

**DEVELOPMENT OF BIO-JET FUEL PRODUCTION
USING PALM KERNEL OIL AND ETHANOL**



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การพัฒนาการผลิตเชื้อเพลิงอากาศยานชีวภาพจากน้ำมันเนื้อเมล็ดปาล์ม
และเอทานอล

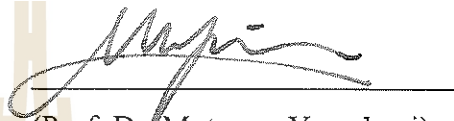


วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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Suranaree University of Technology has approved this thesis submitted in partial fulfillment of the requirements for a Master's Degree.

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จุดประสงค์หลักของงานวิจัยนี้คือ เพื่อศึกษาความเป็นไปได้ในการใช้น้ำมันเนื้อเมล็ดปาล์ม
และเอทานอลเป็นสารตั้งต้นหลักในการผลิตน้ำมันเชื้อเพลิงชีวภาพสำหรับเครื่องยนต์เจ็ท
ด้วยกระบวนการกลั่นลำดับส่วน โดยปฏิกิริยา ทรานส์เอสเทอร์ฟิเคชันเกิดจากการผสมระหว่าง
น้ำมันปาล์มและเอทานอลโดยใช้โพแทสเซียมไฮดรอกไซด์เป็นตัวเร่งปฏิกิริยา โดยได้ผลิตภัณฑ์
ซึ่งเป็นผลพลอยได้คือ เอทิลเอสเทอร์ของกรดไขมัน (FAEE) ที่รวมตัวกับกลีเซอรอล งานวิจัยนี้
ได้ศึกษาตัวแปรที่ส่งผลกระทบต่อปฏิกิริยา ทรานส์เอสเทอร์ฟิเคชันของปาล์มน้ำมันและทดลอง
ภายใต้ห้องปฏิบัติการอีกด้วย ด้วยเหตุนี้ จึงทำให้สามารถใช้การวิเคราะห์พื้นผิวตอบสนอง
เพื่อศึกษาปัจจัยสำคัญที่มีผลต่อปริมาณการผลิตของเอทิลเอสเทอร์ การหาเงื่อนไขที่เหมาะสมที่สุด
ในกระบวนการผลิตถูกกระทำ โดยการประยุกต์ใช้การออกแบบแฟคตอเรียลและวิธีการ
พื้นผิวตอบสนอง ผลกระทบของพารามิเตอร์ที่หลากหลายรวมถึงสัดส่วนเชิงโมลระหว่างน้ำมัน
และเอทานอล อุณหภูมิ เวลาที่ทำปฏิกิริยา และความเข้มข้นของตัวเร่งปฏิกิริยา อยู่ในช่วง 1:6
ถึง 1:12; 40 °C ถึง 60 °C; 60 ถึง 120 นาที และ 0.5 ถึง 1.5% ตามลำดับ งานวิจัยนี้ได้แสดงให้เห็นว่า
วิธีการพื้นผิวตอบสนองนั้นเป็นวิธีการที่เหมาะสมสำหรับการหาค่าที่เหมาะสมที่สุดของเงื่อนไข
ปฏิบัติการ เพื่อที่จะได้รับปริมาณผลผลิตของเอทิลเอสเทอร์สูงสุด พารามิเตอร์ที่เหมาะสมที่สุด
สำหรับการผลิตเอทิลเอสเทอร์ของกรดไขมันที่มีความเข้มข้นสูงสุด อยู่ที่สัดส่วนเชิงโมล
ของเอทานอลต่อน้ำมันเท่ากับ 9:1 อุณหภูมิ 50 °C ความเข้มข้นของตัวเร่งปฏิกิริยาเท่ากับ 1%
ภายในเวลาทำปฏิกิริยา 120 นาที ภายหลังจากได้รับเงื่อนไขที่เหมาะสมที่สุดแล้ว จะถูกนำไปผลิต
จำนวน 120 ลิตรด้วยเครื่องทำปฏิกิริยา ทรานส์เอสเทอร์ฟิเคชันในห้องปฏิบัติการ กระบวนการ
กลั่นลำดับส่วนถูกใช้เพื่อที่จะให้ได้เอทิลเอสเทอร์ของกรดไขมัน C8-C14 ซึ่งกระบวนการนี้
ถูกจำลองด้วยโปรแกรม Aspen Plus V8.4 ภายหลังกระบวนการกลั่นพบว่า น้ำมันเชื้อเพลิงชีวภาพ
สำหรับเครื่องยนต์เจ็ทนี้ มีความเข้มข้นเท่ากับ 96.84 wt.% ซึ่งอยู่ในช่วงที่ยอมรับได้ เมื่อเปรียบเทียบกับ
ค่าที่การคาดการณ์ไว้ด้วย โปรแกรม Aspen (97 wt.%) จึงสรุปได้ว่า การกลั่นลำดับส่วน
คือวิธีการที่ดีที่สุดในการผลิตน้ำมันเชื้อเพลิงชีวภาพสำหรับเครื่องยนต์เจ็ท

คุณสมบัติของเอทิลเอสเทอร์ของกรดไขมันถูกวิเคราะห์ด้วยวิธีการต่างๆ รวมถึงมาตรฐาน
ASTM และ EN เอทิลเอสเทอร์ที่ถูกผลิตด้วยสภาวะที่เหมาะสมนั้นมีคุณสมบัติที่ยอมรับได้
โดยมีซัลเฟอร์ (<0.0001 wt.%) เถ้าซัลเฟต (0.005 wt.%) กากคาร์บอน (0.02 wt.%) และฟอสฟอรัส

(<0.00008 wt.%) ต่ำกว่ามาตรฐาน อย่างไรก็ตาม ค่าความร้อนของน้ำมันเชื้อเพลิงชีวภาพสำหรับเครื่องยนต์เจ็ท (38.3 MJ/kg^{-1}) มีค่าใกล้เคียงกับค่าความร้อนของน้ำมันเชื้อเพลิงเครื่องยนต์เจ็ททั่วไป (42 MJ/kg^{-1}) จุดวาบไฟของน้ำมันเชื้อเพลิงชีวภาพสำหรับเครื่องยนต์เจ็ทเท่ากับ 105°C ซึ่งสูงกว่าจุดวาบไฟของน้ำมันเครื่องยนต์เจ็ททั่วไปซึ่งเท่ากับ 51°C ด้วยเหตุนี้ น้ำมันเชื้อเพลิงชีวภาพสำหรับเครื่องยนต์เจ็ทจึงมีความปลอดภัยและไม่เป็นอันตรายในการขนส่งรวมถึงการจัดเก็บ นอกจากนี้ น้ำมันเชื้อเพลิงชีวภาพยังมีการปล่อยแก๊ส CO, NO, HC ซึ่งเป็นมลพิษที่ต่ำ เนื่องจากการเผาไหม้ที่สมบูรณ์มากกว่าน้ำมันเชื้อเพลิงเครื่องยนต์เจ็ทแบบทั่วไป

สุดท้ายนี้ จึงสรุปได้ว่า น้ำมันเชื้อเพลิงสำหรับเครื่องยนต์เจ็ท เหมาะสมกับการเป็นน้ำมันทางเลือกโดยไม่จำเป็นต้องคิดแปลงอุปกรณ์ภายในเครื่องยนต์ใดๆ เนื่องจากเมทานอลที่ใช้ในการผลิตเชื้อเพลิงชีวภาพแบบทั่วไปนั้นมาจากฟอสซิล งานวิจัยนี้จึงเป็นนวัตกรรมการผลิตเชื้อเพลิงชีวภาพจากพลังงานหมุนเวียน 100% ซึ่งเกิดจากการนำน้ำมันปาล์มและเอทานอลมาผสม ซึ่งผลที่ได้คือน้ำมันเชื้อเพลิงชีวภาพสำหรับเครื่องยนต์เจ็ท



NHAN THI THUC TRUONG : DEVELOPMENT OF BIO-JET FUEL
PRODUCTION USING PALM KERNEL OIL AND ETHANOL.

THESIS ADVISOR : ASSOC. PROF. APICHAT BOONTAWAN, Ph.D.,
111 PP.

BIO-DERIVED JET FUEL/GAS TURBINE ENGINE/PALM KERNEL OIL/
TRANS-ESTERIFICATION/FATTY ACID ETHYL ESTER

The main objective of this study was to demonstrate the feasibility of using palm kernel oil and ethanol as main substrate for bio-jet fuel production process by fractional distillation. The transesterification reaction was carried out between palm kernel oil and ethanol in the presence of potassium hydroxide as catalyst, fatty acid ethyl ester (FAEE) was formed with glycerol as by-product. This research studies the variables affecting palm kernel oil trans-esterification and was carried out under laboratory conditions. Consequently, using response surface analysis, it was possible to study effect of key parameters on the ethyl ester yield conversion. Process optimization was accomplished by applying factorial design and response surface methodology. The effects of multiple parameters including molar ratio between oil and ethanol, temperature, residence time and concentration of catalyst were investigated in the range of 1:6 to 1:12; 40 to 60 °C; 60 to 120 minutes and 0.5 to 1.5 wt.%, respectively. This study clearly showed that response surface methodology was a suitable method to optimize the operating conditions in order to maximize the ethyl ester yield production. The optimum parameters for the highest concentration of fatty acid ethyl ester was achieved at molar ratio ethanol/oil 9:1, 50 °C with 1 wt.% of catalyst concentration within 120 minutes. The optimal conditions were then applied in 20 L trans-esterification reactor laboratory.

To purify fatty acid ethyl esters C8-C14 of the bio-jet production, the fractional distillation process from laboratory experimental and process simulation design using Aspen Plus V8.4 were carried out. As expected, high concentration of 96.84 wt.% bio-jet was purified from the distillation laboratory system. It was acceptable compared to the predicted result from the model of Aspen (97 wt.%), indicating that the fractional distillation was the best process to purify FAEE production with efficient column.

The FAEE properties were then analyzed by different methods including ASTM and EN standard. The ethyl ester which produced at optimum conditions had acceptable properties. It had lower sulfur content (<0.0001 wt.%), sulfated ash (0.005 wt.%), carbon residue (0.02 wt.%) and phosphorus (<0.00008 wt.%) than the limit standard for biofuel, but kinematic viscosity and heating value of jet fuel is some better relative to bio-jet 42 and 38.3 MJ/kg^{-1} , respectively. The flash point of bio-jet 105°C is higher than the conventional jet fuel 51°C , which is safe and non hazardous for transport purpose and constituted a safety guarantee from the point view of storage. Furthermore, bio-jet fuel was performance with lower emission of CO, NO, HC with the completely burning compared to the conventional jet fuel.

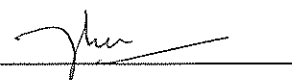
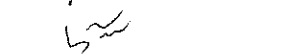
Finally, we can conclude which bio-jet will be a suitable alternative for replacement of gas turbine engine without any modification in engine. Since methanol used for biofuel production is produced from fossil fuels, the innovation in this study is the combined of palm kernel oil and ethanol to produce a bio-jet fuel from 100% renewable energy sources.

School of Biotechnology

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Student's Signature

Advisor's Signature

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LIST OF ABBRVIATIONS

% (w/v)	=	Percentage weight by volume
ANOVA	=	Analysis of variance
ASTM	=	American Section of the International Association for Testing Materials
CCD	=	Central composite design
cm ²	=	Centimeter square
EN	=	European standard
F	=	F-value, test statistic of F distribution
FAEE	=	Fatty acid ethyl ester
g	=	Gram
kg/m ³	=	Kilogram per cubic meter
mbar	=	Millibar
min	=	Minute
MJ/kg ⁻¹	=	Mega joule per kilogram
°C	=	Degree Celsius
°F	=	Degree Fahrenheit
p	=	P-value, smallest level of significance that would lead
R ²	=	Coefficient of determination
rpm	=	Revolutions per minute
RSM	=	Response surface methodology
wt.%	=	Weight by weight

CHAPTER I

INTRODUCTION

1.1 Significance of the study

The limited fossil fuel resources along with the need to reduce greenhouse gas emissions were major impulses to the development of alternative fuels. Nowadays, a large amount of biodiesel is produced around the world; however, it was not used for every types of engine. While biodiesel is used worldwide as a renewable replacement of diesel fuel, no comparable replacement is available for jet engine fuel (kerosene) at sufficient volume. Since biodiesel is too heavy for running the gas turbine engine, there are several projects that intend to produce the replacement of jet fuel, which is bio-derived jet fuel (bio-jet fuel). Bio-jet is an alternative, renewable fuel used for gas turbine engine which the main focus is not only in air traffic, but also in power. Modern gas turbines burn the fuel at very high temperatures and can reach very high speeds with a high stability and short start-up time (<http://www.bladonjets.com/technology/gas-turbines/>). It is a special liquid petroleum that is required higher energy contents per unit volume than gas and easier to handle and distribute when compare to solids (Dunn *et al.*, 2010 and Dunn *et al.*, 2011). Small variations of gas turbines have been used in hybrid vehicles, the company Jaguar, to charge the battery of the electric motor, and so the usage was significantly increased. The Jaguar C-X75 (Figure 1) showed the developers that even with the use of electric motors, a very high performance can be achieved. Several studies indicated that the synthetic alcohols (bioethanol or methanol),

synthetic hydrocarbons from sugars and hydrogen could be possibly used as gas turbine alternative fuels. However, the usage of these fuels is still in limitation since the high quality requirements for the commercial aviation fuels strictly limit the wide application of these alternative fuels for all exiting aircrafts (Gupta *et al.*, 2010; Waynick, 2001). Moreover, with the declining petroleum resources and large fluctuation in the price of fuels, combined with the increasing in environmental concern and the current economic downturn, it is necessary to develop renewably clean and energy efficient technologies for producing sustainable products of bio-jet fuels (Lee *et al.*, 2009; Mayor and Tol, 2010; Pejovic *et al.*, 2008 and Saidur *et al.*, 2009).

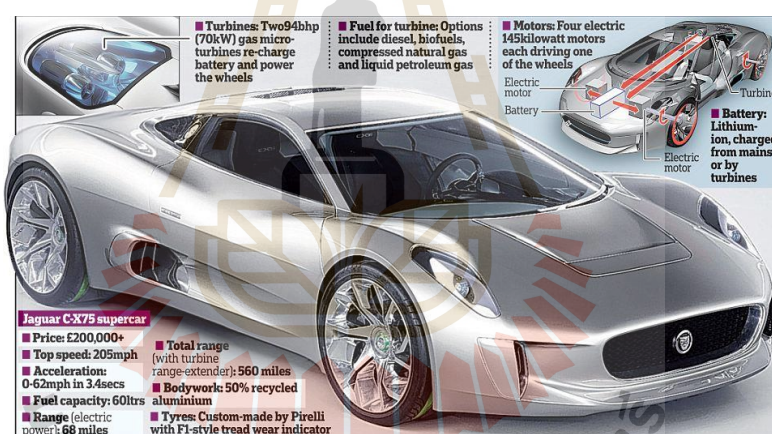


Figure 1.1 The electrically driven Jaguar C-X75 Blaydon Jet with gas turbines engine (http://i.dailymail.co.uk/i/pix/2010/09/30/article13162730B6848CD00005DC321_964x523.jpg).

Fuels were produced from the second generation of biomass sources including camelina, jatropha and algae, reducing the fuel's carbon footprint by 80% relative to jet fuel without competing for resources with food production (Bailis and Baka, 2010). Aviation liquid fuels can be derived from different materials by different methods (Edwards, 2003). One of these technologies is the conversion of vegetables oils as

agricultural sources into bio-jet fuel through trans-esterification reaction with ethanol to form fatty acid ethyl esters (FAEEs). Several feedstock sources have been used for producing FAEE such as palm oil, palm kernel oil, coconut oil, rapeseed oil, soybean oil, etc. Oil palm is the highest vegetable oil production in Thailand, followed by coconut oil and soybean oil (Attanatha *et al.*, 2004). Palm kernel oil (PKO) is obtained from the kernel oil of the palm fruit and it is located inside the hard shell. It is reported that palm oil production within Thailand in 2012 is approximately 0.64 million tons per year and still increased by the year. The oil comprises of various fatty acids ranging from medium chain to long chain fatty acids. As a result, the boiling point of FAEEs is expected to be different, and could be fractionated to produce bio-jet fuel production. Thus, it is pertinent to analyze the potential of palm kernel oil for bio-jet production.

In this work, a new feasible development of bio-jet production using palm kernel oil as a substrate was studied including optimization parameters for high conversion of fatty acid ethyl esters product from trans-esterification reaction between palm kernel oil and anhydrous ethanol, fractionation distillation of FAEE leads to the physicochemical properties of bio-jet fuel to meet the commercial jet fuel standard, and the engine testing coupled with the emission determination. Fuel characterization results for the produced PKO bio-jet through the ASTM and EN standard fuel tests are reported.

1.2 Research objectives

1.2.1 To optimize the conditions of trans-esterification reaction to achieve high conversion of fatty acid ethyl esters using palm kernel oil material as the main substrate with the reactant ethanol in the presence of potassium hydroxide as catalyst.

1.2.2 To design an efficient fractional distillation process of high purity of bio-jet fuel from palm kernel oil fatty acid ethyl esters using a simulation program ASPEN plus.

1.2.3 To compare the physic-chemical properties of the produced bio-jet fuel of palm kernel oil material with the standard biofuel ASTM and EN.

1.2.4 To test the produced bio-jet fuel on the combustion performance in gas turbine engine and analyze the gas emission from the engine during its performance.

1.3 Research hypothesis

Palm kernel oil as agricultural source could produce alkyl esters fuel through trans-esterification reaction with a high conversion and high yield at the optimal conditions. Bio-jet fuel could be obtained as medium chain fatty acid ethyl esters, a main product of trans-esterification reaction using fractional distillation process. Bio-jet fuel then could be used for gas turbine engine with high performance, and lower emission.

1.4 Scope and limitation of the study

This work involves the investigation reaction conditions including molar ratio between ethanol and palm kernel oil, temperature, reaction time, and concentration of catalyst to obtain the optimal conditions with high conversion of trans-esterification reaction; fractional distillation process was investigated to get high purity of bio-jet fuel. Physical chemical properties were compared between the produced bio-jet with the conventional jet, and combustion performance by gas turbine engine was with emission analysis. The ultimate objective of the whole thesis is to improve the value of

agricultural product for the efficient production process of bio-jet fuel by trans-esterification. Finally, trans-esterification between palm kernel oil and ethanol, and process simulation and fractionation distillation were performed to obtain bio-jet and engine testing. Its performances in terms of product yield and purity were investigated, and compared with the conventional product.

1.5 Expected results

1.5.1 High fatty acid ethyl esters yield from trans-esterification reaction under optimum condition can be obtained.

1.5.2 High purity of bio-jet fuel can be achieved through an efficient fractional distillation process.

1.5.3 The obtained bio-jet fuel possesses physico-chemical properties as same as conventional jet fuel.

1.5.4 The model gas turbine engine can be operated using the bio-jet fuel that are synthesized in the laboratory and produced in low gas emission with high energy density.

CHAPTER II

LITERATURE REVIEW

2.1 Jet engine (Gas turbine engine)

A turbojet engine is a gas turbine engine that works by compressing air with an inlet and a compressor, mixing fuel with the compressed air, burning the mixture in the combustion chamber, and then passing the hot, high pressure air through a turbine as the exhaust. The compressor is powered by the turbine, which extracts energy from the expanding gas passing through it. The engine converts internal energy in the fuel to kinetic energy in the exhaust, producing driving force or “thrust”. All the air ingested by the inlet is passed through the compressor, combustor, and turbine as shown in figure.

2.1

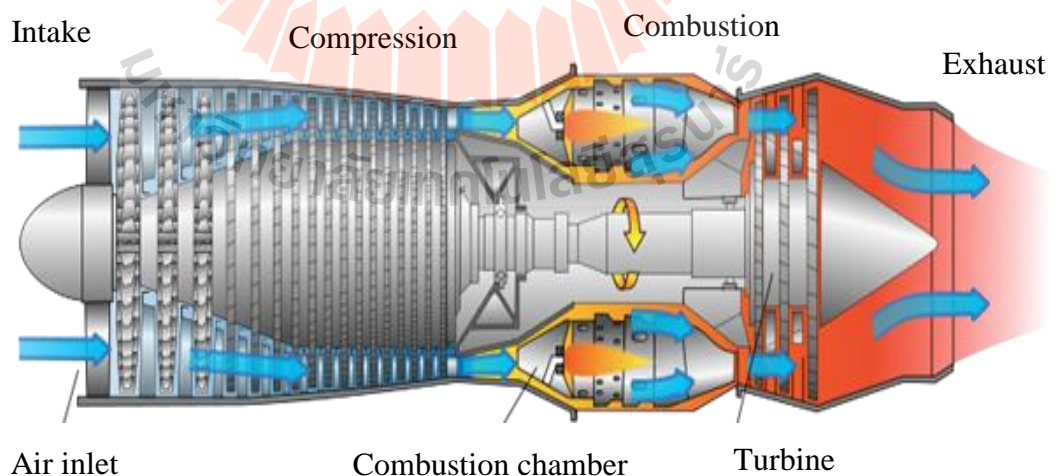


Figure 2.1 Basic principle of a gas turbine engine (Mattingly and Jack, 2006).

2.2 Fuel for gas turbine engine and fractionation distillation

Petroleum or crude oil, a natural resource that is found naturally in rock of some areas of the world, consists of various hydrocarbons and heavy metals. They are mixed with the hydrocarbon constituents and varied based on the source of crude dug up. Generally, their components are very simple, most is alkane, cyclopentadienyl alkane (cycloalkane), and aromatic compounds. Concentration of each element approximately is as follows: including 83-89% carbon, 10-14% hydrogen, 0.1-2% nitrogen, 0.1-1.5% oxygen, 0.5-6% sulfur, and metals which are about 1000 ppm. The first kind of hydrocarbons is the paraffin. This is known as a compound of the alkane, whose molecular formula is C_nH_{2n+2} , roughly be characterized by a long-chain molecule. The binding of carbon atoms is a single bond. The smallest type of paraffin is methane (CH_4), which is the main component of natural gas. Naftin is cycloalkane compound which is a ring of carbon atom. Carbon ring can have 1 or more rings such as cyclohexane, etc. The aromatic compounds are chemical group that has a ring of carbon and six atoms held together by double bonds and single bonds alternately called aromatic ring (benzene ring), for example benzene, toluene and xylene, etc. The last type is asphalt or bitumen, which is the last remaining of fractional distillation column of crude oil. It is a viscous black liquid, often used in the paving of asphalt, as shown in Fig.2.2.

Petroleum is a natural product derived from the decomposition of living organisms, both plants and animals. These compounds are compressed at high temperature under the Earth's crust for several million years in anaerobic conditions. Crude oil pumps up to the surface will be refined respectively. Fractional distillation is the most common form of separation technology used in petroleum refineries,

petrochemical and chemical plants, natural gas processing and cryogenic air separation plants (Kister and Henry Z, 1992; Perry *et al.*, 1984).

