethanol is the catalytic steam reforming of ethanol (SRE) as Equation (1.2).

$$\text{SRE: } CH_3CH_2OH + 3H_2O \rightleftharpoons 6H_2 + 2CO_2 \qquad (1.2)$$

The selection of a suitable catalyst for SRE is important, as the catalyst must be stable, active, selective, and maximize hydrogen production while the least byproducts products. Nickel is the most studied metals in the reforming of fuels and biofuels. The high dispersion of nickel more confident selectivity for hydrogen, and decreased selectivity for methane (Guerrero, Castilla, and Cobo 2014). However, many other reactions can occur concurrently with hydrogen production reactions, for example; ethanol decomposition (ED) to CH_4, CO, and H_2, ethanol hydrogenolysis to CH_4, and H_2O, ethanol dehydration to ethylene, ethanol dehydrogenation to acetaldehyde, acetaldehyde decomposition to CH_4, and CO, acetone formation via aldolic condensation, water gas shift (WGS), methane steam reforming, dry reforming of methane, and methanation (Mattos et al. 2012). In this case, refer to only some reactions that can occur in the same temperature range used in this research.

Ethanol decomposition: $C_2H_5OH \rightleftharpoons CH_4 + CO + H_2$ (1.3)

Acetaldehyde decomposition: $C_2H_4O \rightleftharpoons CH_4 + CO$ (1.4)

Methanation: $CO + 3H_2 \rightleftharpoons CH_4 + H_2O$ (1.5)

Carbon dioxide formation: $2CO \rightleftharpoons CO_2 + C$ (1.6)

In research studies reaction network of steam reforming of ethanol over Ni-based catalysts, at low temperatures (50-100 °C), ethanol decomposes to form the C_1 molecules CH_4, and CO as well as H_2 Equation (1.3). Nickel encourages the C-C bond separation of ethanol, and a methyl group is independent to form methane gas by an increase to a hydrogen atom from the surface. Ni also causes dehydrogenation reaction of ethanol, and decomposition of acetaldehyde cause CH_4, and CO Equation (1.4). The adsorption of ethanol is completed as temperature increases, and temperatures between 150, and 200°C, the prominent reaction is the ethanol decomposition Equation (1.3). In the temperature range of 200 to 300 °C, the concentrations of CO, and H_2 a rapid decrease, furthermore a sharp peak of CH_4 rise; methanation reaction Equation (1.5). In the same temperature range, a large CO_2 peak appears, which can be predicted as water gas shift reaction ($CO + H_2O \rightleftharpoons CO_2 + H_2$), but the fact that H_2 does not increase suggests that CO_2 formation is related to the Boudouard reaction Equation (1.6). This reaction may be explicated significant carbon deposition on the catalyst surface (Fatsikostas, and Verykios 2004).

1.2.4.2. Hydrogenation

In the petroleum industry, several processes implicated in the manufacture of gasoline, and petrochemical products are founded on the destructive hydrogenation of hydrocarbon (Catalyst, Homla-or, and Petroleum 2017). Hydrogenation in Figure 1.2. is the main process that has usually been used to make renewable diesel, and Figure 1.3. shown the hydrogenation ways of fatty acid compositions. It is also widely used to upgrade highly unsaturated oils in the oils, and fats industry. The hydrogenation of vegetable oils is a chemical process in which hydrogen is added to a double bond of carbon-carbon in the glycerides of oil molecule. The reaction takes place in the presence of a catalyst, such as nickel, after that the product is oil of stability, oxidation resistance, and higher consistency (Munoz, Gerpen, and He 2012).

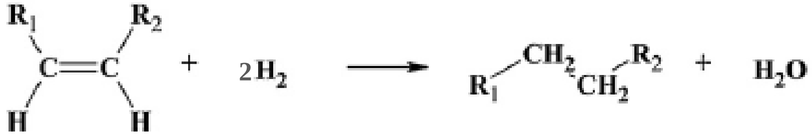


Figure 1.2. Schematic representation of hydrogenation reaction.

(Mortensen et al. 2011)

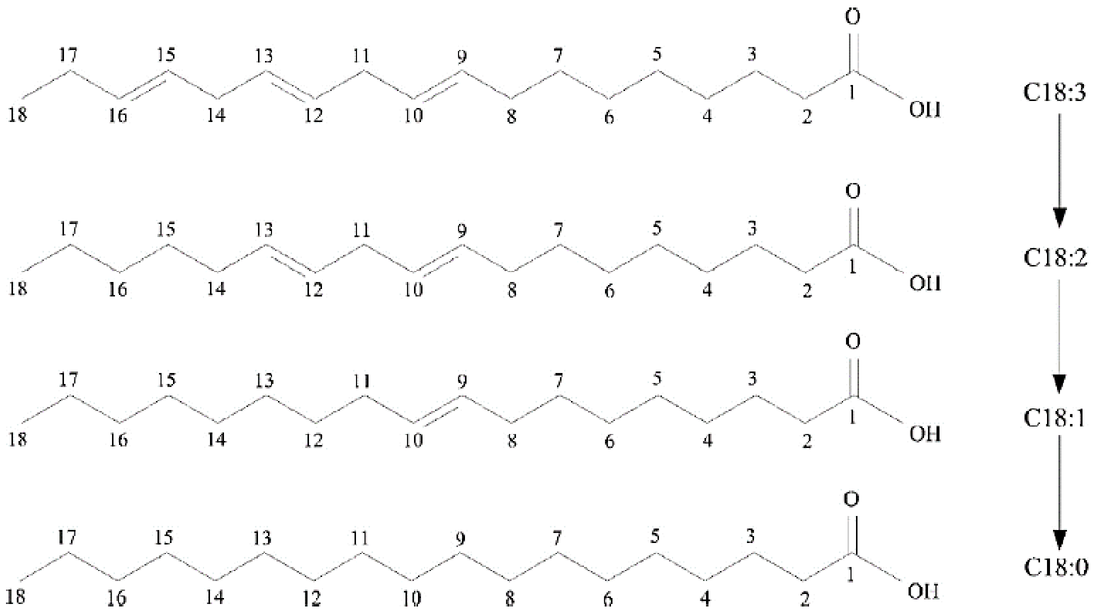


Figure 1.3. Fatty acid transformation induced by the hydrogenation process.

(Adu-Mensah et al. 2019)

1.2.4.3. Hydrodeoxygenation

Hydrodeoxygenation and hydrocracking are the two main reactions for upgrade of bio-oil to hydrocarbons (W. Shi et al. 2014). Hydrodeoxygenation as shown in Figure 1.4. is a reaction that takes away oxygenated compounds from the molecule normally in form of water using catalysts such as cobalt-molybdenum, and nickel-molybdenum supported on alumina, and zeolite materials were used most widely where hydrogen is used to separate carbon-carbon or carbon-heteroatom bonds in a molecule. Oil from vegetables has high oxygen content plays a major role in fuel properties causes in terms of chemical, and thermal instability, low heating value, and decadent. Accordingly, oil from vegetable that has long-chain glyceride ester compose of carbonyl oxygen could be removed by hydrodeoxygenation (Furimsky 2000; Catalyst, Homla-or, and Petroleum 2017).

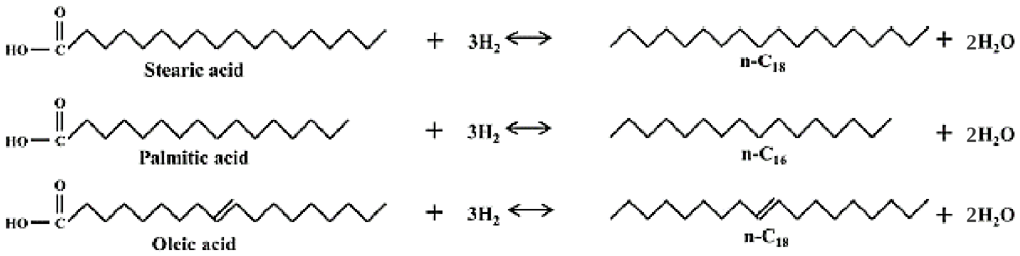


Figure 1.4. Schematic representation of hydrodeoxygenation reaction.

