HYDROPROCESSING OF PALM OIL FOR SECOND GENERATION BIODIESEL PRODUCTION

By

Songphon Phimsen

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree
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Department of Chemical Engineering
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กระบวนการไฮโดรโพรเซสซิ่งของน้ำมันปาล์มสำหรับการผลิตไบโอดีเซลยุคที่ 2

โดย
นายทรงพล พิมเสน

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี
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The Graduate School, Silpakorn University has approved and accredited the Thesis title of “Hydroprocessing of palm oil for second generation biodiesel production” submitted by Mr.Songphon Phimsen as a partial fulfillment of the requirements for the degree of Master of Engineering in Chemical Engineering.

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SONGPHON PHIMSEN : HYDROPROCESSING OF PALM OIL FOR SECOND GENERATION BIODIESEL PRODUCTION. THESIS ADVISORS : ASST.PROF. WORAPON KIATKITTIPONG, D.ENG., AND PROF. SUTTICHAI ASSABUMRUNGRAT, Ph.D.. 104 pp.

Hydroprocessing of crude palm oil (CPO) and its physical refining including degummed palm oil (DPO) and palm fatty acid distillate (PFAD) used to produce diesel with 5 wt.% Pd/C catalyst was studied in this work. The effect of operating parameters such as reaction time, operating temperature, and pressure, was examined in order to determine suitable operating condition for each feedstock. When using CPO as feedstock, the highest diesel yield of 51% was achieved at 400°C and 40 bar with reaction time of 3 h. When gum is removed from CPO, named DPO, the highest diesel yield of 70% was obtained in shorter reaction time of 1 h. In case of PFAD, which mainly contains free fatty acids, maximum diesel yield of 81% could be obtained with milder conditions of 375°C and reaction time of 0.5 h. The main liquid products are *n*-pentadecane and *n*-heptadecane, which contain one carbon atom shorter than the total length of corresponding fatty acid $C_{(n-1)}$ i.e. palmitic and oleic acid, respectively, which are obtained via decarboxylation/decarbonylation pathways.

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Department of Chemical Engineering Graduate School, Silpakorn University Academic Year 2011

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งานวิจัยนี้ได้ทำการศึกษาปฏิกิริยาไฮโดรโพรเซสซิ่งของน้ำมันปาล์มดิบ น้ำมันปาล์มที่ถูกเอายางออก และกรดไขมันที่ได้จากกระบวนการกลั่นน้ำมันปาล์ม เพื่อใช้ในกระบวนการผลิตน้ำมันดีเซลโดยใช้ 5% โดยน้ำหนักของแพลลาเดียมบนตัวรองรับถ่านกัมมันต์เป็นตัวเร่งปฏิกิริยา โดยในการทดลองนี้ได้ทำการศึกษาหาสภาวะที่เหมาะสมในการทำปฏิกิริยาของสารตั้งต้นแต่ละชนิดได้แก่ ระยะเวลาในการทำปฏิกิริยา อุณหภูมิ และความดันของการเกิดปฏิกิริยา จากผลการทดลองพบว่าเมื่อใช้น้ำมันปาล์มดิบเป็นสารตั้งต้น ทำปฏิกิริยาที่อุณหภูมิ 400 องศาเซลเซียส และความดัน 40 บาร์ เป็นเวลา 3 ชั่วโมงจะให้ผลได้ของน้ำมันดีเซล 51% และเมื่อใช้น้ำมันปาล์มที่ถูกเอายางออกเป็นสารตั้งต้นพบว่าจะให้ผลิตภัณฑ์ของน้ำมันดีเซลที่สูงถึง 70% และใช้เวลาในการทำปฏิกิริยาเพียง 1 ชั่วโมง และเมื่อใช้กรดไขมันที่ได้จากกระบวนการกลั่นน้ำมันปาล์มเป็นสารตั้งต้นในการทำปฏิกิริยาพบว่าให้ผลิตภัณฑ์ของน้ำมันดีเซลสูงที่สุดคือ 81% โดยใช้สภาวะในการทำปฏิกิริยาที่ไม่รุนแรงนั้นคือใช้อุณหภูมิ 375 องศาเซลเซียสและใช้เวลาในการทำปฏิกิริยาเพียง 30 นาที เนื่องจากกรดไขมันที่ได้กระบวนการกลั่นน้ำมันปาล์มมีองค์ประกอบหลักเป็นกรดไขมันอิสระ นอกจากนี้ยังพบว่าองค์ประกอบหลักที่พบในผลิตภัณฑ์เฟสของเหลวคือนอร์มัลแอลเคนที่มีคาร์บอนอะตอม 15 และ 17 อะตอม ซึ่งมีคาร์บอนอะตอมน้อยกว่าคาร์บอนอะตอมในกรดไขมันของกรดปาล์มิติกและโอเลอิกอยู่ 1 อะตอม ตามลำดับ นั้นแสดงให้เห็นว่าปฏิกิริยาที่เกิดขึ้นเกิดผ่านปฏิกิริยาดีคาร์บ็อคซิลเลชั่นและดีคาร์บอนิลเลชั่นเป็นหลัก

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ลายมือชื่อนักศึกษา..

ลายมือชื่ออาจารย์ที่ปรึกษาวิทยานิพนธ์ 1. .... 2. ....

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CHAPTER 1

INTRODUCTION

Nowadays, most of world's energy comes from fossil because fossil are considered convenient and effective (Schlager et al., 2006). However, fossil fuel burning is a big contributor to increase carbon dioxide (CO_2) concentration in the atmosphere, the main greenhouse gas cause global warming problem, leading to climatic change, rise in sea levels, changes in the rain-fall (Honjo, 1996) and serious health effects (infectious diseases) (Khasnis and Nettleman, 2005). Because the adverse effects of greenhouse gas emission on the environment together with an increase of oil prices as well as shortage petroleum reserves (Naik et al., 2010), an innovative solution for future fuel has therefore been recognized. Fuels derived from renewable recourses, such as biomass (i.e. vegetable oil, wood) are considered as an alternative. Because it have many advantage than fossil fuels such as reduce greenhouse gas emissions, decreased dependence on fossil fuels and environmentally friendly. The most popular of alternative energy is a biodiesel because it has high combustion efficiency (Snare et al., 2006). The using vegetable oil as an alternative diesel fuel is restricted by their high viscosity due to oxygen-containing species so several routes have been tried for reducing this viscosity, such as diluted vegetable oil with diesel fuel, microemulsification with alcohols, crushing and solvent extraction, as well as transesterification (Lestari et al., 2010). However, the obtain fuel from these process were not popular for use as transportation fuel so the biodiesel have been developed as alternative fuel. Traditional process for biodiesel production was transesterification shown in Figure 1.1. Triglyceride reacts with an alcohol in the presence of either a homogeneous or heterogeneous catalyst to form a mixture of fatty esters (biodiesel) and glycerol. Methanol is mainly used in commercial biodiesel production because of its low cost and availability. In comparison with conventional diesel fuels, biodiesel can reduce particulate matter (PM), un-burnt hydrocarbon

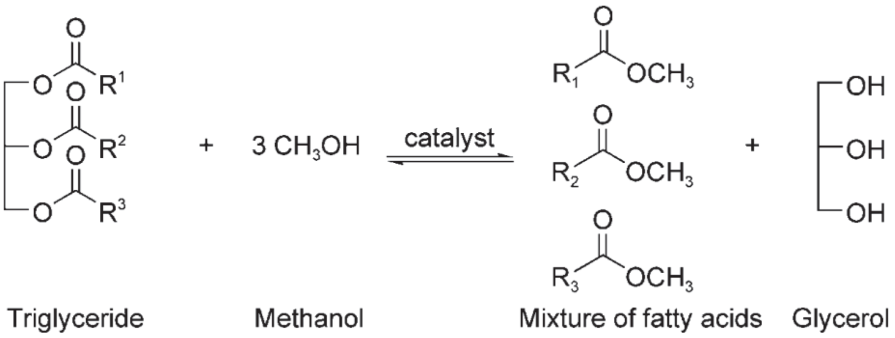


Figure 1.1 Transesterification reaction (Lestari et al., 2009).

(UHC) and carbon monoxide (CO) emissions. These benefits occur because biodiesel contains 10% oxygen by weight which can promote a more complete combustion (Zheng et al., 2008). Besides the analysis of a life cycle, the overall carbon-dioxide (CO_2) emission was calculated to be decreased by 78% in modern four-stroke compression-ignition diesel engines (Atadashi et al., 2010). Conventional biodiesel or FAME is used either in pure form, or in mixtures with mineral diesel up to 5 vol% according to EN 590 (Simacek et al., 2009). Although FAME has been used as diesel fuel for many years, the use of FAME is connected with some drawbacks as compared to the use of petroleum-based diesel fuel such as limited compatibility with conventional diesel engines, use of high quality food feedstock (Kubicka et al., 2009), increased amount of glycerol as a byproduct (Huber et al., 2007), increased NO_x emissions, physical property limitations or low-temperature properties (higher viscosity and cloud point), oxidative stability, gum formation and possible engine problems due to their higher acid number than that of conventional diesel fuels. This fuel is called to 1st generation biodiesel. To avoid the disadvantageous physical properties of FAME oxygenated fuel, catalytic cracking or pyrolysis has been investigated as an alternative pathway of biofuel production. The catalytic cracking technology is used to break down large hydrocarbon molecules into smaller hydrocarbon molecule in the presence of catalyst at a high temperature. The main product of this process is a mixture of hydrocarbons and oxygenated compounds, including carboxylic acid, ketones, and aldehydes as well as water and gaseous products. However, low selectivity is the drawback of catalytic cracking. Pyrolysis of biomass is the direct thermal decomposition of organic matrix in the absence of oxygen supply, to produces a gas mixture (containing mainly carbon oxide and some methane), carbon rich solid residue (char and coke) and liquid oil (bio-oil) including alkanes, alkenes, alkadienes, aromatics and carboxylic acids (Chew and Bhatia, 2008). Many investigators have studied the pyrolysis of triglycerides to obtain products suitable for diesel engines. The bio-oil from this process has similar chemical components to conventional petroleum diesel fuel. However, the major problem for direct utilization of bio-oil as transportation fuels are low heating value, high water content, high viscosity, coking, corrosiveness and cold-flow problems (Srivastava and Prasad, 2000). The drawbacks of technology like pyrolysis or catalytic cracking could be overcome by the developed process named hydroprocessing processes. In this process, triglyceride and fatty acids are converted to straight chain alkane ranging from n-C_{15}-n-C_{18} which is known as middle distillates. Theses straight chain alkanes are found to be suitable as alternative diesel fuels as they have a high cetane number (> 98) than typical diesel fuel, which has a cetane number around 45. Previously, this process is usually used in a petroleum refinery, designed to remove contaminants such as sulfur, nitrogen, condensed ring aromatics, metals from petroleum-derived feedstocks. Conventional hydrotreating catalysts containing sulfided mixes oxides such as NiMo, NiW, and CoMo can be used in the process. The obtained hydrocarbon products refer to as “second generation biodiesel” (Lestari et al., 2009). Besides the aforementioned term ‘‘second generation biodiesel’’, the terms ‘‘green diesel’’ and ‘‘renewable diesel’’ have been used interchangeably for petrodiesel-like fuels derived from biological sources (Knothe, 2010).

In this study, hydroprocessing of crude palm oil (CPO) and its physical refining, i.e. degummed palm oil (DPO) or palm fatty acid distillate (PFAD), catalyzed by 5%wt Pd/C was investigated. The experiments were performed in a small batch shacking reactor. The effect of operating parameters, e.g. residence time, operating temperature, and pressure, are varied in order to examine optimal operating condition and effect of operating parameters on catalyst activity (conversion, selectivity and diesel yield) for each feedstock.

Objective of the Research

To convert the crude palm oil (CPO) and its derivatives into straight chain hydrocarbons in the middle distillate boiling range, which is known as green biodiesel, by hydroprocessing.

CHAPTER 2

THEORY

In this chapter, we provide some background information of hydroprocessing for biodiesel production, vegetable oil mechanism and properties of diesel production.

2.1 Palm oil

Palm oil, palm kernel oil are edible oils derived from the fruits of palm trees (from the African oil palm, *Elaeis guineensis*), which is a local plant in the tropical rain forest region of West Africa. The individual fruit (Figure 2.1) are made up of an outer skin (the exocarp), a pulp (mesocarp) containing the palm oil in a fibrous matrix; a central nut consisting of a shell (endocarp); and the kernel, which itself contains an oil, quite different to palm oil. Palm oil is extracted from the mesocarp of the palm *Elaeis guineensis*.

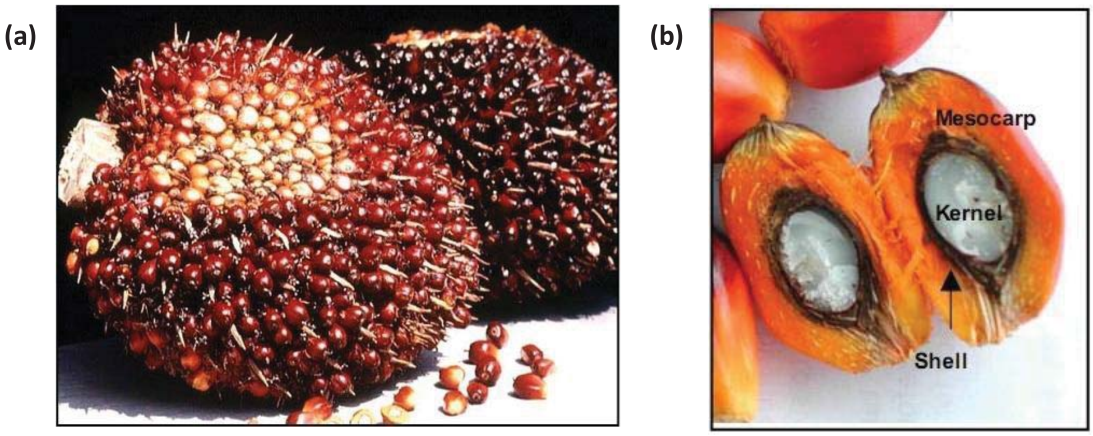


Figure 2.1 (a) Fresh fruit bunches (FFB) **(b)** Cross section of a fruitlet (WWF Malaysia, 2002)

The mesocarp comprises about 70 - 80% by weight of the fruit and about 45 -50% of this mesocarp is oil. The rest of the fruit comprises the shell, kernel, moisture and other non fatty fiber. The extracted oil is known as crude palm oil (CPO) which until quite recently was known as the golden commodity. The palm oil comprises mainly of triglycerides, mono and diglycerides. Free fatty acids, moisture, dirt and minor components of non oil fatty matter referred to collectively as unsaponifiable matter.

2.1.1 Triglyceride

A triglyceride or triacylglycerol, triacylglyceride is chemically an ester derived from a glycerol and three fatty acids. The glycerol being an alcohol has three hydroxyl (-OH) groups while each fatty acid being an acid has carboxyl (COOH) groups, shown as Figure 2.2. While constituting triglycerides the hydroxyl groups of glycerol join with the carboxyl groups of fatty acids to from ester bonds.

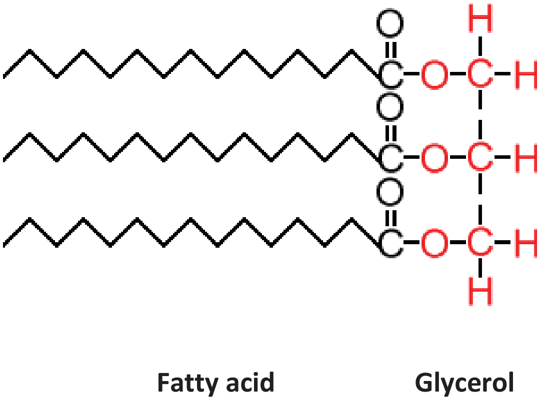


Figure 2.2 structure of triglyceride.

Palm oil has high in saturated fatty acids, 16-carbon saturated fatty acid palmitic acid, as shown in Table 2.1. The property of triglyceride depends on the different fatty acids that combine to form the triglyceride. If the triglyceride is composed of saturated fatty acid, it will be in solid form at room temperature and are thus difficult to apply as transportation fuels, whereas the use of unsaturated fatty acid leads to excessive carbon deposits in the engine. The fatty acids themselves are different depending on their chain length and degree of saturation. The short chain fatty acids are of lower melting point and are more soluble in water than the long one. Whereas, the longer chain fatty acids have higher melting points. Moreover, the melting point is also dependent on degree of unsaturation. Unsaturated fatty acids have a lower melting point compared to saturated fatty acids of similar chain length. The two most predominant fatty acids in palm oil are C16:0 (saturated) palmitic acid and C18:1 (unsaturated) oleic acid, as shown in Table 2.1. Compared to soybean oil, palm oil has a higher amount of saturated fatty acids but this makes it more stable and less prone to oxidation at high temperature (WWF Malaysia, 2002).

Table 2.1 Distribution of fatty acid in palm and soy oil. **(**Eksomtramage et al., 2009 and WWF Malaysia, 2002**)**

Fatty acid	CPO	PFAD	RPO	RPS	Soy Oil
C 8:0 (caprylic acid)	-	-	-	-	
C 10:0 (Capric acid)	-	-	-	-	
C 12:0 (Lauric acid)	-	0.3	-	-	
C 14:0 (Myristic acid)	1.1	1.3	1.0	1.3	
C 16:0 (Palmitic acid)	43.5	47.1	39.8	54.0	6.5
C 18:0 (Steric acid)	4.3	4.5	4.4	4.7	4.2
C 18:1 (Oleic acid)	39.8	35.7	42.5	32.3	28.0
C 18:2 (Linoleic acid)	10.2	9.3	11.2	7.0	52.6
C18:3 (Lonolenic acid)	0.3	0.5	0.4	0.1	8.0
Iodine number	53.0	-	58.0	39.9	133.0

CPO = Crude palm oil
PFAD = Palm fatty acid distillate
RPO = Refined palm olein
RPS = Refined palm stearin

2.1.2 Mono and di-glycerides and FFA

The hydrolysis reaction was considered when presences of heat and water, the triglycerides break up to form FFA thus yielding mono and di-glycerides and FFA. The reaction were shown in Figure 2.3.

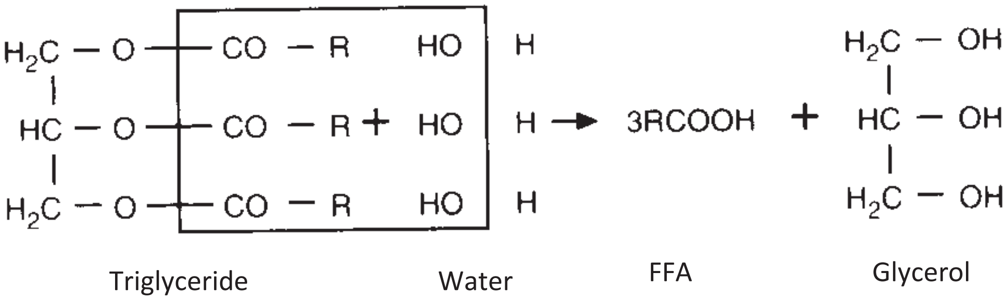


Figure 2.3 Hydrolysis of triglyceride.

2.1.3 Moisture and dirt

This is a result of milling practice. Good milling will reduce moisture and dirt in palm oil but normally it is in the range of 0.25wt%.

2.1.4 Minor component

The minor component is the other components that are not really oils i.e. Carotineoids, Tocopherols, Sterols, Polar Lipids, and Impurities. They are referred to as unsaponifiable matter.

2.2 Physical refinery

Palm oils consist mainly of glycerides and variable content of non-glyceride components. In order to render the oils to an edible form, some of these non-glycerides need to be either removed or reduced to acceptable levels.

The objective of the physical refining is therefore to convert the crude palm oil to quality edible oil by removing objectionable impurities to the desired levels in the most efficient manner. This also means that, where possible, losses in the desirable component are kept minimal. The impurities in the crude palm oil (CPO) are shown in Table 2.2:

Table 2.2 The impurities are contained in the crude palm oil (CPO)

Substances	**Content**
Free Fatty Acid (FFA)	3 - 5%
Gums (phospholipids, phosphotides)	300 ppm
Dirt	0.01%
Shell	Trace
Moisture and Impurities	0.15%
Trace metal	0.50%
Oxidation Products	Trace
Total Carotenoids	500 - 1000 mg/kg

Currently, palm oil in Thailand produced by extraction process and physical refining process, shown as Figure 2.4.

2.2.1 Degumming: The CPO is pumped through a plate heat exchanger and steam heater to increase the CPO temperature to 90 – 130 °C. Then, the CPO feed is pumped to static mixers and the phosphoric acid is added ca. 0.35 – 0.45 kg/ton. Inside there, the intensive mixing is carried out with the crude oil for precipitation up the gums. The precipitation of gums will ease the later filtration process, avoid the scale formation in deodorizer and heating surface. The DPO then will go into bleacher.