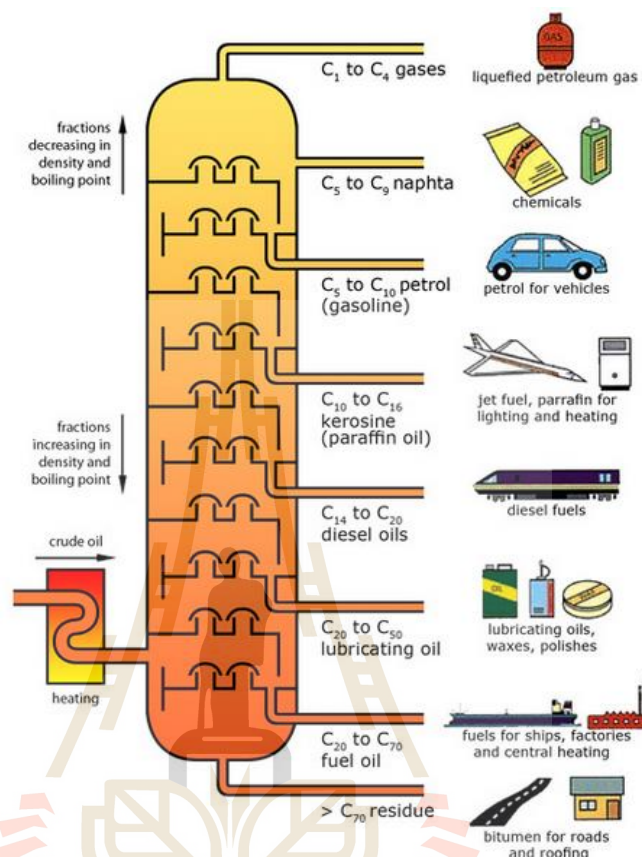


Figure 2.2 Fractional distillation column of petroleum products to different products (<http://en.wikipedia.org>).

In most cases, the distillation is operated at a continuous steady state. New feed is always being added to the distillation column, and products are always being removed. Unless the process is disturbed due to changes in feed, heat, ambient temperature, or condensing, the amount of feed being added and the amount of product being removed are normally equal. This is known as continuous, steady-state fractional distillation. Large-scale industrial towers use “reflux” to achieve a more complete separation of products. Reflux refers to the portion of the condensed overhead liquid product from a distillation or fractionation tower that is returned to the upper part of the tower as in the

schematic diagram of a typical, large-scale industrial distillation tower. Inside the tower, the reflux liquid flowing downwards provides the cooling needed to condense the vapors flowing upwards, thereby increasing the effectiveness of the distillation tower. The more reflux is provided for a given number of theoretical plates, the better the tower's separation of lower boiling materials from higher boiling materials. Alternatively, the more reflux provided for a given desired separation, the fewer theoretical plates are required. Fractionation distillation was used to separate the different types of fuel such as LPG (Liquefied petroleum gas), gasoline, jet fuel (kerosene), diesel fuel, and bitumen, etc. The jet fuel oil grade is divided into two military jets using military affairs. The composition of light hydrocarbons is very volatile. The aircraft can accelerate speed and jet fuel will be used in commercial aircraft with high speed in gas turbine engines, which use fuel at high burn rate. Thus, to get the most effective results, these fuel types are called Jet A-1 and JP-1, which are in line with kerosene oil but have better quality kerosene sold in the market and also colorless like water (Leckel, 2007). Jet fuel or kerosene is fractionated from crude oil through a refining process with the boiling point between 150 °C and 275 °C. The sulfur compounds and contaminated additives were needed to control amount of aromatic substances in limited quantities to induce the incomplete combustion, more smoke and carbon deposits in the engine as well. The dominant feature of the jet fuel is including heat of combustion, and the density in which the density of the fuel is a measure of mass per unit volume. Fuel with high density will be high heat per unit volume. The heating value of combustion is the heat of combustion. Fuel and oxygen that affects the performance of the engine, is also features stability to heat (thermal stability) and features low temperature (low temperature properties), which is a great feature to take into account a lot of oil, aircraft engine. The physical

and chemical properties of the conventional jet fuel's standard are given at Table 2.1 as follow.

Table 2.1 The physical chemical properties of commercial jet fuel

(<http://www.ncbi.nlm.nih.gov/books/NBK231234/>).

Properties	Units	Characteristic	Test method
Physical State		liquid	
Color		colorless	
Odor		kerosene-like	
Density @15°C	kg/lt	0.775-0.840	ASTM D 1298
Sulphur	wt %	0.3 max	IP 336 or ASTM D 1266
Boiling point/range	°C	175-300	ASTM D 86
Flash point	°C	40	ASTM D 328 or D 56
Kinematic viscosity @ 20°C	cSt	2-3.5	ASTM D 445
Energy density	MJ/L	34.7	
Specific energy	MJ/kg	42.15	

2.3 Synthetic jet fuel

Nowadays, many countries now have focused on the research, development of fuels production from renewable energy such as diesel oil, petrol for vehicles, naphta in chemical. It aims to produce fuel to be used on gas turbine engine, for example in aircraft or electric car. The fuel-specific features have dominated the high performance and the need to be safe to fly high for fuel from renewable energy which used on aircraft. In addition to the performance features as the original fuel, it also has other features, such

as jet fuel remaining unchanged as well for jet fuel from potential renewable energy. From the literature, technology for the bio-jet synthesis can be divided into various categories as follows to decompose biomass as fuel for aircraft and synthesis of a new bio-jet fuel.

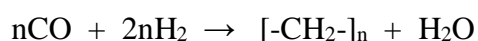
2.3.1 Synthetic jet fuel using Fischer-Winthrop France (Fischer-Tropsch process)

Fischer-Tropsch (F-T) process is a collection of chemical reactions that converts a mixture of carbon monoxide and hydrogen into liquid hydrocarbons. F-T process is often regarded as the key technological component for converting synthesis gas (or “syngas”) to transportation fuels and other liquid products (Jalama *et al.*, 2011). German researchers Franz Fischer and Hans Tropsch developed this method bearing their names in 1922 as a method for making liquid fuels from coal with alkalized under high pressure (>100 bar) (Khodakov *et al.*, 2007). Demirbas (2008) and Lobo *et al.* (2011) showed that nowadays, several major companies have announced plans to build large plants and these projects would yield about 1 million barrels per day of total product by 2020 when it completed, some of which could potentially be used as aviation fuel. F-T fuels have several characteristics that make them attractive as a jet fuel such as their higher specific energy, it leads to a small reduction in the amount of energy required to fly a given distance with a given payload and could allow for increased payload capacity (Martínez *et al.*, 2003). Following by the studies of Yang *et al.* (2010) and Bermúdez *et al.* (2011), the advantages of F-T fuels are clean burning without sulfur dioxide (SO₂) or sulfuric acid (H₂SO₄) aerosol emissions, thus leading to increased combustor and turbine life, and meanwhile their improved thermal stability should

reduce deposits on engine components and fuel lines. Furthermore, this aromatic-free fuel emits fewer particulates than conventional jet fuel. However, being no aromatic fuels, F-T fuels still has some disadvantages. Firstly, F-T kerosene has minimum density requirement. Secondly, the absence of aromatic compounds can cause fuel leaks in certain system. However, these disadvantages can be solved by blending synthetic fuel with traditional jet fuel in various ratios to resolve such problems.

The F-T process involves a series of chemical reactions that produce a variety of hydrocarbons, ideally having the formula C_nH_{2n+2} when n is typically 10-20. The F-T process has three main steps as shown on Fig. 2.3 F-T process scheme (Liu *et al.*, 2013). The first step is the production of synthesis gas, which is a mixture of hydrogen and carbon monoxide, that can be produced from many different sources, including coal (which is used to produced liquid fuels call Coal to liquid: CTL), natural gas (Gas to liquid: GTL), biomass (biomass to liquid: BTL) and synthesis gas will be applied into chemical reactions for the next steps.

The second step is removed undesired compounds such as CO_2 as well as impurities from synthesis gas stream. This stage can produce straight-chain hydrocarbon compounds. The size and length depend on the ratio of carbon monoxide and hydrogen. Catalysts and the conditions of the reaction, the equilibrium of the reaction is:



The third step is F-T synthesis, which makes mainly straight chain hydrocarbons, and to improve the quality of liquid fuels to synthetic cruel oil, which can lead to some processes such as cutting chain is shortened (cracking) from long chain

into small units, and rearranging some of the atoms (isomerizing) to get the desired synthetic fuels such as naphtha for producing gasoline, kerosene for aircraft and diesel for cars, etc. The product composition will vary depending on the hydrogen to carbon monoxide ratio, the catalyst and process conditions. The advantage of this process is enabling the combustion of the engine clean, no soot and no pollution emitted as well. However, there is drawbacks to even synthetic jet fuel in this way to meet the specific items, but all other features are less dense than conventional jet fuel

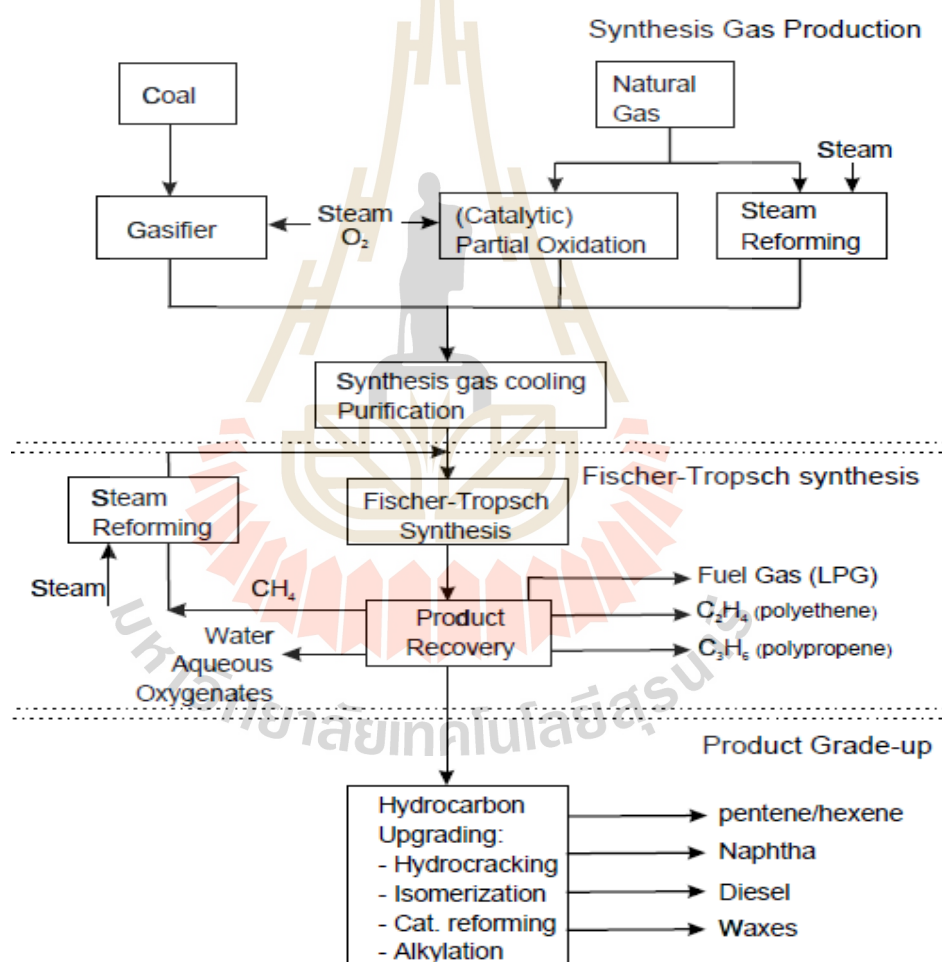


Figure 2.3 Fischer-Tropsch process scheme (Liu *et al.*, 2013).

2.3.2 Hydro-processed Renewable Jet fuel: HRJ fuel

For the HRJ fuel pathways, oil seed farming, oil extraction, and HRJ fuel production stages generate the majority of Green House Gas (GHG) emissions (Stratton *et al.*, 2010; Elgowainy *et al.*, 2012). Major sources of GHG emissions in oil seed farming include nitrogen fertilizer and fossil fuel use. In 2013, Han *et al.* indicated that nitrogen fertilizer used is a major source of GHG emissions. Plant oils are already familiar oils, such as the current crop oil soybean or rapeseed or the micro-organism oil that has received more attention nowadays is oil from algae. This oil will be brought into the process to produce jet fuel. In HRJ production, triglyceride in vegetable oil is hydrogenated to saturate the double bonds and then breaking its glycerin backbone, which co-produces propane to release the fatty acids. Oxygen in free fatty acids is removed by either hydro-deoxygenation (producing water) or decarboxylation (producing CO₂), which generate straight chain alkanes then add hydrogen to make synthetic fuel as needed. The second major step of the reaction steps is starting from the vegetable oil which goes through the process of cleaning. The long chain-shaped of triglycerides free fatty acid and oxygen is introduced into the molecular structure into shorter chains, then eliminating oxygen molecules out in the form of water and carbon dioxide. The steps are made of synthetic fuel. Length of the chain is a diesel (Diesel-range paraffin), and then put them into a synthetic fuel with hydrogen to make synthetic fuel. Han *et al.* (2013) has introduced the chain length of jet fuel (jet-range paraffin) by synthetic fuel for aircraft, however it is still a stub. Molecules are in the same format as the existing synthetic fuel. By synthetic fuel through reactions steps will be taken to a refinery. This will yield for a jet fuel gasoline and diesel for cars. The schematic diagram for hydro-processed renewable jet fuel (HRJ) is given in Fig. 2.4.

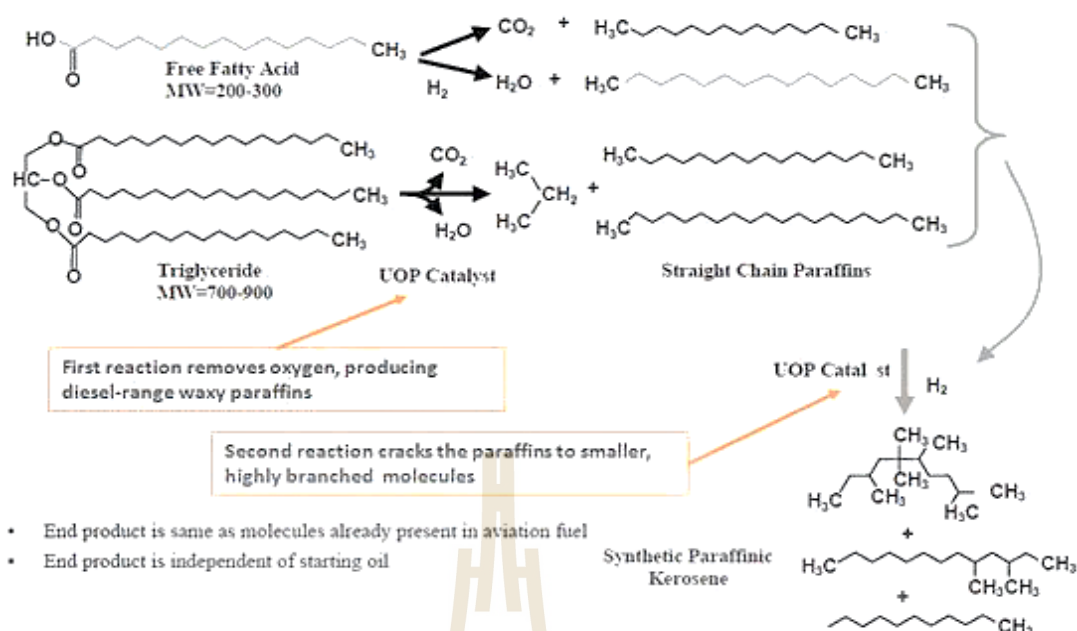


Figure 2.4 Schematic diagram for the production process of HRJ fuel (Kalnes *et al.*, 2010).

The saturation of double bonds, the removal of glycerin backbone, the hydro-deoxygenation, and hydrocracking consume a significant amount of H₂. This hydrogen is a major source of GHG emissions during its production from natural gas via steam methane reforming. However, discussions in the literature of the process assumptions in the production of HRJ fuel are still limited (Bailis and Baka, 2010; Stratton *et al.*, 2010; Agusdinata *et al.*, 2011; Pearlson *et al.*, 2013). Moreover, the basis for most cited studies is the Universal Oil Products (UOP) hydro-deoxygenation process, which was designed for soy oil, and these studies do not concern about the variation in oil characteristics from various feedstock sources. The advantages of HRJ fuel are not only new replacements for traditional jet fuel, but also they offer a lower-emission option for fueling commercial. However, it still has high cost since it has to blend with conventional jet fuel and this blending ratio of traditional jet fuels is high. The process HRJ is complicated and difficult to handle since lots of conditions for

process hydro-cracking. Thus it's leading to further research that need to reduce the price of jet fuel with the optimum blending ratio.

2.4 Ester based bio-jet fuel production process (Bio-derived jet fuel)

Biomass-based biofuel production represents a pivotal approach to face high energy prices and potential depletion of fossil fuels, to reduce greenhouse gas emissions and to enhance a sustainable economy (Zinoviev *et al.*, 2010). Renewable jet fuel comes from feedstock produced by green plants, which absorb atmospheric CO₂ and convert it to other sources such as sugars and oils which can be made into low-carbon jet fuel.

2.4.1 Trans-esterification reaction

Through our knowledge, the production of bio-jet based on trans-esterification process has not been reported so far. Biodiesel, mixture of fatty acid alkyl esters is a nontoxic, biodegradable, and renewable fuel which can be prepared from a range of organic feedstock, including new or waste vegetables oil, animal fats, and oilseed plants (Graboski *et al.*, 1998). Biodiesel has significantly lower emission than petroleum-based diesel when it is burned, it does not contribute to a net rise in the level of atmospheric carbon dioxide with a minimal greenhouse effect (Antolin *et al.*, 2002). Well-known methods for fatty acid alkyl esters biodiesel are micro-emulsions (Sharma *et al.*, 2008) and trans-esterification of oil to ester (Kusdiana *et al.*, 2004). Among these processes, trans-esterification has proven to be the simplest and economical route to produce biodiesel, with physical characteristics similar to the fossil diesel, forming little or no deposits when used in diesel engine. Due to its literature review, transesterification

can be a feasible and efficient method that can use to produce esters in bio-jet production process.

Trans-esterification reaction is a process in which short chain alcohol in the presence of catalyst (strong acid or base) is used to chemically break the molecule of the triglycerides into a mixture of fatty acids alkyl esters and glycerol. The glycerol layer settles down at the bottom of the reaction vessel. Diglycerides and monoglycerides are the intermediates in this process. The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction (Freedman *et al.*, 1984). Due to this reason, together with the fact that the alkaline catalysts are less corrosives than acidic compounds, industrial processes usually favor base catalysts, such as alkaline metal alkoxides (Schwab *et al.*, 1987) and hydroxides (Wimmer *et al.*, 1994). Alkaline metal alkoxides (as CH_3ONa for the methanolysis) are the most active catalysts, since they give very high yields (>98%) in short reaction times (30 min) even if they are applied at low molar concentrations (0.5 mol%). However, they require the absence of water which makes them inappropriate for typical industrial processes (Freedman *et al.*, 1984). Alkaline metal hydroxides (KOH and NaOH) are cheaper than metal alkoxides, but less active. Nevertheless, they are a good alternative since they can give the same high conversions of vegetable oils just by increasing the catalyst concentration to 0.5 or 1.5 mol%. It has been reported that the most desirable biodiesel properties were obtained using KOH as the catalyst in many studies (Refaat *et al.*, 2008; Roy *et al.*, 2003). The excess amount of sodium hydroxide catalyst leads to saponification resulting in lower biodiesel yield and lower biodiesel quality. Moreover, palm oil biodiesel or soybean oil biodiesel have successfully been produced by Darnoko and Cheryan (2000) and Zagonel *et al.* (2005) through KOH-catalyzed trans-esterification processes. In this study, fatty

acid alkyl ester production through trans-esterification reaction of triglycerides and ethanol in the presence of potassium hydroxide as catalyst was carried out, as shown in Fig. 2.5.

The stoichiometric reaction requires 1 mole of a triglyceride and 3 mole of the alcohol. However, an excess of the alcohol is used to increase the yields of the alkyl esters, and to allow its phase separation from the glycerol formed. The most important steps are alcohol that used in process must be anhydrous and the byproduct glycerol must be removed out the reactor. The key factor affecting the production of FAEEs in terms of production yield and purity of FAEEs was resulted in the process removing of glycerol byproduct from reaction (Attantho *et al.*, 2004). The more glycerol byproduct was removed from reaction, the higher yield of FAEEs was formed.

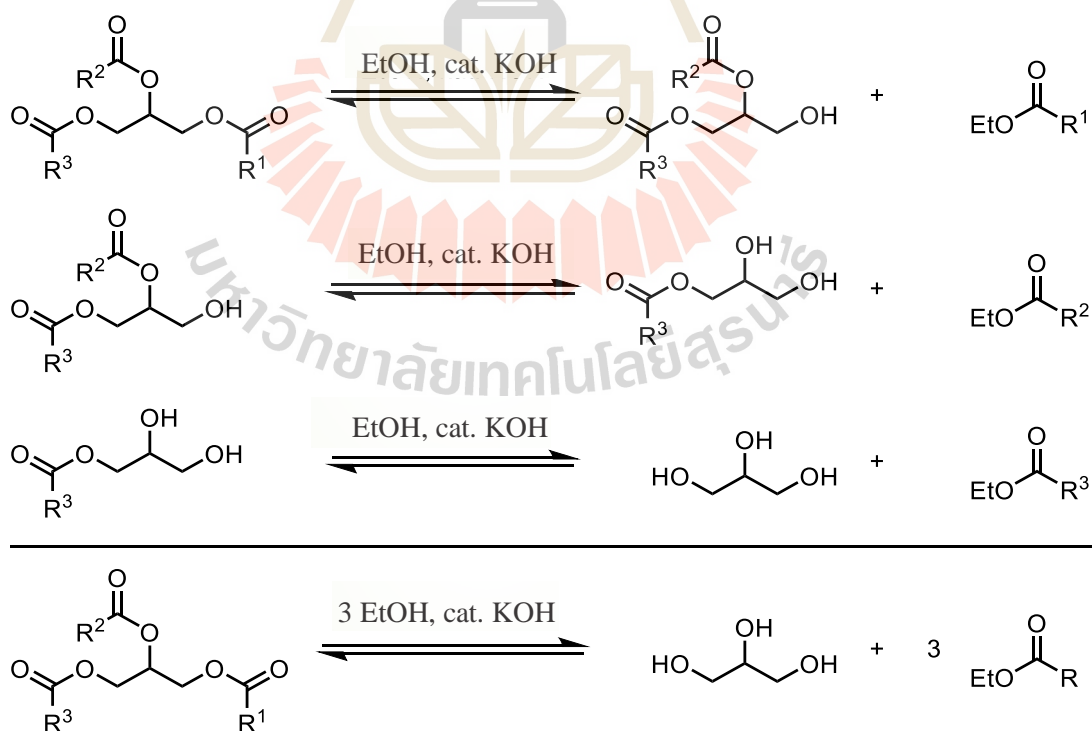


Figure 2.5 Trans-esterification reaction (Nambiar, 2003).

2.4.2 Palm kernel oil

Nowadays, biodiesel is produced a large amount around the world. Since the boiling of biodiesel is too high for the application as bio-jet fuel for the gas turbine engine, it is needed to find new material. Alternatively, the boiling point of the esters can be reduced by achieving the shorter chain or medium chain of triglycerides through the trans-esterification reaction. Operating condition used in bio-jet production, and property of bio-jet produced depend on the feedstock source. Numerous feedstock sources have been used for producing esters, such as palm oil, coconut oil, rapeseed oil, etc. In which, oil from palm fruit is the highest vegetable oil production in Thailand followed by coconut oil and soybean oil. It is reported that the total crude palm oil production within Thailand is approximately 0.64 million tons per year in 2012. Palm kernel oil is one of the vegetable oil obtained from oil palm (Fig. 2.6). Palm kernel oil contained 80% of saturated fatty acid mainly lauric acid. Around 5.086 tons of palm kernel oil is excess from domestic used and export to other country (www.oae.go.th). Fatty acid profiles of vegetable oils from several agricultural sources was shown on Table 2.2. It was illustrated that both coconut oil and palm kernel oil are able to synthetic jet fuel production. High concentration of medium chain fatty acid is the desired characteristic for bio-jet fuel production process.