(Sotelo-boyás, Trejo-zárraga, and Hernández-loyo 2012)

1.2.4.4. Hydrocracking

Hydrocracking in Figure 1.5. is a catalytic process upgrade petroleum crude oil for changing high boiling component hydrocarbon to lighter clean fuels for instance gasoline, kerosene, and diesel oil by adding hydrogen-rich at elevated temperature, and pressure (Catalyst, Homla-or, and Petroleum 2017; Ghosh et al. 2015). The reaction in hydrocracking is that has two types of active sites: acidic sites for isomerization, and cracking reaction of carbon-carbon bonds from high molecular weight hydrocarbons; metal sites for hydrogenation, and dehydrogenation function of olefins, aromatic rings, oxygen compound, nitrogen compound, and sulfur compound (Ali, Tatsumi, and Masuda 2002).

Figure 1.5. Schematic representation of hydrocracking reaction.

(Mortensen et al. 2011)

1.2.4.5. Hydroisomerization

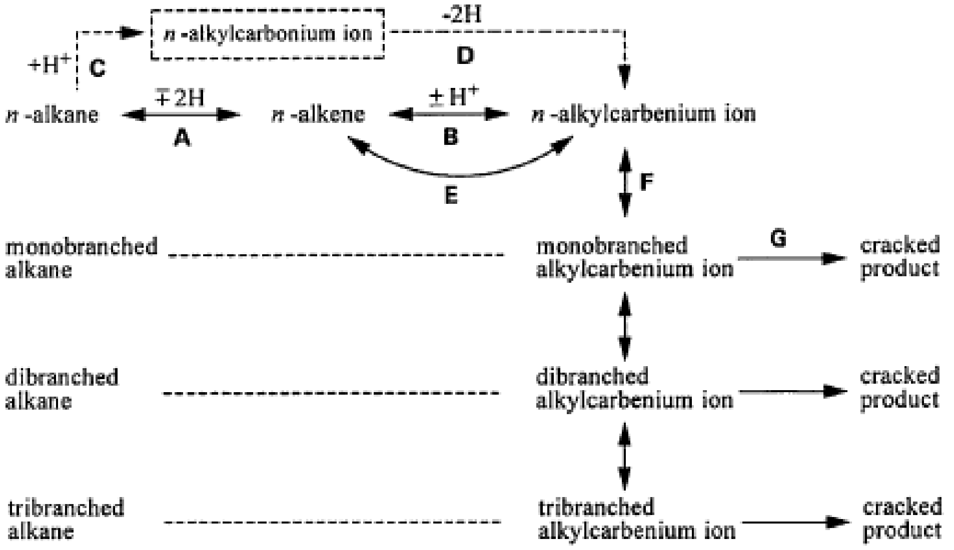
For the production of environmentally clean high-quality transportation fuels have process, the hydroconversion of long-chain paraffin is a well-established process that plays an important role in the petroleum industry (Chen, Li, Chen, Liu, and Liang 2018). The purpose of hydroisomerization to raise the cold flow plugging point, and cetane number is applied to increasing the isomer content in the diesel. Isomerization of C_7-C_{15} paraffin applies to production of diesel fuel with high cetane number, and improved cold flow properties, such as viscosity, pour point, and freezing point (Deldari 2005). Hydroisomerization Figure 1.6. used bifunctional catalysts containing both metallic sites, and acidic sites for dehydrogenation-hydrogenation, and carbon-carbon bond rearrangement. Platinum (Pt) or palladium (Pd) over-acidic supports is verified to be useful for the hydroisomerization of n-paraffins (Chen, Li, Chen, Liu, Tsang, et al. 2018).

1.2.5. Catalyst for biodiesel upgrading

1.2.5.1. ZSM-5

Zeolites have been normally used as ion-exchangers, adsorbents, and heterogeneous catalysts or catalyst supports in petrochemical industries, owing to inherent acidity, large surface area, and great hydrothermal stability (Song et al. 2017). Zeolites are crystalline, microporous three-dimensional aluminosilicates, comprised of corner-sharing TO_4 tetrahedra (T = Si, Al). The normal formula is $M_{x/n}[(AlO_2)_x(SiO2)_y]_zH_2O$, where M is an extra-framework cation that balances the anionic charge of the framework. The oxygen atoms are doubly-bridging, and connect two metal centers; the tetrahedra are arranged into n-membered rings, where n = 4 or larger. A six-membered ring, for example, contains six "T-atoms" (Si or Al), and six oxygen atoms.

For simplification, the latter is ignored in this nomenclature, as well as in structural representations of zeolites, where metal centers are joined by a straight line (http://chemiris.chem.binghamton.edu/chem445/zsm5/zsm5.htm).



A : Hydrogenation-dehydrogenation on metallic sites.

B : Protonation-deprotonation on acid sites.

C : Addition of proton to form alkylcarbonium ion on acid sites.

D : Dehydrogenation to form alkylcarbenium ion.

E : Competitive adsorption-desorption of alkene and carbenium ion on acid sites.

F : Rearrangement of alkylcarbenium ion.

G : Cracking of alkylcarbenium ion.

Figure 1.6. Modified bifunctional pathways of hydroisomerization and cracking of n-paraffins. (Deldari 2005)

1.2.5.2. 10% Ni/HZSM-5

HZSM-5 has been widely applied in the oil cracking process of organic liquid fuel production giving generally aromatic hydrocarbon due to its strong acidity pore size, and shape-selective (Charusiri, Yongchareon, and Vitidsant 2006). HZSM-5 zeolite can be modified by integration of metal or metal oxides in order to get catalysts for selective hydrocarbon conversions. Nickel on HZSM-5 has been found to be active in the aromatization, hydrocracking, and isomerization of hydrocarbon (Yin, Zhao, and Liu 2005). The primal HZSM-5 was previously used to hydrotreat vegetable oils for producing liquid alkane fuels, but an important number of aromatics and violent carbon deposition were observed, while NiMo supported on HZSM-5, significantly cracking C_1-C_4 alkanes and dehydrogenated olefins were obtained. Recently, an investigation showed that transition metal supported HZSM-5 catalysts presented an excellent performance in hydrodeoxygenation of xylitol to gasoline (N. Shi et al. 2012).

1.2.5.3. Amberlyst 15

The production of biodiesel from raw material is high in FFA commonly used acid catalyst such as sulfuric acid is a homogeneous acid catalyst for esterification. The use of a homogeneous acid catalyst causing trouble in recovery and produces toxic (Park, Kim, and Lee 2010). Heterogeneous catalysts reduce these problems as they are slight of recover, and operate with mild conditions in its use (Hykkerud, and Marchetti 2016). Amberlyst-15, an ion exchange resin catalyst functionalized with sulfonic acid groups, has been extensively used as a solid catalyst (Jeon et al. 2016).

Table 1.3. Properties of Amberlyst 15.

Properties	**Value**
Type	Strong acid
Ionic form	Hydrogen
Surface area (m^2/g)	53
Concentration of acid site (meq/g)	4.7
Temperature limit (°C)	120
Moisture content (wt.%)	≤1.6%

1.2.6. Response surface methodology (RSM)

Response surface methodology (RSM) is a technique for experimental designing, model building, evaluating the effects of many determinants, and accomplishing the optimal conditions for desirable responses with the limit of the number for experiments. The advantage of RSM show how a specific response is affected by a given set of input parameters over some specified region, and what input values will be given a maximum or minimum for a specific response. RSM useful for determining optimal conditions in a variety of fields; chemical industry, physical, and engineering sciences, clinical, biological, and social sciences (Khuri 2001; Andre I. Khuri, John A. Cornell 2019).

Response Surface Methods (RSM), that to be applied in this research, present a series of experimental designs, and multiple regression-based techniques that are used to analyses problems response is constraint by several factors, and measure the quality characteristics of the system. RSM technique is based on sequential steps using two-level, and three-level factorial designs to identify important variables by passing on the characteristics of the response surface by the polynomial model and using that model to show the direction of optimum (Nelson, P. R., Coffin, M., & Copeland 2003).