2.2.2 Bleaching: The DPO is mixed with the bleaching earth clay inside bleacher in order to remove any undesirable impurities (all pigments, trace metals, oxidation products) from CPO and to improve the initial taste, final flavor and oxidative stability of product. This process also helps to overcome problems in subsequent processing by adsorption of soap traces, pro-oxidantion metal ions, decomposition of peroxides, color reduction, and adsorption of other minor impurities. The slurry containing the oil and bleaching earth is then passed through the filter to give a bleached palm oil (BPO)

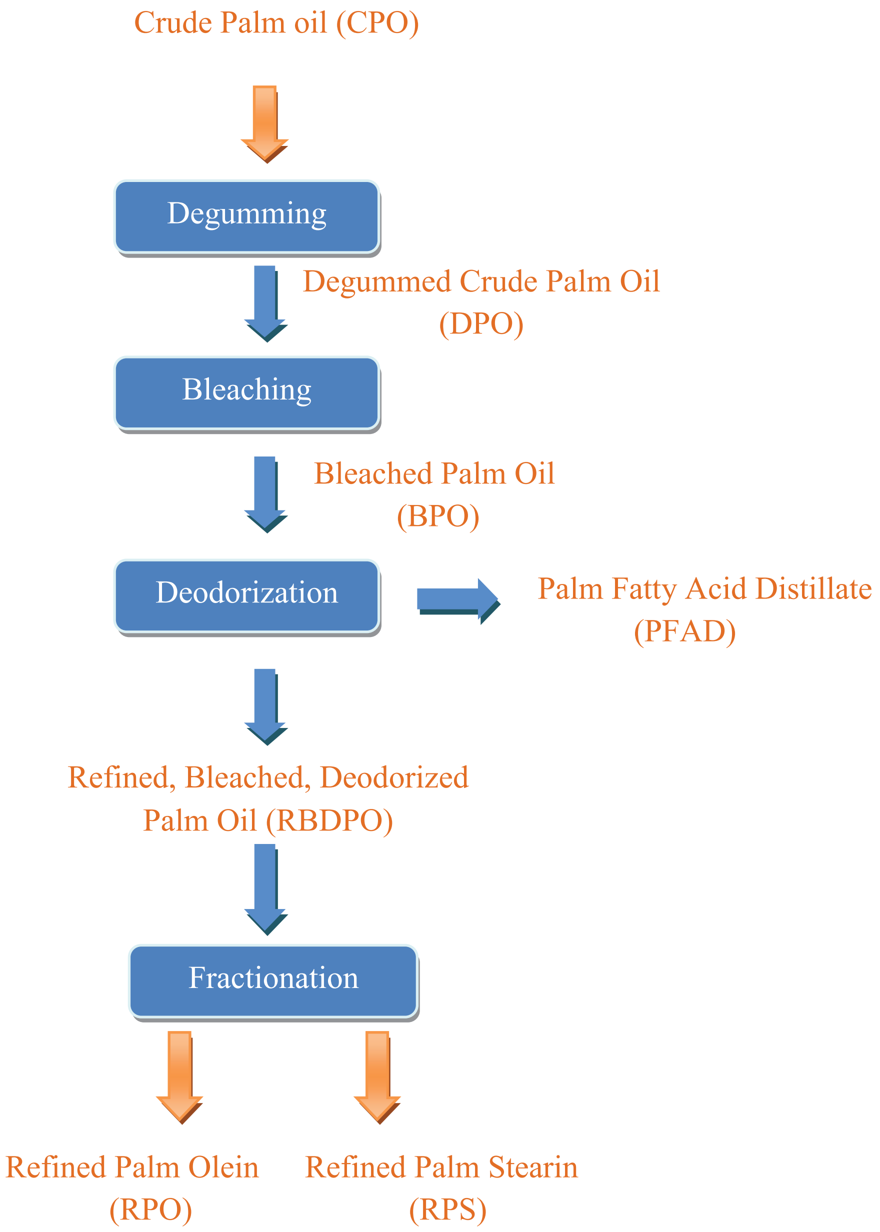


Figure 2.4 Physical refining process of crude palm oil

2.2.3 Deodorization: In this step, bleached palm oil deodorized to produce a product which has mild favor and become more stable. In addition, besides this objective, this process also aids to reduce free fatty acid content and color. Deodorization is a high temperature, high vacuum and steam distillation process. The use of direct steam ensures readily removal of residue free fatty acids, aldehydes and ketones which are responsible for unacceptable odor and flavors. The lower molecular weight of vaporized fatty acids rises up the column and pulls out by the vacuum system. The fatty acid vapor leaving the deodorizer are condensed and collected in the fatty acid condenser. The fatty acids is then cooled in the fatty acid cooler and discharged to the fatty acid storage tank as palm fatty acid distillate (PFAD), a by-product from refinery process. The bottom product is Refined, Bleached, Deodorized Palm Oil (RBDPO)

2.2.4 Fractionation: The dry fractionation is used to separate the palm olein and palm stearin from the RBDPO produced by physical treatment. The RBDPO is passed through the further fractionation process to get various grade of palm olein and palm stearin (http://www.andrew.cmu.edu/user/jitkangl/Palm Oil/Refinery of Palm Oil.htm)

2.3 Diesel product properties

For test physiochemical properties of the obtained biodiesel which are performed by two alternative standards that are American Society for Testing and Materials (ASTM) and European Standards (EN), as shown in Table 2.4.

Table 2.3 Standard test physiochemical properties of the organic liquid products. (Walendziewski et al., 2009; Guzman et al., 2010)

Properties	**Solution**	**Method**	
		European diesel fuel standard (EN)	**ASTM**
Density (15°C)	aerometer	EN ISO 3675, EN ISO 12185	ASTM D-4052
Kinematical viscosity (40 °C)	Ubbelohde viscosimeter	EN ISO 3104	ASTM D-445
Fractional composition		EN ISO 3405	
Flash point	Pensky-Martens-closed cup	EN ISO2719	ASTM D-93
Cloud point			ASTM D-2500
Pour point			ASTM D-97
Corrosion			ASTM D-130
Color			ASTM D-1500
Cold filter plugging point (CFPP)		EN 116	
Bromine number	PN-68/C-04520		ASTM D-1159
Total acid number (TAN)	titration of the sample with KOH solution PN 85/C-04066		ASTM D-664 ASTMD974
Carbon and hydrogen			ASTM D-5291
Cetane index			ASTM D-4737
Thermal stability			ASTM D-6468
Simulated distillation			ASTM D-7213 ASTM-2887-D86

The physiochemical properties of the organic liquid products can be comparison with European diesel fuel standard EN590, NExBTL biodiesel, GTL diesel and FAME shown in Table 2.5. The cetane number for each hydrocarbon component was show in Table 2.6.

Table 2.4 The physiochemical properties standard of the organic liquid products from hydroprocessing. (Technical Research centre of Finland 2005)

Fuel properties	**NExBTL biodiesel**	**GTL diesel**	**FAME**	**EN590/2005**
density @ 15°C (kg/m^3)	775-785	770-785	≈ 885	≈ 835
viscosity @ 40°C (mm^2/s)	2.9-3.5	3.2-4.5	≈ 4.5	≈ 3.5
Cetane index	84-99	73-81	≈ 51	≈ 53
Distillation 10 vol% (°C)	260-270	≈ 260	≈ 340	≈ 200
Lower heating value (MJ/kg)	≈ 44	≈ 43	≈ 38	≈ 43
Lower heating value (MJ/litres)	≈ 34	≈ 34	≈ 34	≈ 36
Polyaromatics (wt%)	0	0	0	≈ 4
Oxygen (wt%)	0	0	≈ 11	0
Sulfur (mg/kg)	≈ 0	< 10	< 10	< 10

Table 2.5 Cetane number of normal and iso-paraffins. (Santana et al., 2006)

N-PARAFFINS	CN	ISO-PARAFFINS	CN
n-Butane	22	2-Methylpentane	33
n-Pentane	30	3-Methylpentane	30
n-Hexane	45	2,3-Dimethylpentane	22
n-Heptane	54	2,4-Dimethylpentane	29
n-Octane	64	2,2,4-Trimethylpentane	14
n-Nonane	72	2,2,5-Trimethylhexane	24
n-Decane	77	2,2-Dimethyloctane	59
n-Undecane	81	2,2,4,6,6-Pentamethylheptane	9
n-Dodecane	87	3-Ethyldecane	47
n-Tridecane	90	4,5-Diehtyloctane	20
n-Tetradecane	95	4-Propyldecane	39
n-Pentadecane	96	2,5-Dimethylundecane	58
n-Hexadecane	100	5-Butylnonane	53
n-Heptadecane	105	2,7-Dimethyl-4,5-diethyloctane	39
n-Nonadecane	110	7,8-Dimethyltetradecane	40
n-Eicosane	110	7-Butyltridecane	70
		7,8-Diethyltetradecane	67
		8-Propylpentadecane	48
		9-Methylheptadecane	66
		5,6-Dibutyldecane	30
		9,10-Dimethyloctadecane	60
		7-Hexylpentadecane	83
		2,9-Dimethyl-5,6-diisopentyldecane	48
		10,13-Dimethyldocosane	56
		9-Heptylheptadecane	88

2.4 Deoxygenation mechanism

The deoxygenation mechanism was discussed by Huber (2007). They studied hydroprocessing of sunflower oil, heavy vacuum oil (HVO) and sunflower oil-HVO mixture at standard hydrotreating conditions (i.e. 300–450 °C, pressure 50 bar, LHSV 4.97 h^{-1} and H_2 to feed ratio of 1600 ml H_2 gas/ml liquid feed) with conventional hydrotreating catalysts (sulfided $NiMo/Al_2O_3$). They found that the vegetable oil–HVO mixtures can be converted into liquid alkanes by hydrotreating. In Fig. 2.5 show the conversion of liquid alkane into free fatty acid of triglyceride. In the first step of this reaction pathway the tri-glyceride is hydrogenated and broken down into various intermediates which they presume as monoglycerides, diglycerides and carboxylic acids. These intermediates are then converted into alkanes by three different pathways: decarboxylation, decarbonylation and hydrodexogenation (or dehydration/hydrogenation).

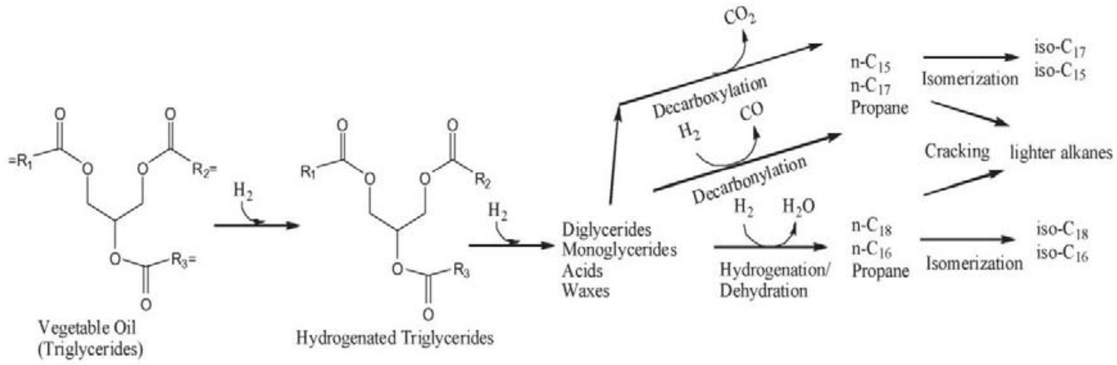


Figure 2.5 Reaction pathways for conversion of tri-glycerides to alkanes.

From Figure 2.5, it can be rewritten with three equations as follows.

$$R-CH_2-COOH \rightarrow R-CH_3 + CO_2 \qquad (1)$$

$$R-CH_2-COOH + H_2 \rightarrow R-CH_3 + CO + H_2O \qquad (2)$$

$$R-CH_2-COOH + 3H_2 \rightarrow R-CH_2-CH_3 + 2H_2O \qquad (3)$$

When Eq. (1) is named as decarboxylation pathway
Eq. (2) is name as decarbonylation pathway
Eq. (3) is name as hydrodeoxygenation pathway

In decarboxylation (deoxygenation) pathway, no hydrogen is required to convert a carboxylic acid group into an alkane involves converting a carboxylic acid into a methyl group and CO_2.

In decarbonylation pathway, carboxylic group is reacted with hydrogen to produce a methyl group, CO and water.

The hydrodeoxygenation pathway involves the reaction of carboxylic acid with hydrogen to produce alkane and water

The selectivity to the decarbonylation plus decarboxylation products (compared to the hydrodeoxygenation pathway) increases with increasing temperature. The straight chain alkanes can undergo isomerization and cracking to produce lighter and isomerized alkanes. Organic acids produced in the hydrotreating process may catalyze the isomerization and cracking reactions. The yield of straight chain alkanes increases when sunflower oil is mixed with HVO, illustrating that dilution of HVO can improve the reaction chemistry. For example, with a 5 wt% sunflower oil–95 wt% HVO feed the maximum theoretical straight chain C_{15}–C_{18} yield from the sunflower oil was higher (87%) than it was with the pure sunflower oil (75%) (Huber et al., 2007). This process has already been in several industrial applications. (Neste Oil Corporation, 2007; HP Innovations, 2006; Hayashi, 2008)

CHAPTER 3

LITERATURE REVIEW

In this thesis, we interested second generation biodiesel production from crude palm oil (CPO) and their derivatives including degummed crude palm oil (DPO) and palm fatty acid distillate (PFAD). The suitable operating parameter and effect of operating parameter on hydroprocessing performance were investigated over 5%wt. Pd/C catalyst. This chapter, we review overview of hydroprocesscing process which can divided into three sections via type of catalysts that are conventional hydroprocessing catalyst, noble metal catalyst and metal nitride/carbide catalyst.

3.1 Conventional hydroprocessing or metal sulfided catalysts (NiMo and CoMo)

Hydroprocessing processes are included in a large group of reaction such as hydrotreating (heteroatom removal such as sulfur (hydrodesulphurization) and nitrogen (hydrodenitrogenation)), hydrocracking, hydrogenation, isomerization and deoxygenation. However, the extent of each of these chemical reactions depends greatly on the type of feedstock, chemicals, catalysts and operating conditions that are involved. The conventional catalysts employed in hydroprocessing are sulfide forms of Mo or W supported on alumina, promoted with Ni or Co. These catalysts have been used for many decades as hydrodesulfurization catalysts for sulfur removal from crude oil streams. Moreover, it has been found that conventional hydrotreating catalysts are suitable for deoxygenation of triglycerides (da Rocha Filho et al., 1993; Gusmão et al., 1989; Huber et al., 2007; Simacek et al., 2009). This process can upgrade bioderived feedstocks, specifically triglyceride and fatty acids with high yields to hydrocarbon middle distillates, which are suitable as alternative diesel fuels (Lestari et al., 2009) and excellent cetane rating. Two general approaches have been proposed: hydrotreating of pure vegetable oil (Bezergianni et al., 2010; Chew and Bhatia, 2008; Huber et al., 2007; Kubicka et al., 2010; Kubička and Kaluža, 2010; Kubicka et al., 2009; Sebos et al., 2009) and co-processing of vegetable oil with crude-oil-based refinery fractions (Bezergianni et al., 2009; Huber et al., 2007). The first approach offers the advantage of high process flexibility, but it requires high investments. In the latter one, the existing apparatus and utilities can be utilized and hence reducing the investments needed. However, the flexibity is reduced as additional issues have to be dealt with e.g. sulfur content of the final product, effect of water and carbon oxide on the catalyst lifetime, separation of carbon oxides from the recycle gas, etc. The wide range of oxygenated molecules were used as starting material such as fatty acids and their esters (Edward, 2000; Laurent and Delmon, 1994; Laurent and Delmon, 1994; Şenol et al., 2005; Viljava et al., 2001) or directly triglycerides (da Rocha Filho et al., 1993; Gusmão et al., 1989).

Kubička and co-workers studied the conversion and selectivity of rapeseed oil over sulfided and unsulfided catalysts. When the activity and selectivity of sulfided $NiMo/Al_2O_3$ catalyst was compared to that of unsulfided Ni/Al_2O_3 at 270-350 °C, the sulfided catalyst was found to be much more active. However, the unsulfided catalysts primary yielded odd number hydrocarbons (decarboxylation/ decarbonylation) while the sulfided catalyst yielded primarily even numbered (hydrodeoxygenation). The activity of sulfided $NiMo/Al_2O_3$ surpassed that of Mo/Al_2O_3 and Ni/Al_2O_3 separately in liquid phase hydrodeoxygenation (HDO) below 300 °C under H_2 atmosphere (Kubicka et al., 2009). Deoxygenation of rapeseed oil over commercial sulfide $NiMo/Al_2O_3$ at 70 bar of H_2 can achieve full conversion above 300 °C, while higher temperature yielded higher selectivity toward odd-number hydrocarbons (Simacek et al., 2009). Supporting sulfided CoMo on mesoporous Al_2O_3 rather than MCM-41 resulted in higher yields of alkanes, but incorporating Al into the framework of MCM-41 did improve yields due to support acidity (Kubicka et al., 2010; Kubicka et al., 2009) .

The disadvantage of using hydrotreating catalyst for deoxygenation reaction of triglyceride is that the high oxygen content of feedstock can increase heat load in the reactor and cause leaching of sulfur from the catalyst surface; water and CO_2 generated during the deoxygenation can induce deactivation of catalyst (Huber et al., 2007). This result is consistent with Senol and co-worker, who studied deoxygenation reaction over sulfide CoMo/Al_2O_3 and NiMo/Al_2O_3 on heptanoic acid, heptanol and heptanoate methyl and ethyl esters and investigated the effect of water on the catalyst performance. They found that the water can inhibit both catalysts, decreases the conversion of the esters and suppresses the oxygen removal reactions on the catalysts. The addition of H_2S effectively compensates the inhibition by water but also changes the product distribution: it shifts the main products towards the C6 hydrocarbons so a sulphiding agent must be added to the reactor to maintain catalyst activity. The amount of H_2S needs to be optimized for the desired activity of the catalyst and the target product quality (Senol et al., 2005). Moreover, the large triglyceride molecules can clog catalysts with pore sizes of less than 2 nm (Tiwari et al., 2011) so the large pore size catalysts were required to overcome diffusion limitations. Mesoporous molecular sieves, such as MCM-41, or alumina can have the advantage of a high surface area and activity, but also have much larger pore diameters than zeolites (Kubicka et al., 2009).

The first work of hydroprocessing for hydrocarbon production was disclosed in U.S Pat. No. 4300009 which does not use metal sulfide catalyst but the crystalline aluminosilicate zeolite was used as catalyst to convert biomass such as corn oil to hydrocarbons like gasoline and para-xylene. These reactions operate at a temperature of 300 to about 650 °C (Haag et al., 1980).

In 1985, the vegetable oil (soy oil) was used as starting material for hydroprocessing process and NiMo supported on silica or/and alumina catalyst were use as catalyst. They found that triglyceride of soy oil hydrolyzed into fatty acid, and then free fatty acid were either hydrocracked, decarboxylated or hydrogenolysed or a combination thereof (Nunes., 1985)

In 1989, U.S. Patent No.4992605, refered to hydroprocessing process, which was proposed by Craig and Soveran. In this patent, two commercial hydroprocessing catalysts i.e. Co-Mo or Ni-Mo were employed to convert many vegetable oil (i.e. canola oil, rapeseed oil, sun flower oil, soybean oil, palm oil and fatty acid fractions of tall oil) into linear hydrocarbon compound mixtures. The obtained products have boiling point in range of diesel (210-343 °C) with carbon atom ranging from C_{15} to C_{18}. It has high cetane number above 100 and is called “SCR” super cetane (The

Saskatchewan Research Council). Many reaction pathway were occurred in this processes i.e. hydrocracking (breaking apart of large molecules) of triglyceride, hydrotreating (removal of oxygen that is deoxygenation reaction) and hydrogenation (saturation of double bonds). It was found that suitable operating condition depend upon type and purity of feed stock so pretreatment step was added before hydrogenation step in order to remove contaminates such as alkali metal from the feed stock. Peter (2008) performed this step in column packed with acidic ion exchange resin such as Amberlyst^{TM}-15. The column was operated in temperature range of 21 °C to 100 °C and pressure range from 172 kPa to 3447 kPa. The amount of metal contaminant after pretreatment step were significantly decreases, example Ca, Fe, Mg, P content were reduce from 73 to 27, 1.6 to 0.6, 65 to 20, 653 to 161 ppm, respectively after pretreatment step (Peter and Marker, 2008). The suitable reaction temperature for deoxygenation ranging between 360 and 390 °C with pressure of 4.8-15.2 MPa and liquid hourly space velocity (LHSV) of 0.5-5.0 hr^{-1}. Generally, cetane number of commercial diesel fuel can be improved by addition of additive such as alkyl nitrates. However, the major drawbacks of these additives are their relatively high cost and a non-linear impact on mixture cetane number. Super cetane has a linear additive effect on cetane number. Therefore, SCR super cetane is a more effective cetane additive than commercial alkyl-nitrate cetane enhancers (Craig, 1989).

The same process was investigated by Monnier (1995) as was proposed as was proposed in U.S. patent No. 5705722. They produced additives for diesel fuels (SCR) from biomass feedstock including tall oil, wood oil and blends of said tall oil with vegetable oil. Crude tall oil, produced as a by-product during kraft pulping of pine and spruce trees, was used as feedstock, in this patent. Typically, crude oil contains 30-60 wt% fatty acid, 20-50 wt% diterpenic acids (rosin or resin acid) and 10-40 wt% unsponifiables. They found that it is not only the unsaturated fatty acids in tall oil can convert into additive (SRC) but also the diterpenic acids and unsponifiables can convert to cetane improver (SRC). The following operating conditions were used: the reaction temperature in ranges of about 370-450 °C, the hydrogen pressure in rang of 4-15 MPa and the liquid hourly space velocity (LHSV) is from 0.5 to 5.0 hr^{-1}. The suitable catalysts for the process were hydroprocessing catalyst, including Co-Mo, Ni-Mo and other transition metal based catalyst (Monnier, 1995).