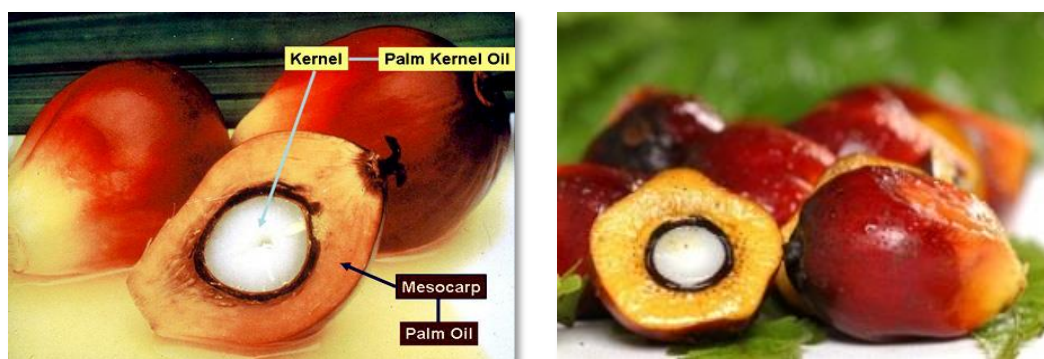


Figure 2.6 Palm kernel oil (<http://naturalnigerian.com/2012/02/pam-kernel-oil>).

Table 2.2 Triglyceride profiles of vegetable oils from soybean, palm, palm kernel, sunflower, etc (Pearlson *et al.*, 2013).

Source of oil	C10	C12	C14	C16	C18	C18:1	C18:2	C20
Coconut	9.5	50	15	10	2.0	7.5	0.5	0.5
Jatropha	-	-	1.0	14	8.5	55	30	0.3
Palm	-	-	2.0	39	5.6	42	8.2	-
Palm kernel	6.2	47	16	8.2	17.3	15	1.5	-
Algae			4.5	36	1	12	1.5	20
Sunflower	-	-	-	5	7	20	65	0.5
Soy bean				7	5	32	52	-
Cotton seed	-	-	0.4	20	2	35	42	-
<i>Y. lipolytica</i>			5	11	1	28	51	1

In this study, palm kernel oil (PKO) was used in trans-esterification reaction. PKO was obtained from the kernel of palm fruit, located inside the hard shell, and is one of the potential raw materials in Thailand. Fatty acids mostly found in palm kernel oil are including several types: lauric acid (C12:0), myristic acid (C14:0), palmitic acid (C16:0), capric acid (C10:0), caprylic acid (C8:0), stearic acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2), etc (Pearlson *et al.*, 2013; Alamu *et al.*, 2008) (Table 2.2). It was described that at the end of trans-esterification reaction, fatty acid alkyl esters were comprised of both medium chain and long chain of fatty acid. However, only medium chain fatty acid ethyl ester is used solely as the bio-jet production, due to kerosene or jet fuel has carbon chains from C10 to C14. Then, from fatty acid alkyl esters of palm kernel oil, bio-jet production could be obtained by

fractionation distillation (obtained as medium chain fatty acid alkyl ester) since these esters have dissimilar boiling points to others long chain.

2.4.3 Ethanol

Short-chain alcohols such as methanol, ethanol, and butanol are the most frequently employed. The selection of the alcohol is based on cost and performance consideration. In this work, the usage of ethanol instead of methanol was emphasized. As known, almost all fatty acid alkyl esters currently produced worldwide come from trans-esterification of oils and methanol, however next logical step is the use of ethanol instead of methanol, since ethanol was produced from agricultural renewable resources, and had lower human toxicity than methanol (Hamelinck *et al.*, 2007). In addition, ethanol is preferable to methanol not only due to its much higher dissolving power oils but also the lower cloud and pour points of the formed fatty acid ethyl esters than the methyl esters (Encinar *et al.*, 2007). Therefore, producing ethyl esters rather than methyl esters is of considerable interest, because, in addition to the entirely agricultural nature of ethanol, the extra carbon atom provided by the ethanol molecule slightly increases the heat content and the cetane number (Vicente *et al.*, 2007). However, limitation of using ethanol as the reactant is the increasing in the mutual solubility of ethyl ester and glycerol, making phase separation more difficult (Mittelbach *et al.*, 2004). This drawback can be solved by addition of glycerol (Encinar *et al.*, 2007) or evaporation of ethanol (Bouaid *et al.*, 2009). For the bio-jet production process, anhydrous ethanol (approximately 99.8 wt.%) is required. Since the concentration of the distilled ethanol was 92-95 wt.%, further step was applied to obtain anhydrous ethanol by dehydration using vapor permeation with membrane. The distilled ethanol was supplied at high

temperatures, and high pressure to the membrane module in order to remove water prior to circulating to the trans-esterification reaction (dehydrated ethanol). Since water is the smallest molecule compared to ethanol, it is possible to use a filter at the molecular level (molecular sieving) to remove water from the system. The technique used is called vapor permeation (VP) (Khunnonkwao *et al.*, 2012). The ethanol contained some water at the concentration of approximately 6 wt.%, and this mixture is called azeotropic concentration. Water was penetrated through the surface of the membrane and condensed on the other side as permeate. In order to make this system economically possible in a more commercial, the system must remove water from the reaction efficiently and at a high dehydration rate. The main purpose is making the separation of water completely occur within a short operating time. In addition, the VP system avoids direct contact of the membrane with the reacting solution which has a high acid condition. This operation can extend the life of the membrane for a longer time. In VP process, the feed side needs to be vaporized prior to enter the vapor permeation module. In addition, the vapor feed can be pressurized and superheated resulting in higher dehydration rate as shown in Fig. 2.7. The materials for preparation of membrane can be varied, but are classified into polymer, and ceramic-based materials. For ceramics, this type of membrane shows superior dehydration performances due to its rigid structure in comparison to polymer membranes. In addition, the molecular sieve property results in a very high separation factor.

The NaA zeolite membrane (Mitsui Engineering and Shipbuilding, Japan) was installed in jacket stainless steel housing. A high pressure piston pump head mounted on a 1/10 hp pump drive was employed to increase the liquid feed pressure with the help of a needle valve. Prior to entering the membrane module, the pressurized

liquid feed was heated to the desired inlet temperature through a shell and tube heat exchanger by using an oil bath. On the downstream side, the permeate vapor was condensed by using two parallel glass cold traps filled with liquid nitrogen to ensure that permeate was completely collected. The downstream pressure was maintained at approximately 3 mbar by using a vacuum pump. This vapor-permeation-assisted esterification system above was studied by Khunnonkwao *et al.* (2012). Thus, anhydrous ethanol could be achieved by using vapor permeation techniques. Membrane was used to enhancing the concentration of ethanol with dehydration process, due to its different pore sizes (2.6 Å of water and 4.4 Å of ethanol molecular Sieve Pore Sizes). Water was completely removed through vapor permeation process with membrane (pore size were at 3 Å).

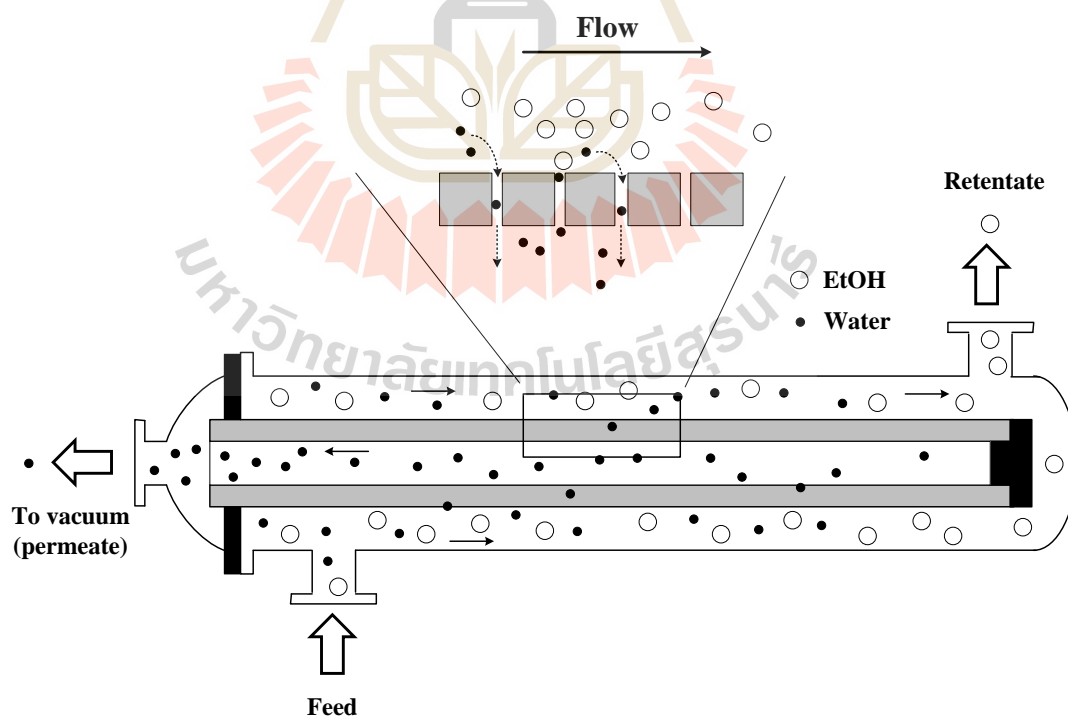


Figure 2.7 The schematic diagram of vapor permeation (Khunnonkwao *et al.*, 2012).

Fatty acid ethyl esters (FAEEs) were produced through trans-esterification of palm kernel oil and ethanol. Anhydrous ethanol was played as an important role in trans-esterification reaction producing FAEEs for bio-jet production. Higher FAEEs production could be obtained with anhydrous ethanol. Prior to distillation process, the by-product glycerol would be removed from the reactor. The higher glycerol was removed out, the more FAEEs were obtained. Due their diverse boiling points, bio-jet or biodiesel could be separated. From one process, both bio-jet and bio-diesel can be obtained, make an efficient process in terms of economic and technical. As mentioned, in HRJ process, people tried to produce jet fuel production from breaking down the long chain fatty acid into short chain, that's required of several conditions and difficult to handle. Vice versa, started from medium chain fatty acid of suitable vegetables oils to get desired bio-jet, this is one of the advantages of ester based bio-jet production process. Ester based bio-jet production is process making bio-jet fuel by fractionation distillation FAEEs from trans-esterification reaction between palm kernel oil and anhydrous ethanol

2.4.4 Factors effecting the trans-esterification reaction

The process of trans-esterification is affected by various factors depending upon the reaction condition used. The effect of these factors are described below.

2.4.4.1 Molar ratio between ethanol and palm kernel oil

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. The stoichiometric ratio for trans-esterification requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid alkyl esters and one mole of glycerol. However, trans-esterification is an

equilibrium reaction in which a large excess of alcohol is required to drive the reaction to the right. The molar ratio has no effect on acid, peroxide, saponification and iodine value of methyl esters (Tomasevic *et al.*, 2003). However, the high molar ratio of alcohol to vegetable oil interferes with the separation of glycerol because there is an increase in solubility. When glycerol remains in solution, it helps drive the equilibrium to back to the left, makes reverse reaction and lowering the yield of esters. The ester yield increased as the molar ratio increased up to a specific volume.

The base catalyzed formation of ethyl ester is difficult compared to the formation of methyl esters. Specifically, the formation of stable emulsion during ethanolysis is a problem. Ethanol is not miscible with triglycerides at ambient temperature, and the reaction mixtures are usually mechanically stirred to enhance mass transfer. During the course of reaction, emulsions usually form. In the case of methanolysis, these emulsions quickly and easily break down to form a lower glycerol rich layer and upper methyl ester rich layer. In ethanolysis, these emulsions are more stable and severely complicate the separation and purification of esters (Zhou *et al.*, 2003).

2.4.4.2 Reaction time and temperature

The conversion rate increases with reaction time. The reaction was slow during the first minute due to the mixing and dispersion of ethanol into palm kernel oil; then reaction is fast and reached the equilibrium at optimal residence time. Trans-esterification can occur at different temperatures, depending on the oil used. Moreover, the rate of reaction is strongly influenced by reaction temperature. However, given enough time, the reaction will process to near completion even at room

temperature. Generally, the reaction is conducted not too high due to high volatile of ethanol and waste electricity or further increase in temperature has negative effect on the conversion (Bajpai and Tyagi, 2006). Several researchers studied about the effect of reaction time and temperature, such as Freedman *et al.* (1984) trans-esterified peanut, cotton-seed, sunflower, and soybean oil under the condition of methanol–oil molar ratio 6:1, 0.5 wt.% sodium methoxide catalyst and 60 °C. An approximate yield of 80% was observed after 1 min for soybean, and sunflower oils. After 1 h, the conversion was almost the same for all four oils (93–98%). Moreover, the reaction was studied with different temperature, the results were indicating that temperature clearly influenced the reaction rate and yield of esters (Ma and Hanna, 1999). Thus, it is important to determine the effect of temperature and reaction time to achieve optimal conditions for the higher conversion of trans-esterification reaction.

2.4.4.3 Concentration of catalyst

Catalyst concentration is a critical factor to be determined in the trans-esterification process. High catalytic activity depends on the catalyst processing strong basic sites (Dorado *et al.*, 2004). Low and high catalyst concentrations may result in undesired FAEEs yield as well as high production costs. The effect of four different concentrations of KOH as catalyst, including 0.5 wt.%, 1 wt.%, 1.5 wt.% and 2 wt.% were investigated in study of Prafulla *et al.* (2009). It showed that, at different amount of KOH, the conversions of trans-esterification were changed as the change of catalyst concentration, the highest yield was achieved at 1 wt.% of KOH catalyst. Thus, it is indicating that at higher catalyst concentrations, the intensification of mass transfer becomes more important than increasing the amount of catalyst. In this study, different

catalyst amounts were evaluated to obtain the optimal concentration of catalyst which is used for the trans-esterification reaction.

2.4.5 Response surface methodology (RSM)

The trans-esterification process is influenced by several operating parameters. The reaction temperature, concentration of catalyst, oil to ethanol molar ratio, reaction time are the main parameters that influence on the FAEE yield (Atabani *et al.*, 2012; Yaakob *et al.*, 2013). As mentioned by many authors, an important stage in the production process is the optimization of operating conditions. Process optimization is often time-consuming and requires repeated expensive experiments. Furthermore, due to simultaneous effects of some operating variables on the system, the design and application of modeling tools such as response surface methodology (RSM) are essential for maximizing the productivity and reducing the production process costs. Moreover, its main advantage is the reduced number of experimental runs required to generate sufficient information for statistically acceptable results. RSM is a set of mathematical and statistical methods for modeling and problem analysis which has been applied in research into complex variation process. The multiple regression and correlation analyses are used as tools to assess the effects of two or more independent factors on the dependent variables. This methodology is suitable for optimizing complicated systems where response is influenced by several parameters (Abd Rabu *et al.*, 2013; Halim *et al.*, 2009; Noshadi *et al.*, 2012; Wu and Leung, 2011). Furthermore, the central composite design (CCD) of the RSM is the most commonly used in the optimization process for several biotechnological and chemical processes (Jeong *et al.*, 2009). RSM has been successfully applied for optimization biodiesel production from

different raw materials and different types of catalysts (Ghadge *et al.*, 2006). The method includes a full fractional factorial design with center points that are augmented with a group of star points. As the distance from the center of the design space to a factorial point is defined as ± 1 unit for each factor. In this study, the central composite design was used to optimize operating variables (temperature, catalyst concentration, residence time and oil to ethanol molar ratio) to achieve high value of FAEE yield.



CHAPTER III

MATERIALS AND METHODS

3.1 Materials

3.1.1 Palm kernel oil

Palm kernel oil was purchased from the Chumporn palm oil industry, Thailand. The palm kernel oil was stored at room temperature before reaction. The concentration of different fatty acids from C8 to C20 of purchased palm kernel oil was specified using Gas Chromatography (Agilent GC, 7890A, USA) (Fig. 3.1).

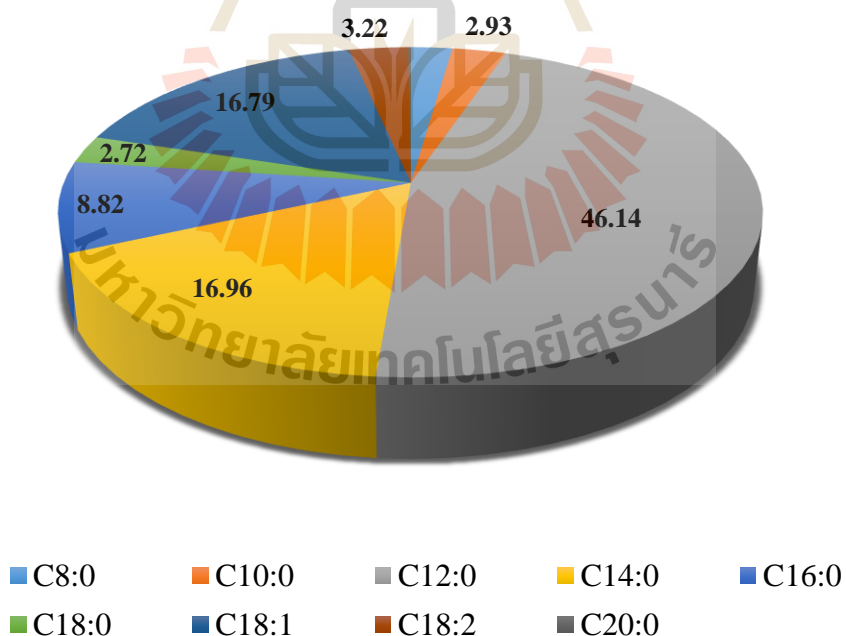


Figure 3.1 Fatty acid contents in palm kernel oil of this study (%).

3.1.2 Ethanol

The ethanol of 99.5% was produced from the Biotechnology's laboratory, Suranaree University of Technology, Thailand (Biofuel Production Laboratory from Biomass Research Unit).

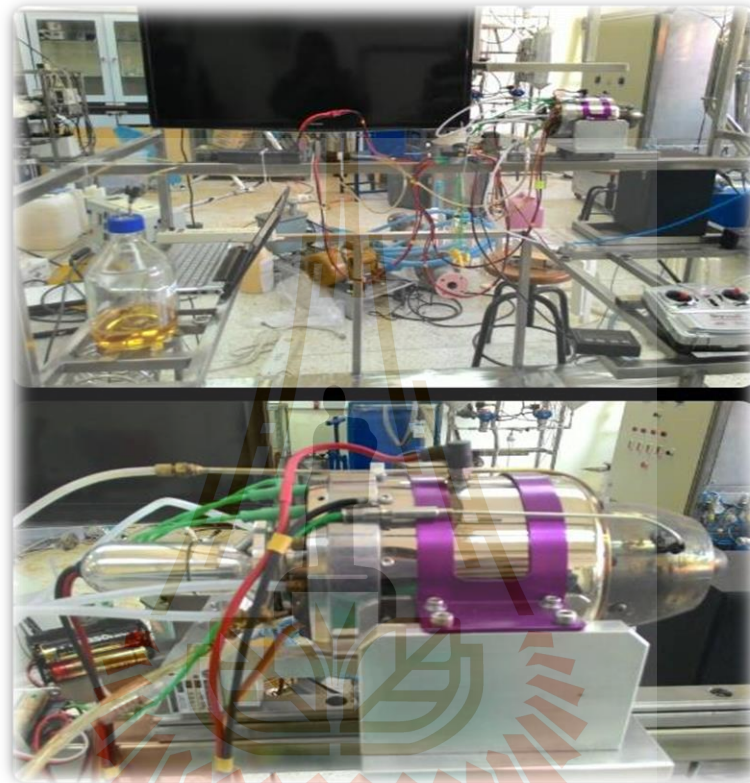


Figure 3.2 Gas turbine engine used in this study.

3.1.3 Gas turbine engine

In this work, a gas turbine engine PST, J 1300R was obtained from PST jet, Thailand. Three parts including compressor, combustion and turbine are the main compartments of the machine. In each parts of the engine, several temperature and pressure sensors were set up. Firstly, compressor compresses air flown into the system to achieve high pressure, and fed into the combustion chamber. Second, combustion chamber with the function of fuel burning is used to increase the speed and pressure of

the gas. The last one is turbine, in which energy change of the gas from the combustion chamber to the rotation. By using this machine, the parameters including temperature and pressure were measured at five different points as shown in Fig. 3.2. In addition, rotational speed and driving force (thrust) were measured and recorded using a data logging system.

3.2 Equipment

All of equipment used in the trans-esterification and fractional distillation process to produce bio-jet fuel production were shown as follow:

Names of equipment	Company
Analytical Balance	PRESICA, USA
Micropipettes 10, 100, 200, 1000 μ L	BRAND, GERMANY
pH Meter	OHAUS, USA
Hot plate and Stirrer	SCIOLOGEX, USA
Reactor 20L	AB GLASS, UK
Stirrer Rotor	IKA, MALAYSIA
Separation funnel	BUDHER, GERMANY
Cold trap	LABTECH, USA
Condenser	KONTES, USA
Oil bath	GRANTS, ENGLAND
Vacuum pump	DAIKAWA, USA
Cooler water	CHILLER, THAILAND
Gas chromatography 7890A	AGILENT, USA
Bomb Calorimeter	IKA, MALAYSIA
Density meter	ANTONPAAR, AUSTRIA
High speed rotation indicator	METROLOGY TECH, THAILAND
Refrigerator -4 $^{\circ}$ C, -20 $^{\circ}$ C	RIVACOLD, THAILAND
Vortex Mixer	DRAGONLAB, CHINA

3.3 Methods

3.3.1 Free fatty acid analysis in palm kernel oil

Prior to trans-esterification reaction, palm kernel oil obtained from market was analyzed for free fatty acid concentration using titration method. Free fatty acid content has an influence on the course of the trans-esterification by reaction. Soap is produced when a higher free fatty acid or a greater number of water molecules is available. Titration method is an analytical technique used to determine free fatty acid (FFA) in oil. It is based on a complete chemical reaction between analyte and reagent of known concentration of which is added to sample. The volume of base required to neutralize the acid in the PKO is an indication of the amount of FFA in oil. Firstly, 10 ml PKO was prepared and put into a 250 ml flask. 20 ml of isopropyl alcohol with 3 drops of phenolphthalein was then added into PKO. Then titrate by using KOH was carried out by dropping KOH solution into PKO until medium in flask change into pink color in 10 seconds. Calculate volume of KOH used for titration. The amount of used potassium hydroxide (dissolved in ethanol) was based on the amount needed to neutralize the unreacted acids (Official Methods and Recommended Practices of the AOCS, 1997). Free fatty acid concentration was calculated using equation as follow:

$$FFA = \frac{V \times M \times W}{m} \times 100$$

Which, FFA: Concentration of free fatty acid (%)

V: Volume of KOH used (ml)

M: Molarity of KOH used (mol/1000ml)

W: Average molecular weight of fatty acid component, g/mol

m: Mass of PKO sample, (g)

3.3.2 Trans-esterification reaction laboratory

The schematic diagram of the experimental set-up for trans-esterification reaction was shown as follows (Fig 3.3)

3.3.2.1 Trans-esterification steps

The transesterification reaction was carried out with ethanol/palm kernel oil molar ratio (6:1, 9:1, 12:1), using (0.5wt.%, 1 wt.%, 1.5 wt.%) of potassium hydroxide as an alkaline catalyst. The reaction was carried out at 40, 50, 60 °C and the reaction time was specified within 60, 90 and 120 minutes. The choice of said variables and their range were selected based on several outside sources and on preliminary studies in our laboratory. The upper reaction temperature level, 60 °C, was determined by its not higher than the boiling point of ethanol. The lower level was 40 °C, normal temperature, since lower temperatures would require a cooling system for reactor, which would increase the cost of the process. Catalyst concentration level were 0.5 and 1.5 wt.%, according to literature data (Freedman *et al.*, 1984). The combination of these variables (temperature, catalyst concentration, reaction time and molar ratio of alcohol to oil) was used in a factorial experimental design for fatty acid ethyl esters production optimization by transesterification of palm kernel oil with ethanol.