The quadratic (second-order) polynomial model is suitable to a parametric model and is defined as a sum of all linear, quadratic, and couple cross-product terms between predictors. That is the approximating function shown in Equation (1.7).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{j=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{j=i+1}^{k} \beta_{ij} X_i X_j + \varepsilon \qquad (1.7)$$

Where Y is the predicted response used as a dependent variable

k is the number of variables studied in the experiments

β_0 is the intercept (grand mean)

β_i is the linear coefficient

β_{ii} is the quadratic coefficient

β_{ij} is the interaction coefficient

X_i and X_j are the independent variables

ε is the error of the model

The RSM's design process is as follows (Aslan, and Cebeci 2007):

1) Designing a series of experiments for adequate, and reliable measurement of the response of interest.

2) Developing a mathematical model of the second-order response surface with the best fittings.

3) Finding the optimal set of experimental parameters that produce a maximum or minimum value of the response.

4) Representing the direct, and interactive effects of process parameters through two, and three- dimensional plots.

It is widely accepted that used experimental designs in manufacturing companies are full, and fractional factorial designs, those study the joint effect of the factors or process parameters on a response. A full factorial designed (FFD) experiment, which was applied in this research study, consists of all feasible combinations of levels for all factors. The total number of experiments for studying k factors at 2-levels is 2^k (Antony 2014).

1.3. Research objectives

1.3.1. To find the best condition of biodiesel upgrading from biodiesel using palm fatty acid distillate as raw material.

1.3.2. To study the effect of mass ratio of biodiesel to ethanol, reaction temperature, reaction pressure, and reaction time on percent increasing yield of ethyl-ester in a high-pressure batch reactor.

CHAPTER 2

RESEARCH METHODOLOGY

2.1. Material

2.1.1. Raw materials

PFAD was supplied by Chumporn Palm Oil Industry Public Company Limited, Thailand. The PFAD consisted of 93 wt.% FFA, and undesirable components: monoglycerides (MG), diglyceride (DG), triglyceride (TG), and impurity.

2.1.2. Chemicals

1.) Ethanol (C_2H_5OH) 99.5 wt.% commercial grade was obtained from Union Intraco (Thailand) Co., Ltd.

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

3.) Zeolite (ZSM-5) was obtained from Zeolyst International, Inc.

4.) Nickel Nitrate (Hexahydrate) 99% AR was obtained from Loba Chemie Pvt. Ltd.

5.) Amberlyst 15 hydrogen form was obtained from Merck Ltd., Thailand.

6.) Methyl heptadecanoate (C17:0) analytical standard was obtained from S.M.Chemical Supplies Co., Ltd.

2.2. Equipment

2.2.1. Biodiesel production

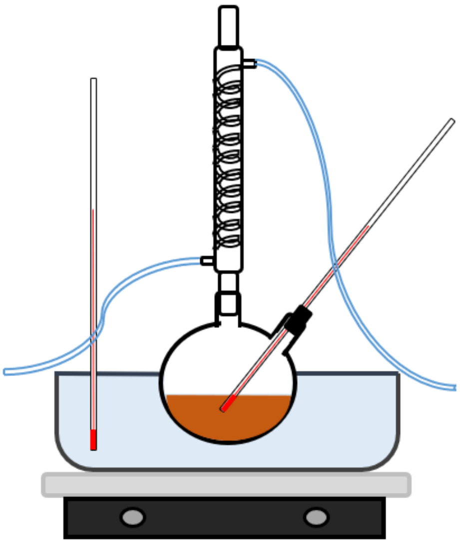


Figure 2.1. Biodiesel production equipment.

Biodiesel production equipment was set in Figure 2.1.

1.) The two-necked round bottom flask has a capacity of 500 mL was used for the batch experiment.

2.) Heater, stirrer, and temperature controller sets were used as the temperature controlling system.

3.) The condenser was used for condense ethanol.

2.2.2. Biodiesel upgrading

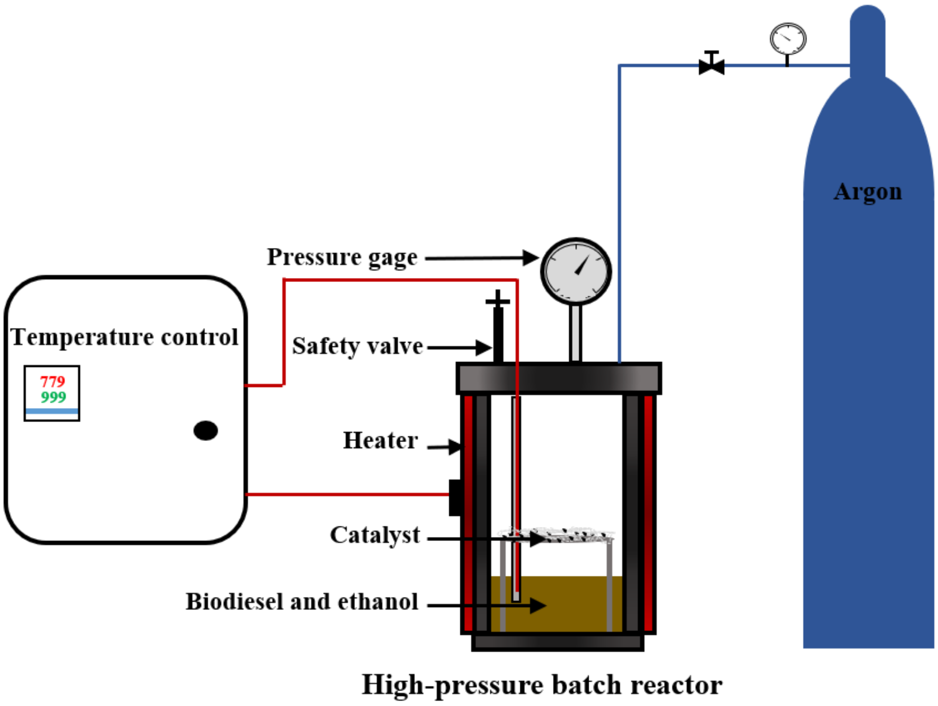


Figure 2.2. Upgrading biodiesel equipment

Upgrading biodiesel equipment was set in Figure 2.2.

1.) A high-pressure batch reactor has a capacity of 1000 mL (diameter 10.1 cm and high 13.5 cm)

2.) A ceramic cylinder heater 2500 W and temperature controller was used as the temperature controlling system.

2.3. Methodology

Batch high-pressure reactor for biodiesel upgrading produces from PFAD biodiesel. Batch process of esterification for produces is raw material was applied from an interesting result of batch process of ethyl ester by esterification from PFAD with ethanol research (Kanjaikaew, Tongurai, and Chongkhong 2015). And another interesting research (Kanjaikaew et al. 2017), ethyl ester production with two-step esterification of palm fatty acid distillate use of sulfuric acid as catalyst was kept constant at 2 wt.% of FFA in the first-step esterification. Batch high-pressure reactor for biodiesel upgrading has 4 factors; mass ratio of biodiesel to ethanol, reaction temperature, reaction pressure, and reaction time that affected procedure were analyzed by to find the best condition.

2.3.1. Catalyst preparation

Preparation of 10% Ni/HZSM-5 is using ZSM-5 zeolites with a SiO_2/Al_2O_3 ratio of 30, and 405 m^2/g of surface area. ZSM-5 zeolites in the ammonium form were calcined in the air at 550°C for 4 hours to HZSM-5 (Yang, Kumar, and Apblett 2016). Then, the zeolite catalyst was further promoted with Ni metal 10 wt.% by wet impregnation method using aqueous solutions of $Ni(NO_3)_2 \cdot 6H_2O$. Next, the catalysts were dried at 103°C for 12 hours and calcined at 600°C for 5 hours (Iliopoulou et al. 2012). Amberlyst 15 was dried at 105°C for 3 hours prior to use (Zhang et al. 2010). After preparing 10% Ni/HZSM-5 catalyst, the properties of 10% Ni/HZSM-5 were characteristic by x-ray fluorescence (XRF) to specify the components in the catalyst and verify the amount of nickel added.

2.3.2. Biodiesel production using PFAD

Base on the batch process of ethyl ester by esterification from palm fatty acid distillate with ethanol (Kanjaikaew, Tongurai, & Chongkhong, 2017), the condition with interesting experimental results is 7:1 molar ratio of ethanol to free fatty acid (FFA), 70 °C reaction temperature, and 70 minutes reaction time. The esterification process was carried in a 500 mL two-neck round-bottom flask. Preheated PFAD, and poured into the flask, and heat up to reaction temperature 70°C. Reaction time was 70 minutes after pouring of ethanol, and sulfuric as catalyst was kept constant at 4 wt.% of FFA into the flask. After that, poured into the separating funnel. The ethyl ester phase was washed with water, and this phase was heated for evaporate water. This process was repeated in order to get enough biodiesel for the next step in high-pressure batch reactor. The raw material biodiesel for upgrading in a high-pressure batch reactor called PFAD biodiesel.