The extensive studies of SCR super cetane were observed by Stumborg (1996). They studied the use of conventional refinery technology to convert vegetable oils, such as canola oil and tall oil, into a straight-chain paraffinic hydrocarbon in diesel range with high cetane number between 55 and 90 (super cetane). Specific gravity of super cetane is very similar to diesel fuel (0.790). Viscosity is higher than fossil diesel fuel but it is similar to FAME. The major drawback of super cetane is the poor cold temperature characteristics as shown by higher value of cloud point or pour point (higher than 20 °C). Emission of carbon monoxide and hydrocarbon was decreased with an addition of SRC super cetane. The SCR super cetane exhibited emission benefit similar to DII-3, the commercial additive cetane improver (Stumborg et al., 1996).

To improve cold flow properties an extended investigation of super cetane in order to convert *n*-paraffin into branched paraffin chain by adding isomerization step was proposed by Neste Oil Oyj (Myllyoja et al., US Patent No.20070006523). The use of catalyst with lowest cracking activities are most suitable, e.g. Pt/SAPO-11/Al_2O_3, Pt/ZSM-22 and 23/Al_2O_3 catalyst. For example, hydrogenation of tall oil fatty acid (TOFA) over NiMo/Al_2O_3 yielded normal alkane, which is when blended with conventional diesel fuel of 10 wt.% gives turbidity point of the mixture very high (25 °C). But after isomerization of such blending, the turbidity point of mixture decreased to -12 °C with high cetane number over 74. The fuel produced from this process, known as NexBTL, is free from sulfur, nitrogen, oxygen, and aromatics and has a very high cetane number. Neste Oil has completed the construction of a biorefinery unit based on hydroprocessing of vegetable oil in Porvoo, Finland (Myliyoja et al., 2006). The previous studies of isomerization were investigated by Weitkamp (1983). They have been reported the hydroisomerization of n-alkenes of C_{10}-C_{16} over Pt and Pd supported with Zeolite Y and HZSM-5. The light hydrocarbon increased with increasing acidity of catalyst because of the high cracking activity thereof (Weitkamp et al., 1983). In 2000, the isomerization of n-hexane and n-heptane was carried out over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (denoted by $Cs_{2.5}$) promoted by Pt. They found that the Pt+Cs2.5 (the mechanical mixture of Pt/Al_2O_3 and $Cs_{2.5}$) were an excellent catalyst and the reactivity increase with the carbon number. The catalyst deactivation cloud be suppressed by the presence of Pt and/or hydrogen gas. The strong acid catalysts exhibited high activity but the stability and selectivity were low, opposite trend was observed for weak acid catalyst (Liu et al., 2000). When compared pollutant emissions of NExBLT to fossil diesel, it was found that NExBLT emitted NO_x 10-20% and particular matter (PM) 20-30% less than fossil diesel and could reduce significantly aldehydes, 1,3-butadiene, benzene (Rantanen et al., 2005).

Walendziewski (2009) was studied hydroprocessing process of co-feed of light gas oil-rapeseed oil mixtures (10 and 20 wt.% of rapeseed oil) over $NiMo/Al_2O_3$. Hydroprocessing of two series mixtures were performed with the same parameter sets, temperature of 320, 350 and 380 °C, hydrogen pressure 3 and 5 MPa, LHSV=2 $h^{-1}$and hydrogen feed ratio of 500.. In the result of the process one can observe over 95% yield of hydrogenolysis and hydrogenation of ester and carboxyl acid bonds as well as hydrogenation of double bonds. The obtained product has lower flash point especially 20 wt% rapeseed oil mixture due to hydrocracking reaction. Improvement of the product properties of the flash point is possible by product stabilization through the separation of low boiling hydrocarbons from the product by distillation (Walendziewski et al., 2009).

In term of mechanism, Donis (2009) described the mechanism of hydroprocessing process which many reactions take place on the catalyst such as hydrodesulfurization, hydrodenitrogenation, hydro-dearomatization, hydrocracking or hydrogenation of olefin. They found that the carboxylic acids are hydrogenated into linear alkanes of same length or 1 carbon atom shorter and the backbone of triglyceride is converted into propane, water, carbon monoxide, carbon dioxide and methane. Hydrodeoxygenation and decarboxylation were used to explain the occurrence of these products. The first reaction refers to the hydrogenation or hydrodeoxygenation (HDO) reaction as shown by the red solid line in Figure 3.1. The products are water, propane and three linear alkanes of the full length of the fatty acid chains. Another reaction, which is usually known as decarboxylation (CO_2-elimination) shown as the blue dashed lines in Figure 3.1. The products are propane, carbon dioxide and/or carbon monoxide and linear alkane of one carbon atom shorter.

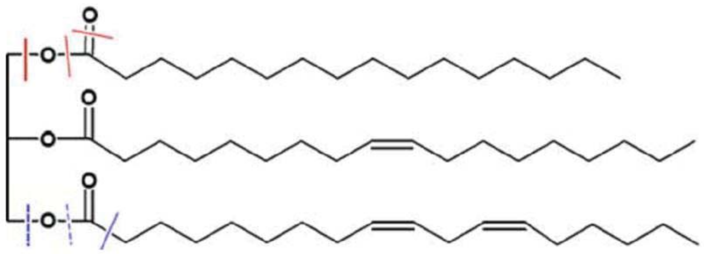
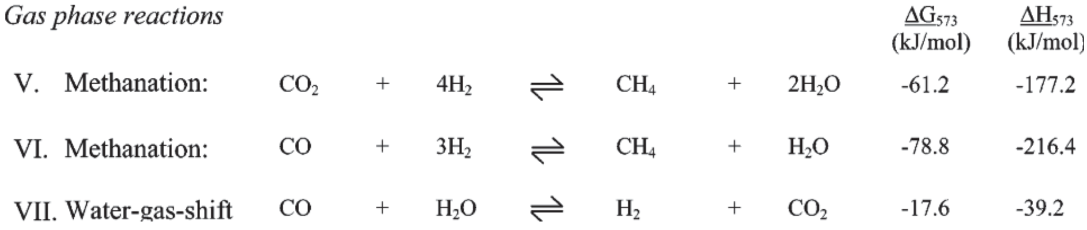


Figure 3.1 Schematic representation of the two different reaction path-ways for the removal of triglyceride oxygen by hydrotreating.

Besides previous reactions, the two additional reactions need to be taken into consideration when carbon dioxide and carbon monoxide are appeares. The processes are water gas shift and methanation reactions shown in Figure 3.2 (Donnis et al., 2009). In some cases the isomerization and cracking reaction can occur in this process.



Gas phase reactions								ΔG_{573} (kJ/mol)	ΔH_{573} (kJ/mol)
V. Methanation:	CO_2	+	$4H_2$	$\rightleftharpoons$	CH_4	+	$2H_2O$	-61.2	-177.2
VI. Methanation:	CO	+	$3H_2$	$\rightleftharpoons$	CH_4	+	H_2O	-78.8	-216.4
VII. Water-gas-shift	CO	+	H_2O	$\rightleftharpoons$	H_2	+	CO_2	-17.6	-39.2

Figure 3.2 Methanation and water-gas-shift reaction (Snare et al., 2006).

Simacek (2009) investigated hydroprocessing of rapeseed oil over a commercial hydrotreating Ni–Mo/alumina catalyst. The process operates at temperature 260–340 °C under hydrogen pressure of 7 MPa. The obtained products composed of the gaseous products of propane, methane (in some cases), carbon dioxide and carbon monoxide, and an organic liquid product (OLP). The OLP contain of *n*-alkanes C15–C18, *i*-alkanes (up to 40 wt.%), small amounts of cycloalkanes and aromatics. Hydrogenation of double bonds is the primary reaction. The reactants and intermediates decreased with increasing reaction temperature. At temperatures higher than about 310 ^{o}C, the mentioned reactants and intermediates were not detected. It is noted that at low reaction temperatures, 260-300 °C, the products were cloudy but the products obtained at reaction temperatures above 300 °C were clear colorless liquids (Simacek et al., 2009). In 2010, they studied the same process and catalyst. The process operate at temperature 310 and 360 °C and under hydrogen pressure of 7 and 15 MPa. The conversion of rapseed oil was over 99% at 310 °C and complete conversion was achieved at 360 °C. The obtained product having carbon atom number ranging from about 14 to 20, where *n*-alkanes C17 and C18 formed more than 75 wt.% of the product. Reaction product obtained at 360 °C and 7 MPa was blended into mineral diesel fuel in several concentration levels ranging from 5 to 30 wt.%. It was found that most of the standard properties i.e. viscosity, density, sulfur content, nitrogen content and cetane index were similar to or better than those of pure mineral diesel (Simacek et al., 2010).

The effect of temperature on product yield, heteroatom removal and hydrocarbon composition for hydrotreating of waste cooking oil, was studied by Bezergianni et al (2010). The catalyst used in this study is a commercial hydrotreating catalyst NiMo/Al_2O_3. They found that the diesel production is dominant at all reaction temperatures. However, it is noted that high temperature are suitable for gasoline production while low reaction temperatures are more suitable for diesel production. Heteroatom removal also investigated in this study. Surfur and nitrogen are most effectively removed in all cases while oxygen removal is favored by hydrotreating temperature. Moreover, the saturation of double bonds is increased with temperature. Moreover, the effect of reaction temperature on the hydrocarbon composition was also studied. It was observed that as the temperature increases the amount of paraffins decreases whereas the amount of iso-paraffins increases. The decrease of *n*-paraffins vs. the increase of iso-paraffins indicate that isomerization reactions are favored by hydrotreating temperature, which is as expected as higher temperatures cause hydrocracking of reactions (which include isomerization and cracking) (Bezergianni et al., 2010).

The shale oil was used as feedstock for hydrotreating process over three difference types of commercial catalyst, including CoMo/Al_2O_3, NiW/Al_2O_3 and NiMoW/Al_2O_3, at different conditions. The results showed that the desulfurization was high for all three catalysts at moderate conditions. However, denitrogenation was much more difficult than desulfurization, even at severe conditions. The NiMoW catalyst was most active for heteroatom removal in comparison to other catalysts. After hydrogenation, produced oil had low sulfur (41 μg g^{-1}), nitrogen (195 μg g^{-1}), and alkene, low density, and high cetane number. The obtained product can be directly used as a domestic transportation fuel (Yu et al., 2010).

The Mo-Co/γ-Al_2O_3 and W-Ni/Al_2O_3 catalysts with different metal loadings were prepared by applying new synthesis technologies that combined ultrasonic-assisted impregnation and temperature-programming methods. Clean liquid oil was obtained from middle-temperature coal tar (complex mixture consisting of aliphatic, aromatic, alicyclic and heterocyclic compounds) via hydrogenation in two-stage fixed beds filled with the laboratory made catalysts. The Mo-Co/γ-Al_2O_3 catalyst with 12.59 wt.% Mo and 3.37 wt.% Co loading, and the W-Ni/γAl_2O_3 catalyst with 15.75 wt.% W and 2.47 wt.% Ni loadings were selected. This process was capable of removing nitrogen and sulfur from 1.69 and 0.98 wt.% in the feed to less than 10 ppm and 100 ppm, respectively in the products. The results showed that the raw coal tar can be considerably upgraded through catalytic hydroprocessing (Kan T., 2011). The effect of pressure on the hydroprocessing performance was investigated at stepwise pressure of 6, 8 and 12 MPa. The nitrogen content of 3 ppm remained in the gasoline product and 1 ppm in the diesel product at 12 MPa. The results reveal that hydrodenitrogenation (HDN) reaction is a strong function of hydrogen pressure, the nitrogen content of both gasoline and diesel decreases from 14 to 3 and 8 to 1 ppm as reaction pressure increases from 6 to 12 MPa, respectively. However, both gasoline and diesel yield decrease as increasing reaction pressure as oxygenated compounds were formed at high reaction pressure.

The deoxygenation of methyl laurate and canola oil is discussed in details in term of various oxygen removal conditions such as reaction temperature, pressure, catalyst amount, and hydrodynamics of heterogeneous reaction mixture in batch reactor. The reaction was performed at 18-85 bar of initial cold hydrogen pressure and 300-400 °C over NiMo/γAl_2O_3 catalyst. Canola oil is converted mainly into heptadecane and octadecane in the presence of hydrogen and NiMo/γ-Al_2O_3 catalyst. Heptadecanic acid is formed as a major intermediate product. Formation of heptadecane, octadecane, and heptadecanic acid increases as amounts of NiMo/γ-

Al_2O_3 catalyst increases, whereas formation of unaccountable products decreases as the amount of the catalyst increases. Both catalysts and hydrogen are needed to convert canola oil to hydrocarbons. Formation of heptadecane, octadecane and gaseous products from canola oil increases as reaction temperature increases, as well as unaccountable product. Formation of heptadecane and octadecan, and consumption of H_2 increases as H_2 pressure increases whereas the formation of unaccountable products decreases as H_2 pressure increases. Elevated hydrogen pressure and prolonged reaction time are required in the presence of catalyst to increase the conversion of canola oil to hydrocarbons such as heptadecane and octadecane (Kwon KC., 2011).

The identification of active sites or their precursors is important information in heterogeneous catalytic reactions. However, analysis of the active site is very complex therefore there is a lack of information about the nature of active sites in the deoxygenation of rapeseed oil over NiMoS-alumina catalysts. The activity and selectivity of hydrotreating catalysts in the deoxygenation of vegetable oils can be expected to be affected by (i) total amount, distribution and crystallite size of Ni and Mo species, (ii) nature and specific surface area of the support and (iii) Ni and Mo precursors and their impregnation order. Several authors have investigated the influence of the impregnation order of hydrotreating catalysts on their catalytic activity in hydrotreating reactions, either as NiMoS on alumina (Hong et al., 2006), on Alpillared clays (Salerno et al., 2004), on AlMCM-41 (Basha et al., 2009) or as CoMoS on activated carbon (Ferrari et al., 2002). However, the results of these studies are varied and inconclusive. Nonetheless, impregnation with the promoter (Ni, Co) prior to impregnation with Mo yields typically more active catalyst. The distribution of Ni sites and their structure can be affected by catalyst pretreatment temperature. It has been studied with respect to catalyst characterization using TPR (Brito and Laine, 1993), electron spectroscopy, XRD (Scheffer et al., 1987), Raman spectroscopy, UV–vis DRS, XPS and HRTEM (Guevara-Lara et al., 2007) and also with respect to its catalytic activity in various chemical reactions, such as thiophene hydrodesulfurization (Reinhoudt et al., 2000; Reinhoudt et al., 2001; Reinhoudt et al., 1998; Vissenberg et al., 2001), acrylonitrile hydrogenation (Li et al., 2001), or oxidative dehydrogenation of ethane (Čapek et al., 2008).

Priecel and co-worker (2011) studied deoxygenation of rapeseed oil over sulfide NiMo-alumina catalysts (NiMoS-alumina). They focused on the preparation of catalyst precursors with different distribution of Ni species in order to contribute to the understanding of the effect of catalyst preparation on the activity/selectivity of NiMoS-alumina catalysts in the deoxygenation of rapeseed oil. They found that the conversion was affected by the population of the octahedral and tetrahedral nickel species in NiMoO-alumina catalysts. It has been found that the catalysts with higher population of octahedral nickel species are more active than those containing higher population of tetrahedral nickel species. The selectivity to oxygenate and hydrocarbons were not affected by the population of Ni species but by the conversion of rapeseed oil. Oxygenates were mainly formed at low conversion of rapeseed oil while hydrocarbons prevailed at high conversion of rapeseed oil. The single Ni alumina catalysts favor almost exclusively deoxygenation through the HDC pathway (the formation of the C17 hydrocarbons) whereas single Mo-alumina catalysts favor the HDO pathway (the formation of the C18 hydrocarbons) (Priecel et al., 2011).

Kubicka and co-worker (2009) investigated deoxygenation of refined rapeseed over a four different mesoporous-alumina-supported CoMo catalysts in a fixed bed reactor. The reactions were operated at temperature in the range of 250-350 °C and pressure 0.7-7 MPa. The results revealed that CoMo/OMA catalysts exhibited higher activity for deoxygenation of triglycerides than CoMo supported on MCM-41 (silica) and ordinary alumina supports. At low reaction temperature, the effect of reaction pressure has strongly effect on conversion (rate) due to hydrogen-mass-transfer limitations. On the other hand, at higher reaction temperature (>310 °C), the reaction proceeds with the rate due to temperature effect rather than the effect of pressure is (Kubicka et al., 2009).

Waste cooking oil is a useful nonfood biomass. These low-grade wastes oils are unsuitable for 1st generation biodiesel production because they sometimes contain high free fatty acid (FFA) content. However, deoxygenation is suitable for converting waste oils into n-paraffin, the so-called “2nd generation biodiesel”, which has the components similar to fossil diesel. Waste oil has also been used in many researches as feedstock (Tiwari et al., 2011; Toba et al., 2011). Toba and co-worker (2011) investigated hydrodeoxygenation of waste cooking oil and trapped grease over sulfide catalysts i.e. NiMo, CoMo and NiW in a hight pressure batch reactor and fixed bed flow reactor. The results revealed that NiMo and NiW catalysts showed high and stable hydrogenation activity whereas the deactivation of hydrogenation activity was observed in case of CoMo catalyst. NiW catalyst gave more hydrocarbons formed by decarboxylation or decarbonylation than NiMo and CoMo catalysts.

Hydroprocessing of waste cooking oil was studied by Bezergianni et al. (2010) over commercial hydrotreating catalyst. They found that the effect of operating temperature is dominant on catalyst activity i.e. conversion or selectivity. At the lowest hydrotreating temperature of 330 °C gave highest diesel yield of 90.1% of the total liquid products. However, gasoline yield increases with temperature due to higher hydrotreatment temperatures favor cracking and therefore the production of light molecules. The effects of temperature on selectivity have the same trend as conversion, conversion and selectivity decreases with increasing reaction temperature. The maximum conversion was found to be 90% at the lowest hydrotreatment temperature of 330 °C. Hydrocracking reaction and heteroatom removal favored by increasing operating temperature.out of place.

Veriansyah and co-worker (2011) studied hydroprocessing of soybean oil with different types of supported catalyst i.e. hydrotreating catalyst (NiMo, CoMo) and noble metal (Pt, Pd, Ni, Ru). In case of Pd or Ni catalyst, the n-paraffin content (n-C_{17} and n-C_{15}) was more than 80 wt.% while it was less than 55.wt% when the CoMo catalyst was used. Enhancing isomerization and cracking reaction activity on the CoMo catalyst could produce lighter and isomerized hydrocarbons. The decarboxylation was a main reaction pathway when the Pd catalyst was used while hydrodeoxygenation was favored when the NiMo or CoMo catalyst was used (Veriansyah et al., 2011).

Lestari and co-worker (2006) studied deoxygenation of model compounds of vegetable oils, stearic acid, over Ni/Zr-laponite catalyst for different amount of Ni loading. The optimum reaction time was achieved at 3 h. The results showed that the maximum absorption of nickel particles inside the pore system of Ni/Zr-laponite catalyst was 12%. Above this percentage, nickel particle tends to blocked pore of the catalyst. Zirconia pillared laponite clays are promising catalyst supports for decarboxylation of vegetable oils as it has large pore size and surface area which is accessible for the large molecule of reactants. Among the catalyst investigated in this work, Ni/Zr-laponite catalyst was successfully converted stearic acid, into smaller C number of hydrocarbons representing direct decarboxylation of stearic acid (Lestari et al., 2006).

The commercial work in this respect was firstly done by Finland's company Neste Oil under commercial name NExBTL (European patent 1 396 531; Patent, 2004/0226; Rantanen et al.) and Ecofinning^{TM}, jointly offered by UOP and Eni, S.p.a under commercial name UOP/Eni Ecofining^{TM} technology (European patent 1728 844; Tom et al., 2008). The UOP and S.p.a started a collaborative research effort in 2005 to develop such a process based on conventional hydroprocessing technology that is already widely deployed in refineries and utilizes the existing refinery infrastructure and fuels distribution system. The obtained product from UOP/Eni Ecofining^{TM} technology is green diesel because it is an aromatic and sulfur free diesel fuel which has a very high cetane blending value. The cold flow properties of the fuel can be adjusted in the process to meet climate-specific cloud point specifications in either the neat or blended fuel. Green diesel is of very high quality when compared with biodiesel (100% FAME) and is similar in both composition and combustion properties to syndiesel, which was produced by Fischer-Tropsch (FT) synthesis of a syngas stream derived from coal (CTL), stranded natural gas (GTL) or biomass (BTL) (Nexant Chem Systems, 2003). A comparison of these fuels with petroleum diesel fuels is reported in this work. Like FT diesel, the boiling range and energy density of green diesel is comparable to typical petroleum diesel products, with substantially higher cetane number (>75) and lower density (0.77). In contrast to FAMEs, whose fuel properties depend on feed origin, green diesel product is independent of feed origin, and cold flow properties can be controlled by adjusting the reactor severity. A blending study is presented in the process economics section of the article to illustrate the additional financial benefit that can be achieved by adding green diesel (or syndiesel) to a typical European refinery distillate pool. GHG emissions from green diesel were more than 80% lower than petroleum diesel and about 40% less than biodiesel. As determined by comprehensive LCA studies, "green diesel" produced via the Ecofining process has environmental benefits over petroleum diesel, biodiesel (100% FAME), and fossil-derived syndiesel (without carbon sequestration). Compared with petroleum diesel, green diesel has savings 66–84% for fossil and 41–85% GHG emissions, respectively, depending upon study assumptions. Producing a ton of green diesel consumes much less biorenewable feedstock when compared with BTL syndiesel, with over twice the savings in GHG savings as BTL syndiesel when calculated per ton of biorenewable feedstock. From an investment standpoint, green diesel is competitive with biodiesel. Moderately sized units consistent with current large-scale biodiesel production can be economical. However, because cost of production is a key to the differential price between crude petroleum and renewable plant oils, the return on investment will depend upon other factors such as plant location, mandated increases in the renewable content, availability of renewable feed, major shifts in crude petroleum pricing, product blending attributes, and of course, (as with biodiesel) government subsidy and carbon tax credits (Kalnes et al., 2009).