The trans-esterification experiment step was carried out with 100g of palm kernel oil, as shown in Figure 3.3. Palm kernel oil was measured into a flask and heated to a temperature of 110 °C (pretreatment step for oil). The flask was maintained at this temperature for 30 minutes to evaporate water in the oil, subsequently oil was cooled down to desired temperature. By the stoichiometry of the trans

esterification process, one mole of PKO is required to react with three moles of ethanol to produce three moles of FAEE and one mole of glycerol.

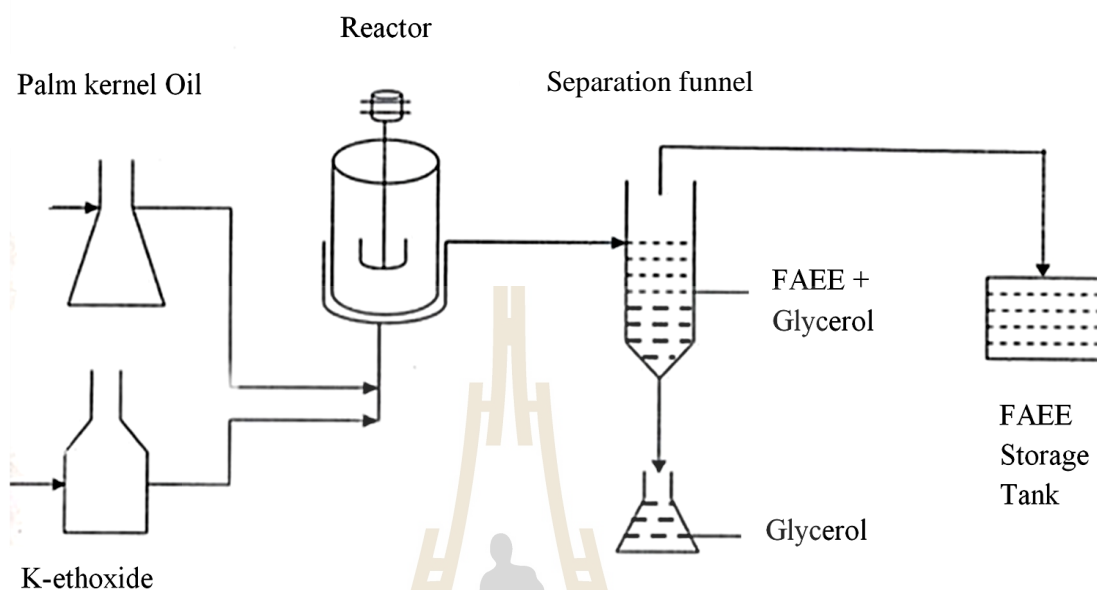


Figure 3.3 The schematic diagram of the unit for FAEE production.

However, an excess of alcohol is required to push the reaction to the forward side (Gerpen, 2005). The K-ethoxide was prepared by mixing the calculated anhydrous ethanol with potassium hydroxide into a flask and heated up to certain temperature. The flask was closed and swirled round thoroughly for about two minutes repeatedly about six times for complete mixing. The K-ethoxide mixture was slowly transferred to mix with PKO and the flask was capped. Reaction time was then recorded as soon as the mixture of KOH/ethanol was added. The speed of the stirrer was kept constant at 400 rpm throughout the experiment. After a specific time, the heating and stirring were stopped, and reactor was removed from the water bath. Since ethanol distributes favorably in the aqueous phase, the more residual ethanol is in the reactor, the more difficult phase separation is formed (Oliveira *et al.*, 2011). Thus, the residual ethanol was subsequently removed out using rotary evaporator.

The trans-esterification reaction was carried out as a batch reaction set-up (Fig 3.4). The reaction products (mixture of FAEEs and glycerol) were transferred to a separator funnel. Then, mixture was allowed to settle and phase separation by gravity overnight. The settling stages were shown in Fig 3.5 (left) and (right). The mixtures were separated into two layers. The top layer is a mixture of FAEEs, and the bottom layer is glycerol as shown on Fig. 3.5 (c).

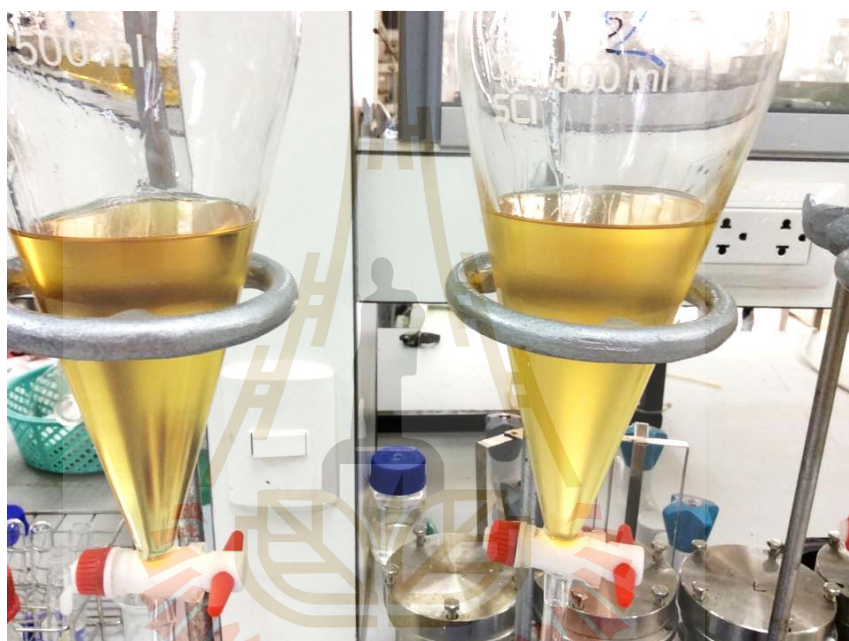


Figure 3.4 Batch trans-esterification reaction set-up.

After separation of the layers by gravity separation, ethyl ester was purified by washing by distilled warm water several times in order to remove catalyst until the washing become clear. Then, the washed ethyl ester was dried at 120 °C for 60 min. The purified fatty acid ethyl esters contents were analyzed using Gas chromatography (GC). An Agilent Technology GC 7890A /MSD 5975C with an Agilent 7693A automated liquid sampler was configured at the following conditions. The column was HP-INNOWAX, 50 m x 0.2 mm id x 0.4 μm , column flow rate of 0.6 mL.min⁻¹ and helium as the carrier gas. The initial oven temperature was 40 °C (holds

for 2 min) with a programming rate of 14 °C /min to 140 °C (holds for 2 min) then 6 °C /min to 290 °C (holds for 9 min). The maximum temperature was 310 °C and run time of 45.143 minutes. The relative fractions of each fatty acid ethyl ester were calculated from the fraction of total peak area attributed to each by the mass spectrum libraries supplied with the GC-MS software. The final analysis was recorded and analyzed by the computer using Acq-Method on the GC Plus The FAEE of biodiesel samples was identified and then the peak areas were utilized to quantify the FAEE content.

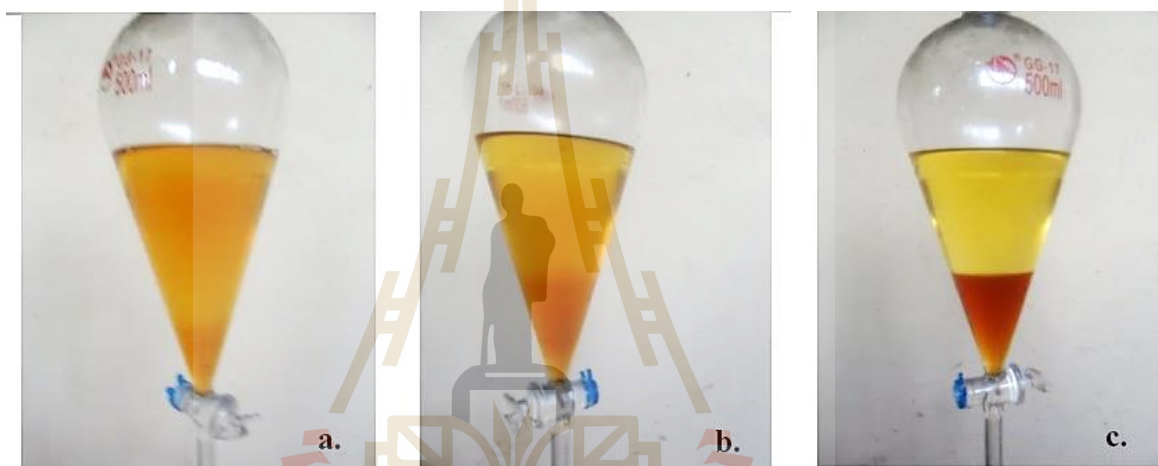


Figure 3.5 Settling stages for separation of the produced palm kernel oil-FAEEs and glycerin, stage (a), stage (b) and stage (c).

The fatty acid ethyl ester content in each experiment was calculated via the following equation:

$$\%FAEE = \frac{\sum C \times 100}{W_i}$$

Which, FAEE: Concentration of fatty acid ethyl esters (%)

C: Calculated weight of fatty acid ethyl esters (g)

W_i: Weight of sample, (g)

3.3.2.2 Experimental design using RSM

The trans-esterification process is influenced by several operating parameters. The reaction temperature, concentration of catalyst, ethanol to oil molar ratio, reaction time are the main parameters that influence on the FAEE yield (Atabani *et al.*, 2012; Yaakob *et al.*, 2013). Response surface methodology was used for statistical analysis of the experimental data using Design Expert software version 10.0.3. Temperature, ethanol to oil ratio, catalyst concentration, and reaction time were chosen as independent variables, and the production of ethyl esters was the dependent variable. The 3 level - 4 factors central composite design (CCD) was employed in trans-esterification step optimization requiring 26 experiments. The code and uncoded levels of the independent variables were shown in Table 3.1.

Table 3.1 Experimental levels of independent process variables for FAEE production.

Independent variables	Symbols (uncoded)	Code levels		
		-1	0	1
Molar ratio	X ₁	6	9	12
Temperature (°C)	X ₂	40	50	60
Catalyst concentration (wt%)	X ₃	0.5	1	1.5
Reaction time (min)	X ₄	60	90	120

For this study, a set of 26 experiments were carried out. Usually a low-order polynomial in some range of independent variables is employed for modeling. If the response is well modeled by a linear function of independent variables, then the approximating function is the first-order model. If there is curvature in the system, then a polynomial of higher degree must be used, such as the second-order

model (Montgomery, 2001). In this study, there was a curvature. Experiments were then employed to fit the second-order polynomial model, which indicated that 26 experiments were required for this process. The coded values of the independent variables for the design of the experiment for FAEE production and glycerol are given in Table 3.2. For statistical calculations, the variables X_i were coded as x_i according to the following relationship:

$$x_i = \frac{(X_i - X_0)}{X}$$

Where, X_0 is the average value of variables in high and low levels

X is (variable at high level - variable at low level)/2

X_1 is a coded variable that represents the molar ratio

X_2 is a coded variable that represents the catalyst concentration

X_3 is a coded variable that represents the temperature

X_4 is a coded variable that represents the time of reaction

The behavior of the system discussed was described by a quadratic equation, Eq. (2), which follows Box *et al.* (1978), Box *et al.* (1951). A multiple regression data analysis was carried out with the statistical package (StatSoft Inc., Tulsa, Okla., USA). The optimum values of selected variables were obtained by solving the regression equation and also by analyzing the response surface contour plots:

$$Y = \beta_0 + \sum_{j=1}^k \beta_j X_j + \sum_{i < j} \sum \beta_{ij} X_j X_i + \sum_{j=1}^k \beta_{jj} X_j^2 + \varepsilon$$

where Y is the predicted FAEE yield; β_0 , β_j , β_{ij} and β_{jj} constant model coefficients; x_i and x_j are the coded independent variables or factors; ε is random error.

Table 3.2 Full factorial central composite design matrix for FAEE production.

Run	Independent variables			
	X_1	X_2	X_3	X_4
1	6	60	1.5	120
2	9	50	1	90
3	6	60	0.5	120
4	12	60	0.5	60
5	12	50	1	90
6	12	40	0.5	120
7	12	40	1.5	120
8	9	50	1	60
9	9	50	0.5	90
10	6	60	1.5	60
11	6	40	1.5	60
12	12	60	1.5	60
13	6	40	1.5	120
14	6	40	0.5	120
15	9	50	1	120
16	9	50	1	90
17	6	40	0.5	60
18	6	60	0.5	60
19	9	40	1	90
20	12	40	1.5	60
21	12	40	0.5	60
22	6	50	1	90
23	12	60	1.5	120
24	12	60	0.5	120
25	9	60	1	90
26	9	50	1.5	90

All results are expressed as mean \pm SD. To determine the effect of treatment, data were analyzed using one-way analysis of variance (ANOVA) repeated measures. Response surface plots were developed using the fitted quadratic polynomial equation obtained from regression analysis, holding one of the independent variables at constant value corresponding to the stationary point and changing the other two variables. P-values of less than 0.05 were regarded as significant.

3.3.3 Fractionation distillation for bio-jet production process

After optimization trans-esterification reaction for FAEE production, purified FAEEs were obtained and continued carrying on distillation. Due to FAEEs in palm kernel oil had different boiling points depending on long chain and medium chain of fatty acids, fractional distillation was used to separate the lower boiling point of fatty acid ethyl esters from the heavy one (Table 3.3). To produce bio-jet production, FAEE from C8 to C14 was needed to distillate out from the mixture. The higher purity of achieved FAEE C8-C14, the more efficient of the distillation system.

Experiment of fractional distillation process for bio-jet production was carried out as following Figure 3.6. Mixture of purified FAEE was put into reactor, which was covered by the first jacket. It was filled up by thermal oil, and connected to the oil bath, which was set up at 165 °C. Vacuum pump was controlled at 25 mbar with the pressure indicator (Fig 3.6).

When the reactor was heat up to desired conditions above, C8-C14 FAEE in the mixture were become a vapor and went to the top of the reactor which was connected to the fractional column. The second jacket was used at fractional column, which was controlled the temperature of the column (Fig 3.6). The fraction column was

set up at 131°C using that jacket, this due to if the came out components had higher boiling point than this such as C20 FAEE, it was not be fractionated out of the system, and was refluxed back into the reactor. The vapor was came to the condenser. The temperature for the condenser was maintained at -4 °C using a water bath, in this case, ethanol was used instead of water, due to ethanol has lower freezing point than water. Reactor was stirred by motor coupled with the controller at 800 rpm. The higher value of stirrer speed was done for mixing well of the mixture and reduce the time for heating up. In order to reducing the losses of the distilled FAEE C8-C14 and extended longer life for the vacuum pump, the cold trap was included in the system to trap all of the losen product which was not condensed from the condensor. The temperature was -30°C at the cold trap.

Table 3.3 Boiling points of organic acid ethyl esters.

Organic acids	Source	Boiling point (°C)
Caprylic acid (C8:0)	Triglyceride	207
Capric acid (C10:0)	Triglyceride	245
Lauric acid (C12:0)	Triglyceride	259
Myristic acid (C14:0)	Triglyceride	265
Palmitic acid (C16:0)	Triglyceride	303
Stearic acid (C18:0)	Triglyceride	215 (15 mmHg)
Oleic acid (C18:1)	Triglyceride	218 (15 mmHg)
Linoleic acid (C18:2)	Triglyceride	224 (17 mmHg)

The distilled FAEE C8-C14 was then determined using GC-MS and was used for further analytical method for fuel properties and engine testing.

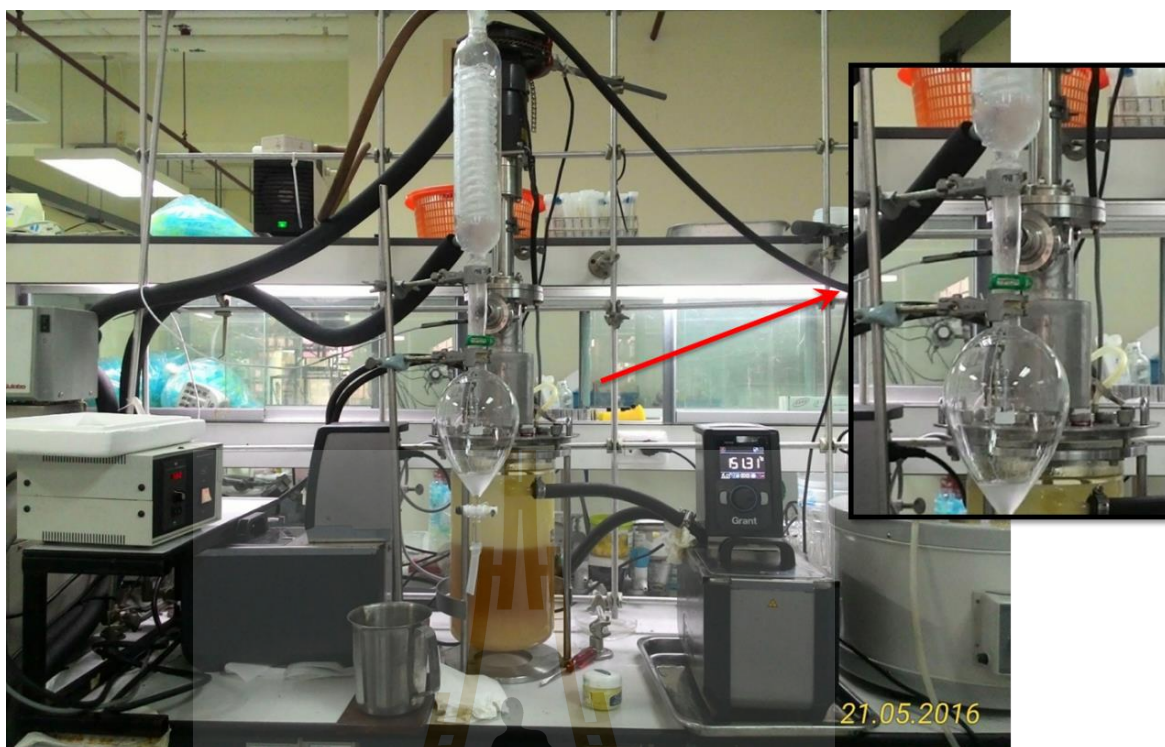


Figure 3.6 Fractionation distillation column laboratory.

3.3.4 Properties of bio-jet fuel and gas turbine engine testing

The FAEE quality was evaluated according to the European standard (EN) and American Section of the International Association for Testing Materials (ASTM) by Scientific Equipment Center Prince of Songkla University, Thailand.

Different properties of the distilled FAEE C8-C14 or bio-jet were determined: density at 15°C (ASTM D1298), kinetic viscosity at 40°C (ASTM D445), carbon residue (ASTM D4530), flash point (ASTM D93), cloud point (ASTM D2500), pour point (ASTM D97), acid number (ASTM D664), copper corrosion (ASTM D130), phosphorus content (ICP-OES), calcium content (ICP-OES), magnesium (ICP-OES), sulfated ash (ASTM D874), total contaminant (ASTM D5452), iodine value (EN 14111), sulfur content (XRF), oxidation stability at 100°C (EN 15751), mono-, di- and triglyceride content (EN 14105), free and total glycerin (EN 14105). Energy density of

the product was measured using bomb calorimeter from Suranaree university of technology.



Figure 3.7 Testo 350 Portable Emission Analyzer

Moreover, the performance of gas turbine engine was carried out using the purified FAEE C8-C14 (bio-jet). It was mixed well with the lubricant in the ratio of 1:18 of FAEE before testing. The concentration of CO, CO₂, NO₂ and hydrocarbon (HC) from the exhausted gas from the engine was measured using Testo 350 Portable Emission Analyzer (Fig 3.7). The value of fuel consumption and the thrust were also determined in this study.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Free fatty acid concentration in palm kernel oil

The experiment was carried out by titration method using KOH as solution. The volume of base KOH required to neutralize the acid in the PKO is an indication of the amount of FFA in oil. The effect of FFA content strongly depends on the type of catalyst used during trans-esterification. The FFA content is a key parameter for determine the viability of the vegetable oil trans-esterification process (Dorado *et al.*, 2002). The results of titration based on the volume of KOH used to neutralize the acid content of the palm kernel oil for the calculation of the percentage FFA content were shown on Table 4.1 as follow:

Table 4.1 Concentration of free fatty acid using titration method.

Run	Volume of KOH used (ml)	Free fatty acid concentration (%)
1	0.6	0.1536
2	1.1	0.2816
3	0.9	0.2304

To carry out the base-catalyzed reaction to completion, a value of free fatty acid in oil lower than 1% is needed. The higher the acidity of the oil is, the smallest the efficiency of conversion is. Above that limit, trans-esterification reaction favors to saponification reaction to formation of soap, undesired product of trans-esterification

resulting in a lower ester yield and against this reaction (Viele *et al.*, 2013; Atadashi *et al.*, 2012; Hingu *et al.*, 2010; Morais *et al.*, 2010). In this study, the concentration of FFA was resulted in lower than 1%, indicating that it is efficient and reasonable to use potassium hydroxide as alkali-catalyzed for trans-esterification reaction between palm kernel oil and ethanol. Ma, Clements, and Hanna (1998) studied the trans-esterification of beef tallow catalyzed by sodium hydroxide (NaOH) in the presence of FFA. Without adding FFA, the apparent yield of beef tallow methyl esters (BTMEs) was the highest. When 1.6% of FFA was added, the apparent yield of BTMEs reached the lowest level (less than 5%). If low qualities of beef tallow or vegetable oil with high FFA are used to produce ester, they must be refined by saponification using NaOH solution to remove FFA. The starting materials used for base-catalyzed alcoholysis should meet certain specifications. In this work, the triglycerides of palm kernel oil with lower acid value was used for trans-esterification in the presence of KOH as base-catalyzed, and all materials are also anhydrous.

4.2 Optimization of fatty acid ethyl ester production from trans-esterification reaction between palm kernel oil and ethanol

4.2.1 Fitting the model and evaluation

As mentioned earlier, RSM was used to optimize trans-esterification reaction from studying the interaction factors, experiments were performed at varying physical parameters by central composite design. The results were presented on Table 4.2. Experimental yield was analyzed to get a regression model.

Table 4.2 CCD arrangement of code level of variables of temperature, molar ratio of ethanol to oil, catalyst concentration and reaction time in RSM design.

Run	Independent variables				FAEE (%)	
	X ₁	X ₂	X ₃	X ₄	Experimental	Predicted
1	6	60	1.5	120	82.88	86.64 [76.27/97.00]
2	9	50	1	90	87.89	88.33 [83.27/93.39]
3	6	60	0.5	120	65.24	71.06 [60.69/81.42]
4	12	60	0.5	60	61.86	64.04 [53.67/74.40]
5	12	50	1	90	75.66	82.60 [73.42/91.78]
6	12	40	0.5	120	73.44	77.16 [67.02/87.31]
7	12	40	1.5	120	83.31	84.75 [74.50/95.01]
8	9	50	1	60	83.22	85.09 [76.27/93.92]
9	9	50	0.5	90	83.07	80.21 [71.03/89.39]
10	6	60	1.5	60	76.58	72.62 [62.26/82.99]
11	6	40	1.5	60	61.64	66.58 [56.22/76.95]
12	12	60	1.5	60	75.52	78.66 [68.30/89.03]
13	6	40	1.5	120	77.99	75.00 [64.64/85.37]
14	6	40	0.5	120	65.12	62.94 [52.68/73.19]

[95% CI low/ 95% CI high]

Table 4.2 Continued.