2.3.3. Upgrading PFAD biodiesel

This part was to investigate the effect of factors on the reaction for biodiesel upgrading from biodiesel. Independent variables for this biodiesel upgrading were mass ratio of biodiesel to ethanol; 0.56:1, 1.12:1, and 1.69:1 (volumetric ratio of biodiesel to ethanol; 0.5:1, 1:1, and 1.5:1), reaction temperature; 160, 205, and 250 °C, reaction pressure; 10, 15, and 20 bar, reaction time; 8,10, and 12 hours, and 10% Ni/HZSM-5 as catalyst kept constant at 5 wt.% base on biodiesel.

In high-pressure batch reactor, biodiesel and ethanol base on volumetric ratio pour into a batch reactor, and the catalyst was placed on the stand in a batch reactor Figure 2.2. Then, reactor was heated up to target temperature and pressure. After the target condition was reached, the reaction time was started. Temperature and pressure were kept constant throughout the reaction time. When the reaction time has elapsed, the heater will stop heating, and set aside for room temperature, and atmospheric pressure. A batch reactor was opened, and the liquid in a batch reactor was analyzed in order to find the amount of increasing yield of ethyl-ester.

2.3.4. Experimental design and the best condition based on response surface methodology

The number of experiments was designed by using RSM with FFD, and the individual significance of factors was measured as the result of a batch experiment. The FFD was operated by determining four dependent factors at two different levels. These variables and their values defined by RSM were shown in Table 2.1. There are 27 experiments from the FFD method. In which each experiment is carried out at various variables to find the relationship in each variable that affects to increasing yield of ethyl-ester as shown in Table 2.2

Table 2.1. Factors and their levels in full factorial design.

Factors	Symbol	Lower level (-1)	Upper level (+1)
PFAD Biodiesel: EtOH (mass ratio)	X_1	0.56	1.69
Reaction temperature (°C)	X_2	160	250
Reaction pressure (bar)	X_3	10	20
Reaction time (hrs.)	X_4	8	12

Table 2.2. Experimental from the FFD method for reaction in high-pressure batch reactor.

Run	Parameter				Increasing yield of ethyl-ester (Y, %)
	X_1 (Mass ratio of Biodiesel: EtOH)	X_2 (°C)	X_3 (bar)	X_4 (hrs.)	
1	-1	-1	-1	-1	
2	-1	-1	-1	1	
3	-1	-1	1	-1	
4	-1	-1	1	1	

Run	Parameter				Increasing yield of ethyl-ester (Y, %)
	X_1 (Mass ratio of Biodiesel: EtOH)	X_2 (°C)	X_3 (bar)	X_4 (hrs.)	
5	-1	0	0	0	
6	-1	1	-1	-1	
7	-1	1	-1	1	
8	-1	1	1	-1	
9	-1	1	1	1	
10	0	-1	0	0	
11	0	0	-1	0	
12	0	0	0	-1	
13	0	0	0	0	
14	0	0	0	0	
15	0	0	0	0	
16	0	0	0	0	
17	0	0	1	0	
18	0	1	0	0	
19	1	-1	-1	-1	
20	1	-1	-1	1	
21	1	-1	1	-1	
22	1	-1	1	1	
23	1	0	0	0	
24	1	1	-1	-1	
25	1	1	-1	0	
26	1	1	1	-1	
27	1	1	1	1	

2.3.5. Studies of gas product from reaction

After reaction under the best condition is finished, collect gas samples for analyzing the gas components, and measuring the amount of gas. Gas-phase product was analyzed with standards gases; hydrogen (H_2), methane (CH_4), and carbon dioxide (CO_2) by Gas chromatography-Thermal Conductivity Detector (TCD) (HP 6890), using HP PLOT-Q column (30 m x 0.53 mm x 40 μm). The initial temperature was operated at 250°C with split mode, and the carrier gas was helium.

2.3.6. Studies of effect on increasing yield of ethyl-ester using other catalysts

After reaction under the best condition from reaction between biodiesel, and ethanol with 10% Ni/HZSM-5 as catalyst, four parameters at the best condition were operated with other catalysts; HZSM-5, Amberlyst 15, and non-catalyst for studies of the effect on increasing yield of ethyl-ester using other catalysts.

2.3.7. Product analysis

2.3.7.1. Analysis of free fatty acid

The American Oil Chemists' Society Official (AOCS) Method Ca 5a-40 was used to determine the free fatty acid (FFA) by titration procedure, and conversion of FFA define as Equation (2.1):

$$\text{FFA conversion, \%} = (1 - A/A_0) \times 100 \qquad (2.1)$$

Where

A_0 is the initial FFA of material, and A is the residual FFA of product.

2.3.7.2. Analysis of acid value

The American Oil Chemists' Society Official (AOCS) Method Ca 3a-63 was used to determine the acid value by titration procedure.

2.3.7.3. Analysis of ester content

EN 14103 method was used to prepare the sample for determining ester content. Determination of ester content defines as Equation (2.2):

$$E = [(\Sigma A - A_{EI})/A_{EI}] \times [(C_{EI} \times V_{EI})/m] \times 100\% \qquad (2.2)$$

Where

E is ester content expressed as a mass fraction in percent

ΣA is total peak area from $C_{14:0}$ to $C_{24:1}$

A_{EI} is peak area of methyl heptadecanoate

C_{EI} is concentration, in mg/mL, of the methyl heptadecanoate solution

V_{EI} is volume, in mL, of the methyl heptadecanoate solution

m is mass, in mg, of the sample

Fatty acid ethyl ester (FAEE) content was analyzed by gas chromatography-Flame Ionization Detector (FID) (Agilent 6890 Plus GC), using Agilent 19091S-413 HP-5ms column (30 m x 0.32 mm x 0.25 µm). The detector temperature was 320°C, the injection volume was 1.0 µL, and the injector was operated at 280°C with a 50:1 split ratio. Temperature program: the initial temperature at 50°C for 1min, 1st ramp at 10°C/min to 240°C (hold for 5 min), 2nd ramp at 4°C/min to 300°C (hold for 10 min). The carrier gas was hydrogen at a constant flow rate of 1 mL/min.

2.3.8. Calculation methods

Percent increasing yield of ethyl-ester was calculated by ester content, and as following is the percent increasing yield of ethyl-ester defined as Equation (2.3):

$$\text{Increasing yield of ethyl-ester (wt.\%)}, Y = [(EP \times WP) - (EI \times WI)] / (EI \times WI) \times 100 \qquad (2.3)$$

Where

EP or ester product (wt.%) is the percent ester of liquid-ethanol after reaction in the high-pressure batch reactor at the best condition

WP or weight product (g) is weight of liquid-ethanol after reaction in the high-pressure batch reactor at the best condition

EI or ester initial (wt.%) is the percent ester at the mixture of PFAD biodiesel and ethanol

WI or weight initial (g) is weight of the mixture between PFAD biodiesel and ethanol before putting into the high-pressure batch reactor

CHAPTER 3

RESULT and DISCUSSION

3.1. Catalyst characterization

The elemental composition of the synthesized 10% Ni/HZSM-5 catalyst consists of four major elements: O, Si, Ni, and Al were in line with SiO_2/Al_2O_3 mole ratio equal to 30 of ZSM-5 zeolites, and nickel metal weight composition by 10% Ni/HZSM-5 preparation. The component of 10% Ni/HZSM-5 catalysts are as follows; O 46.693%, Si 37.355%, Ni 10.098%, and Al 2.351%. This result was strongly consistent with XRF analysis.

3.2. Biodiesel production

Combining the biodiesel produced in each batch, and analytical the FFA conversion is 95.06%, and the ester content base on the GC-FID analysis is 80.04 wt.%. Some properties of PFAD biodiesel is presented in Table 3.1. The results were shown properties of PFAD biodiesel; ester content 80.04 wt.%, viscosity 5.98 mm^2/s, and acid value 10.07 mgKOH/g cannot meet biodiesel standard EN 14214. Density 886.7 kg/m^3 and water content 0.032 wt.% can met standard EN 14214. Then biodiesel upgrading was further conducted and investigated.