3.2 Noble metal catalysts (Pd, Pt)

Non-sulphided catalysts are interested for the production of biofuels because they eliminate the need to add a sulphur compound to a biomass-derived feedstock in order to prevent the deactivation of sulphided metal catalysts. Deoxygenation reactions also occur during the hydroprocessing of petroleum fractions along with hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodemetallization (HDM) and the saturation of olefins/aromatics. These hydroprocessing reactions use high pressure hydrogen to remove S, O and N heteroatoms out of petroleum feedstocks through a series of hydrogenolysis and hydrogenation steps. Since, the oxygen in petroleum is typically less than 3000 ppmw, less attention has been paid to deoxygenation as compared to HDS as far as petroleum upgrading research is concerned. However, in the hydroprocessing of biomass feedstocks, deoxygenation is a critical reaction step since a neat biomass feedstock may contain up to 500,000 ppmw oxygen with minimal amounts of sulfur. The oxygen speciation within these feedstocks varies significantly with the type of biomass and upgrading methods employed (Choudhary and Phillips, 2011). The catalytic deoxygenation of different fatty acids and their derivatives has been intensively investigated in both gas phase and liquid phase.

Maier et al. (1982) demonstrated that octanaic acid was converted to heptane with 97% yield at 330 °C over Pd/SiO_2 in H_2 flow. The results revealed that Pd/SiO_2 is highly active and selective catalyst for gas phase deoxygenation of carboxylic acid.

Snare et al. (2006) investigated the screening experiments of different heterogeneous-supported metal catalyst for deoxygenation of stearic acid. Several active metals, such as Pd, Ni, Ru, Ir, Os, Rh, supported on silica, alumina, active carbon as well as some alloys and bimetallic catalysts have been studied. They found that palladium (Pd) and platinum (Pt) metals supported on microporous active carbon are the most selective and active catalysts for deoxygenation of stearic acid. They offer 100% and 86% of conversion and 95% and 87% of C_{17} selectivity, respectively, at reaction temperature of 300 °C and 6 bar. Furthermore, the gas phase analysis demonstrated that the decarboxylation reaction was more pronounced over the Pd/C catalyst, while the decarbonylation reaction was more evident over the Pt/C catalyst (Snare et al., 2006).

Deoxygenation of stearic acid was performed over 4 wt.% Pd/C in temperature range of 270-330 °C under 17 bar of helium. There are two main component in a liquid product i.e. *n*-heptadecane (cetane number is 105) and *n*-pentadecane (cetane number is 96), which were formed parallelly at the beginning of the reaction. From figure 3.4 (b) show that the selectivity of *n*-C17 independent with conversion. The initial reaction rate of stearic acid deoxygenation increased with increasing reaction temperature. At the same time the time needed form full conversion of stearic acid decreased with increasing reaction temperature (Lestari et al., 2008).

The deoxygenation of different feedstock i.e., pure palmitic acid, stearic acid etc., and a technical grade stearic acid (a mixture of 59% of palmitic and 40% of stearic acid) was investigated by Lestari et al. (2009). It was performed over 4 wt% Pd/C mesoporous catalyst at 300 °C under 17 bar of 5% H_2 in argon. The main products were hydrocarbons with one carbon less than the corresponding acid that is *n*-C15 was the main product in the deoxygenation of palmitic acid, while *n*-C17 was formed in the deoxygenation of stearic acid. In case of technical grade stearic acid both n-C15 and n-C17 were formed. Moreover, the reaction rates of different fatty acids were independent of the fatty acid chain length. If fatty acids contain other impurities, the deoxygenation rates decreased. Therefore, in this work the impurities of the reactants were analyzed by the ICPOES analysis (Lestari et al., 2009).

The same reaction and catalyst were performed at 360 ^{o}C under 10 bar of argon or 5% hydrogen in argon by Lestari (2009). The results showed stable catalyst performance along 25 h of reaction period, giving about 15% conversion of stearic acid. The main product in liquid phase was *n*-C17 and in gaseous phase were CO and CO_2. Moreover, methanation of CO occurred during the deoxygenation under both argon and 5 vol% hydrogen in argon; a 70% smaller methane peak was observed in Ar compared to 5 vol.% hydrogen in argon. The present of hydrogen in small quantities in the liquid phase made the reaction of fatty acid faster than the case of inert atmosphere. This phenomenon indicates that hydrogen is able to preserve the catalyst activity for longer time. The presence of hydrogen also diminished the consecutive aromatization, which is undesirable in diesel fuel and they probably form coke which can lead to deactivation of catalyst. Moreover, studies of the effect of hydrogen pressure revealed that a low partial pressure of hydrogen was beneficial in increasing the turnover frequency (TOF) and final conversion compared to pure hydrogen or an inert reaction atmosphere (Lestari et al., 2009).

Deoxygenation of unsaturated fatty acid, such as oleic acid, methyl oleate, and linoleic acids, can also lead to saturated diesel-fuel-range hydrocarbons. The reaction occurs initially via hydrogenation of double bonds and subsequent deoxygenation of the corresponding saturated feed. Comparison of the deoxygenation activity was performed for semibatch and continuous modes at similar reaction conditions, showing higher productivity in semibatch operation, which was attributed to mass transfer limitations in the tubular fixed-bed reactor. Furthermore, a better performance was observed in a semibatch reactor compared to a batch reactor due to the use of a flow purging gas in the former reactor, thus flushing the formed gaseous products, CO and CO_2, away from the reactor (Snåre et al., 2007).

Supported metal nanoparticles (SMNPs) have attracted attention over the past decade due to their superior physicochemical properties compared to their bulk materials. The ability to control the particle size, shape, and metal dispersion as well as the advantage of nanoparticle aggregation inhibited by immobilization/separation on the heterogeneous support offer the potential to enhance selectivity and activity in catalytic applications (Astruc et al., 2005; White et al., 2009). Many immobilization methods and support materials have been reported in the literature. Han et al (2007). investigated synthesis of Pd/SBA-15 by one step direct synthesis method through sol–gel reaction leading to a catalyst which exhibited high catalytic activity and better recycling in the Suzuki and Heck coupling reactions. (Han et al., 2007). This catalyst was reprepared by Lestari and used for deoxygenation of stearic acid. The experiments were performed at 300 ^{o}C under 17 bar of 5 vol% H_2 in Ar as a carrier gas in a semibatch reactor. The SBA-15 poses high surface area and large pore volume of 850 m^2/g and 1.4 cm^3/g, respectively. The most active catalyst was 3wt% Pd-SBA-15 with average pore diameter of 6.8 nm exhibiting high TOF of 0.72 s^{-1}. This value is slightly higher from those reported previously (Simakova et al., 2009; Zhao et al., 1998). Pd/SBA-15 catalyst showed higher catalytic performance than that of Pd/C for deoxygenation of stearic acid. In the case of 3wt% Pd/SBA-15 with the stearic acid to Pd mass ratio was 933 , TOF of 0.72 s^{-1} with 96% conversion could be obtained after 300 min of reaction time whereas for 5 wt% Pd/C the mass ratio of stearic acid to Pd of 900 giving TOF of 0.126 s^{-1} and 62% conversion of stearic acid after 360 min. The main products in gaseous phase were CO and CO_2. The CO is well known for poisoning the metal catalyst surface. Therefore, the use of semibatch reactor by purging out the gaseous product gases could help to maintain the catalytic activity. The main product in liquid phase was n-heptadecane with over 90% selectivity at above 95% conversion. Furthermore, trace amounts of isomer *n*-C17 i.e. 3-heptadecene and/or 8-heptadecene were also formed in the liquid phase (Lestari et al., 2010).

Ultra-large pore volum silica mesocellular foam was used as the catalyst support for deoxygenation of stearic acid and ethyl stearate. Palladium nanopaticles were successfully synthesized according to Han et al., (2007) within the support, with 55-60% dispersion in a 5 wt.% palladium material. Reaction was performed at 300 ^{o}C for up to 6 h under nitrogen atmosphere. Conversion of stearic acid was 85-90% after 6 h with 100% selectivity to *n*-heptadecane. Lower conversion (<15%) was observed after 6 h for ethyl stearate with 87% selectivity to n-heptadecane and 13% as the intermediate stearic scid (Ping et al., 2010).

Saka et al. (2004) suggested a two step process for biodiesel production of low-cost feedstocks, such as waste cooking oil and waste greases. The first step is hydrolysis of the triglyceride in the water to produce free fatty acid. The second step is esterification of the fatty acids to alkyl esters (biodiesel) (Kusdiana and Saka, 2004). An alternative to esterification as the second step in this envisioned process is catalytic deoxygenation of the fatty acids to produce alkanes. The deoxygenation was done in the same medium (hot water) as the hydrolysis step. Fu et al. (2010) demonstrated the first time that deoxygenation can be accomplished in near-and supercritical water by using the two heterogeneous catalysts, 5% platinum, and 5% palladium, on activated carbon. Palmitic acid was employed as a model fatty acid. It was very effective although H_2 were not added into the reactions system. Pt/C is more active catalyst than Pd/C in this reaction. The catalyst could be reused without significant activity loss, and the selectivity was greater than 90% toward pentadecane (deoxygenation product). The kinetics for Pt/C catalyzed deoxygenation of palmitic acid was first-order in fatty acid, and the activation energy was 79 ± 5 kJ mol^{-1} (Fu et al., 2010).

Maki-Arvela et al. (2008) investigated the deactivation of Pd/C catalyst for hydroprocessing of lauric acid in continuous flow reactor. The results showed catalytic activity declined during the first 20 min of time-on-stream to a steady state conversion level of about 4–6%. The catalyst stability slightly increased enhanced by using lower boiling point solvents such as mesitylene and decane instead of dodecane. The initial concentration of lauric acid was decisive for the catalyst deactivation, the higher was the initial concentration of fatty acid the more extensive catalyst deactivation occurred. The reason for the catalyst deactivation is the poisoning of the catalyst by the product gases, i.e., CO and CO_2 and coking (Maki-Arvela et al., 2008).

Smejkal (2009) investigated the thermodynamic analysis comparing to the hydrogenation of rapeseed oil. Tristearate was chosen as a model compound to represent vegetable oils in the calculations. The C17 and C18 concentration were calculated and it was found that their concentration is affected by temperature and particularly by pressure. Moreover, the model predictions are in a good agreement with experimental data at high temperature (above 300 °C). Below 300 °C, the discrepancy of the measured and predicted hydrocarbons concentration is increased.

Additionally, the estimations suggest that the reaction is limited by hydrogen transfer. However, this finding is currently being examined experimentally (Smejkal et al., 2009).

Snare et al. (2008) studied liquid-phase deoxygenation reaction of mono-, di-unsaturated fatty and monounsaturated fatty acid ester in a semi-batch reactor. They found that at high pressure and low temperature favour the hydrodeoxygenation pathway. In comparison with hydrodeoxygenation pathway decarboxylation offers the advantage of lower hydrogen consumption. Thus, decarboxylation of fatty acids and their methyl esters has been studied extensively over Pd/C. The saturated fatty acid (oleic acid, methyl oleate and linoleic acid) give high selectivity to saturated diesel fuel range hydrocarbons. The unsaturated reactants were hydrogenated with H_2 and subsequently deoxygenated. Parallel to hydrogenation formation of diunsaturated acids occurred. Under hydrogen rich atmosphere the hydrogenation was enhanced and the deoxygenation reaction became predominant. Additionally, isomerisation (double bond migration) of oleic acid occurred prior to hydrogenation and deoxygenation. Analogous to isomerisation, hydrogenation and deoxygenation trends were observed in experiments conducted under H_2 atmosphere with other unsaturated feeds. Furthermore, the deoxygenation of unsaturated feeds was performed in continuous mode under conditions of strong mass transfer influence to confirm stability and potential of the catalyst applicable in inducting. (Snare et al., 2008).

The deoxygenation of triglyceride (tristearin, triolein and soybean oil) under nitrogen atmosphere was investigated by Morgan (2010). This reaction was performed over 20 wt% Ni/C, 5 wt% Pd/C and 1 wt% Pt/C catalyst. They found that all three catalysts, CO is a primary product in gaseous phase so the decarbonylation pathway is a main pathway. Ni/C catalyst shows slightly higher selectivity for light hydrocarbons and H_2 than the Pt and Pd catalysts. The liquid products were analyzed via simulated distillation gas chromatography. The desirable fraction is C8-C17 fraction so the efficiency of catalysts can be follows the order Ni>Pt>Pd. 20% Ni/C is the most active catalyst for tristerin and triolein deoxygenation and higher C-C cracking activity. The aromatics formation during the deoxygenation of ethylstearate over Pd/C was strongly dependent on catalyst alkalinity that alkaline catalyst tended to form aromatics, whereas acidic catalysts did not. The distribution of carbon chain lengths in the product is strongly influenced by the degree of unsaturation of the constituent fatty acid chains in the triglyceride and by the nature of the catalyst (Morgan et al., 2010).

In 2011, Simacek and co-worker (2011) studied hydroprocessing of sunflower oil over a commercial hydrocracking catalyst in a fixed bed reactor. They found that the desired product i.e. *n*-alkane C_{17} and C_{18} decreased with increasing reaction temperature. On the other hand, the content of the aromatic, i-alkanes and cycloalkanes increased with the increase of reaction temperature. At low reaction temperature (360 °C), the content of aromatics in the hydroprocessing product was negligible (0.1 wt%). Moreover, monoaromatics were formed more than 90% of all aromatic hydrocarbons in hydroprocessing products. Simacek's results were similar to Maki-Arvela (Maki-Arvela et al., 2011). They used Pd/C as catalyst and tall oil as feedstock. They suggested that the catalyst activity dropped at high reaction temperature because of increasing aromatic compound. Moreover, they found that when increases of the metal loading from 1wt.% to 4wt.% led to an increase of catalyst activity (both conversion and selectivity) but a decrease of aromatic compounds. When compared between 1 vol.% hydrogen in argon and pure hydrogen, the results revealed that 1 vol% hydrogen gave low conversion (35%) but pure hydrogen gave higher catalyst activity (conversion = 59% and selectivity = 91%) at the same condition (after 330 min, 350 °C). The formation of C_{18} isomers as well as the aromatics could be suppressed using pure hydrogen.

The effect of saturated fatty acid (stearic acid) and unsaturated fatty acid (oleic and linoleic acid) were investigated by Immer and co-worker (2010). The process was performed at 300 ^{o}C under 1vol% hydrogen in argon over 1 wt% Pd/C in dodecane as solvent. They found that the initial reaction rate (during 5 min) for oleic and linoleic acids were 150 fold that of stearic acid and deoxygenation rates for oleic and stearic acids were the same, whereas in case of using linoleic acid as feedstock the catalyst deactivation occurred at 5 min reaction time. This is due to the formation of C17 aromatic hydrocarbon.

The deoxygenation of methyl eaters and triglycerides over a series of supported Pt catalysts were performed in a reactive distillation (RD) under He flow. They found that the PtSnK supported on silica was the best selectivity for desired product of α-olefins. No cyclic or aromatic products were observed under these experimental conditions (Chiappero M., 2011).

The using of Jatropha as feedstock was performed over Pt-Re/H-ZSM-5 catalyst at temperature rang 543-573 K. Rhenium-modified Pt/H-ZSM-5 catalysts were found to be much more effective for hydrotreating jatropha oil even at high jat/cat ratio of 10 as 80% conversion and 70% C18 selectivity were achieved. The reaction pathway involves hydrogenation of the C=C bonds of the triglycerides followed by C15-C18 alkane production through hydrodeoxygenation with decarbonylation and decarboxylation (Murata et al., 2010).

3.3 Metallic nitride and carbide catalysts

Platinum (Pt) and palladium (Pd)-based materials (noble catalysts) are one of the most practical catalysts. However, these catalysts are too expensive so the alternative catalysts were of interest, such as metallic nitride and carbide catalysts. Recently, metallic oxycarbide and oxynitride-supported system, such as, transition metal carbides and nitrides, have demonstrated to improve performance over the convensional hydroprocessing catalysts, which have shown excellent performance for use in hydrodenitrogenation (HDN), hydrodesulfurization (HDS) and hydrodeoxygenation (HDO) reactions.

Metal carbides and nitrides have more superior HDS activities when compared to sulfided Mo catalysts. It was found that the carbide was more active than the nitride, Sajkowski and Oyama (1996) observed that Mo_2C/Al_2O_3 had activity over two times greater than commercial sulfides Mo-Ni- S/Al_2O_3 catalyst. Kapoor et al., (1997) found the bimetallic compounds showed activity and stability compared with the corresponding monometallic carbides. The supported bimetallic oxycarbide was synthesized by temperature-programmed reaction (TPR). The catalysts were characterized by CO chemisorption, BET surface area measurement, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), nearedge X-ray absorption fine structure (NEXAFS). The supported bimetallic materials were tested in HDN of quinoline and HDS of dibenzothiophene. It was found that the HDN and HDS activity have higher activities than the monometallic when compared at the same active site. The HDS activity increases with higher amounts of molybdenum metal ratio, HDS conversion increases with the concentration of carbidic carbon on the surface observed from NEXAFS. The catalysts did not deactivate with time on stream because amount of sulfur occupies small fraction on the surface in from metal sulfide after the hydroprocessing reaction. Moreover, the electronic properties of the oxycarbide were modified by the interaction with the Al_2O_3 (Kapoor et al., 1997).

Hydrodeoxygention (oxygen removal) by transition metal nitrides was studied by Ramanathan and Oyama (1995) using a model liquid feed mixture containing dibenzothiophene, quinoline, benzofuran and tetralin in aromatics and alkanes. Vanadium nitride (VN) exhibited excellent activity and selectivity for hydrodeoxygenation of benzofuran. Claridge et al. (2000) performed an extensive study on the synthesis of transition metal carbide and nitride catalysts from oxide precursors. Hydrodeoxygenation of oleic acid and canola oil over Nitrides of molybdenum, tungsten, and vanadium supported on γ-Al_2O_3 were investigated by Monnier et al. (2010). The reaction was performed at 380-410 ºC under H_2 atmosphere. The molybdenum nitride (Mo_2N) supported on γ-Al_2O_3 showed superior performances for the hydrodeoxygenation of oleic acid (with almost 100% and oxygen removal) and higher production of normal alkanes (380 ºC and 8.35 MPa H_2). Experimental results indicated that Mo_2N favours the hydrodeoxygenation three times out of four for the removal of oxygen from oleic acid over hydrodecarbonylation. On theother hand, oleic acid was mostly deoxygenated by decarbonylation and decarboxylation in the case of vanadium nitride supported catalyst. A 450-h hydrotreating test performed with Mo_2N/γ-Al_2O_3 and canola oil as feedstock indicated high oxygen removal throughout the test (exceeding 90%). Improvements are nevertheless required in terms of product distribution in order to maximize the yield of high-cetane middle distillates (diesel fuel range hydrocarbons) (Monnier et al., 2010).

CHAPTER 4

RESEARCH PROCEDURE

4.1 Experimental

4.1.1 Chemicals

5 wt% Pd/C was purchased from Aldrich Chemical Co. Starting materials i.e. CPO, DPO and PFAD were obtained from Pathum Vegetable Oil, Co. Ltd. (Thailand). The distribution of fatty acids in feedstocks are provided in Table 4.1 CPO consist of triglyceride higher than 95 wt.% while PFAD consists of 93.2 wt.% free fatty acid (FFA). Noted that composition of CPO was similar to DPO only the gum in CPO was removed. Calibration mixture for ASTM-2887 was purchased from Restex Co. All of calibration gas was purchased from Thai industrial gases (TIG) public company limited.

4.1.2 Reactor and operational detail

For routine experiments, Hydroprocessing of CPO, DPO and PFAD were performed in a small batch (5.8 ml) shaking reactors, as shown in Figure 4.1. The reactor has the inner diameter of 2.35 mm and a length of 9 mm. The system is heated by furnace (shown in Figure 4.2) that can shake the material to touch each other more. Prior to the experiments, the catalyst was reduced by hydrogen flow (10 ml/min) at 200 ^{o}C ramp 5 ^{o}C/min for 2 h. After the reduction, the catalyst was cooled to 30 ^{o}C under N_2 flow. The reduced catalyst was removed from the reduction apparatus and weighed by analytical balance. The 0.1 g of reduced catalyst and 2 ml of reactant were loaded into the reactor. Sealed reactors were purged by hydrogen gas for several times and pressurized by H_2 in the range of 20-80 bar. The furnace was heated to desired temperature then brings the reactor into the furnace and shakes in the maximum speed (70 rpm). After complete reaction, the reactors were removed from the furnace and submerged in a water bath at ambient temperature to stop reaction.

Table 4.1 Distribution of fatty acid in CPO, DPO and PFAD.

Fatty acid	**CPO* (wt.%)**	**DPO* (wt.%)**	**PFAD** (wt.%)**
C 12:0 (Lauric acid)	0.8	0.8	-
C 14:0 (Myristic acid)	1.2	1.2	1.1
C 16:0 (Palmitic acid)	44.5	45.4	49.0
C 16:1 (Palmitoleic acid)	0.1	0.1	0.2
C 18:0 (Steric acid)	3.8	3.8	4.1
C 18:1 (Oleic acid)	39.7	39.0	35.8
C 18:2 (Linoleic acid)	9.3	9.1	8.3
C 18:3 (Lonolenic acid)	0.2	0.2	0.3
C 20:0 (Arachidic acid)	0.3	0.3	0.3
C 20:1 (Eicosenoic acid)	0.1	0.1	0.2
C 24:1 (Tetracosenoic acid)	-	-	0.6

* The weight percent of fatty acid in triglyceride.
** The weight percent of free fatty acid.