Run	Independent variables				FAEE (%)	
	X ₁	X ₂	X ₃	X ₄	Experimental	Predicted
15	9	50	1	120	98.21	97.96 [89.78/106.15]
16	9	50	1	90	90.28	88.26 [83.20/93.32]
17	6	40	0.5	60	48.63	50.63 [40.27/60.99]
18	6	60	0.5	60	53.72	54.22 [44.08/64.36]
19	9	40	1	90	75.65	80.11 [70.93/89.29]
20	12	40	1.5	60	84.47	77.80 [67.54/88.05]
21	12	40	0.5	60	69.53	66.47 [56.11/76.84]
22	6	50	1	90	79.78	73.65 [64.82/82.48]
23	12	60	1.5	120	93.55	90.74 [80.37/101.10]
24	12	60	0.5	120	83.98	79.74 [69.37/90.10]
25	9	60	1	90	87.84	84.36 [75.18/93.54]
26	9	50	1.5	90	89.93	93.78 [84.60/102.96]

[95% CI low/ 95% CI high]

The FAEE production from trans-esterification reaction was investigated at different molar ratio of ethanol to oil, concentration of catalyst, temperature, and reaction time, which is known as the most important parameters affecting the efficiency

of the fatty acid ethyl esters production. The empirical model was constructed from experimental data and the significant of each variable term in the model was analyzed through p and F – value. The reliability of fitted models was determined by analysis of regression coefficient including F-value, p-value, R^2 , adjusted R^2 , predicted R^2 , and %C.V., respectively as represented in Table 4.3 and 4.4.

confidence.

Table 4.3 Regression analysis (ANOVA).

Sources of variation	Sum of squares	Degrees of freedom	Mean squares	F-value	Probability (P)
Model	3360.45	14	240.03	7.13	0.0012
Residual	370.09	11	33.64		
Total	3730.54	25			

For Table 4.3, the model F-value of 7.13 was implied that this model is significant. There was only a 0.12% chance that an F-value could occur due to noise. Values of probability p-value was shown less than 0.0500, indicated that this model terms are significant. The lack of fit F-value of 12.86 implies the lack of fit is not significant relative to the pure error. There is a 21.40% chance in lack of fit F-value, this large could occur due to noise. Non-significant lack of fit is good since the model is required to be fitted. This fit of the model was checked with the coefficient of determination R^2 , which was calculated to be 0.941, revealed that 94.1% of the response variability could be explained by the previously discussed model and the model adequately represented the experimental results. This study indicated that the model can be considered statistically significantly according to the F-test with 95%

The effect of the variables as linear, quadratic or interaction coefficients on the response was tested for significance by ANOVA. Table 4.4 illustrated F-value and p-value for each variable in the polynomial model. The p-value associated with a test statistic at least as extreme as the one that was actually observed that the null-hypothesis of observing a test statistic was true. The p-value lower than 0.05 indicated the dependent variables were significantly difference at 95% confident interval. In this experiment, the p-value of all models was lower than 0.0001, indicated that the model fitness was highly significant. The p-value for lack of fit showed the undesirable characteristic of the model, whereas p greater than 0.05 indicate that the lack of fit was not significant. It means that, the variation of the data around the fit model was small and the predicted models fitted the experimental data sufficiently.

Table 4.4 shows the linear, interaction, and quadratic regression coefficient of the models. The mark of the regression coefficient specified trends effect to the dependent variables as positively and negatively. Evaluations of independent parameter in fitted model for each dependent variable were determined. According to Table 4.4, three factors including molar ratio (X_1), catalyst concentration (X_3), and retention time (X_4) affected to ethyl esters FAEE concentration. Considering the concentration of FAEE, molar ratio of ethanol to oil, catalyst concentration and retention time were significant term while temperature was non-significant term. This implied that the temperature of reaction in this experiment could overcome the high yield of FAEE with no matter how the temperature was. The relations between these three above parameters were described as the quadratic term. In which, catalyst concentration and molar ratio of ethanol to oil are the most significant variables for FAEE production

(effect of $X_3= 24.29$ and effect of $X_1 = 19.46$). Catalyst concentration has a substantially higher effect on ethyl esters production compared to the molar ratio.

Table 4.4 F-value and p-value, regression coefficient of the predicted models for each variable and standard errors

Factors	FAEE (%)	Sources	Standard error	F-value	P-value
β_0	88.42	Model	2.30	7.13	0.0012
Linear					
β_1	4.99	X_1	1.37	19.46	0.0010
β_2	2.30	X_2	1.37	2.83	0.1207
β_3	6.74	X_3	1.37	24.29	0.0005
β_4	6.03	X_4	1.37	13.30	0.0038
Interaction					
$\beta_1 \beta_2$	-1.30	$X_1 X_2$	1.45	0.81	0.3874
$\beta_1 \beta_3$	-1.15	$X_1 X_3$	1.45	0.62	0.4460
$\beta_1 \beta_4$	-0.48	$X_1 X_4$	1.45	0.11	0.7443
$\beta_2 \beta_3$	0.82	$X_2 X_3$	1.45	0.32	0.5854
$\beta_2 \beta_4$	1.40	$X_2 X_4$	1.45	0.93	0.3555
$\beta_3 \beta_4$	-0.91	$X_3 X_4$	1.45	0.39	0.5442
Quadratic					
β_1^2	-10.48	X_1^2	3.62	8.35	0.0147
β_2^2	-6.45	X_2^2	3.62	3.17	0.1027
β_3^2	-1.70	X_3^2	3.62	0.22	0.6489
β_4^2	2.52	X_4^2	3.62	0.48	0.5015
R^2	0.9408		-	-	-
Adj. R^2	0.9013		-	-	-
Pred. R^2	0.8520		-	-	-
C.V.%	7.51		-	-	-

According to the estimated coefficient exhibited as following, catalyst concentration has a positive effect on the ethyl esters yield. It means increase in the catalyst concentration accelerates the speed of the trans-esterification reaction. The same results were reported by Bouaid *et al.* (2007) and Yuan *et al.* (2008) in the optimization of FAEE conversion from waste canola oil and used frying oil, respectively. Temperature is not significant for ethyl esters production at the confidence interval considered (95%). Note that, the chosen optimum conditions took into the consideration temperature which are important in defining the operational cost of bio-jet production on an industrial scale.

The coefficient of variation (C.V.) is the standard deviation expressed as a percentage of standard error of predicted value to the mean value of observed response. A model can be considered logically reproducible if the C.V. is less than 10% (Ahmad *et al.*, 2007). Resulted at 7.51%, the FAEE concentration in this model were in acceptable range of C.V.

The mathematical model generated from the experimental data using Design-Expert software is expressed by the following quadratic equations:

$$\begin{aligned}
 A = & -216.42 + 26.039X_1 + 6.490X_2 + 31.218X_3 - 0.427X_4 - 0.0435X_1X_2 \\
 & - 0.764X_1X_3 - 0.005X_1X_4 + 0.163X_2X_3 - 0.004X_2X_4 - 0.06X_3X_4 \\
 & - 1.164X_1^2 - 0.064X_2^2 - 6.785X_3^2 + 0.002X_4^2
 \end{aligned}$$

In order to confirm the suitable precision, the point prediction of the model was carried out by measuring the dependent variables at the point of the interests in triplicate experiments. The average values for each triplicate were compared to the

predicted value or must be in range of 95% CI value which the upper and lower bound of the 95% confidence interval that surrounded the coefficient estimated for the center point. The point predictions of the models were completed (Table 4.2). All of experimental values of FAEE concentration were in a range of 95% confident interval. As a result, the empirical model of FAEE production were extremely confident and suitable for application.

4.2.2 Analysis of response surface

Response surface had been applied successfully for optimization of biodiesel production in fat and oil feedstock, including mahua oil (Ghadge and Raheman, 2006), jatropha oil (Tiwari *et al.*, 2007) and waste rapeseed oil (Yuan *et al.*, 2008). The 3-dimension response surface and the 2-dimension contour plots were the graphical representations of regression equation. Due to interaction effects between the variables, the parameters could not be analyzed independently. The significance of the parameters in the model was obtained using statistical techniques. They provided a method to reveal the relationship between responses and experimental levels of each variable and the type of interactions was between two test variables. The shape of the contour plots such as circular or elliptical, indicated whether the mutual interactions between the variables were significant or not. Circular contour plot indicated the interactions between the corresponding variables are negligible while, elliptical contour plot indicated that the interactions between the corresponding variables were significant (Zhong and Wang, 2010).

The relationship between independent and dependent variables was illustrated in 3-dimensional representation of the response surfaces and two-

dimensional contour plots generated by the model of FAEE production. RSM was illustrated with three-dimensional plots by presenting the response in function of two factors and keeping the other constant. It is visualized by the yield of FAEE in relation to the temperature, ethanol to oil ratio and catalyst concentration and reaction time in Figure 4.1 to 4.3.

Figure 4.1 was shown the response for the interactive factor temperature and catalyst concentration. As expected, Fig. 4.1 showed that ethyl esters conversion increased when high catalyst concentration was applied. However, as with the work of Vicente *et al.* (1998), it was observed that temperatures (>60 °C) and catalyst concentrations ($>1.5\%$) led to the production of large amounts of soaps in this study. Furthermore, the addition of an excessive amount of catalyst increased emulsion formation. The response surface corresponding to the second-order model indicated that for low temperatures, ethyl esters production increased with an increasing catalyst concentration. Maximum ethyl ester conversions were therefore obtained from large catalyst concentrations (1 wt.%). This was due to the second most significant factor being the catalyst concentration, and to its effect being positive (Table 4.4).

When palm kernel oil reacted with KOH dissolved in ethanol, there were two reaction pathways: transesterification to produce FAEE and saponification to produce soap; therefore, forecasting the temperature effect was not straightforward. There were two equilibrium reactions. When saponification reaction was favored, KOH was lost and the overall process rate decreased. KOH was a catalyst on transesterification reaction and also a reagent on saponification reaction. On the other hand, the trans-esterification reaction could be favored when adequate temperature was used.

Low temperature decreased the rate of saponification reaction, thus trans-esterification reaction was favored.

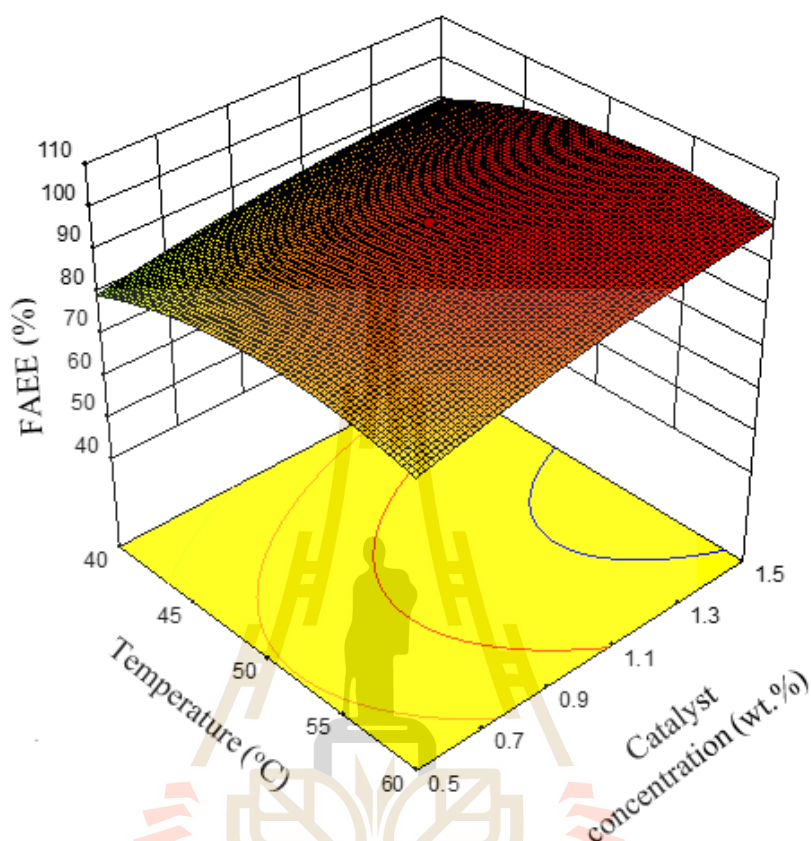


Figure 4.1 Response surface contour for interaction on ethyl esters production between temperature and catalyst concentration.

When temperature increased, the reaction rates were obviously higher because molecules had more energy, transesterification reaction was faster than the saponification reaction, thus KOH was again a catalyst, therefore the ethyl ester concentration increased. That could be compensated for eventually through an increase of selectivity for FAEE concentration, but that was not the case (see Figure 4.1). When operating at much higher temperature, the saponification reaction rate speeded up also, therefore the transesterification reaction yield decreased. Therefore, temperature was tested as an important variable to enhance the reaction in FAEE production and reduce

the cost of reaction process. In summary, defining the best temperature was clearly an optimization problem.

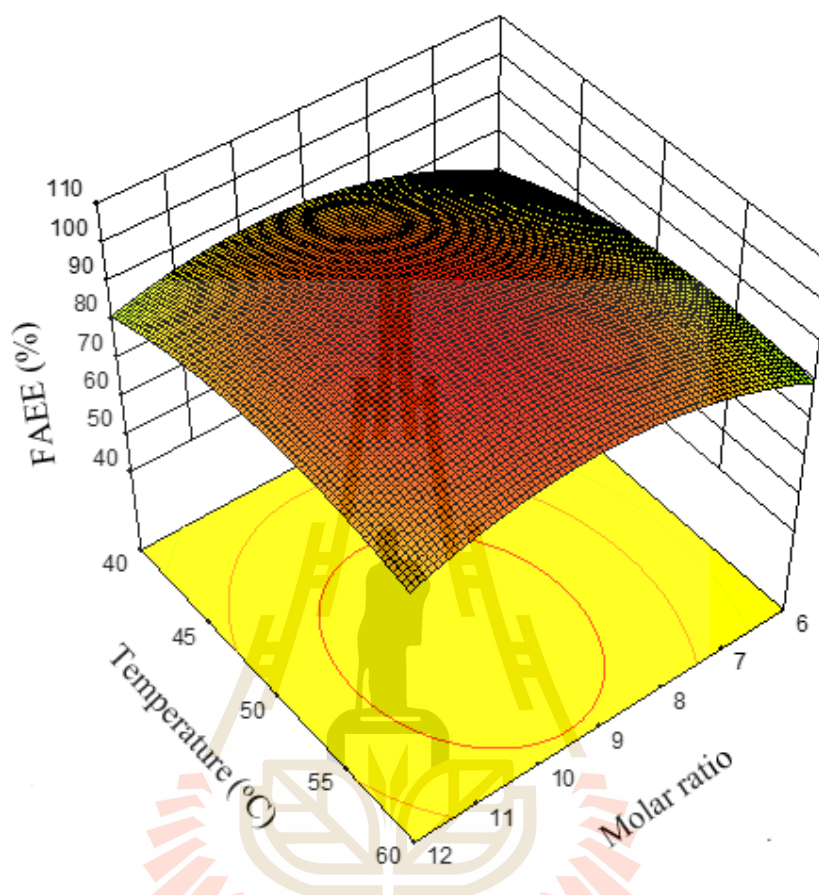


Figure 4.2 Response surface contour for interaction on ethyl esters production between molar ratio and temperature.

Figure 4.2 showed the response for the interactive factors of temperature and molar ratio. Figure 4.3 presented the response for the interactive factor of time and molar ratio. The 3D response surface plots indicated that the ethyl esters production increases when ethanol concentration increases (molar ratio: ethanol/oil) (Figure 4.2). Therefore, the maximum fatty acid ethyl esters conversions were obtained for the high molar ratio. This was caused by the stoichiometry of trans-esterification, which requires a 3:1 M ratio of alcohol to triglyceride, since this reaction involved the conversion of

one ester and an alcohol towards another ester and another alcohol, as an excess of alcohol was used to drive the reaction near the completion.

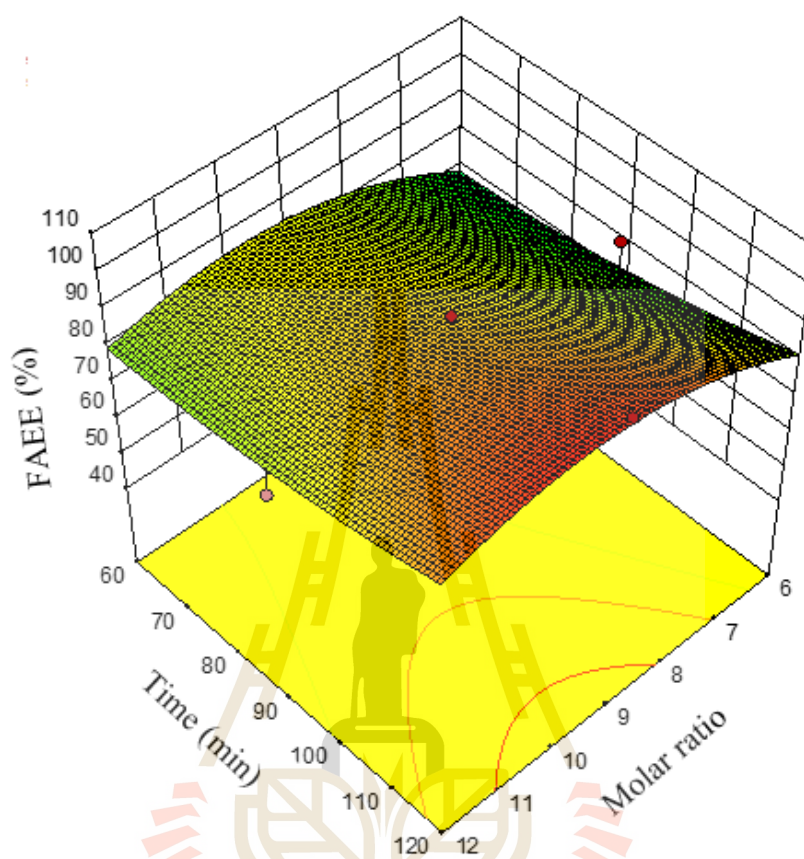


Figure 4.3 Response surface contour for interaction on ethyl esters production between molar ratio and time.

Consequently, the ethanol concentration resulted in a greater ethyl ester conversion within longer time (Figure 4.3), which is similar to Silva *et al.* (2010). However, Tanaka *et al.* (1981) reported that the FAEE conversion was achieved high yield at shorter time of reaction, this due to the reaction was quite difficult for ethanol compare to the methanol. On the other hand, an excessive amount of alcohol made the recovery of glycerol difficult (Ma *et al.*, 1998; Schuchardt *et al.*, 1998); therefore the ideal alcohol/oil ratio had to be established empirically, considering each individual

process. Fillieres *et al.* (1995) found a molar ratio between 9:1 and 12:1 to be the best for ethanol.

Higher production of ethyl esters was strongly favored when high molar ratio was employed for a certain time of reaction (X_4), temperature (X_2) and catalyst concentration (X_3) (Figs. 4.2 and 4.3). The molar ratio (ethanol/oil) was a fundamental variable in the trans-esterification of the ethyl esters production. This said molar ratio affects the separation and recovery of glycerol. A molar ratio of 6:1 is generally considered the most appropriate for methanol, although in this work, as has been indicated, we found the molar ratio 9:1 to be the best for ethanol. As well, the results are quantitatively similar to those of the literature (Ma *et al.*, 1998; Antolin *et al.*, 2002; Vicente *et al.*, 1998).

Moreover, Fillieres *et al.* (1995) and Nouredin *et al.* (1997) had hypothesized that the quality of ethyl esters depends on the large excess of alcohol. However in this study, the high molar ratio of ethanol to palm kernel oil only was resulted in the interfered in the glycerol separation, since there was an increase in solubility. When glycerol remained in solution, it helped driving the equilibrium back to the left, thereby lowering the yield of esters. The transesterification of palm kernel oil with ethanol was studied at molar ratios between 6:1 and 12:1. When temperature was high, higher ethyl ester yield was achieved (Fig. 4.2), mainly when the molar ratio increased to values of 12:1. On the other hand, at lower temperatures (40 °C), the best results were for molar ratios between 9:1 and 12:1. For molar ratios less than 9:1, the reaction was incomplete, resulted in lower FAEE conversion. For a molar ratio of 12:1, the glycerol separation was difficult and the apparent yield of esters decreased, since some of glycerol remained in the ethyl ester phase. Therefore, molar ratio 9:1 seemed

to be the most appropriate. Several researchers had found similar results for fatty acid ethyl ester production (Fillieres *et al.*,1995; Freedman *et al.*, 1982; Tomasevic *et al.*, 2003).

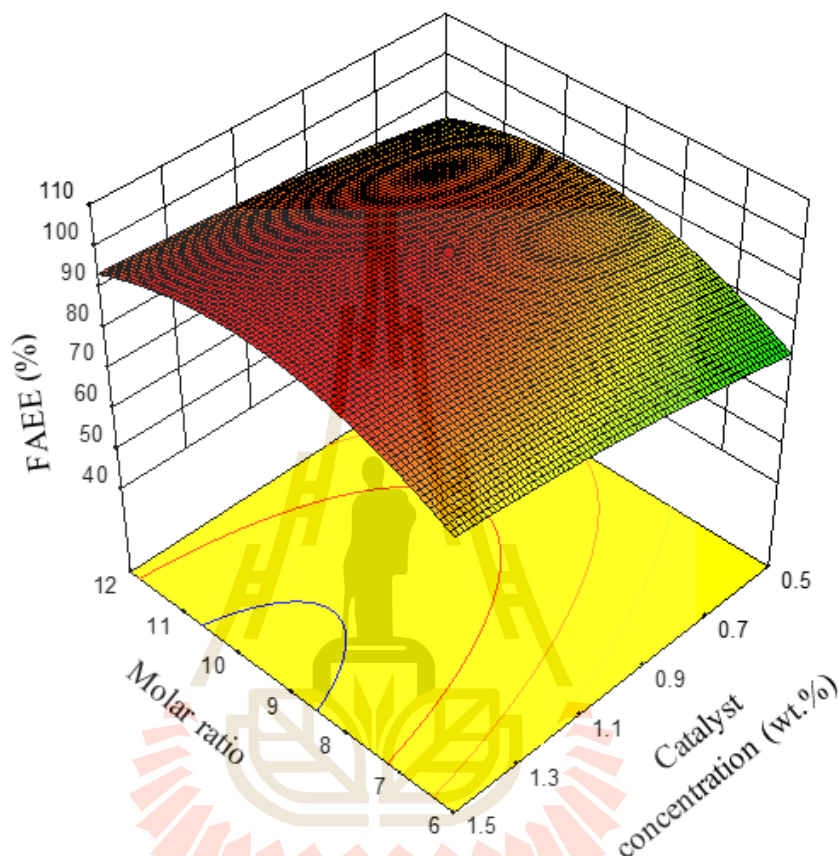


Figure 4.4 Response surface contour for interaction on ethyl esters production between catalyst concentration and molar ratio

Figure. 4.4 showed the ethyl ester yield as function of molar ratio and catalyst concentration under experimental conditions defined by factorial design. It is possible to observe that higher ethyl ester yields occurred at higher molar ratio (9:1) and at higher catalyst concentration (>1 wt.%). When molar ratio values were low (6:1), yields increased with catalyst concentration. However, when molar ratio was kept in its higher level (9:1), a higher ethyl ester yield was always achieved. Thus, catalyst

concentration was the most important factor in improving ethyl ester yields. However, excess catalyst could produce emulsions and the FAEE that was produced had difficulty in the separation phase. It has been reported that low catalyst concentration increases conversions with methanol-to-oil ratio (Ghadge *et al.*, 2006). In this present study, applying response surface design, we observed that for ethanol, ethyl esters production increases when catalyst concentration increases for low molar ratio.