Table 3.1. Properties of PFAD biodiesel.

Properties	Unit	Test method	Diesel	Biodiesel standard (EN 14214)	PFAD biodiesel
Ester content	wt.%	EN 14103	-	≥ 96.5	80.04
Density at 15°C	kg/m^3	ASTM D1298	820-845	860-900	886.7
Viscosity at 40°C	mm^2/s	ASTM D445	2-4.5	3.5-5.0	5.98
Water content	wt%	ASTM D6304	-	≤ 0.05	0.032
Calorific value	MJ/kg	ASTM D4809	44	-	39.03
Acid value	mgKOH/g	ASTM D664	-	≤ 0.5	10.07
Free fatty acid content	%FFA	AOCS Ca 5a-40	-	-	4.59

3.3. Experimental results and the best condition for biodiesel upgrading

When upgrading of biodiesel with high-pressure batch reactor for 8-12 hours over a temperature range 160-250°C under pressure 10-20 bar and the biodiesel to ethanol mass ratio around 0.56:1-1.69:1 (the biodiesel to ethanol volumetric around 0.5:1-1.5:1), it was found that the percentage of increasing yield of ethyl-ester responses were obtained from 27 experimental runs according to the full factorial design shown in Table 3.2. At the best condition was achieved at mass ratio of biodiesel to ethanol 0.56:1 (volumetric ratio of biodiesel to ethanol 0.5:1), reaction temperature 250°C, reaction pressure 10 bar, and reaction time 12 hours. The best increasing yield of ethyl-ester was 52.77% from the experiment, and 50.48% from the model prediction in the same run. The verified percent increasing yield of ethyl-ester was 52.48±0.34% which did not differ greatly. Accordingly, the best condition could be achieved by an experimental design by RSM.

Table 3.2. Experimental design and results of the increasing yield of ethyl-ester response for the reaction in high-pressure batch reactor.

Run	Parameter				Increasing yield of ethyl-ester (Y, %)	
	X_1 (Mass ratio of Biodiesel: EtOH)	X_2 (°C)	X_3 (bar)	X_4 (hrs.)	Experimental	Predicted
1	-1	-1	-1	-1	42.76	41.12
2	-1	-1	-1	1	33.89	35.82
3	-1	-1	1	-1	24.81	28.25
4	-1	-1	1	1	26.33	24.80
5	-1	0	0	0	37.01	34.96
6	-1	1	-1	-1	35.07	37.74
7	-1	1	-1	1	52.77	50.48
8	-1	1	1	-1	40.70	39.91
9	-1	1	1	1	18.77	21.56
10	0	-1	0	0	23.26	23.94
11	0	0	-1	0	28.62	30.49
12	0	0	0	-1	33.61	28.03
13	0	0	0	0	27.35	26.82
14	0	0	0	0	22.44	26.82
15	0	0	0	0	25.50	26.82
16	0	0	0	0	29.75	26.82

Run	Parameter				Increasing yield of ethyl-ester (Y, %)	
	X_1 (Mass ratio of Biodiesel: EtOH)	X_2 (°C)	X_3 (bar)	X_4 (hrs.)	Experimental	Predicted
17	0	0	1	0	27.76	23.15
18	0	1	0	0	29.36	29.70
19	1	-1	-1	-1	18.14	20.01
20	1	-1	-1	1	10.87	7.775
21	1	-1	1	-1	15.62	14.03
22	1	-1	1	1	17.70	19.69
23	1	0	0	0	14.66	18.68
24	1	1	-1	-1	23.70	21.34
25	1	1	-1	0	28.42	29.64
26	1	1	1	-1	19.12	21.84
27	1	1	1	1	17.33	15.09

3.4. Regression model, statistical analysis and response surface contour plots for percent increasing yield of ethyl-ester

From experimental, and predicted results shown in Table 3.3, regression analysis was used to derive the relationship between the increasing yield of ethyl-ester, and four independent parameters in the form of a polynomial equation model obtained in Equation (3.1).

$$Y = 26.82 - 8.142X_1 + 2.881X_2 - 3.672X_3 - 1.214X_4 + 0.420X_1X_2 + 2.658X_1X_3 + 0.582X_1X_4 - 1.428X_2X_3 + 0.702X_2X_4 - 1.650X_3X_4 - 1.070X_1X_2X_3 + 0.313X_1X_2X_4 + 2.005X_1X_3X_4 - 4.118X_2X_3X_4 \quad (3.1)$$

The analysis of variance (ANOVA) was used to verify the regression model for statistical significance. The ANOVA for the response surface model is shown in Table 3.4. The F_{signif} value of the model equal to 0.000151, which was less than 0.05, so the model was significant at a 95% confidence level. P-values lower than 0.05 represent that a given model variable concerned, and encourages significant towards the response.

Table 3.3. Estimated regression coefficients for regression model.

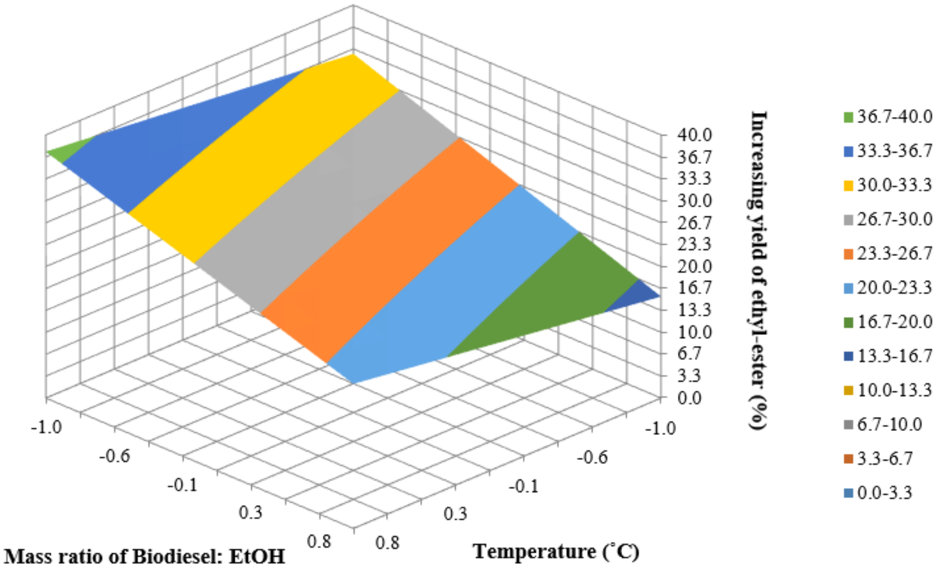
Source	Sum of square	P-value	Remark
Intercept	26.82	1.72761E-13	Significant
X_1	-8.142	1.48499E-06	Significant
X_2	2.881	0.00925	Significant
X_3	-3.672	0.00194	Significant
X_4	-1.214	0.229	Not significant
X_1X_2	0.420	0.678	Not significant
X_1X_3	2.658	0.01957	Significant
X_1X_4	0.582	0.566	Not significant
X_2X_3	-1.428	0.174	Not significant
X_2X_4	0.702	0.490	Significant
X_3X_4	-1.650	0.120	Significant
$X_1X_2X_3$	-1.070	0.300	Not significant
$X_1X_2X_4$	0.313	0.757	Not significant
$X_1X_3X_4$	2.005	0.06495	Not significant
$X_2X_3X_4$	-4.118	0.00129	Significant

Table 3.4. ANOVA for the response surface model.

Source	Sum of square	Mean square	F_0	F_{signif}	Degree of freedom
Regression	2171.1	155.08	9.9510	0.000151	14
Residual	187.01	15.58			12
Lack of fit error	158.47	17.61	1.8509	0.333	9
Pure Error	28.54	9.51			3
Corrected total	2358.1				26
R^2 = 0.921, adjusted R^2 = 0.828					

Figure 3.1.-3.3. presents the three-dimensional (3-D) response surface, and contour plots for the upgrading biodiesel demonstrate changes of the percent increasing yield of ethyl-ester by mass ratio of biodiesel to ethanol, reaction temperature, and reaction pressure which are the significance of the independent variables for the increasing yield of ethyl-ester within their experimental range while other variables were kept constant at its center point. The increasing yield of ethyl-ester can be enhanced by increasing reaction temperature, reducing mass ratio of biodiesel to ethanol, and reaction pressure in the high-pressure batch reactor, thus upgrading of biodiesel should select the condition that has the best value, and maximum yield 52.77%.