Figure 4.1 Batch reactor

Figure 4.2 Furnace

4.1.3 Analysis of hydroprocessed product

Hydroprocessed products were contained two phase that gaseous phase and liquid phase. The gaseous product from each experimental test were collected in gas sampling bag (figure 4.3.) and analyzed by gas chromatography (GC 14-B, Shimadzu Corporation) by injecting 10 μl pass Porapak Q column with a thermal conductivity detector (TCD).

Figure 4.3 gas sampling bag

The GC was calibrated for all of the products, including CO, CO_2 and CH_4. The moles of the gaseous product were determined by calibration curve. The reaction pathways were investigated by a mole ratio of CO/CO_2. The liquid products from each experiment test were collected from reactor. It was analyzed using offline Shimadzu GC-14B gas chromatograph equipped with an Agilent DB-2887 column (10 m× 0.53 mm × 3.00 μm) and Flame ionization detector (FID). The operating conditions for each instrument are shown in the tables 4.2 and 4.3, respectively. The Peak Integrations (SimDist) were performed using Distillation GC software version 2.00 from Shimadzu Corp. The boiling point range from SimDist can divided into four fractions. The products in the temperature range of 250-380°C is a suitable for diesel range (*n*-C15-*n*-C18). The 0.1 μl of liquid samples were injected into the column inlet (40 kPa). The injector and detector temperature were maintained at 350 ^{o}C. The GC oven used temperature programs following: 40-350 ^{o}C (15^{o}C/min) hold for 20 min.

The effectiveness of hydrotreating reactions was measured in term of product yields of desired product (middle distillate yield). The conversion and selectivity of the products is determined by simulated distillation (according to ASTM 2887) data as follows:

$$\text{Conversion (\%)} = \frac{\text{Feed}_{360+} - \text{Product}_{360+}}{\text{Feed}_{360+}}.100$$

where: Feed_{360+} is the weight percent of the feed which have a boiling point higher than 360 ^{o}C. Product_{360+} is the weight percent of the product which have a boiling point higher than 360 ^{o}C.

As diesel is the main product, the measure of selectivity is also employed. Diesel selectivity is based on the boiling point range and is defined by the following equation:

$$\text{Diesel selectivity (\%)} = \frac{\text{Product}_{180\text{-}360} - \text{Feed}_{180\text{-}360}}{\text{Feed}_{360+} - \text{Product}_{360+}}.100$$

where $Feed_{180–360}$ and $Product_{180–360}$ are the weight percent of the feed and product, respectively, which have a boiling point between 180 and 360 °C (diesel molecules) (Bezergianni et al., 2010).

Table 4.2 The condition of GC-TCD.

Gas chromatograph	**Shimadzu GC-14B**
Detector	TCD
Column	Porapak Q
Carrier gas	He (UHP) flow 30 ml/min
Detector temperature	150 °C
Injector temperature	150 °C
Column temperature	40 °C

Table 4.3 The condition of GC-FID.

Gas chromatograph	**Shimadzu GC-14B**
Detector	FID
Carrier gas	N_2 (UHP)
Column	DB-2887
Split/Splitless	Split (30 ml/min)
Purge flow rate	10 ml/min
Make up pressure	40 kPa
Carrier pressure	40 kPa
Injector temperature	350 °C
Detector temperature	320 °C
Column temperature	40 °C ramp 15 °C/min to 350 °C hold for 20 min

CHAPTER 5

RESULTS AND DISCUSSION

In this chapter, the effect of operating parameters, including reaction time, operating temperature, and operating pressure, was investigated to determine optimal operating condition for different feedstocks, CPO, DPO, and PFAD of hydroprocessing over 5wt.% Pd/C. In addition, the effect of the operating parameters on catalyst activity in terms of conversion, selectivity and yield, were investigated.

We also analyzed some of specific products including the straight chain alkanes, CO, CO_2 and CH_4. Additionally, we used simulated distillation to analyze the straight chain alkanes products that occur under hydroprocessing conditions. For all feedstocks in this study, similar product distribution in both liquid and gas phases are obtained. The major liquid products are *n*-pentadecane (C15) and *n*-heptadecane (C17) containing one carbon atom shorter than the total length of the fatty acid $C_{(n-1)}$. The hydrocarbons that contain carbon atom with the same number as the fatty acid $C_{(n)}$ were formed less than 5wt% in all cases. In this study, the compositions of liquid hydrocarbons are considered in four fractions; the 65–150 ^{o}C fraction is most likely alkanes ranging from C5 to C8, the 150–250 ^{o}C fraction is most likely alkanes ranging from C9 to C14, the 250–380 ^{o}C fraction is most likely alkanes ranging from C15 to C18 (desired product know as middle distillate) and the 380-520 ^{o}C fraction is defined as those compounds having high boiling point above the boiling point of *n*-heptadecane including unconverted triglyceride starting material, as well as high boiling hydrocarbon and oxygenated products, shown in Table 5.1 (Huber et al., 2007).

Table 5.1 Distillation data in specified temperature range. (Huber et al., 2007)

The straight chain alkanes	Range of temperature (°C)
Alkanes C_5-C_8	65-150
Alkanes C_9-C_{14}	150-250
Alkanes C_{15}-C_{18}	250-380
Intermediates, the tri-glycerides and fatty acids	380-520

5.1 Hydroprocessing of CPO

The studies of product quality and yields were performed on hydroprocessing of CPO feedstock. All experiments were done duplicate. The reaction time is am identified parameter for regulating catalyst effectiveness and catalyst deactivation. First of all, optimum reaction time was determined to find the point which showed the highest diesel-range yield as shown in Figure 5.1 (a). CPO conversion increases with increasing residence time (from 0.25 to 5 h), the conversion increases rapidly from 17 to 69 % at the beginning of the reaction up to 3 h after that it gradually increases to 74 %. However, maximum diesel yield (51%) was observed at a reaction time of 3 h. This is due to a decrease of diesel selectivity after 3 h. As depicted in Figure 5.1 (b), lighter hydrocarbons, i.e. 65-150 °C and 150-250 °C fraction, obviously increase with increasing reaction time but middle distillate and heavy hydrocarbon, i.e. 250-380 °C**,** 380-520 °C fraction, decrease with increasing reaction time. The reason for reduction of middle distillate fraction was suggested that heavy molecules including triglyceride and some molecules of middle distillate are cracked into light hydrocarbons.

The effect of operating temperature was investigated in the range of 350-450°C. The results shown in Figure 5.2 (a) revealed that no conversion was observed at temperatures of 350°C and 375°C which were not high enough to give reasonable conversion and diesel yield. However, when temperature was increased to 400°C, conversion of CPO and yield increase significantly to 70% and 51%, respectively. The reason of this behavior might be due to an increase of the rate of deoxygenation. At higher temperature, CPO conversion increases as a function of temperature but

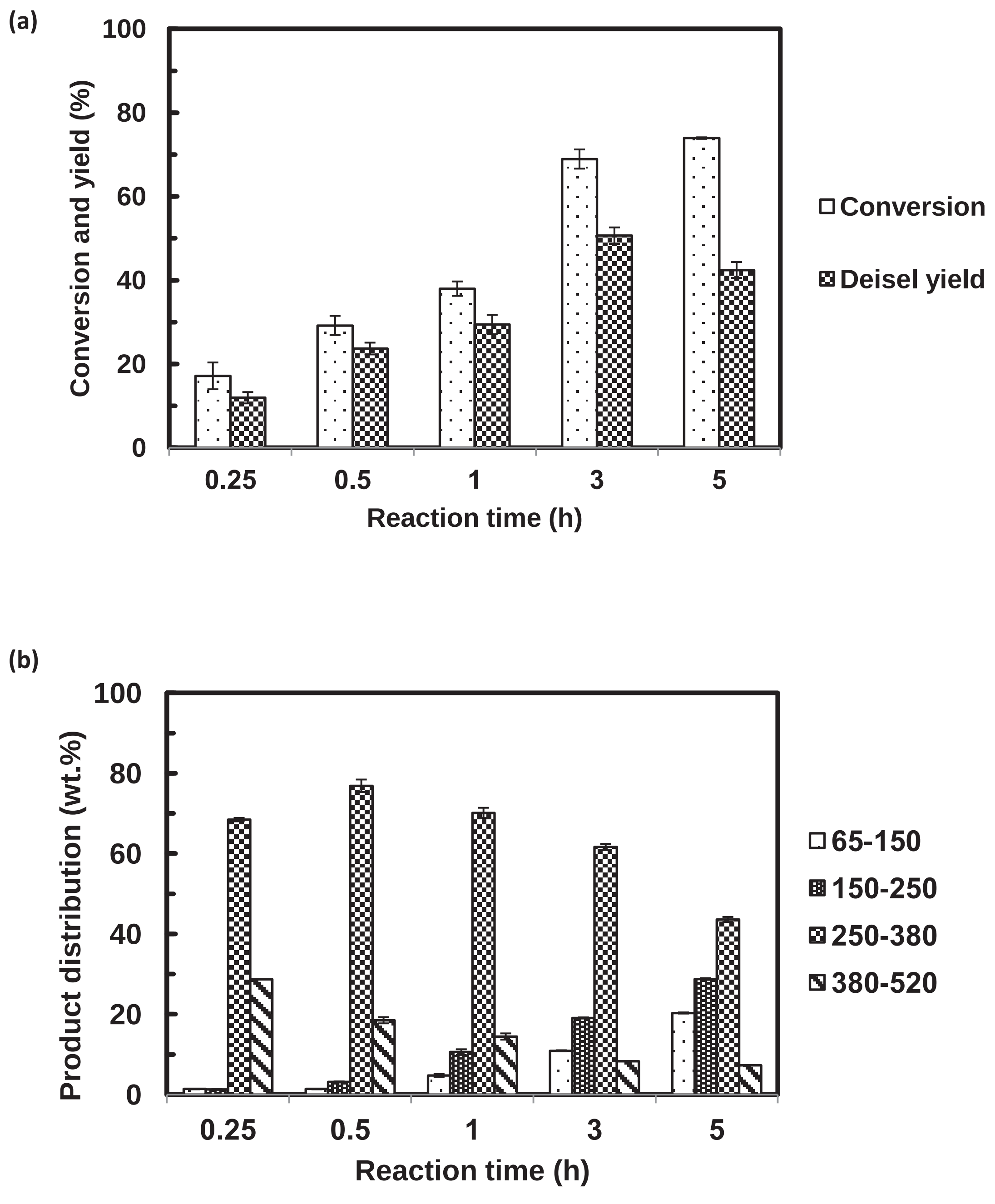


Figure 5.1 The effect of reaction time on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of CPO feedstock. (operating temperature = 400 °C, operating pressure = 40 bar).

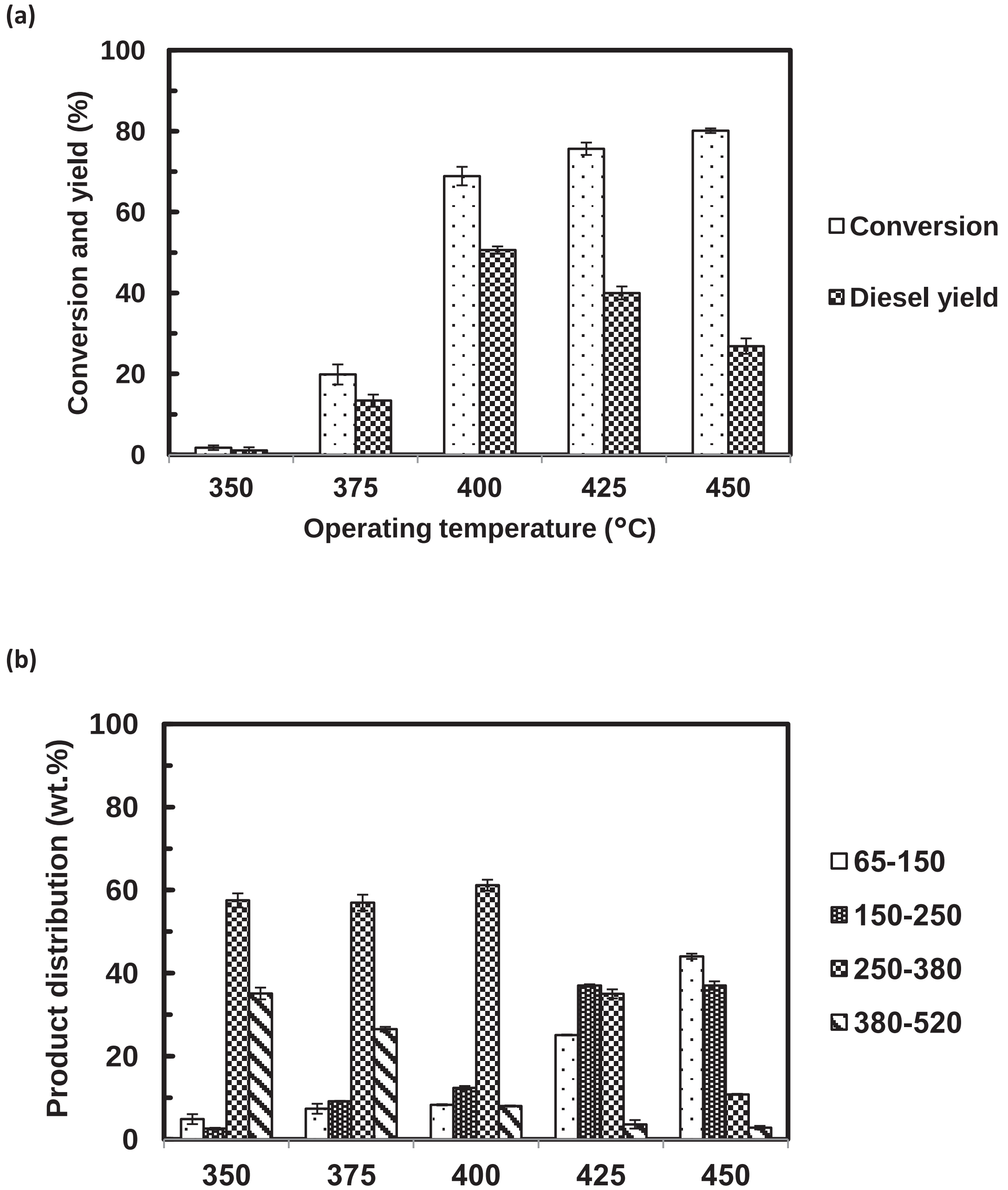


Figure 5.2 The effect of operating temperature on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of CPO feedstock. (reaction time = 3 h, operating pressure = 40 bar).

diesel yield starts to decrease. As demonstrated in Figure 5.2 (b), the middle distillate of 250-380°C was found to be satisfactorily high at operating temperature of 350-400°C while the fraction of lighter hydrocarbon was still low but slightly increase with increasing temperature due to the conversion of heavier hydrocarbons. Beyond this temperature range, the middle distillate decreases suddenly as it may be cracked to lighter fraction. This effect is more pronounced at 450°C as shown by the highest yield of the 65-150°C fraction. The effect of pressure on conversion and diesel yield is shown in Figure 5.3 (a). As pressure was increased from 20 to 60 bar, CPO conversion continually increases whereas diesel yield increases to the maximum value at 40 bar and then levels off at higher pressure. Therefore, to obtain reasonable diesel yield from hydroprocessing of CPO, one can choose to operate at temperature of 400°C and pressure at 40 bar with the reaction time of 3 h. The effect of reaction pressure on catalyst activity was lower than the effects of reaction time and operating temperature. The effects of operating pressure on liquid product distribution were shown in Figure 5.3 (b)

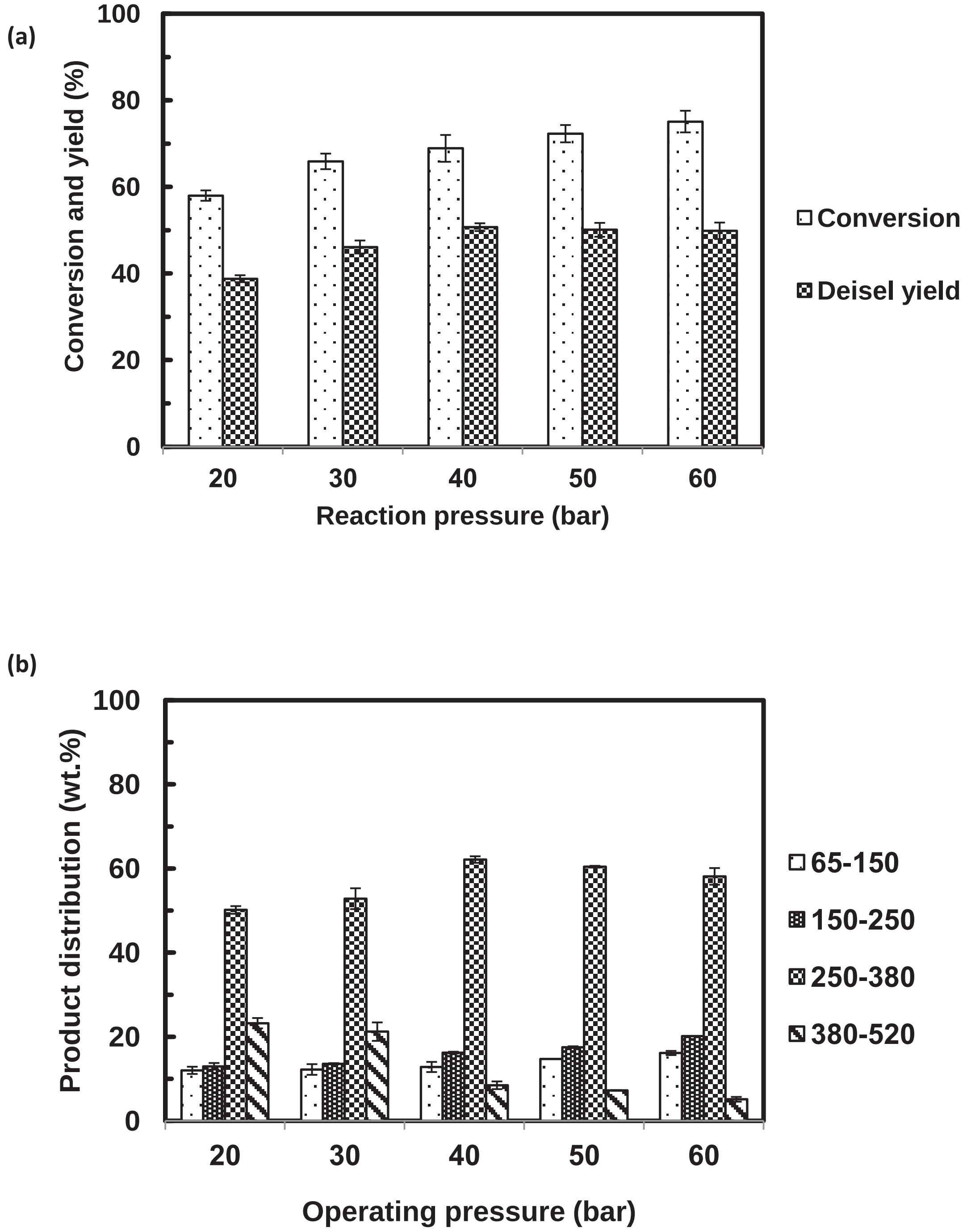


Figure 5.3 The effect of operating pressure on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of CPO feedstock. (reaction time = 3 h, operating temperature = 400 °C).

5.2 Hydroprocessing of DPO

Figure 5.4 (a) showns conversion and diesel yield as a function of reaction time for DPO feedstock. Similar tendency to the case of CPO was observed, conversion increases with increasing residence time and maximum yield was observed at a certain time. However, using DPO can provide higher conversion and diesel yield as well as less reaction time. When compared to CPO, the maximum diesel yield of 70% can be obtained in 1 h. This result indicates that CPO feedstock was more difficult to be converted than DPO because CPO contains gum (Phospholipids, phosphotide). The middle distillate selectivity increases from 67 to 80 wt.% with increasing residence time from 0.3 to 1 h but significantly decreases to 66 wt% at 3 h. In case of temperature, at low temperature of 350 and 375°C, moderate conversion (ca.50%) and diesel yield (ca.45%) can be achieved while these were not observed in case of CPO. As demonstrated in Figure 5.5 (b), the fraction of middle distillate suddenly drops with increasing operating temperature over 400°C. Therefore, temperature of 400°C is a suitable operating temperature as the highest yield is obtained as shown in Figure 5.5 (a). At high temperature, heavy molecules and some diesels molecules are cracked into lighter molecules. Therefore, at milder hydroprocessing temperature (350-400 ^{o}C) promote diesel rather gasoline (light hydrocarbon 40-200 ^{o}C) production, which is in accordace to literature (Bezergianni and Kalogianni, 2009). Reaction pressure was observed to offer slight increase in conversion but not diesel yield as shown in Figure 5.6 (a). This is due to a slightly decrease of diesel selectivity. If we consider in the view point of archiving high conversion and diesel product, a possible operating pressure would be 20 bar. The middle distillate fraction slightly decreases as initial cold hydrogen pressure, as shown in Figure 5.6 (b). In comparison to CPO, as expected, higher diesel yield would be obtained at less severe operating condition in the case of using DPO as the feedstock. This is because DPO is more pure than CPO as the contaminations of phospholipid compounds were removed. Although, DPO offers higher diesel yield with milder operating condition than that of CPO but for further development to industrial scale, the energy consumption during degummed process is needed to be taken into account in comparison of the energy saving during the hydroprecessing period.