4.2.3 Optimization parameters for trans-esterification reaction

The optimum values of selected variables were obtained by solving the regression. The optimum values of the process variables for maximum ethyl esters production are shown on Table 4.5, when a yield of 97% was achieved. The ester yield increased as the molar ratio ethanol to oil also increased. The best results were for molar ratios between 9:1 and 12:1. The reaction was incomplete for molar ratios less 6:1. For a molar ratio of 12:1, the glycerol separation was difficult and the apparent yield of esters decreased, because of a portion of the glycerol remaining in the ester phase.

Table 4.5 indicated that the value molar ratio for ethanol (9:1) was higher than the molar ratio found by Freedman *et al.* (1984) in the methanol (6:1). However, it was lower than the molar ratio found by Encinar *et al.* (2002), who studied the trans-esterification of Cynara oil with ethanol (12:1). Therefore, molar ratio 9:1 was seemed to be the most appropriate. Thus, reaction with ethanol used a molar ratio higher than the reaction with methanol. Therefore, the phase separation became more difficult when molar ratio of ethanol increased due to its miscibility increasing for both phases (glycerol and ethyl ester).

Table 4.5 Optimum values of the process parameter for maximum efficiency.

Parameters	Optimum values
Ethyl esters (%)	97
Molar ratio (X_1)	9:1
Temperature (X_2)	50
Catalyst concentration (wt.%) (X_3)	1
Time (min) (X_4)	120

The optimum-value temperature was 50 °C. This temperature was far below the boiling point of ethanol. Therefore, molar ratio (ethanol/oil) was used between 6:1 and 12:1, since it did not evaporate. The transesterification rate increased as the temperature increased. However, the maximum operating temperature cannot exceed the boiling point of the reactants. Encinar *et al.* (2002) had studied about the ethanolysis of refined *Cynara cardunculus* oils achieved the best results at 75 °C. This temperature was higher than the one in this present experiment. However, transesterification reaction may occur at different temperatures, depending on the oil used. In addition, ethanol/oil molar ratio was presented the difference in solubility as a function of temperature.

The highest ethyl ester yields were achieved when the reaction time was 120 min. Other authors reported that similar yields of biodiesel may be obtained following ethanolysis or methanolysis; however, the reaction times required to attain them are very different: methanolysis is quicker than ethanolysis (Meneghetti *et al.*, 2006).

The optimum value of catalyst concentration was at 1% w/v. This value agrees with the values duly presented in the literature (Noureddin *et al.*, 1997). As a typical catalyst concentration for transesterification reactions (0.5 to 1.5 wt.%), the

results that were obtained agreed with those obtained from the response surface analysis, confirming that the RSM was effectively used to optimize FAEE production.

4.2.4 Trans-esterification reaction followed by the optimization

Process optimization of trans-esterification reaction between palm kernel oil and ethanol was indicated that the best parameters or conditions for higher FAEE production were 9:1 molar ratio of ethanol/oil, 1 wt.% catalyst concentration at 50 °C within 120 minutes. Trans-esterification reaction was carried out with longer reaction time in order to confirm that the highest FAEE was achieved at these parameters and resulted in an equilibrium phase. Figure 4.5 was shown about the FAEE concentration during the reaction time. FAEE production was analyzed using Gas chromatography 7890A. As expected, the conversion of FAEE production was reached the highest value within 120 min (98.21%). The rate of reaction is strongly influenced by reaction temperature (Bajpai and Tyagi, 2006). However, given enough time, the reaction will proceed to near completion. In this study, the optimal reaction time for the completion conversion to FAEE production was achieved at 120 min. Shorter reaction time (<90 min), the conversion was incomplete. On the other hand, longer reaction time was also performed at high conversion of FAEE production, nevertheless it was not much changed compared to 120 min. The increasing in FAEE production (>120 min) then was not significantly increased, indicating that FAEE conversion reached the equilibrium and the conversion was almost completed.

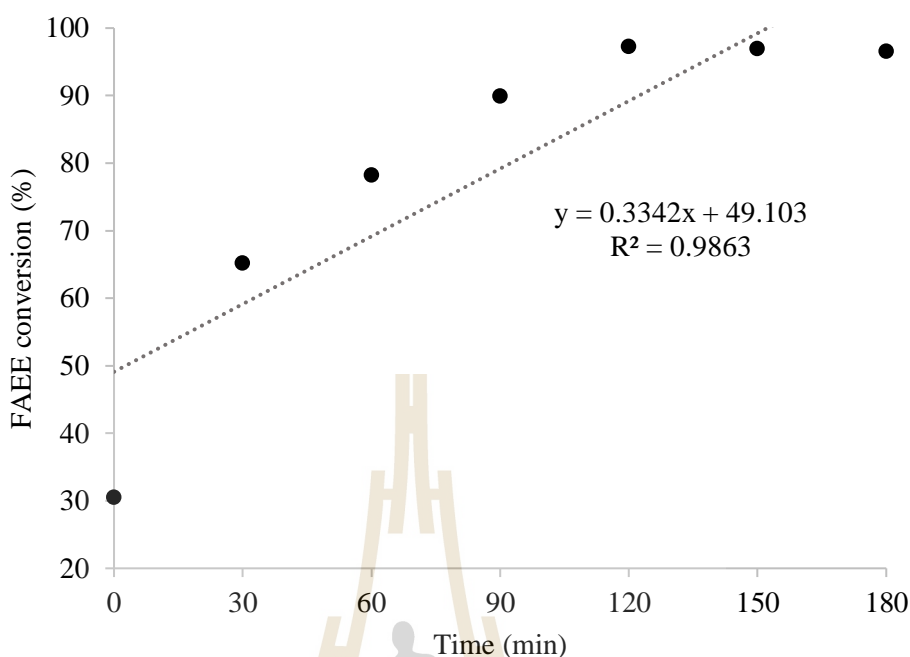


Figure 4.5 FAEE concentration through trans-esterification at 9:1 molar ratio, 1 wt.% catalyst concentration and 50 °C

4.3 Fractionation distillation process from 20L trans-esterification reaction

Trans-esterification reaction was carried out in 20 L reactor at the optimal parameters 9:1 molar ratio ethanol/oil, 1 wt.% potassium hydroxide, 50 °C (Fig 4.6). Phase separation was occurred between palm kernel oil ethyl esters and glycerol at certain time (Fig 4.7). Ethanol was removed from the mixture, and it was recovered by dehydration system using membrane. After glycerol was removed out of reactor due to its high gravity, FAEE was achieved and used for further process which was fractionation distillation to achieve FAEE from C8 to C4 or bio-jet. As mentioned above, components of fatty acid ethyls ester had different boiling, the lighter boiling point of FAEE C8-C14 were in the range from 207 to 265 °C. While the boiling point

of FAEE C16-C20 or biodiesel was shown at higher due to its high viscosity and higher molecule weight compared to C8-C14 (Table 3.3).



Figure 4.6 20L Trans-esterification reactor of PKO and ethanol

By tran-esterification reaction, fatty acid ethyl esters were produced in terms of hydrocarbon chains from C8 to C20. However for bio-jet production, medium chain of fatty acid ethyl esters was required (C8-C14) (Fig 2.2), thus FAEEs C8-C14 were needed to be separated from the mixture. The most common used purification process for ethyl esters is distillation since it allows the increase in ester content, eliminating color and smells in it, improve the filterability test and furthermore reduce the content of mono-, di- and triglycerides. On the other hand, it had increase of energy

consumption as it was a process that involves the transfer of heat which therefore require energy.



Figure 4.7 Phase separation between FAEE and glycerol.

The distillation system laboratory was carried out by high vacuum distillation with a cold trap to increase the final product avoiding thermal degradation with the use of high temperature and reduce the product loss through the pump during the fractionation. The system also included the use of enhancements to increase energy efficiency, this way of system was designed with the use of low pressure steam generation 25 mbar to reduce the heating costs of the raw material prior to distillation.

The vapor liquid equilibrium of myristic acid ethyl ester (the highest boiling point in mixture of FAEEs C8-C14) and palmitic acid ethyl ester (the lowest boiling point of mixture FAEEs C16-C18) were shown on figure 4.8. It was formed an ideal system

without azeotrope between two components. Therefore, the distillation process with fractionation column was not too difficult to separate these components.

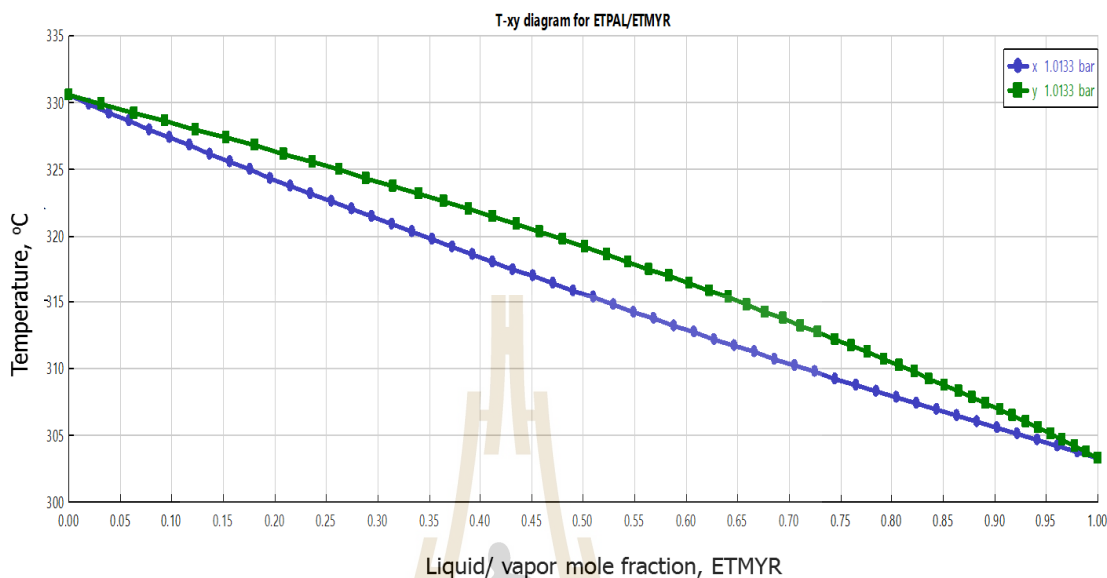


Figure 4.8 Vapor liquid equilibrium of myristic acid ethyl ester (C14) and palmitic acid ethyl ester (C16).

The fractional distillation column was designed by the simulation software AspenTech AspenPlus™ version V8.6 (Figure 4.9). After removing ethanol, phase separation was occurred in the decantor and glycerol was then take out from the system. Thus, stream product that was feeded into the column included mixture of FAEEs. The distillation process was carried out with the column including 15 stages, pressure was set up at 25 mbar with the feed stages in above 3 (feed stage is the stage that feed was put into the column) with the reflux ratio was 1.5. The Reflux ratio is the ratio between the boil up rate and the take-off rate. Or in the orther words, it is the ratio between the amount of reflux that goes back down the distillation column and the amount of reflux that is collected in the receiver (distillate). The smaller reflux ratio, the more efficiency the distillation column. In this study, the low reflux ratio was used, indicating that the

distillation column was efficient and suitable with the economical analysis since higher reflux ratio caused an expensive system for distillation.

The component profiles of fractional distillation was shown on Figure 4.10. Four components including 2 lighter boiling point components (Lauric acid ethyl ester C12- the blue line and myristic acid ethyl ester C14- green line) and 2 heavier boiling point components (Stearic acid ethyl ester C18:0- pink line and linoleic acid ethyl ester C18:2- purple line) during the each fractionation stages was chosen to be reported how the process and the concentration of components could happen in each stages.

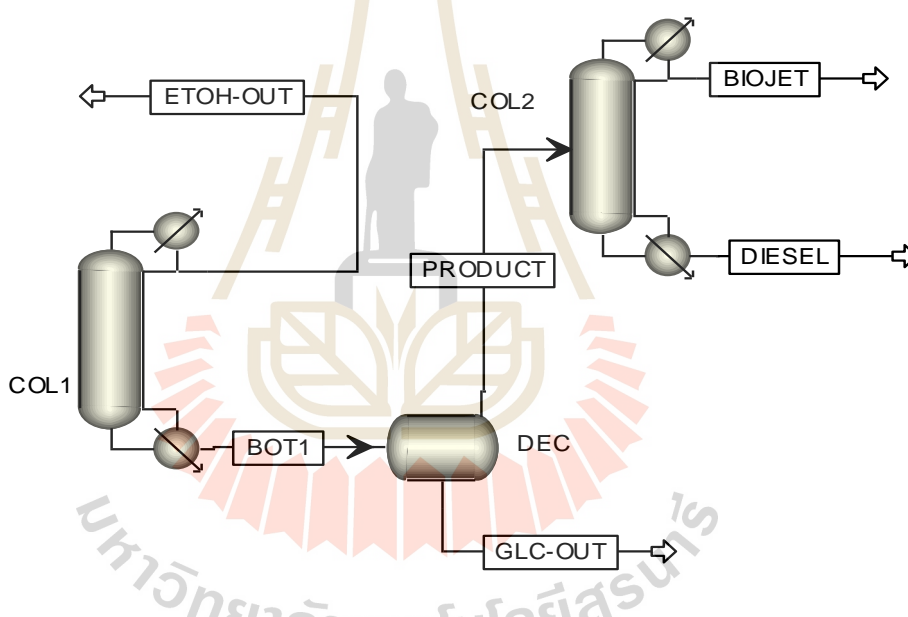


Figure 4.9 Fractionation distillation column for bio-jet production.

As shown on Figure 4.10, the distillation was performed as high process for purify bio-jet production. It was uncomplicated to separate C12 out from the mixture due to at the stages 7, almost C12 was taken out at the top of the column. However, for the myristic acid ethyl ester C14, the distillation process was carried out harder compared to C12. It took 13-15 stages to reach the equilibrium to completing system. The profiles was shown only C12 and C14, however we wanted to separate out all of FAEE C8-C14

since in PKO, around 72% of fatty acid was C12-C14 which had higher boiling point than C8-C10. Thus, by column with 15 stages, completion distillation 98.2% was achieved, around 97.6% of C8-C14 was fractionated. Then, the FAEE C8-C14 or bio-jet production from the experimental was analyzed using Gas chromatography (Figure 4.11) and compared to the predicted data from ASPEN software.

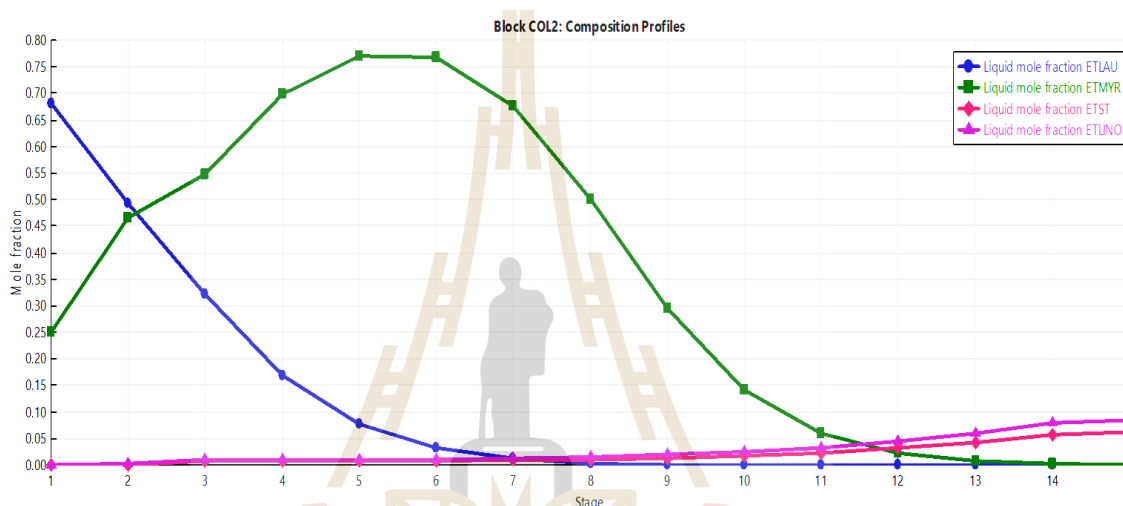


Figure 4.10 Components profiles in each stages of fractionation column, including FAEE C12, C14, C18:0 and C18:2.

As expected, the FAEE C8-C14 concentration using GC method was achieved 96.84 wt.% with the distilled conversion achieved at 97%, such an acceptable result compared to the predicted value, indicating that the fractionated distillation was efficiency process to purify bio-jet production. Around 3 wt% of fatty acid ethyl esters C16 and C18:1 was residual in the distillate stream due to high composition of these components in PKO and high temperature with high pressure was maintained to completely take out all of the desired product. Bio-jet production then was analyzed the

physical-chemical properties and compared to the conventional jet fuel that used in gas turbine engine.

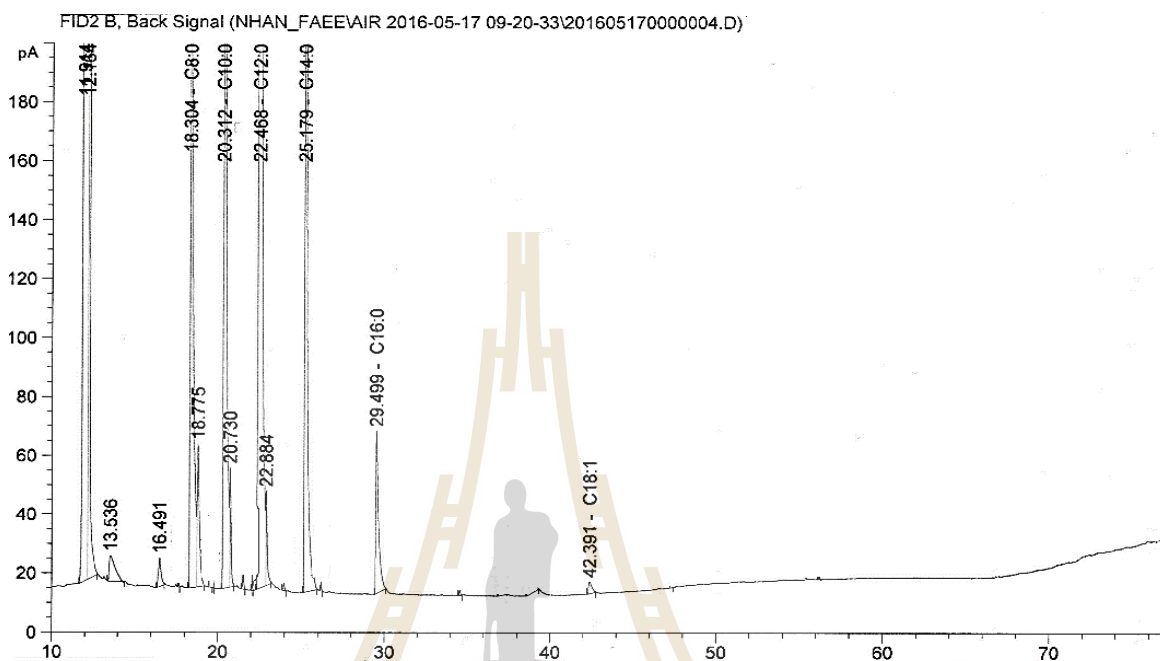


Figure 4.11 Gas chromatography of distilled bio-jet production.

4.4 Properties of bio-jet fuel production

The product of fractional distillation process, bio-jet production was shown Fig 4.12 as following. Since bio-jet fuel is produced in quite differently scaled plants from vegetable oils of varying origin and quality, it was necessary to install a standardization of fuel quality to guarantee engine performance without any difficulties. As standardization is a prerequisite for successful market introduction and penetration of bio-jet fuel, the standards or guidelines for the quality of bio-jet had also been defined in other countries like United states, European.

The parameters, which defined the quality of bio-jet fuel, were divided into two groups. One group contained general parameters, which were also used for mineral oil

based fuel and the other group especially described the chemical composition and purity of fatty acid ethyl esters (Mittelbach, 1996). Table 4.6 contained the general and the FAEE from C8-C14 according to the standards above countries.

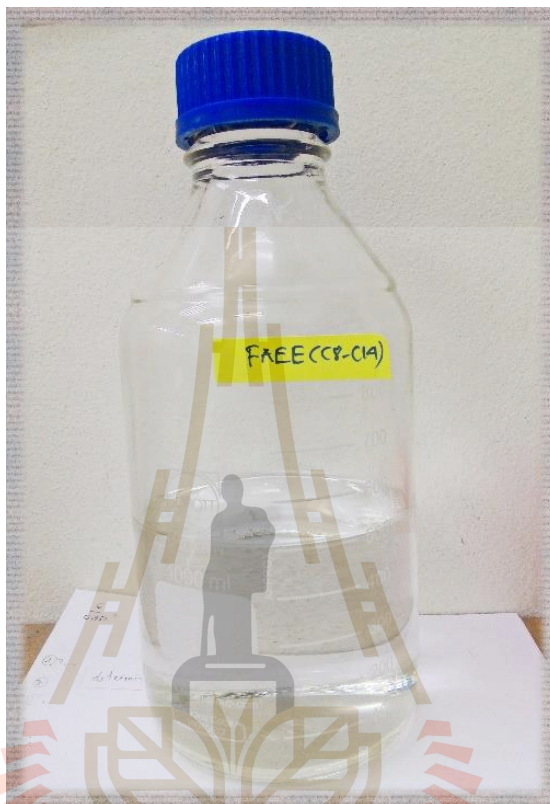


Figure 4.12 Distillated FAEE C8-C14 (bio-jet) production.

In evaluating the suitability of the PKO-biojet as alternative jet the ASTM biofuel, standard test procedures was used to characterize the PKO-biojet. The test results and the standard limit as recommended by ASTM and EN. The standard limits ASTM and EN above was reported by George *et al.* (2009); Viele *et al.* (2014) and Meher *et al.* (2006).

Table 4.6 General and specific parameters of the quality of bio-jet fuel.

Parameters	Unit	Bio-jet	Methods	ASTM limits	EN limits
Density at 15°C	kg/m ³	866.3 ± 0.0	ASTM D1298	865-885	-
Viscosity at 40°C	cSt	2.658 ± 0.001	ASTM D445	≤ 3.5 – 5.0	-
Carbon residue	% wt.	0.0190 ± 0.0014	ASTM D430	≤ 0.05	-
Acid value	mg KOH/g	1.611 ± 0.008	ASTM D664	≤ 0.8	-
Phosphorus (P)	% wt.	< 0.0000837	ICP-OES	≤ 0.0010	
Calcium (Ca)	mg/kg	<1.748	ICP-OES	≤ 5.0	
Magnesium (Mg)	mg/kg	<0.080	ICP-OES	≤ 5.0	
Sulfated Ash	% wt.	<0.005	ASTM D874	≤ 0.02	
Total contaminant	% w/v	0.00003 ± 0.00003	ASTM D5452	≤ 0.0024	
Iodine value	g Iodine/100g	1.71 ± 0.02	EN14111	-	≤ 120
Sulfur content	% wt.	<0.0001	XRF	≤ 0.0010	
Mono-glyceride	% wt.	Not detected	EN 14105		≤ 0.70
Di-glyceride	% wt.	0.21 ± 0.00	EN 14105		≤ 0.20
Tri-glyceride	% wt.	Not detected	EN 14105		≤ 0.20
Free glycerin	% wt.	0.02 ± 0.00	EN 14105		≤ 0.02
Total glycerin	% wt.	0.06 ± 0.00	EN 14105		≤ 0.25
Water content	% wt.	0.147 ± 0.003	ISO 12937		≤ 0.05
Oxidation stability at 100°C	Hours	> 10	EN 15751		≥ 10
Flash point	°C	105	ASTM D93	51	
Cloud point	°C	-10	ASTM D2500	-17	
Pour point	°C	-15	ASTM D97	-44	
Copper corrosion		No. 1a	ASTM D130		
Energy density	MJ/kg	38.3			

XRF= X-Ray Fluorescence Spectrometer

Among the general parameters for bio-jet, the viscosity controlled the characteristics of the injection from the gas engine injector. The viscosity of fatty acid ethyl esters could go very high levels and hence it was important to control it within an acceptable level to avoid negative impacts on fuel injector system performance. Therefore, the viscosity specifications proposed are nearly same as that of the jet fuel. The kinematic viscosity at 40°C for the produced PKO bio-jet fuel was 2.658 cSt. This result was acceptable within the requirement of ASTM specification for biojet fuel, not so much higher than the conventional jet fuel (2.37 cSt), indicating that PKO bio-jet produced could be used in gas turbine engines. Higher viscosity fuels can cause poor fuel combustion that leads to deposit formation as well as higher in cylinder penetration of the fuel spray. Viscosity is a measure of the fuel's adhesive or cohesive property and a minimum viscosity is required for some engines because the potential for power loss caused by injection pump and injector leakage.