(A)



(B)

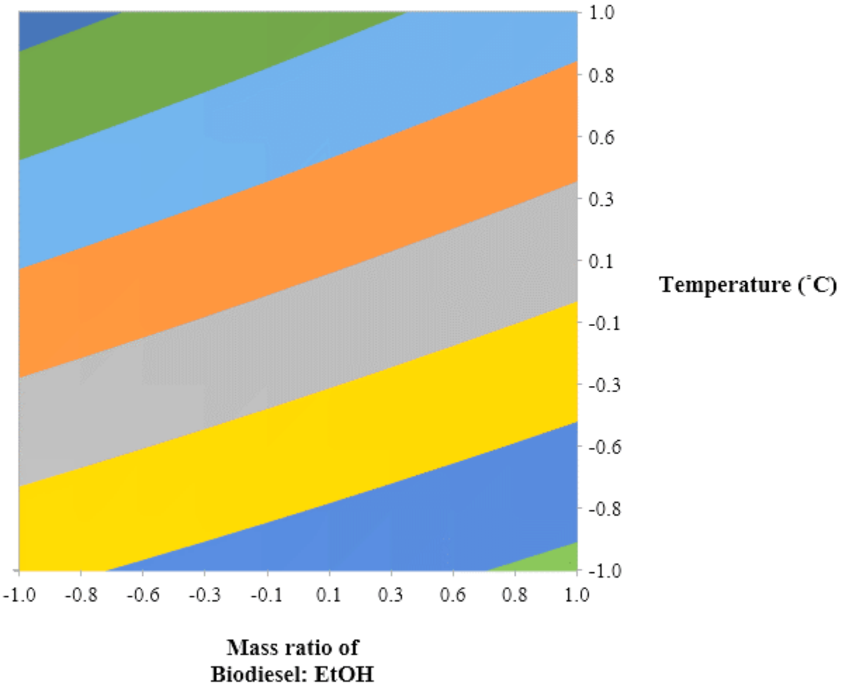


Figure 3.1. Effect of mass ratio of biodiesel to ethanol and reaction temperature on percent increasing yield of ethyl-ester (reaction pressure 10 bar and reaction time 12 hours); (A) 3-D respond surface plot and (B) 2-D contour plot.

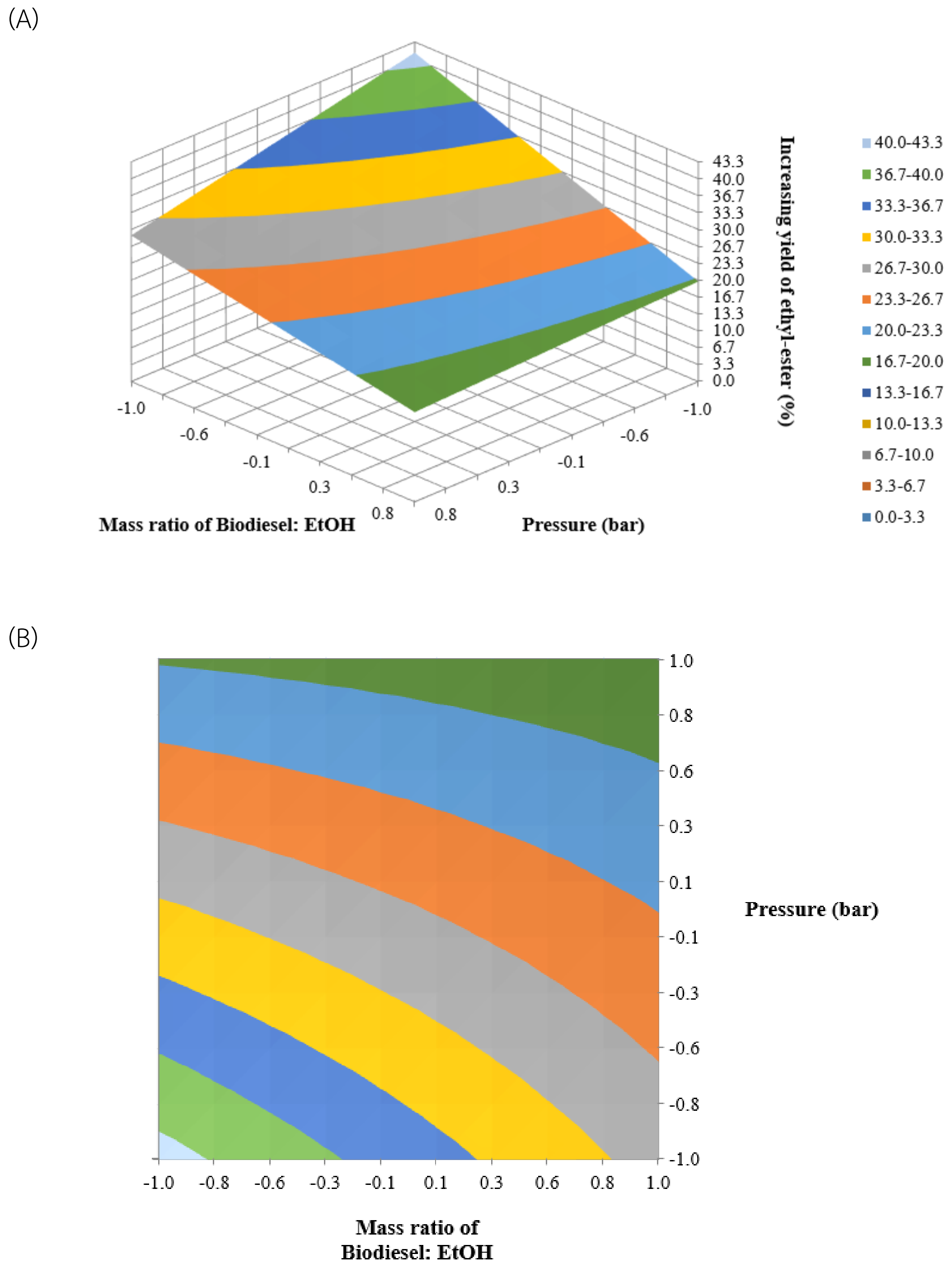


Figure 3.2. Effect of mass ratio of biodiesel to ethanol and reaction pressure on percent increasing yield of ethyl-ester (reaction temperature 250°C and reaction time 12 hours); (A) 3-D respond surface plot and (B) 2-D contour plot.