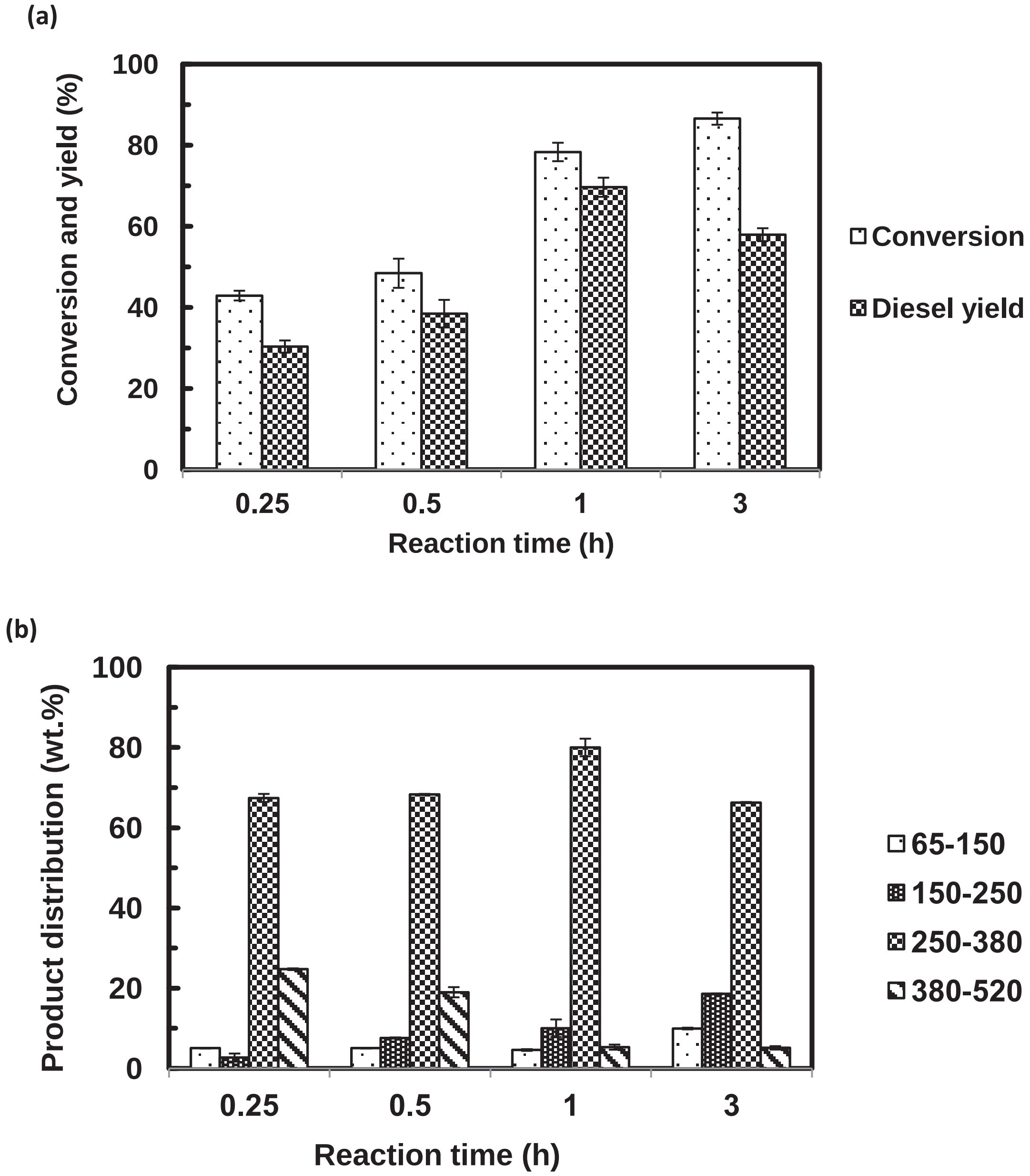
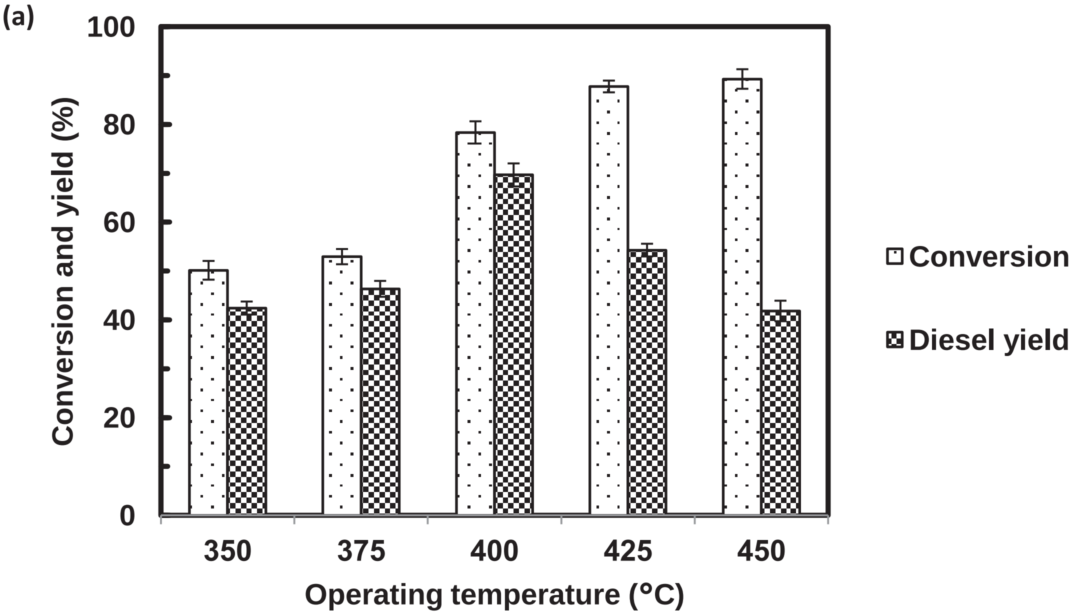


Figure 5.4 The effect of reaction time on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of DPO feedstock. (operating temperature = 400 °C, operating pressure = 40 bar).



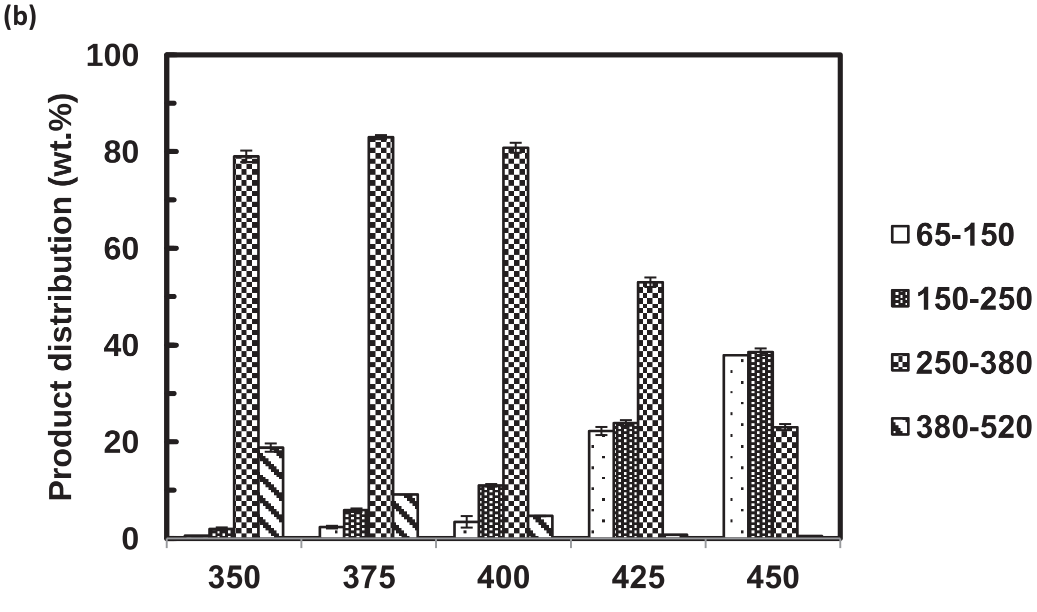
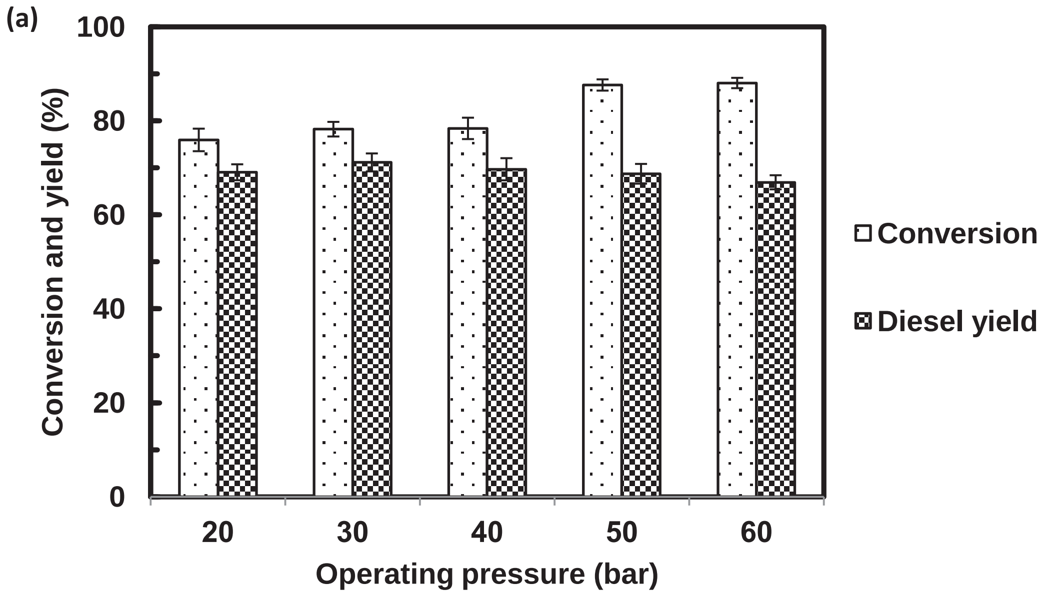


Figure 5.5 The effect of operating temperature on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of DPO feedstock. (reaction time = 1 h, operating pressure = 40 bar).



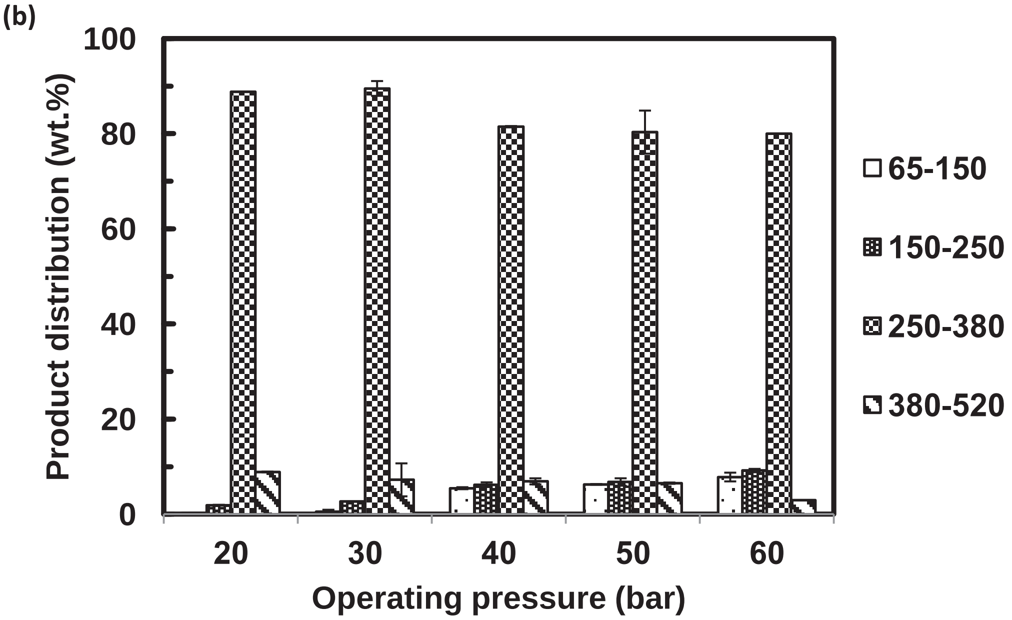


Figure 5.6 The effect of operating pressure on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of DPO feedstock. (reaction time = 1 h, operating temperature = 400 °C).

5.3 Hydroprocessing of PFAD

The conversion of PFAD increases from 82 to 91% with increasing residence time from 0.5 to 5 h and diesel yield decreases from 81 to 58% as shown in Figure 5.7 (a). Figure 5.7 (b) demonstrates the decrease of middle distillate selectivity as a function of residence time. This observed phenomenon might be because some molecules of middle distillate were cracked into light hydrocarbons (C_6-C_{14}). The PFAD conversion in all residence times are found to be higher than either DPO or CPO due to the most compositions of PFAD are free fatty acid, i.e. palmitic acid, oleic acid, and linoleic, that could be converted to aliphatic alkane easier than triglyceride. For this type of feed stock, it is obvious that at temperature of 375°C is the best choice as the maximum diesel yield of 81% was obtained. In case of pressure, increasing pressure can increase conversion as depicted in Figure 5.9 (a). The suggested operating pressure for PFAD is 40 bar as at this pressure the maximum diesel yield can be obtained. It is noted that adversed effect from too high pressure has a pronounced effect on diesel yield when compared to DPO and CPO.

Immer and co-worker studied deoxygenation of stearic, oleic and linoleic acids over a 5wt.% Pd/C catalyst. At operating condition of 300 ºC, 15 bar, 1.6 g of reactant, 23 g of dodecane solvent and 350 mg of 5% Pd/C catalyst under 10% H_2, almost complete conversion of stearic and oleic acid could be obtained within 0.5 h. It was proposed that such rate could occur only when the unsaturated C18 free fatty acids, oleic and linoleic, are hydrogenated to stearic acid before decarboxylation. However, since the hydrogenation of the unsaturated C18 free fatty acids to saturated fatty acid occurred at milder condition and could complete during heating up, the decarboxylation rate is therefore merely independent of the degree of saturation of raw materials (Immer et al., 2010). Moreover, Lestari and co-worker investigated deoxygenation of stearic (C18:0) and palmitic acid (C16:0) over 4 wt.% Pd/C catalyst using dodecane as a solvent. At 300 ºC and 17 bar of 5% H_2 in Ar, 95% stearic conversion and 98% palmitic conversion could be obtained after 12 h. Therefore, this might conclude that the deoxygenation rates of different saturated fatty acids are independent of carbon chain length of its fatty acids (Lestari et al., 2009). As can be seen, deoxygenation of free fatty acids: palmitic acid, stearic, oleic, and linoleic, can

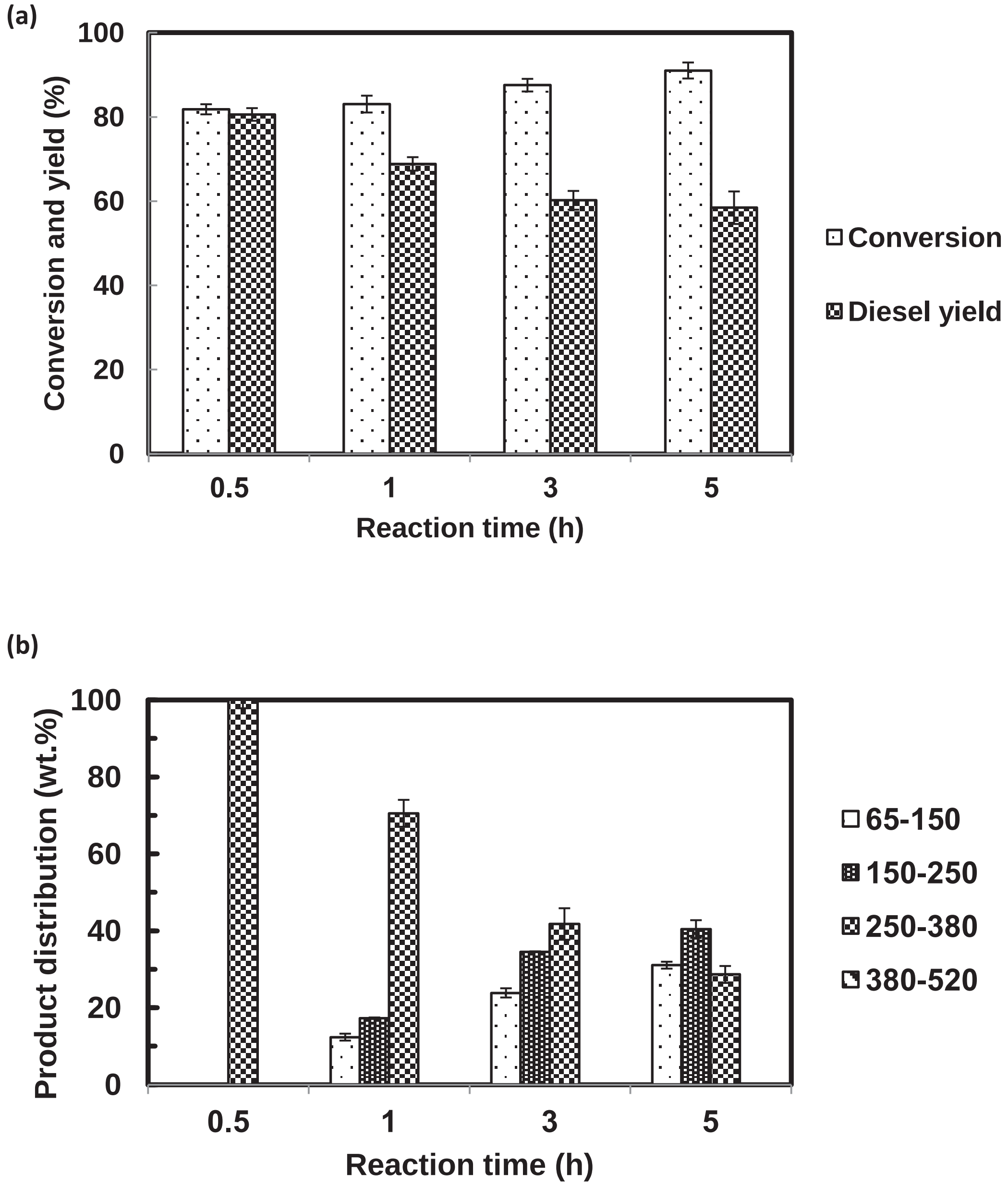


Figure 5.7 The effect of reaction time on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of PFAD feedstock. (reaction time = 0.5 h, operating temperature = 375 °C).

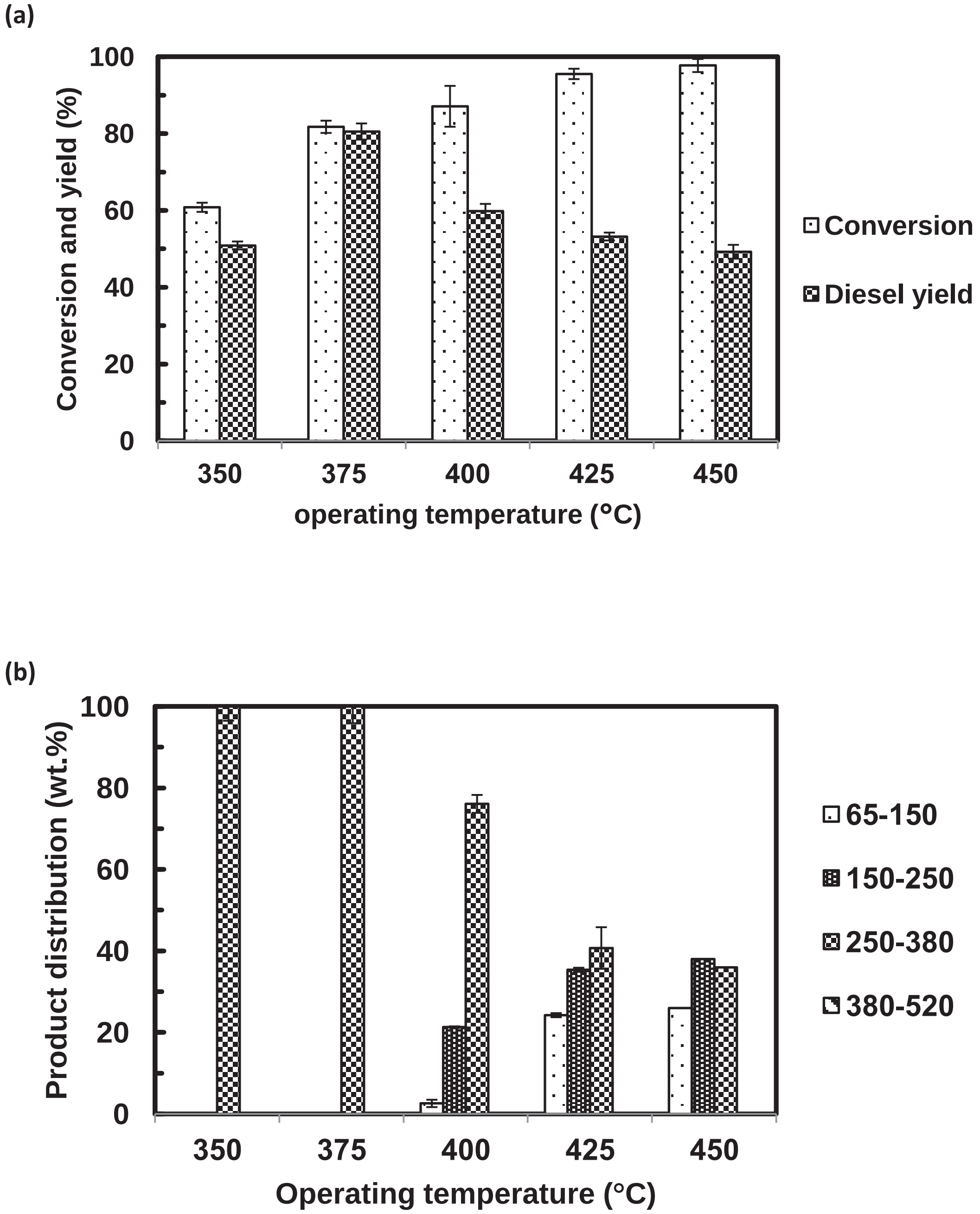


Figure 5.8 The effect of operating temperature on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of PFAD feedstock. (reaction time = 0.5 h, operating pressure = 40 bar).