Carbon residue of the fuel is indicative of carbon depositing tendencies of the fuel and an approximation of the tendency for carbon deposits to form in engine. The carbon residue measured according to the ASTM standard for the PKO bio-jet was 0.2%. This result was in the agreement with the requirement of ASTM standard. Conradsons carbon residue for bio-jet is more important than that in the jet fuel since it showed high correlation with the presence of free fatty acids, glycerides, soaps, polymers, higher unsaturated fatty acids and inorganic impurities. The acid value of the esters ranged higher than the limits specified by the standard (0.8 mg KOH/g), indicating that the acid value did not meet the standard ASTM, this due to the process neutralize was not complete and needed to be improved for using in the engine.

The phosphorus and the sulfur content was proven to be almost at zero for the ethyl esters sample. The limit set by the ASTM standard was 0.05%. The requirement is necessary to reduce sulfate and sulfuric acid pollutant emissions and to protect exhausted catalyst systems when they were developed on the gas turbine engine in the future. Yet, bio-jet proved to be unsatisfactory in terms of ISO 12937 specifications set to measure the content of water, as they surpassed 0.05 wt%. The water content in bio-jet fuel was high due to the dehydration process which used to remove water out reach the equilibrium phase, and due to the storage conditions. However, one of the most commonly thought of sources of water contamination is through condensation of atmospheric moisture to form liquid water. A research study showed that an empty 200 gallon fuel tank could contain a maximum amount of 22.8 grams of water vapor at 86 °F, and 12.92 grams at 50 °F (<http://www.yachtsurvey.com/mythofcondensationinfuel tanks.htm>). Condensation is only one of the many ways in which water can contaminate fuel.

The flash point of a fuel is the temperature at which it will ignite when exposed to a flame or spark. Conventional aviation fuel is a complex mixture of a few hundred different hydrocarbons and as such, the molecular interactions that may govern the temperature at which the flash point occurs are difficult to predict. The flash point of the PKO bio-jet was 105 °C. This value falls within the acceptable limit required by the ASTM standard. A lower flash point is an indication of the presence of alcohol not properly removed from the biojet. A higher flash point means that the alcohol which is of lower flash point had been removed and the fuel may only ignite at higher temperature. The flash point of bio-jet fuel is higher than the conventional jet fuel, which is safe and non hazardous for transport purpose (Bajpai and Tyagi, 2006). From the

perspective of storage and fire hazard, bio-jet is much safer than jet fuel. Association expressed concern that the oxidative stability of jet fuel, oxidative stability is major industry issue for jet and bio-jet fuels. The result was in agreement with the requirements of ASTM standard. Unlike biodiesel, some types of biodiesel was instable in oxidation, it may result in fuels that have unacceptable low flash point after storage. Some biodiesel had excellent storage histories; others had tended to oxidize rapidly. The degree of saturation of the fatty acid chains tended to be correlated with its stability. The stability of fatty acid was influenced by factors such as presence of air, heat, traces of metal, etc.

The values of cloud point and pour point in Table 4.6 were very high. However for the conventional jet fuel, the cloud point and pour point were -17 and -44 °C, respectively. On the other hand, the cloud point is higher than the pour point which is in agreement with the findings of Alptekin and Canakci (2008). The cloud point and pour point are properties affecting the low temperature operability of bio-jet. The cloud point of a fuel is the temperature at which the fuel becomes cloudy due to the formation of crystals which can clog fuel filters and supply lines as the fuel cooled, while the pour point is the lowest temperature at which the fuel will flow or the temperature at which the fuel contains so many agglomerated crystals that it is essentially a gel and will no longer flow.

Sulfated ash content is a measure of the amount of residual alkali catalyst in the bio-jet as well as any other ash-forming compounds that could contribute to injector deposits or fuel system fouling. The palm kernel oil bio-jet showed ash content of less than 0.005%. This result is below the maximum value of 0.02% set by the ASTM standard.

Mono- and diglycerides as well as triglycerides were referred to as bound glycerol. They were present in the feedstock oil and could remain in the final product in small quantities. A high excess of alcohol in the trans-esterification should ensure that all of triglycerides (the major component of palm kernel oil) are reacted. Moreover, the presence of high level of ethanol in bio-jet cause accelerated deterioration of natural rubber seals and gaskets. Therefore, control of alcohol content is required. A higher content of glycerides in the ester, especially triglycerides, may cause formation of deposits at the injection nozzles and at the valves (Felizardo *et al.*, 2006; Vicente *et al.*, 2006). As shown on Table 4.6, the values of mono-, di- and triglycerides were found to agree with the specified EN limits. Regarding the free and total glycerol contents, the measured values for palm kernel oil were found below the specification limits standard.

The energy density of a potential fuel impacts on the range with payload and a high energy density is vital in trying to maximize the passenger and cargo capacity while retaining range. Where weight capacity is the limiting factor, as is the case with most civil aviation flights, it is desirable to have a fuel that produces the most energy per unit mass whereas in applications where range is to be maximized, the volumetric energy content of the fuel is the most important parameter, and a higher volumetric energy content is desirable (Blakey *et al.*, 2011). The bio-jet in this study was found to have an energy content of 38.3 MJ.kg^{-1} , lower when compared to the conventional jet fuel. This may affect to the fuel consumption of the engine also due to fuel consumption was proportional to the volumetric energy density of the fuel based on the lower heating value.

4.5 Emission characteristics of bio-jet fuel production

In the combustion process, bio-jet fuel is mixtures of hydrocarbons, compounds that contain hydrogen and carbon atoms. In perfect engine, oxygen in the air would convert all of the hydrogen in fuel to water and all of carbon in fuel to carbon dioxide. In reality, the combustion process is not perfect and the engines emit several types of pollutants. The emission of the produced bio-jet fuel was measured and compared to the conventional jet fuel by one group from school of Mechanical Engineering, Suranaree University of Technology, Thailand using TESTO 350. The difference value between two of these types fuel was obtained on Table 4.7.

Table 4.7 The difference of emission level between the produced bio-jet and the conventional jet fuel.

Emission	Level	% Difference
CO ₂	High	0.7% - 1.8%
CO	Low	30% - 66%
NO ₂	Low	18% - 43%
HC	Low	11% - 41%

The amount of CO₂ produced when a fuel is burned is a function of the carbon content of the fuel. Carbon dioxide does not directly impair human health, but it is considered a “greenhouse gas”. The heat content, or the amount of energy produced when a fuel is burned, is mainly determined by the carbon (C) and hydrogen (H) content of the fuel. Heat is produced when C and H combine with oxygen (O) during combustion. During complete combustion, carbon and hydrogen combine with oxygen

(O₂) to produce carbon dioxide (CO₂) and water (H₂O). As shown on the table, the produced bio-jet was obtained at higher content CO₂ than the conventional jet with the acceptable value (<5%), indicating that bio-jet was resulted in efficiency fuel for engine with completely burning.

Nevertheless, incomplete combustion occurs when the supply of air or oxygen is poor. During incomplete combustion, water is still produced but part of the carbon is not completely oxidized producing soot or carbon monoxide (CO). As mentioned, bio-jet fuel was burned with completely process, resulted in lower CO than conventional jet around 35%, strongly confirmed that the produced bio-jet fuel would become the replacement for conventional jet fuel in the future. Furthermore, incomplete combustion resulted in the using fuel inefficiently and the carbon monoxide produced is a health hazard. It reduces the flow of oxygen in the bloodstream and is particularly dangerous to persons with heart disease.

For the hydrocarbon (HC) emissions, HC result when fuel molecules in the engine do not burn or burn only partially. Hydrocarbons react in the presence of nitrogen oxides (NO₂) and sunlight to form ground-level ozone, a major component of smog. Ozone can irritate the eyes, damage lungs, and aggravate respiratory problems. It is our most widespread urban air pollution problem. Some kinds of exhaust hydrocarbons are also toxic, with the potential to cause cancer. The conventional jet fuel was produced in high value of HC, strongly effect to the environment (Table 4.7).

With the difference value in nitrogen oxides about 18-43%, bio-jet fuel was achieved as clean burning compared to the conventional jet fuel. Under the high pressure and high temperature conditions in an engine, nitrogen and oxygen atoms in the air we breathe react to form various nitrogen oxides, collectively known as NO_x. In this study,

nitrogen dioxide was measured. Nitrogen dioxide like hydrocarbons, are precursors to the formation of ozone. They also contribute to the formation of acid rain. Thus, since greenhouse gas emission and pollutant concern were increasing, bio-jet fuel production was achieved as perfect replacement for the gas turbine engine instead of using conventional jet fuel in the next future.



CHAPTER V

CONCLUSIONS

Bio-jet has become more attractive to replace petroleum jet fuel. As per the reported literature, most of trans-esterification studies have been done on vegetable oils such as rapeseed, soybean, sunflower, etc by using methanol and NaOH/KOH as catalyst. There are few studies reported on palm kernel oil, which are produced worldwide and achieved at high yield per year. The main objective of this study was to investigate the feasibility of using palm kernel oil materials as main substrate to produce bio-jet fuel production by trans-esterification reaction and fractional distillation. The trans-esterification of palm kernel oil and ethanol was carried out on laboratory scale experiments using potassium hydroxide as catalyst. In order to obtain FAEE with high conversion, the reaction conditions, such as catalyst concentration, reaction temperature, molar ratio of ethanol/oil and reaction time were optimized on the conversion of palm kernel oil. Consequently, using response surface analysis, it was possible to study the effect of key parameters on the FAEE conversion. Process optimization was then accomplished by applying factorial design and response surface methodology. The high regression coefficient of the polynomial showed that the model was well fitted to the experimental data. Moreover, this study clearly showed that response surface methodology was a suitable method to optimize the operating conditions in order to maximize the ethyl esters production. Graphical response surfaces

were used to locate the optimum point. A full factorial central-composite design (26 assays) was successfully employed for experimental design and results analysis.

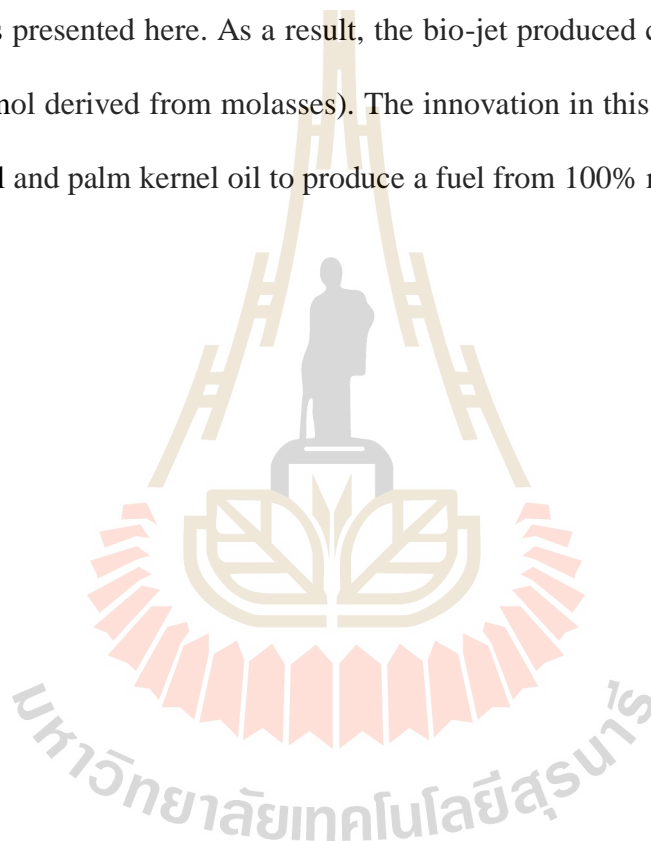
Satisfactory prediction equations were derived for the ethyl esters using RSM. The optimum concentration for molar ratio ethanol to oil, catalyst, reaction time and temperature were, 9:1, 1 wt.%, 120 min and 50 °C, respectively. At the optimum conditions, the maximum FAEE concentration was 98.21 wt.%, which was also confirmed the model prediction of 97.96 wt.%.

Subsequently, the mixture of FAEEs from trans-esterification reaction was distilled in order to separate or purify fatty acid ethyl ester C8-C14. The fractional distillation was carried out using Aspen Plus software and the column was designed followed by the process simulation for the experimental. The results were shown that with the distilled column included 15 stages, mixture of ethyl esters was feed in above stage 3, a high concentration of 96.84 wt.% bio-jet was purified from the distillation laboratory system with an agreement within process simulation by Aspen (97.6 wt.%), indicating that the distillation fractionation was successful applied process used to purify FAEE C8-C14 or bio-jet from the mixture of ethyl esters.

The ethyl ester which was produced at optimal condition and fractionated at efficient column had acceptable properties and compared well with jet fuel. It had lower sulfur content, sulfated ash, carbon residue and phosphorus than the limit standard for biofuel, but kinematic viscosity and heating value of jet fuel were some better relative to bio-jet 42 and 38.3 MJ/kg⁻¹, respectively. The flash point of bio-jet 105 °C was higher than the conventional jet fuel (51 °C), which is constituted a safety guarantee from the point view of storage.

Moreover, bio-jet fuel was obtained at lower emission of CO, NO, HC with the burning which was not only completely but also clean at the same condition testing compared to the conventional jet fuel, indicating that bio-jet production could become the replacement for gas engine in the future.

Based on the study results, the conclusion was that ethanol could substitute for the methanol in trans-esterification with palm kernel oil, when it was applied in optimized conditions, as presented here. As a result, the bio-jet produced comes from renewable sources (ethanol derived from molasses). The innovation in this work is the combined use of ethanol and palm kernel oil to produce a fuel from 100% renewable energy.



REFERENCES

- Abd Rabu, R., Janajreh, I., Honnery, D., 2013. Transesterification of waste cooking oil: process optimization and conversion rate evaluation. **Energy Convers. Manag.** 65,764–769
- Agusdinata, D. B., Zhao, F., Ileleji, K., & Delaurentis, D. (2011). Life cycle assessment of potential biojet fuel production in the United States. **Environmental Science and Technology**, 45(21), 9133-9143.
- Alptekin E., Canakci M. Characterization of the key fuel properties of methyl ester-diesel fuel blends. **Fuel**, 88 (1), pp 75-80, 2008.
- Antolín G., Tinaut F.V., Briceño Y., Castaño V., Pérez C., Ramírez A.I. Optimization of biodiesel production by sunflower oil transesterification, **Bioresour. Technol.** 83 (2) (2002) 111-144
- Atabani, A., Silitonga, A., Badruddin, I.A., Mahlia, T., Masjuki, H., Mekhilef, S., 2012. A comprehensive review on biodiesel as an alternative energy resource and its characteristics. **Renew. Sustain. Energy Rev.** 16, 2070–2093.
- Atadashi, I., Aroua, M., Abdul Aziz, A., Sulaiman, N., 2012. Production of biodiesel using high free fatty acid feedstocks. **Renew. Sustain. Energy Rev.** 16, 3275–3285
- Bailis, R. E., & Baka, J. E. (2010). Greenhouse gas emissions and land use change from *Jatropha curcas*-based jet fuel in Brazil. **Environmental Science and Technology**, 44(22), 8684-8691.

- Bajpai, D. and Tyagi, V.K. (2006) Biodiesel: Source, production, composition, properties and its benefits. **Journal of Oleo Science**, 55, 487-502
- Bermúdez, V., Lujan, J. M., Pla, B., & Linares, W. G. (2011). Comparative study of regulated and unregulated gaseous emissions during NEDC in a light-duty diesel engine fuelled with Fischer Tropsch and biodiesel fuels. **Biomass and Bioenergy**, 35(2), 789-798.
- Blakey S., Wilson CW., Farmery M., Midgley R. Fuel effects on range versus payload for modern jet aircraft. **Aeronaut J** 2011:115:627-34
- Bouaid, A., Martinez, M., Aracil, J., 2007. A comparative study of the production of ethyl esters from vegetable oils as a biodiesel fuel optimization by factorial design. **Chem. Eng. J.** 134, 93–99
- Box G.E.P., Hunter W.G., Hunter J.S., *Statistics for Experimenters: An Introduction to Design, Data Analysis and Model Building*, John Wiley, New York, 1978.
- Box G.E.P., Wilson K.B. On the experimental attainment of optimum conditions, **J. R. Stat. Soc. B** 13 (1951) 1–45
- Darnoko D., Cheryan M. “Kinetics of palm oil transesterification in a batch reactor”. **JAOCS**, 77 (12) (2000), pp. 1263–1267
- Demirbas, A. (2008). Biofuels sources, biofuel policy, biofuel economy and global biofuel projections. **Energy Conversion and Management**, 49(8), 2106-2116.
- Dorado MP, Ballesteros E, Mittelbach M, Lopez FJ. Kinetic parameters affecting the alkali-catalyzed transesterification process of used olive oil. **Energy Fuels** 2004; 18:1457-1462.

- Dorado, M.P., Ballesteros, E., Almeida, J.A., Schellert, C., Lohrlein, H.P. and R. Krause. 2002. An alkali-catalyzed transesterification process for high free fatty acid waste oils. **Transactions of ASAE** 45(3): 525-529
- Dunn, P. F., Thomas, F. O., Davis, M. P., & Dorofeeva, I. E. (2010). Experimental characterization of aviation-fuel cavitation. **Physics of Fluids** (1994-present), 22(11).
- Dunn, P. F., Thomas, F. O., Leighton, J. B., & Lv, D. (2011). Determination of Henry's law constant and the diffusion and polytropic coefficients of air in aviation fuel. **Fuel**, 90(3), 1257-1263.
- Edwards, T. (2003). Liquid fuels and propellants for aerospace propulsion: 1903-2003. **Journal of Propulsion and Power**, 19(6), 1089-1107.
- Elgowainy, J. Han, M.Q. Wang, N. Carter, R.W. Stratton, J.I. Hileman, A. Malwitz, S. Balasubramanian. Life Cycle Analysis of Alternative Aviation Fuels in GREET (No. ANL/ESD/12-8). **Argonne National Laboratory, Argonne, IL** (2012)
- Encinar J.M., Gonzalez J.F., Rodriguez J.J., Tejedor A., Biodiesel fuels from vegetable oils: transesterification of *Cynara cardunculus* L. oils with ethanol, **Energy Fuels** 16 (2002) 443-450.
- Felizardo, P., Correia, M.J.N, Raposo, I, Mendes, F.J, Berkemeier, R., Bordaro, J.M. Production of biodiesel from waste frying oils. **Waste Manage.** 2006, 26, 487-494.
- Fillieres R., Benjelloun-Mlayeh B., Delmas M. Ethanolysis of rapeseed oil quantitation of ethyl-esters, mono-glycerides, di-glycerides, and triglycerides and glycerol by high-performance size-exclusion chromatography, **J. Am. Oil Chem. Soc.** 72 (1995) 427-432

- Freedman B., Pryde E.H. Fatty esters from vegetable oils for use as diesel fuel, Proceedings Book of International Conference on Plant and Vegetable Oils as **Fuel**, ASAE, Fargo, 1982, p. 117
- Freedman B., Pryde E.H., Mounts T.L. Variables affecting the yield of fatty esters from transesterified vegetable oils. **J Am Oil Chem Soc**, 61 (10) (1984), pp. 1638–1643
- Geogre A., Ypatia Z., Stamoulis S., Stamatis K. Transesterification reaction of vegetable oils with ethanol and characterization of the key fuel properties of ethyl esters. **Energies** 2009,2,362-376.
- Gerpen, J. V. (2005). Biodiesel processing and production. **Fuel Processing Technology**, 86(10), 1097-1107.
- Ghadge S.V., Raheman H. (2006). Process optimization for biodiesel production from mahua (*Madhuca indica*) oil using response surface methodology. **Bioresource Technology**, 97, 379-384.
- Graboski, M. S.; McCormick, R. L. Prog. **Energy Combust. Sci.** 1998, 24, 125-164
- Gupta, K. K., Rehman, A., & Sarviya, R. M. (2010). Bio-fuels for the gas turbine: A review. **Renewable and Sustainable Energy Reviews**, 14(9), 2946-2955.
- Halim, S.F.A., Kamaruddin, A.H., Fernando, W., 2009. Continuous biosynthesis of biodiesel from waste cooking palm oil in a packed bed reactor: optimization using response surface methodology (RSM) and mass transfer studies. **Bioresour. Technol.** 100, 710–716.
- Hingu, S.M., Gogate, P.R., Rathod, V.K., 2010. Synthesis of biodiesel from waste cooking oil using sonochemical reactors. **Ultrason. Sonochem.** 17, 827–832

- Jalama, K., Coville, N. J., Xiong, H., Hildebrandt, D., Glasser, D., Taylor, S. and Hutchings, G. J. (2011). A comparison of Au/Co/Al₂O₃ and Au/Co/SiO₂ catalysts in the Fischer–Tropsch reaction. **Applied Catalysis A: General**, 395(1–2), 1-9.
- Jeong G.T., Yang H.S., Park D.H. (2009). Optimization of transesterification of animal fat ester using response surface methodology. **Bioresource Technology**, 100, 25-30.
- Kalnes, T. N., McCall, M. M., & Shonnard, D. R. (2010). Renewable diesel and jet-fuel production from fats and oils. **Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals**, 468-495.
- Khodakov, A. Y., Chu, W., & Fongarland, P. (2007). Advances in the development of novel cobalt Fischer-Tropsch catalysts for synthesis of long-chain hydrocarbons and clean fuels. **Chemical Reviews**, 107(5), 1692-1744.
- Khunnonkwao, P., Boontawan, P., Haltrich, D., Maischberger, T., & Boontawan, A. (2012). Purification of l-(+)-lactic acid from pre-treated fermentation broth using vapor permeation-assisted esterification. **Process Biochemistry**, 47(12), 1948-1956.
- Kister, Henry Z. (1992). *Distillation Design* (1st ed.). McGraw-Hill. ISBN 0-07-034909-6.
- Leckel, D. (2007). Low-Pressure Hydrocracking of Coal-Derived Fischer–Tropsch Waxes to Diesel. **Energy & Fuels**, 21(3), 1425-1431.
- Lee, D. S., Fahey, D. W., Forster, P. M., Newton, P. J., Wit, R. C. N., Lim, L. L. and Sausen, R. (2009). Aviation and global climate change in the 21st century. **Atmospheric Environment**, 43(22–23), 3520-3537.