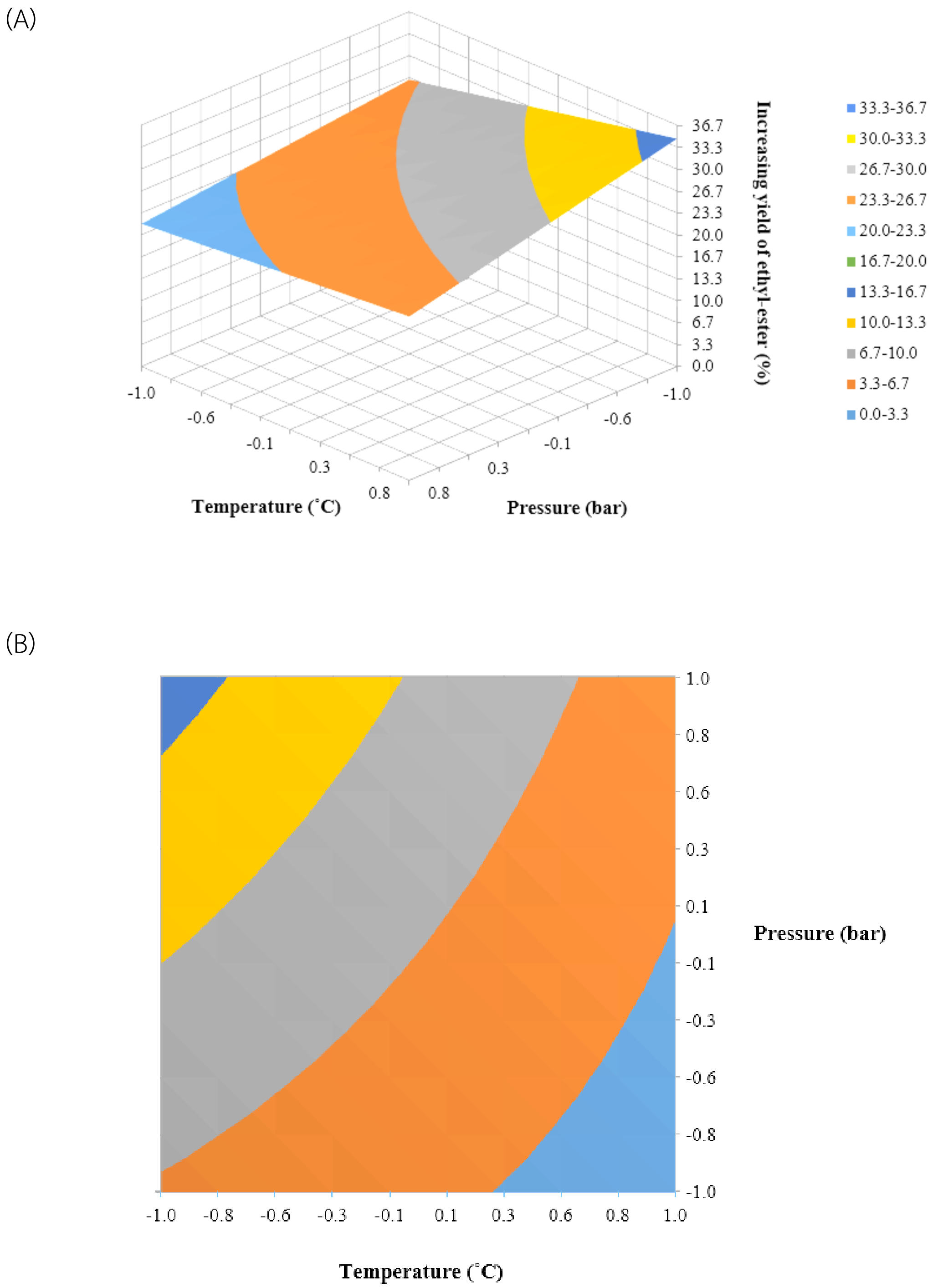


Figure 3.3. Effect of reaction temperature and reaction pressure on percent increasing yield of ethyl-ester (mass ratio of biodiesel to ethanol 0.56:1 and reaction time 12 hours); (A) 3-D respond surface plot and (B) 2-D contour plot.

3.5. Studies of gas product from reaction

From sampling analysis of production gas after cooling down to room temperature base on the best condition; mass ratio of biodiesel to ethanol 0.56:1 (volumetric ratio of biodiesel to ethanol 0.5:1), reaction temperature 250°C, reaction pressure 10 bar, and reaction time 12 hours, the quantitative of gas as percent area under the peak is carbon dioxide 13.12%, hydrogen 0.93%, and methane 0.20%. This result was strongly consistent with the decomposition of ethanol at temperature range 100°C to 250°C give hydrogen, methane, carbon dioxide, and carbon monoxide (Fatsikostas, and Verykios 2004).

3.6. Studies of effect on increasing yield of ethyl-ester using other catalysts

The effect catalyst on percent increasing yield of ethyl-ester was studied in the best condition. The result in Figure 3.4. showed that the percent increasing yield of ethyl-ester from reaction was operated with 10% Ni/HZSM-5 as a catalyst has the highest values, and followed by HZSM-5, Amberlyst 15, and non-catalyst respectively. By using 10% Ni/HZSM-5 and HZSM-5 as a catalyst, the values of the percent increasing yield of ethyl-ester are close while using Amberlyst 15 as a catalyst gives the percentage increasing yield of ethyl-ester less than about triple compare with using 10% Ni/HZSM-5, and HZSM-5 as a catalyst. This is probably because the Amberlyst 15 can only tolerate 120°C but at the best condition up to 250°C may cause the performance of Amberlyst15 greatly reduced.

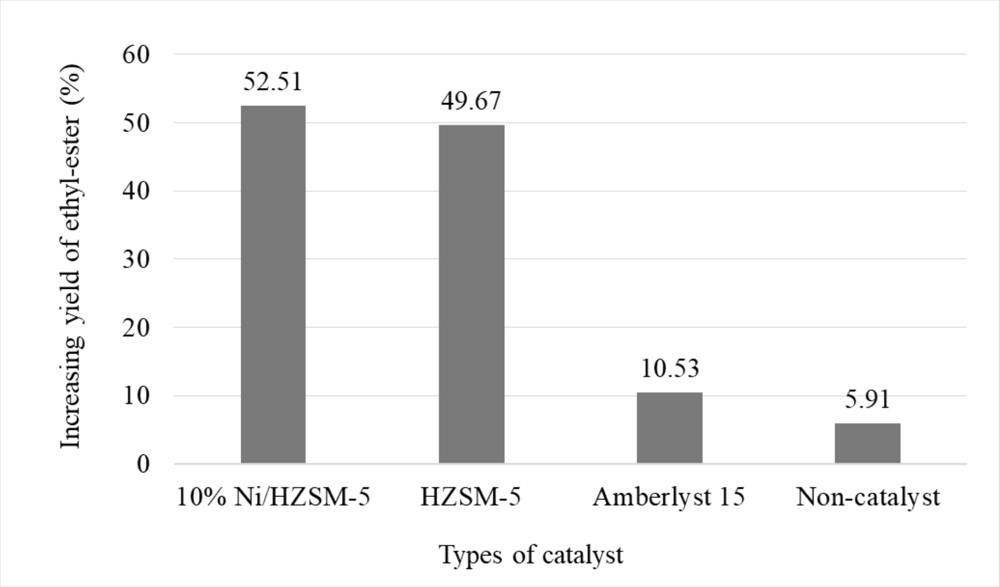


Figure 3.4. Effect of catalyst on percent increasing yield of ethyl-ester by the best condition from reaction between biodiesel and ethanol.

3.7 Analytical of product

A summary of the properties of PFAD biodiesel and upgrading of biodiesel in this work are presented in Table 3.5. As the percent increasing of ethyl-ester from the reaction was operated with 10% Ni/HZSM-5 and HZSM-5 as catalyst is in the same direction. Therefore, both properties of upgrading biodiesel with 10% Ni/HZSM-5 and upgrading biodiesel with HZSM-5 are investigated. FFA content reduced to half may be the result of esterification reaction by subcritical ethanol (Lermontov, and Yurkova 2009; Go et al. 2014; Sales, Ghirardi, and Jorquera 2017). The calorific value to decrease may be the result of short-chain hydrocarbon from catalytic cracking reaction and the increased water. Water content increases a lot in upgrade biodiesel may be the result of methanation reaction as part of the reaction to convert ethanol into hydrogen as shown in Equation (1.3) to Equation (1.5) (Mattos et al. 2012).

Table 3.5. Properties of PFAD biodiesel and upgrading biodiesel in this work.

Properties	Unit	Test method	Diesel	Standard: EN 14214	PFAD biodiesel	Upgrading biodiesel with 10% Ni/HZSM-5	Upgrading biodiesel with HZSM-5
Ester content	wt.%	EN 14103	-	$\geq$ 96.5	80.04	96.53	85.38
Density at 15°C	kg/m^3	ASTM D1298	820-845	860-900	886.7	874.7	884.50
Viscosity at 40°C	mm^2/s	ASTM D445	2-4.5	3.5-5.0	5.98	5.47	4.55
Water content	wt%	ASTM D6304	-	$\leq$ 0.05	0.032	0.05	0.05
Calorific value	MJ/kg	ASTM D4809	44	-	39.03	35.73	36.48
Acid value	mgKOH/g	ASTM D664	-	$\leq$ 0.5	10.07	5.02	6.09
Free fatty acid content	%FFA	AOCS Ca 5a-40	-	-	4.59	2.51	3.37

CHAPTER 4

CONCLUSIONS

Under high-pressure batch reactor for upgrading biodiesel derived from PFAD was successfully performed by partial hydrogenation using 10% Ni/HZSM-5 as a catalyst, and ethanol as a hydrogen source. The best condition for upgrading biodiesel derived from PFAD was followed: reaction temperature 250°C, pressure 10 bars, reaction time 12 hours, mass ratio of biodiesel to ethanol 0.56:1 (volumetric ratio of biodiesel to ethanol 0.5:1), and 5 wt.% of 10% Ni/HZSM-5 base on weight of biodiesel. The product of partial hydrogenation of biodiesel derived from PFAD was optimized using RSM with a maximum increasing yield of ethyl-ester 52.77 wt.%, and the percent ester content up to 96.53% which met the requirements of the international standard (EN14214). The model equation in terms of the variable parameters was pointed out that mass ratio of biodiesel to ethanol, temperature and pressure were significantly affected by the increasing yield of ethyl-ester in upgrading biodiesel from PFAD. Overall, the work demonstrated that increasing yield of ethyl-ester, and high conversion of FFA, partial hydrogenation using ethanol as a hydrogen source, and 10% Ni/HZSM-5 as catalyst was found to be an effective approach for the catalytic upgrading of biodiesel derived from PFAD.