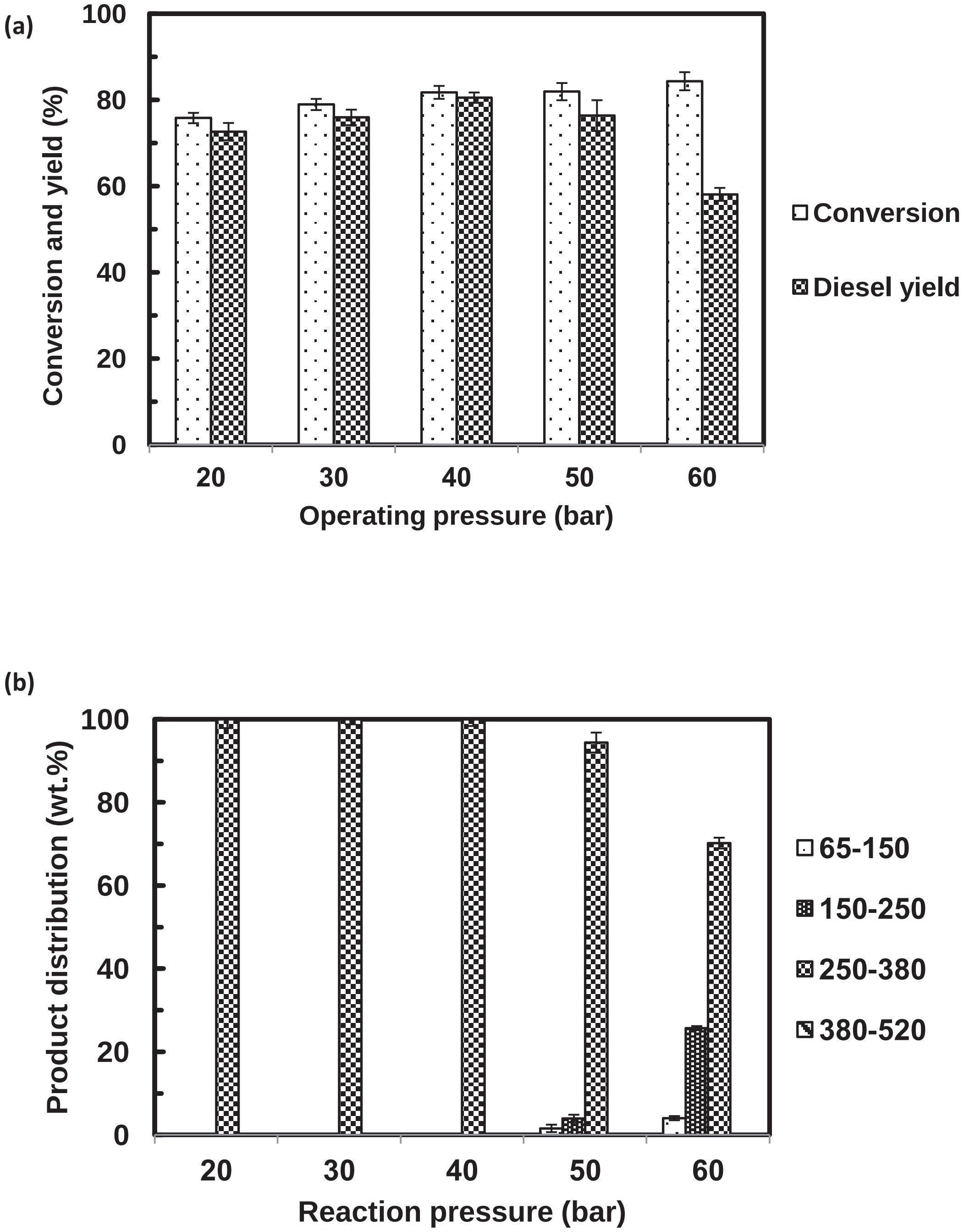


Figure 5.9 The effect of operating pressure on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of PFAD feedstock. (reaction temperature = 375 °C, reaction time = 0.5 h).

mostly proceed at temperature around 300°C, however, for our PFAD case, higher operating temperature is required. From the above reasons, higher operating temperature (375 °C) in the case of our PFAD might be resulted from the containing of mono-, di-, and tri-glycerides. Moreover, others impurities in PFAD can lead to the decrease of the deoxygenation rates (Lestari et al., 2009). In addition, the difference of the reaction performance among the literatures and also our work was also due to the difference in the ratio of catalyst to reactant.

Our results demonstrated that PFAD, a by-product from physical refining of edible palm oil, is another attractive feedstock to produce bio-diesel via hydroprocessing.

5.4 Analysis of deoxygenation reaction pathways.

The products obtained from hydroprocessing of palm oil can be attributed to the elimination of oxygen. Three principle deoxygenation pathways are composed of decarboxylation, decarbonylation and hydrodeoxygenation, as shown in Chapter 3. In our work the major liquid products are *n*-pentadecane (C_{15}) and *n*-heptadecane (C_{17}), which contain one carbon atom shorter than the total length of the fatty acid $C_{(n-1)}$. Such $C_{(n-1)}$ can be produced by two parallel pathways: decarboxylation and decarbonylation. On the other hand, the hydrodeoxygenation pathway produces alkanes with the same number of carbon atom as the starting material or even number of carbon atom ($C_{(n)}$) of less than 5wt.% by converting the carboxylic acid with hydrogen and releasing water. Thus, the ratio of *n*-alkanes with odd numbers of carbon atoms to *n*-alkanes with even numbers of carbon atoms can serve as an indicator for evaluating the reaction pathways of decarboxylation/decarbonylation and hydrodeoxygenation. In this section, we will discuss on the effect of operating temperature and pressure on the behavior of the reaction by examining on the ratio of $n\text{-}C_{15}/n\text{-}C_{16}$ and $n\text{-}C_{17}/n\text{-}C_{18}$ as these are the major products in this study.

For all feedstocks, operating temperature and reaction pressure can affect the ratio of C_{15}/C_{16} and C_{17}/C_{18}, as shown in Figures 5.10 and 5.11, respectively. Regardless the feedstocks, either C_{15}/C_{16} or C_{17}/C_{18}, the mole ratio decreases with increasing reaction temperature indicating that decarboxylation/decarbonylation is not favor at high temperature. These results are inconsistent with other works such as

Hancsok (2011), Kovacs (2011), Krar (2010) and Kikhtyanin (2010) Hancsok (2011) reporting that the ratio of $C_{(n-1)}/C_{(n)}$ increases as a function of temperature. However, our observation is consistent with the thermodynamic model suggested by Smejkal (2009) that increasing of C15/C16 mole ratio at high temperature might be due to the limitation of hydrogen diffusion to the active phase and side reactions such as isomerization and cracking. As such the contrary of our finding might be because our experiments were performed in a small batch shacking reactor so the reaction would occur without limited diffusion.

In case of reaction pressure, regardless of the feedstocks, either the mole ratio of C15/C16 or C17/C18 decreases with increasing reaction pressure indicating that decarboxylation/decarbonylation is not favor at high pressure. This trend is similar to those found with previous studies such as Hancsok (2011), Kovacs (2011), Krar (2010) and Kikhtyanin (2010).

It is noted that the range of $C_{(n-1)}/C_{(n)}$ value observed in this study is higher than other previous studies. Theses might be due to the difference of some parameters such as type of reactors (batch or continuous) and type of catalyst (NiMo, CoMo and Pd). The $C_{(n-1)}/C_{(n)}$ ratio varies with catalyst such as 0.13 for CoMo (Krar M., 2010), 1 for NiMo (Hancsok J., 2011; Sankaranrayanan T.M., 2011), 4 for Pd (Kikhtyanin O., 2010), in case of using sunflower oil as feedstock (temperature = 300 $^{\circ}$C, LHSV = 1 h^{-1}, H_2/feedstock volume ratio = 600 Nm^3/m^3, pressure = 20 bar). In addition, the type of reactor has also a significant effect on this ratio. In 2011, Kwon and co-worker studied hydroprocessing of canola oil and methyl laurate over $NiMo/Al_2O_3$ catalyst in a batch reactor. They found that value of $C_{(n-1)}/C_{(n)}$ ratio was constant at 3 over the range of T = 350-400 ^{o}C and P = 18-85 bar of H_2. In case of batch reactor, higher $C_{(n-1)}/C_{(n)}$ ratio was obtained at the same catalyst. From our results, the higher $C_{(n-1)}/C_{(n)}$ ratio might be due to the use of Pd/C as catalyst and performing the reaction in batch mode.

For gas-phase products, CO, CO_2 and methane are the main contribution. Although, the present of CO and CO_2 could be attributed to decarbonylation ordecarboxylation, however, it cannot be concluded that the hydroprocessed products obtained only from the decarbonylation or decarboxylation. Because of the presence

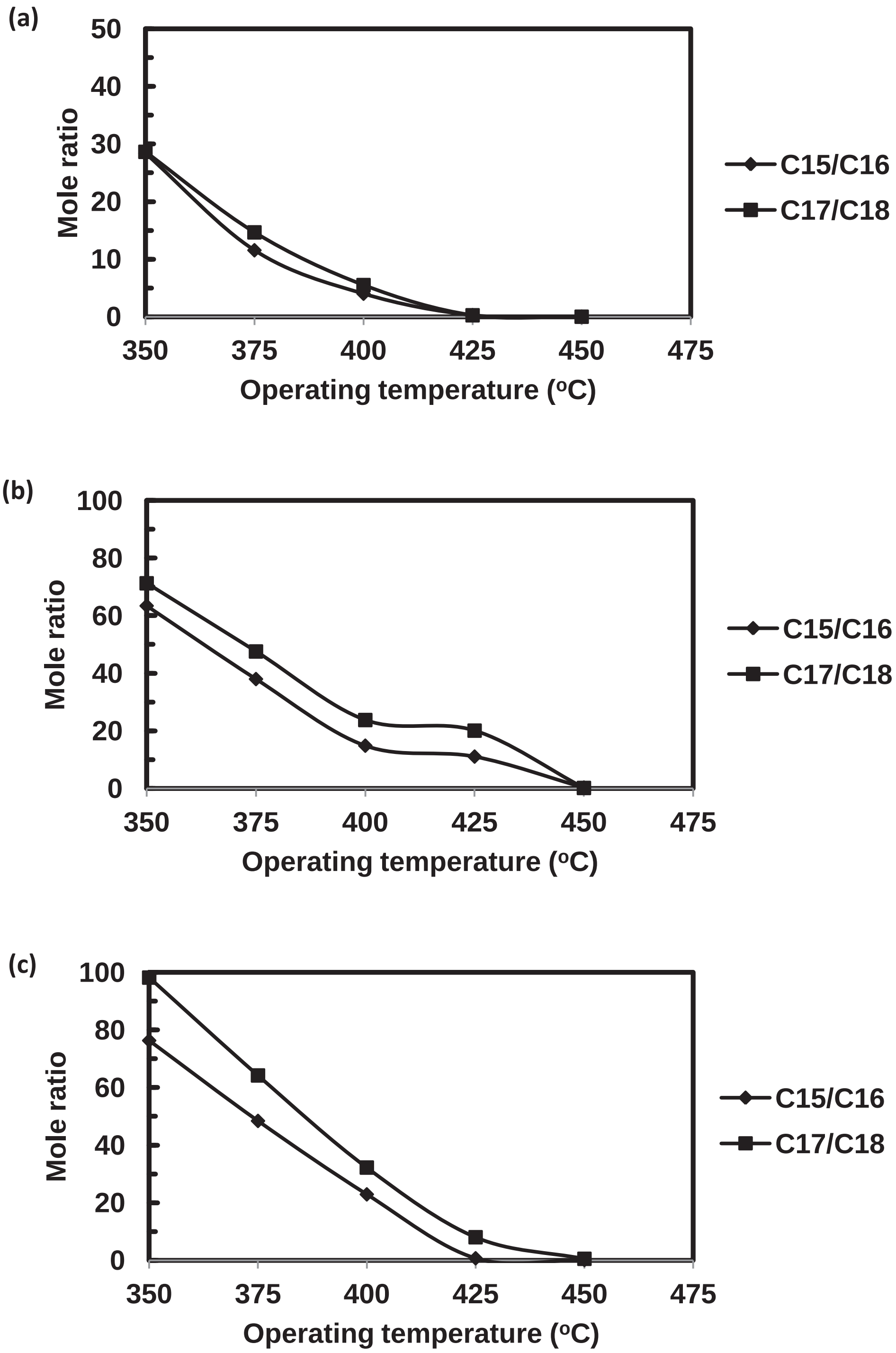


Figure 5.10 The ratio of C(n-1)/C(n) paraffins as a function of the operating temperature a) used CPO as feedstock b) used DPO as feedstock and c) used PFAD as feedstock.

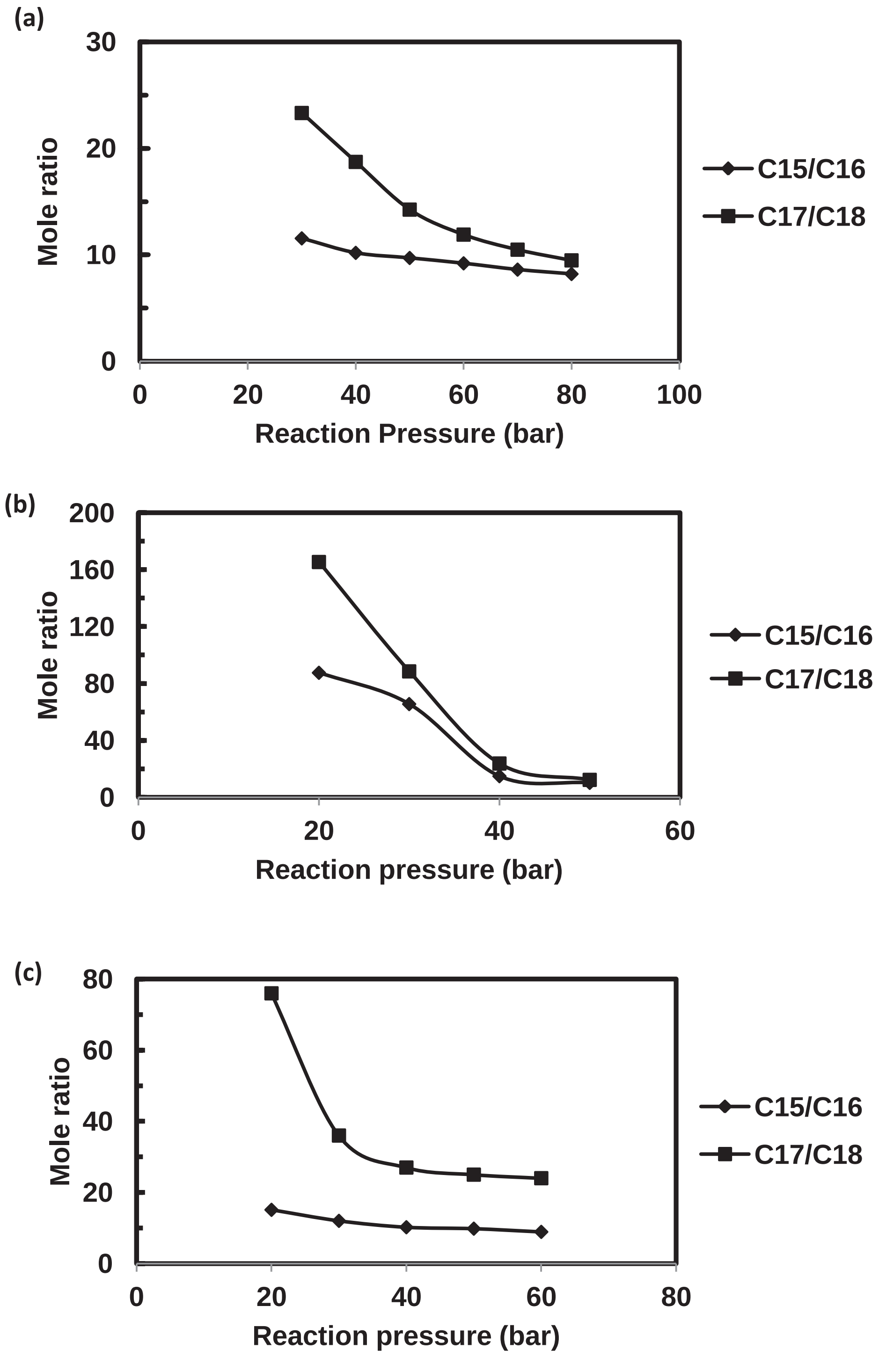


Figure 5.11 The ratio of C(n-1)/C(n) paraffins as a function of the reaction pressure a) used CPO as feedstock b) used DPO as feedstock and c) used PFAD as feedstock.

of CO, CO_2, water and hydrogen, it is noted that the reactions such as water gas shift and methanation could also take place. Therefore identifying the reaction between decarboxylation and decarbonylation are difficult. However, the gaseous products of CO_2 and CO confirm the results of liquid products which contain one shortage of carbon atom, $C_{(n-1)}$ so the decarboxylation/decarbonylation are the main pathways. It is worthy to note that the beneficial of decarboxylation/decarbonylation over hydrodeoxygenation is the less demand of hydrogen consumption as shown in Eqs. (1) - (3), respectively.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusion

6.1.1 Hydroprocessing of palm oil

In this study, hydroprocessing of CPO and its physical refining, i.e. DPO or PFAD, catalyzed by 5%wt Pd/C was investigated. The obtained products contain two phases, gas phase and liquid phase. The product distribution were found similar in both liquid and gas phases from all feedstocks. For all experiments, the liquid products were found to be composed mainly of middle distillate in the range of 250-380 °C, which are mostly C_{15}-C_{18} hydrocarbon. Particularly, the major liquid products are *n*-pentadecane (C_{15}) and *n*-heptadecane (C_{17}), which contain one carbon atom shorter than the total length of corresponding fatty acid $C_{(n-1)}$ i.e. palmitic and oleic acid. Such $C_{(n-1)}$ can be produced from two parallel pathways: decarboxylation or decarbonylation. Insignificant amount of less than 5wt.% are alkanes containing the same number of carbon atom as the starting material or even number of carbon atom ($C_{(n)}$). These products formed by the hydrodeoxygenation pathway of which the carboxylic acid reacted with hydrogen and releasing water.

For gas phase, CO, CO_2 and methane are the main products of this reaction. However with the present of CO, CO_2, CH_4, H_2O and H_2, the reaction such as water gas shift and methanation could also take place. Hence, decarboxylation or decarbonylation pathway cannot be identified as the main reaction. It is noted that the gaseous products of CO_2 and CO confirm the results of liquid products which contain one shortage of carbon atom, $C_{(n-1)}$ indicating the decarboxylation and decarbonylation are the main pathways. It is worthy to note that the beneficial of decarboxylation/decarbonylation over hydrodeoxygenation is the less demand of hydrogen consumption.

6.1.2 Optimal operating condition

The operating parameters, such as reaction time, operating temperature, and pressure, are varied in order to examine optimal operating condition for hydroprocessing of each feedstock using 5 wt.% Pd/C catalyst. In case of CPO, the optimal operating conditions (maximum diesel yield of 51%) were observed at operating temperature of 400°C and pressure at 40 bar with the reaction time of 3 h. In the case of using DPO as feedstock, the reaction given higher diesel yield of 69% at the same operating temperature but required less severe operating condition, operating pressure at 20 bar and reaction time of 1 h, as shown in Table 6.1. This is because DPO is purer than CPO as the contaminations of phospholipid compounds were removed. Although, DPO offers higher diesel yield with milder operating condition than that of CPO but for further development to industrial scale, the energy consumption during degummed process are needed to take into account and compared to the energy saving during the hydroprecessing period. The remaining feedstock PFAD gave 73% of diesel yield at less severe operating condition of lower operating temperature (375 °C) with low reaction pressure (20 bar) and shorter reaction time (30 min) when compared to DPO and CPO, respectively. The optimal operating condition can summarize in Table 6.1.

Table 6.1 Comparing diesel yield for each feedstock.

Feedstock	Time (h)	T (°C)	P (bar)	Diesel yield (%)
CPO	3	400	20	39
			40	51
DPO	1	400	20	69
			40	70
PFAD	0.5	375	20	73
			40	81

6.2 Recommendations

From our results, we found that the free fatty acid (FFA) can convert to *n*-alkanes easier than triglyceride so the addition of hydrolysis reaction before sequential deoxygenation is suggested for future work. The hydrolysis of triglyceride can yield FFA and glycerol, and then the FFA intermediates are further reacted in deoxygenation reaction. The addition of such hydrolysis step can improve diesel yield in case of using triglyceride as feedstock.

Commonly, the commercial catalysts, i.e. NiMo, CoMo or Pd, etc., are used in deoxygenation so the synthesis and development of new catalysts are interesting. The new methods for catalyst preparation, such as flam spray pyrolysis, sovothermal and other may enhance the efficiency of and its performances.