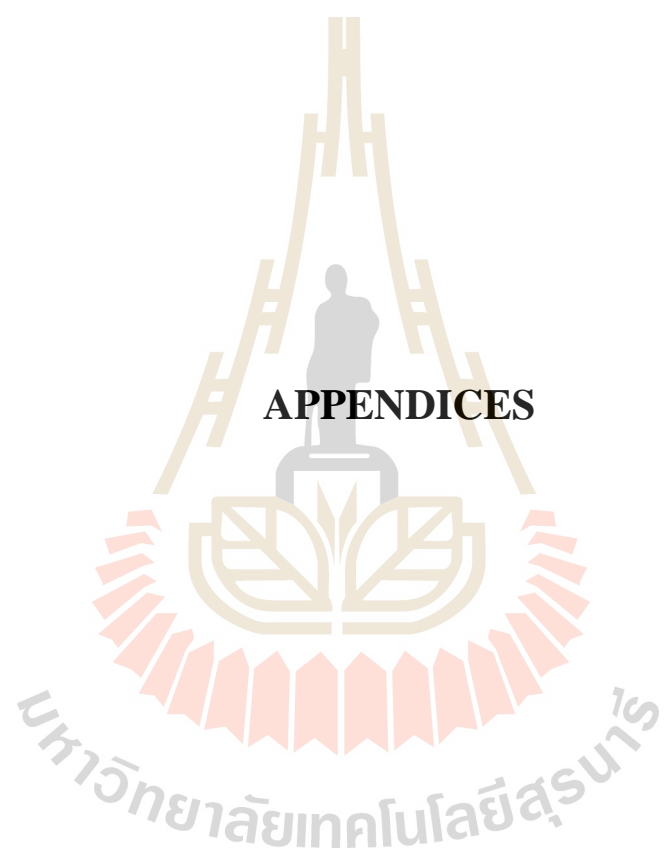
- Lee, D. S., Pitari, G., Grewe, V., Gierens, K., Penner, J. E., Petzold, A. and Sausen, R. (2010). Transport impacts on atmosphere and climate: Aviation. **Atmospheric Environment**, 44(37), 4678-4734.
- Ma F, Clements L, Hanna M. The effects of catalysts, free fatty acids and water on transesterification of beef tallow. **Transactions of ASAE**, 1998, 41(5): 1261–1264
- Ma F. and Hanna M.A. Biodiesel production: a review. **Bioresour Technol**, 70 (1999), pp. 1–15
- Martínez, A. n., López, C., Márquez, F., & Díaz, I. (2003). Fischer–Tropsch synthesis of hydrocarbons over mesoporous Co/SBA-15 catalysts: the influence of metal loading, cobalt precursor, and promoters. **Journal of Catalysis**, 220(2), 486-499.
- Mayor, K., & Tol, R. S. J. (2010). The impact of European climate change regulations on international tourist markets. **Transportation Research Part D: Transport and Environment**, 15(1), 26-36.
- Meher L.C, Vidya Sagar D., Naik S.N. Technical aspects of biodiesel production by transesterification: a review. **Renewable and Sustainable Energy Reviews**, 10(2006), 248-268.
- Meneghetti S.M.P., Meneghetti M.R., Wolf C.R., Silva E.C., Lima G.E.S., Silva L.L., Serra T.M., Cauduro F., Oliveira L.G., Biodiesel from castor oil: a comparison of ethanolysis versus methanolysis, **Energy Fuels** 20 (2006) 2262–2265.
- Mittelbach M. Diesel fuel derived from vegetable oils, VI: Specifications and quality control biodiesel. **Bioresour Technol** 1996; 27(5):435:7
- Montgomery D.C. Design and Analysis of Experiments, 5th ed. Wiley, New York, 2001

- Morais, S., Mata, T.M., Martins, A.A., Pinto, G.A., Costa, C.A., 2010. Simulation and life cycle assessment of process design alternatives for biodiesel production from waste vegetable oils. **J. Clean. Prod.** 18, 1251–1259
- Noshadi, I., Amin, N., Parnas, R.S., 2012. Continuous production of biodiesel from waste cooking oil in a reactive distillation column catalyzed by solid heteropolyacid: optimization using response surface methodology (RSM). **Fuel** 94, 156–164
- Noureddini H., Zhu D. Transesterification of soybean oil, **J. Am. Oil Chem. Soc.** 74 (1997) 1457–1463
- Oliveira, M. E. S., Pantoja, L., Duarte, W. F., Collela, C. F., Valarelli, L. T., Schwan, R. F., & Dias, D. R. (2011). Fruit wine produced from cagaita. *Eugenia dysenterica* DC) by both free and immobilized yeast cell fermentation. **Food Research International**, 44(7), 2391-2400.
- Pearlson, M., Wollersheim, C., & Hileman, J. (2013). A techno-economic review of hydroprocessed renewable esters and fatty acids for jet fuel production. **Biofuels, Bioproducts and Biorefining**, 7(1), 89-96.
- Pejovic, T., Noland, R. B., Williams, V., & Toumi, R. (2008). Estimates of UK CO₂ emissions from aviation using air traffic data. **Climatic Change**, 88(3-4), 367-384.
- Perry, Robert H. and Green, Don W. (1984). *Perry's Chemical Engineers' Handbook* (6th ed.). McGraw-Hill. ISBN 0-07-049479-7.
- Refaat AA, El Sheltawy ST, Sadek U. Optimum reaction time, performance and exhaust emissions of biodiesel produced by microwave irradiation. **International Journal of Environmental Science and Technology** 2008;5 315-322.

- Roy, I. and Gupta, M. N. (2003) Applications of microwaves in biological sciences. **Curr. Sci.** 85, 1685-1693.
- Saidur, R., Rahim, N. A., Masjuki, H. H., Mekhilef, S., Ping, H. W., & Jamaluddin, M. F. (2009). End-use energy analysis in the Malaysian industrial sector. **Energy**, 34(2), 153-158.
- Schuchardt U., Sercheli R., Matheus V.R., Transesterification of vegetable oils: a review, **J. Braz. Chem. Soc.** 9 (1998) 199–210.
- Schwab AW, Baghy MO, Freedman B. Preparation and properties of Diesel fuel from vegetable oils. **Fuel.** 1987; 66:1372–1378.
- Silva G.F., Castro M.S., Silva J.S., Mendes J.S., Ferreira A.L.O., Simulation and optimization of biodiesel production by soybean oil transesterification in non-ideal continuous stirred-tank reactor, **Int. J. Chem. Reactor Eng.** 8 (A34) (2010) 1–20
- Stratton, R. W., Wolfe, P. J., & Hileman, J. I. (2011). Impact of aviation non-CO2 combustion effects on the environmental feasibility of alternative jet fuels. **Environmental Science and Technology**, 45(24), 10736-10743.
- Stratton, R.W., Wong, H.M., Hileman, J.I., 2010. Life Cycle Greenhouse Gas Emissions from Alternative Jet Fuels. **Partnership for AiR Transportation Noise and Emissions Reduction**. Massachusetts Institute of Technology, Cambridge, MA.
- Tanaka Y., Okabe A., Ando S. Method for the preparation of a lower alkyl ester of fatty acids. **US Patent** 4,303–590, 1981.
- Tiwari AK, Kumar A, Raheman H (2007) Biodiesel production from Jatropha oil with high free fatty acids: An optimized process. **Biomass Bioenergy** 31: 569-575.

- Tomasevic A.V., Marinkovic S.S. Methanolysis of used frying oils, **Fuel Process. Technol.** 81 (2003) 1–6.
- Vicente G., Coteron A., Martinez M., Aracil J., Application of the factorial design of experiments and response surface methodology to optimize biodiesel production, **Ind. Crops Prod.** 8 (1998) 29–35.
- Vicente, G; Martiner, M.; Aracil, J. A comparative study of vegetable oils for biodiesel production in Spain. **Energy Fuels** 2006, 20, 394-398.
- Vicente, G; Martiner, M.; Aracil, J. Optimization of integrated biodiesel production. Part I. A study of the biodiesel purity and yield. **Bioresour. Technol.** 2007, 98, 1724-1733
- Viele, E. L., Chukwuma, F. O and Uyigue, L. Production and characterization of biodiesel from crude palm kernel oil and bioethanol using potash from ash of empty oil palm bunch residue as catalyst. ”, **International Journal of Application or Innovation in Engineering & Management (IJAIEM)**, 3, pp 355-363, 2014
- Viele, E. L., Uyigue, L. and Chukwuma, F. O., “Esterification of High Free Fatty Acid Crude Palm Kernel Oil as Feedstock for Base-Catalyzed Transesterification Reaction”, **International Journal of Application or Innovation in Engineering & Management (IJAIEM)**, 2, (12), pp 361-365, 2013
- Waynick, J. A. (2001). The development and use of metal deactivators in the petroleum industry: A review. **Energy and Fuels**, 15(6), 1325-1340.
- Wimmer, T. PCT. Ind. Appl. WO 9309,212 (Cl C11C3/04), 1993; **Chem. Abstr.** 120: P10719b (1994)

- Wu, X., Leung, D.Y., 2011. Optimization of biodiesel production from camelina oil using orthogonal experiment. **Appl. Energy** 88, 3615–3624
- Yaakob, Z., Mohammad, M., Alherbawi, M., Alam, Z., Sopian, K., 2013. Overview of the production of biodiesel from Waste cooking oil. **Renew. Sustain. Energy Rev.** 18, 184–193.
- Yang, J. H., Kim, H.-J., Chun, D. H., Lee, H.-T., Hong, J.-C., Jung, H., & Yang, J.-I. (2010). Mass transfer limitations on fixed-bed reactor for Fischer–Tropsch synthesis. **Fuel Processing Technology**, 91(3), 285-289.
- Yuan, X., Liu, J., Zeng, G., Shi, J., Tong, J., Huang, G., 2008. Optimization of conversion of waste rapeseed oil with high FFA to biodiesel using response surface methodology. **Renew. Energy** 33, 1678–1684
- Zagonel, G.F., Peralta-Zamora, P.G., and Ramos, L.P., 2005. Production of Ethyl Esters from Crude Soybean Oil: Optimization of Reaction Yields Using a 23 Experimental Design and Development of a New Analytical Strategy for Reaction Control, report from Research Center in Applied Chemistry (CEPESQ), Department of Chemistry, Federal University of Parana, Brazil.
- Zhou W., Konar S.K., D.G.V. Boocock. Ethyl esters from the single-phase base-catalyzed ethanolysis of vegetable oils. **J Am Oil Chem Soc**, 80 (4) (2003), pp. 367–371
- Zhou, A., & Thomson, E. (2009). The development of biofuels in Asia. **Applied Energy**, 86, Supplement 1(0), S11-S20.



APPENDICES

APPENDIX A

STANDARD FAEE ANALYSIS CURVE

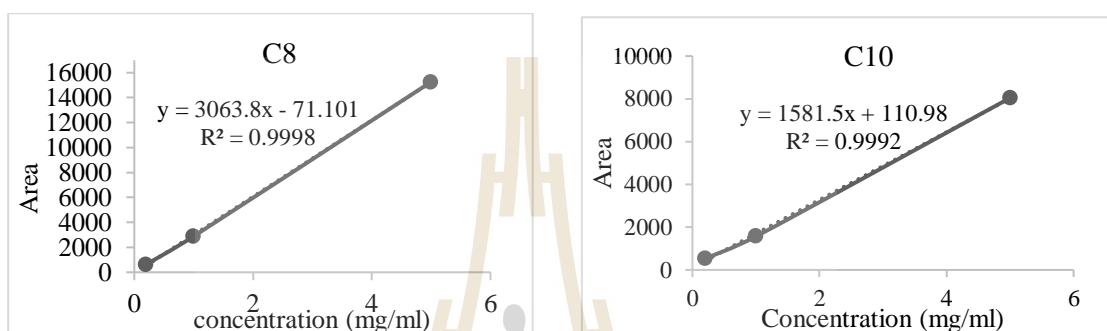


Figure 1A Standard curve of FAEE C8 and C10 using Gas Chromatography (GC).

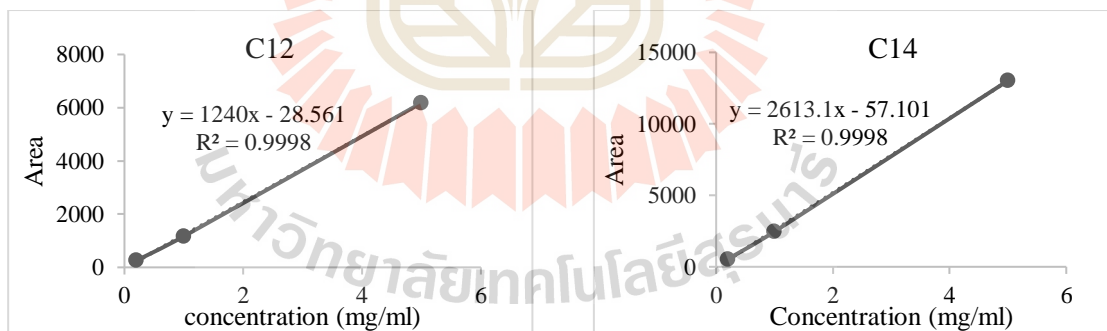


Figure 2A Standard curve of FAEE C12 and C14 using Gas Chromatography (GC).

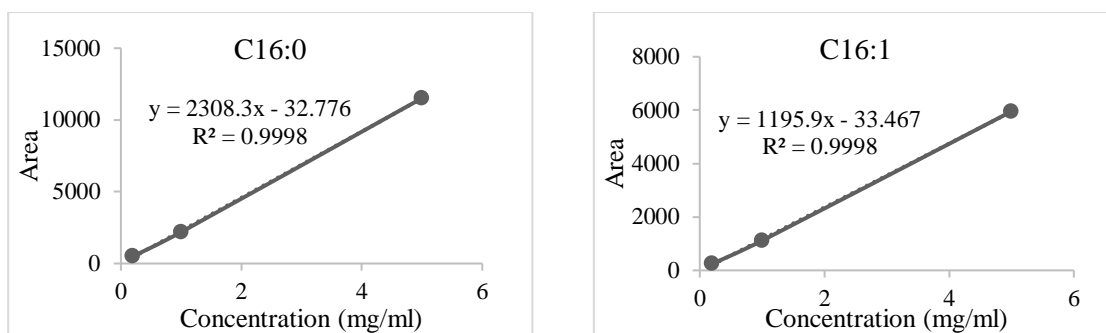


Figure 3A Standard curve of FAEE C16:0 and C16:1 using Gas Chromatography (GC).

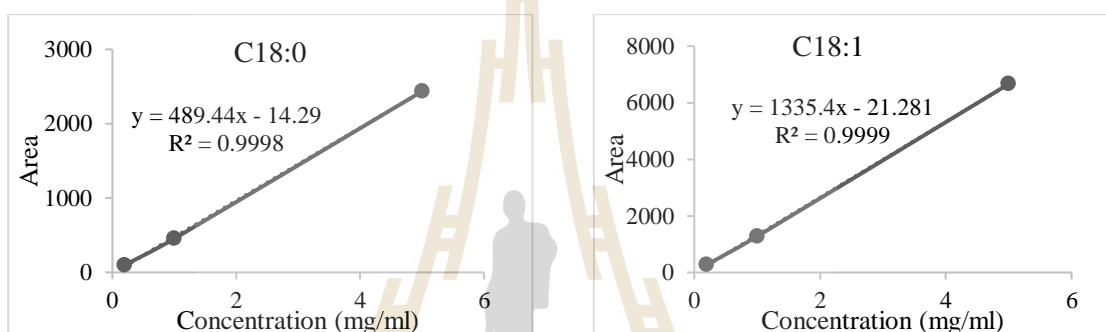


Figure 4A Standard curve of FAEE C18:0 and C18:1 using Gas Chromatography (GC).

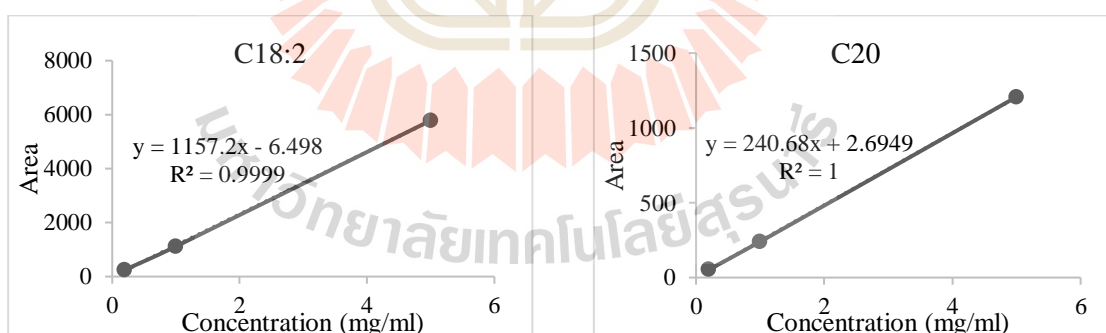


Figure 5A Standard curve of FAEE C18:2 and C20:0 using Gas Chromatography (GC).

APPENDIX B
EMISSION ANALYSIS OF BIO-JET FUEL
PRODUCTION

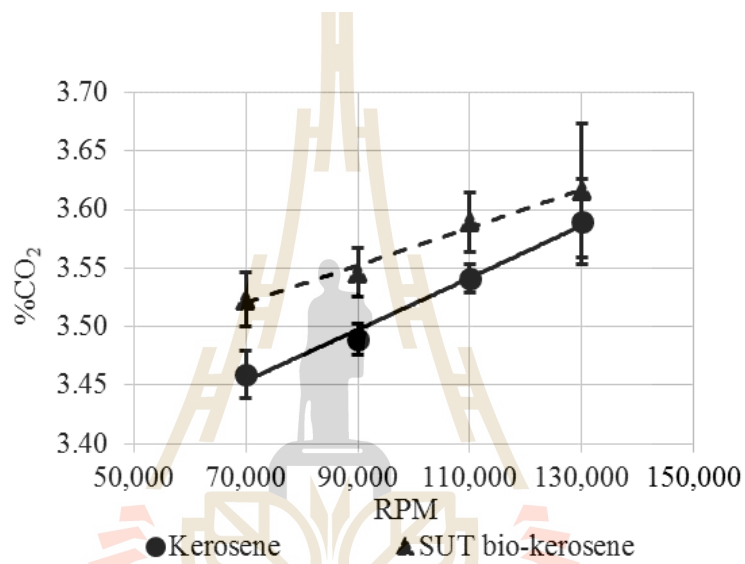


Figure 1B CO₂ emission from exhaust gas of gas turbine engine.

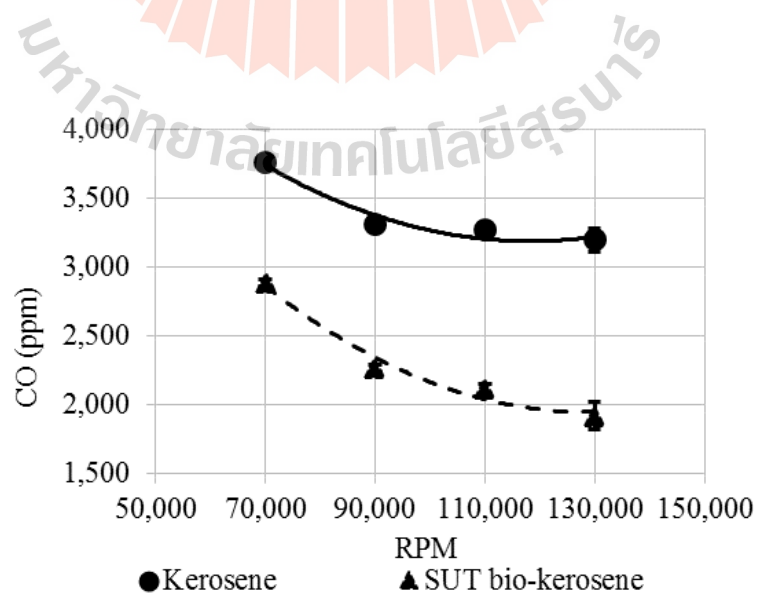


Figure 2B CO emission from exhaust gas of gas turbine engine.

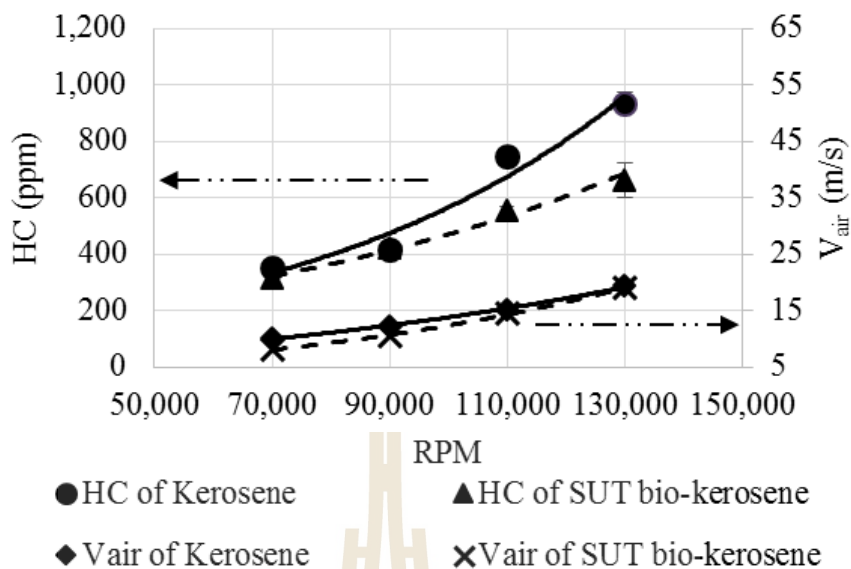


Figure 3B HC emission from exhaust gas of gas turbine engine.

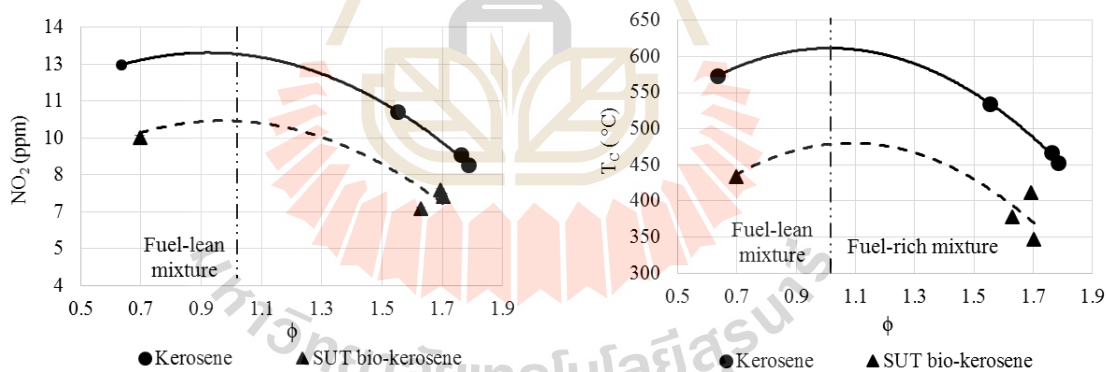


Figure 4B NO₂ emission from exhaust gas of gas turbine engine.

BIOGRAPHY

Ms. Nhan Thi Thuc Truong was born on April 22, 1991 at Thua Thien Hue, Vietnam. She obtained her Bachelor degree of Engineering in Post-Harvest from Department of Post-Harvest and Food Technology, Hue Agriculture and Forestry, Hue university, in 2009. After graduation, she decided to further study for master degree in the field of Biofuels at school of Biotechnology, Institute of Agricultural Technology, Suranaree University of Technology, Nakorn Ratchasima, Thailand. During study, she received scholarship from Thai-German cooperative between Suranaree University of Technology, Thailand and Oldenburg University, Germany to do some part of her research in Germany from 7th, July to 5th, September. During this time, she had experience to practice skills in improvement of simulation process using Aspen plus software with the additional calculation. She researches topic was Development of bio-jet fuel production using palm kernel oil and ethanol. The results from part of thesis have been presented as an innovation process to produce bio-jet fuel production, renewable energy from agricultural sources at the 8th Northeast Thailand Innovation contest, Suranaree University of Technology, Nakorn Ratchasima, Thailand.