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APPENDIX

APPENDIX A

CATALYST PREPARATION

A1. 10% Ni/HZSM-5 preparation

Find the amount of nickel nitrate (hexahydrate) in 10% Ni/HZSM-5 preparation

Molecular weight

$Ni(NO_3)_2•6H_2O$ = 290.8 g/mol

Ni = 58.69 g/mol

Basis 100 g of 10% Ni/HZSM-5 (10 g of Ni, and 90 g of HZSM-5)

If Ni 58.69 g in $Ni(NO_3)_2•6H_2O$ equal to 290.8 g

Ni 10 g in $Ni(NO_3)_2•6H_2O$ equal to (290.8/58.69) x 10 = 49.55 g

So, 49.55 g of nickel nitrate (hexahydrate) was used in 100 g of 10% Ni/HZSM-5 preparation

Find the amount of water in 10% Ni/HZSM-5 preparation

Basis 100 g of 10% Ni/HZSM-5 (10 g of Ni, and 90 g of HZSM-5)

If HZSM-5 0.101 g requires water amount of 0.1529 g

HZSM-5 90 g requires water amount of (0.1529/0.101)x90 = 136.25 g

So, 136.25 g of water was used in 100 g of 10% Ni/HZSM-5 preparation

APPENDIX B

BIODIESEL PRODUCTION

B1. Molecular weight

PFAD = 312.76 g/mol

Ethanol = 46.07 g/mol

Sulfuric acid = 98.08 g/mol

Fatty acid

- Myristic acid = 228 g/mol
- Palmitic acid = 256 g/mol
- Stearic acid = 284 g/mol
- Arachidic acid = 312 g/mol
- Palmitoleic acid = 254 g/mol
- Oleic acid = 282 g/mol
- Ecosenoic acid = 310 g/mol
- Tetracosenoic acid = 367 g/mol
- Linoleic acid = 280 g/mol
- Linolenic acid = 278 g/mol

Average of molecular weight of FFA

= 93/[(1/228) + (45.6/256) + (3.8/284) + (0.3/312) + (0.2/254) + (33.3/282) + (0.2/310) + (0.6/367) + (7.7/280) + (0.3/278)] = 268 g/mol

Base on wt.% of FFA in PFAD = 93

B2. Density

PFAD = 0.897 g/cm^3

Ethanol = 0.789 g/cm^3

Sulfuric acid = 1.84 g/cm^3

B3. Batch biodiesel production

Find the amount of PFAD, and ethanol in batch biodiesel production 7:1 molar ratio of ethanol to free acid (FFA)

Base on wt.% of FFA in PFAD = 93

PFAD 100 g have FFA 93 g

FFA 93 g = 93/268 = 0.347 mol

Ethanol = 0.2974 x 7 = 2.0815 mol of ethanol = 95.89 g

Find the amount of sulfuric acid in batch biodiesel production Sulfuric acid 2 wt.% of FFA

Sulfuric acid = (2 x 0.93 x 100)/98 = 1.90 g

Sulfuric acid 4 wt.% of FFA

Sulfuric acid = (4 x 0.93 x 100)/98 = 3.80 g

APPENDIX C

BIODIESEL UPGRADING

C1. Calculation of percent increasing yield of ethyl-ester

For example, calculations at the best condition for biodiesel upgrading

$$\text{Increment of ester (\%)} = \frac{[\text{Ester product x Wight product}] - [\text{Ester initial x Wight initial}]}{[\text{Ester initial x Wight initial}]} \text{ x } 100$$

Where

EP or ester product (wt.%) is the percent ester of liquid-ethanol after reaction in the high-pressure batch reactor at the best condition

WP or weight product (g) is weight of liquid-ethanol after reaction in the high-pressure batch reactor at the best condition

EI or ester initial (wt.%) is the percent ester at the mixture of PFAD biodiesel and ethanol

WI or weight initial (g) is weight of the mixture between PFAD biodiesel and ethanol before putting into the high-pressure batch reactor

C2. Ester content of biodiesel upgrading

Calculations at the best condition for biodiesel upgrading.

Ester product = 56.75 % (Base on biodiesel and ethanol)

Ester product 12.91 g -> Oil 7.59 g, and Ethanol 5.32 g

Oil = (4.59/12.91) x 100 = 58.79 %

So, 58.79 % consist of ester, and hydrocarbon

56.75 % consist of ester

Ester in oil = (56.75/58.79) x 100 = 96.53 %

APPENDIX D

ANALYTICAL METHODS

D1. Determination of ester content

This method determines the percentage of ester present in the sample by gas chromatography with internal calibration (methyl heptadecanoate) method (EN 14103). Each sample (approximately 50 mg) was dissolved in a 1.5 ml vial with 1 mL of methyl heptadecanoate solution (10 mg/mL).

Fatty acid ethyl ester content was analyzed by gas chromatography-flame ionization detector (Agilent 6890 Plus GC), using Agilent 19091S-413 HP-5ms column (30 m x 0.32 mm x 0.25 μm). The detector temperature was 320 °C, the injection volume was 1.0 μL, and the injector was operated at 280 °C with a 50:1 split ratio. Temperature program: initial temperature at 50 °C for 1min, 1st ramp at 10°C/min to 240 °C (hold for 5 min), 2nd ramp at 4 °C/min to 300 °C (hold for 10 min). The carrier gas was hydrogen at a constant flow rate of 1 mL/min.

D2. Determination of free fatty acid by titration

This method determines the free fatty acids existing in the sample by acid-base titration method (AOCS Ca 5a-40). Each sample (approximately 1-10 g) was dissolved in 50 mL of isopropanol, and titrated with 0.1 M sodium hydroxide solution, using phenolphthalein solution as an indicator.

D3. Determination of acid value by titration

This method determines the acidic constituents in the sample by titration method (ASTM D664). Each sample (approximately 1-5 g) was dissolved in 25 mL of isopropanol, and titrated with 0.1 M potassium hydroxide solution, using phenolphthalein solution as an indicator.

D4. Component analysis in liquid phase product

After removing the ethanol from the liquid phase product, it was analyzed by gas chromatography-mass spectrometry, using HP-5ms Ultra Inert column (30 m x 250 μm x 0.25 μm). the injection volume was 1.0 μL with a 50:1 split ratio. Temperature program: the initial temperature at 50 °C for 1min, 1st ramp at 10°C/min to 240 °C (hold for 5 min), 2nd ramp at 4 °C/min to 300 °C (hold for 10 min).

D5. Gas-phase product analysis

Gas-phase product from reactor was analyzed by gas chromatography (HP 6890), using HP 19095P-004 HP-PLOT Q column (30 m x 530 um x 40 um). The detector temperature was 250 °C, and the injector was operated at 250 °C with a 50:1 split ratio. The carrier gas was helium.

VITAE

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Educational Attainment

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Bachelor of Engineering (Chemical Engineering)	Prince of Songkla University	2018

Scholarship Awards during Enrolment

Engineering Graduate Scholarship

Graduate School Research Support Funding for Thesis

List of Proceedings

Title	Upgrading Biodiesel Derived from Palm Fatty Acid Distillate (PFAD) using 10%Ni/HZSM-5 as Catalyst
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