Most experiments of deoxygenation use edible oil as feedstock, which would compete food resources. Hence, applying the edible oil to this technology in large scale is needed to consider. The utilization of alternative nonfood sources and lignocelluloses such as grass, microalgae, agricultural waste products, low-quality vegetable oils as well as heavier side products of kraft pulping industries are of interest.

In our experiment, the conversion CPO and DPO is not completes therefore some residue of triglyceride and free fatty acid containing might effect to physiochemical properties of liquid product. For future work, analyzing the effect of residue this contaminant on diesel properties should be investigated. In addition, in the case of PFAD as starting material, conversion of triglyceride and free fatty acid should be calculated individually. The silylation technique is necessary for the calculation.

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APPENDIX

APPENDIX A

APPENDIX A

SIMULATED DISTILLATION

SimDist is a gas chromatography (GC) technique often employed in the petrochemical industry for quickly determining the boiling range distribution of petrochemical products. This technique separates individual hydrocarbon components in the order of their boiling points, and is used to simulate the time-consuming laboratory-scale physical distillation procedure known as true boiling point (TBP) distillation. In contrast to classic physical distillation, SimDis exhibits a range of advantages that include comparatively very rapid, reproducible, and easily automated, requires only a small microlitre sample volume, and can better define initial and final boiling points. SimDist are of great importance in fields of research and in the development of novel fuels (Bachler et al., 2010). Knowledge of the boiling range distribution of finished products has been an essential part of quality determination. The separation is accomplished with a nonpolar (hydrocarbon-like) chromatography column using a gas chromatograph equipped with an oven and injector that can be temperature programmed. A flame ionization detector (FID) is used for detection and measurement of the hydrocarbon analytes. The result of SimDist analysis provides a quantitative percent mass yield as a function of boiling point of the hydrocarbon components of the sample. The chromatographic elution times of the hydrocarbons are calibrated to the atmospheric equivalent boiling point (AEBP) of the paraffins reference material. In this study, used calibration mixture 1%wt/wt -An accurately weighed mixture of approximately equal mass quantities of *n*-hydrocarbons dissolved in carbon disulfide (CS_2). The mixture shall cover the boiling range from *n*-C5 to *n*-C44, but does not need to include every carbon number. The composition in this calibration mixture was shown in Table A1 The SimDist method ASTM (American Society for Testing and Materials) D2887 covers the boiling range 55–538 °C (100–1000 °F) which covers the *n*-alkanes (*n*-paraffins) of chain length about C5–C44. SimDist and laboratory-scale physical distillation procedures are routinely used for determining boiling (Villalanti et al., 2000).

Table A.1 Components of n-C_5 to n-C_{44} alkanes in calibration mixture. (Restek, 2011: online)

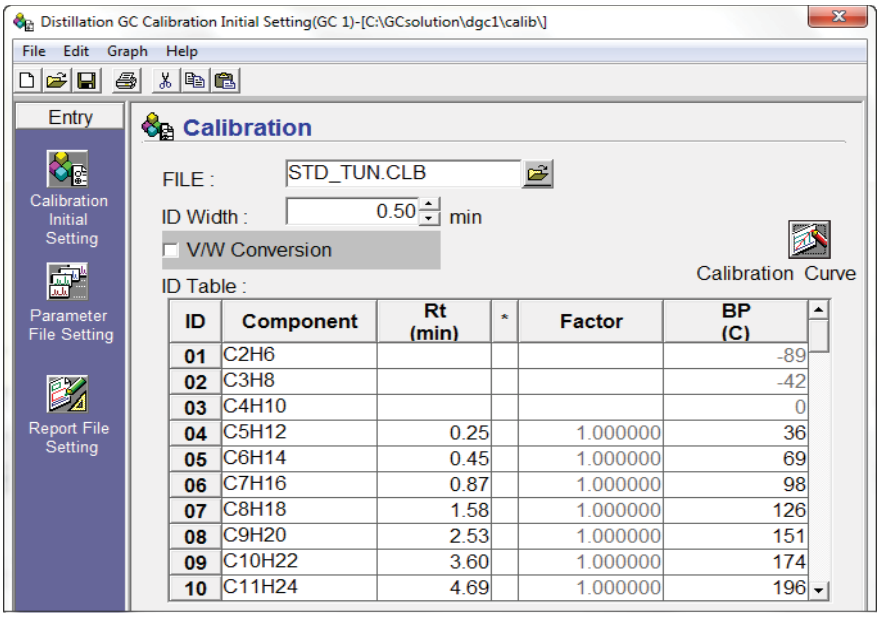
Elution order	Compound	CAS#	Percent Purity	Concentration (wt.%)
1	n-Pentane (C5)	109-66-0	99%	0.9995 wt./wt.%
2	n-Hexane (C6)	110-54-3	99%	0.9995 wt./wt.%
3	n-Heptane (C7)	142-82-5	99%	0.9995 wt./wt.%
4	n-Octane (C8)	111-65-9	99%	0.9995 wt./wt.%
5	n-Nonane (C9)	111-84-2	99%	0.9995 wt./wt.%
6	n-Decane (C10)	124-18-5	99%	0.9995 wt./wt.%
7	n-Undecane (C11)	1120-21-4	99%	0.9995 wt./wt.%
8	n-Dodecane (C12)	112-40-3	99%	0.9995 wt./wt.%
9	n-Tetradecane (C14)	629-59-4	99%	0.9995 wt./wt.%
10	n-Pentadecane (C15)	629-62-9	99%	0.9995 wt./wt.%
11	n-Hexadecane (C16)	544-76-3	99%	0.9995 wt./wt.%
12	n-Heptadecane (C17)	629-78-7	99%	0.9995 wt./wt.%
13	n-Octadecane (C18)	593-45-3	99%	0.9995 wt./wt.%
14	n-Eicosane (C20)	112-95-8	99%	0.9995 wt./wt.%
15	n-Tetracosane (C24)	646-31-1	99%	0.9995 wt./wt.%
16	n-Octacosane (C28)	630-02-4	99%	0.9995 wt./wt.%
17	n-Dotriacontane (C32)	544-85-4	98%	0.9991 wt./wt.%
18	n-Hexatriacontane (C36)	630-06-8	99%	0.9995 wt./wt.%
19	n-Tetracontane (C40)	4181-95-7	97%	0.9986 wt./wt.%
20	n-Tetratetracontane (C44)	7098-22-8	99%	0.9995 wt./wt.%
Solvent	Carbon Disulfide	75-15-0	99%	

Table A.2 GC- FID condition for calibration curve.

Condition	Value
Air (kPa)	60
H_2 (kPa)	50
Carrier and make up (kPa)	40
Split (ml/min)	30
Pert (ml/min)	40

Table A.3 Retention time for each hydrocarbon component in calibration mixture.

Components	Retention time (Average)
n-pentane (C5)	0.25
n-hexane (C6)	0.45
n-Heptand (C7)	0.87
n-Octane (C8)	1.58
n-Nonane (C9)	2.53
n-Decane (C10)	3.6
n-Undecane (C11)	4.69
n-Dodecane (C12)	5.74
n-Tetradecane (C14)	7.71
n-Pentadecane (C15)	8.61
n-Hexadecane (C16)	9.45
n-Heptadecane (C17)	10.26
n-Octadecane (C18)	11.02
n-Eicosane (C20)	12.43
n-Tetracosane (C24)	14.88
n-Octacosane (C28)	16.96
n-Dotriacontane (C32)	18.76
n-Hexatriacontane (C36)	20.32
n-Tetracontane (C40)	21.98



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☐ V/W Conversion

ID Table :

ID	Component	Rt (min)	*	Factor	BP (C)
01	C2H6				-89
02	C3H8				-42
03	C4H10				0
04	C5H12	0.25		1.000000	36
05	C6H14	0.45		1.000000	69
06	C7H16	0.87		1.000000	98
07	C8H18	1.58		1.000000	126
08	C9H20	2.53		1.000000	151
09	C10H22	3.60		1.000000	174
10	C11H24	4.69		1.000000	196

Figure A.1 Data base of simulated distillation.

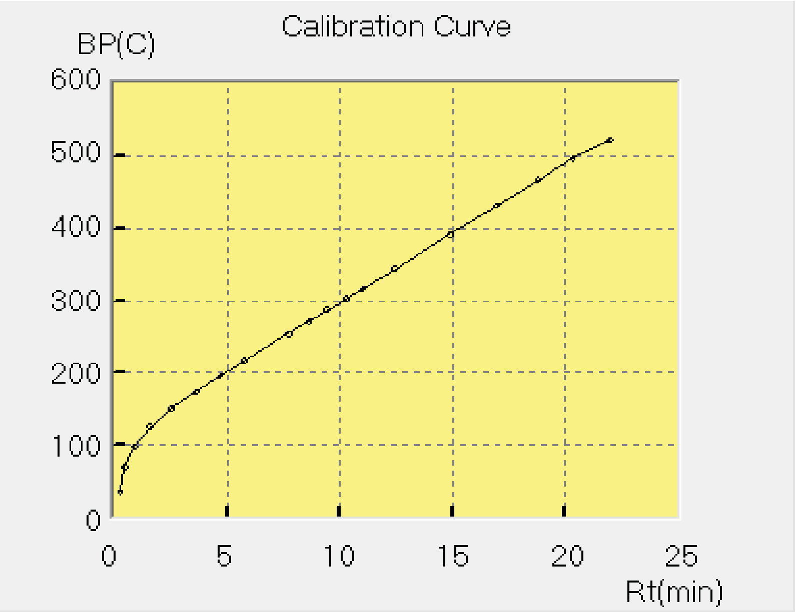


Figure A.2 Calibration curve for simulated distillation.

Calculation for amount of mole

For example:

Volume of injected *n*-pentane (C5) is 0.1 µL

$$[\mathbf{0.1\ \mu l}]\left[\frac{\mathbf{1\ l}}{\mathbf{10^{6}\mu l}}\right]\left[\frac{\mathbf{1000\ cm^{3}}}{\mathbf{1\quad l}}\right]\left[\frac{\mathbf{1.1593\ g_{sol}}}{\mathbf{1\ \ cm^{3}}}\right]\left[\frac{\mathbf{1\ g_{C5}}}{\mathbf{100\ g_{sol}}}\right]\left[\frac{\mathbf{1\ mole_{C5}}}{\mathbf{72.15\ g_{C5}}}\right]$$

$$= \mathbf{1.6068 \times 10^{-8}\ mole_{C5}}$$

Table A.4 Density and molecular weight for each component in calibration mixture.

Component	Density (g/cm^3)	Molecular weight (g/mol)
n-pentane (C5)	0.626	72.15
n-hexane (C6)	0.659	86.18
n-Heptand (C7)	0.684	100.20
n-Octane (C8)	0.703	114.23
n-Nonane (C9)	0.718	128.26
n-Decane (C10)	0.730	142.28
n-Undecane (C11)	0.740	156.31
n-Dodecane (C12)	0.749	170.33
n-Tetradecane (C14)	0.763	198.39
n-Pentadecane (C15)	0.769	212.42
n-Hexadecane (C16)	0.773	226.44
n-Heptadecane (C17)	0.777	240.47
n-Octadecane (C18)	0.777	254.50
n-Eicosane (C20)	0.789	282.55
n-Tetracosane (C24)	0.797	338.66
n-Octacosane (C28)	0.8067	394.76
n-Dotriacontane (C32)	0.812	450.87
n-Hexatriacontane (C36)	0.7795	506.97
n-Tetracontane (C40)	0.7785	563.08
n-tatratatracontane (C44)	0.8200	
Carbondisulfide (sovent)	1.261	76.139

Calculation for density of calibration mixture

$(0.626X0.001)+(0.659X0.001)+(0.684X0.001)+(0.703X0.001)+(0.718X0.001)+$

$(0.730X0.001)+\ldots+(1.261X0.8) = 1.1593\ g_{sol}/cm^3$

APPENDIX B

APPENDIX B

CALIBRATION CURVE FOR GASEOUS AND LIQUID PRODUCT

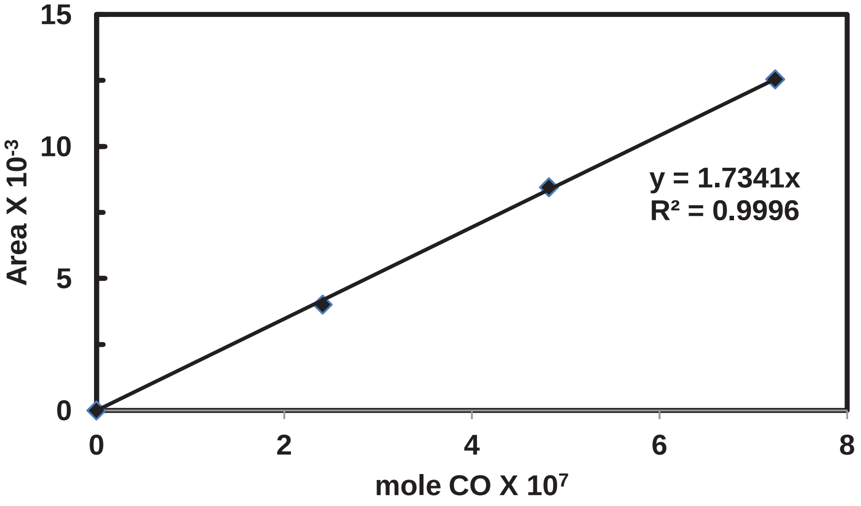


Figure B.1 Calibration curve of carbonmonoxide (CO).

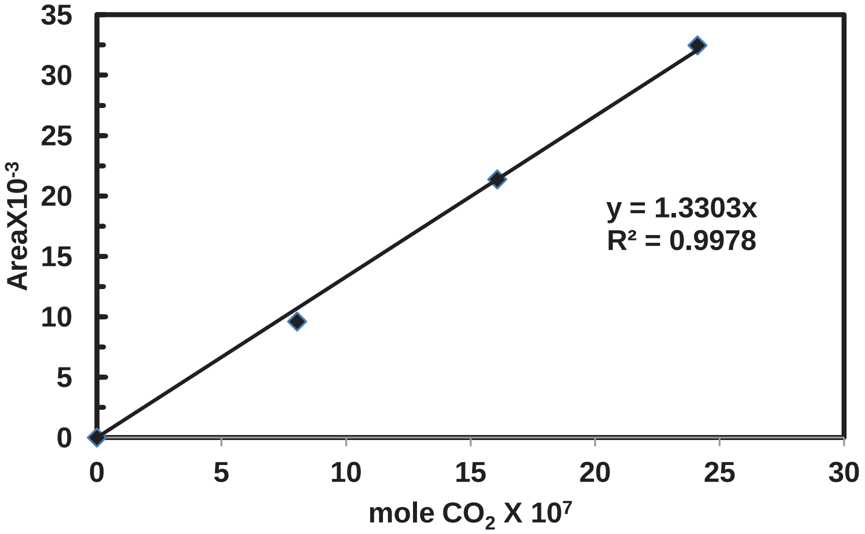


Figure B.2 Calibration curve of carbondioxide (CO_2).

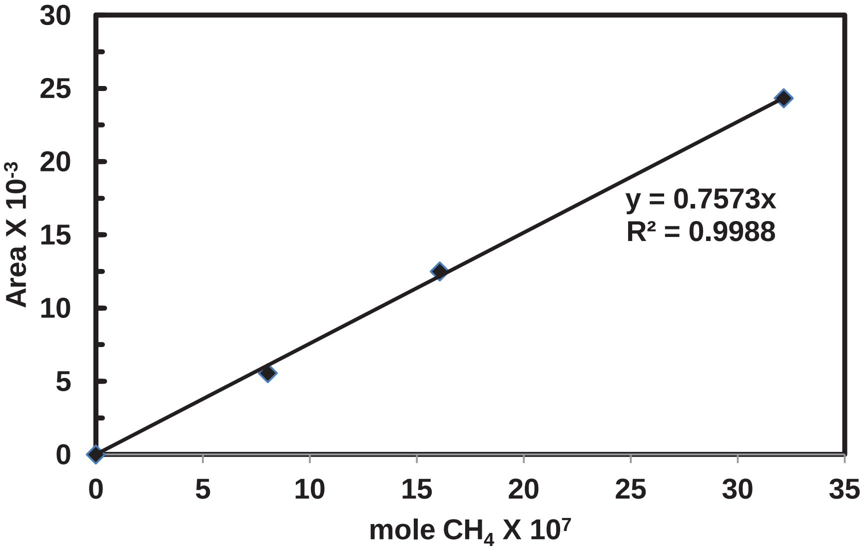


Figure B.3 Calibration curve of methane (CH_4).

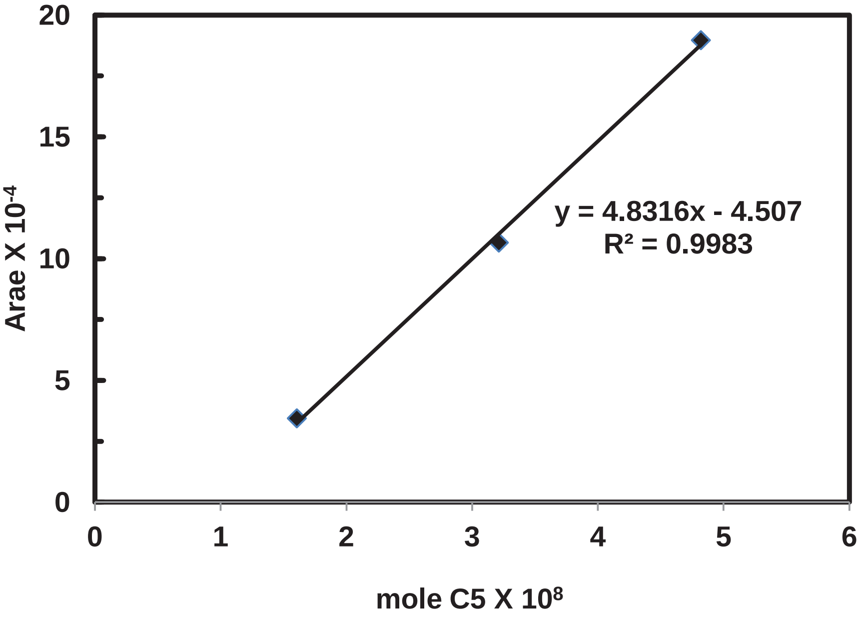


Figure B.4 Calibration curve of *n*-pentane (C5).

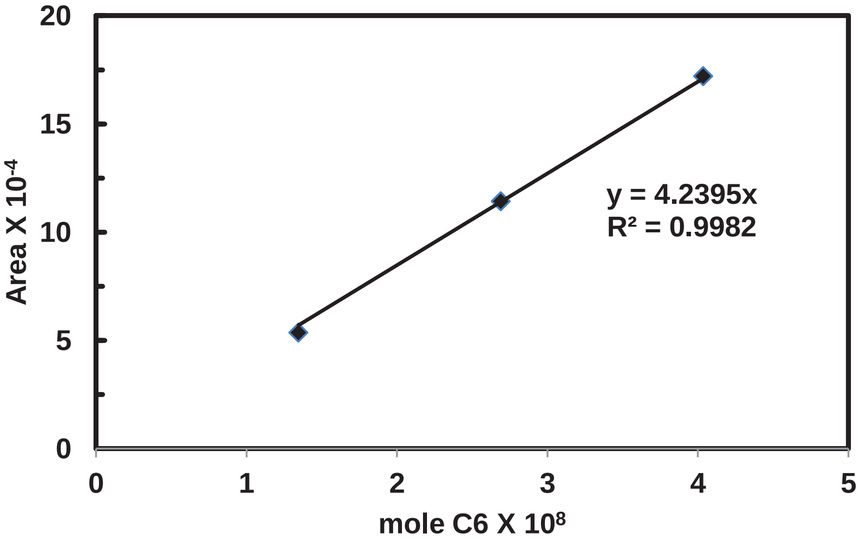


Figure B.5 Calibration curve of *n*-hexane (C6).

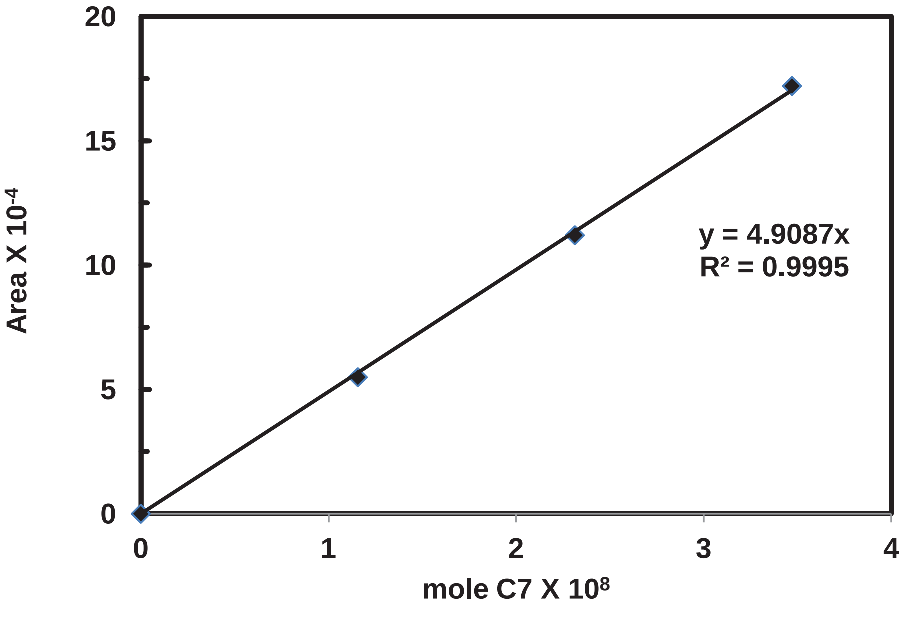


Figure B.6 Calibration curve of *n*-heptane (C7).

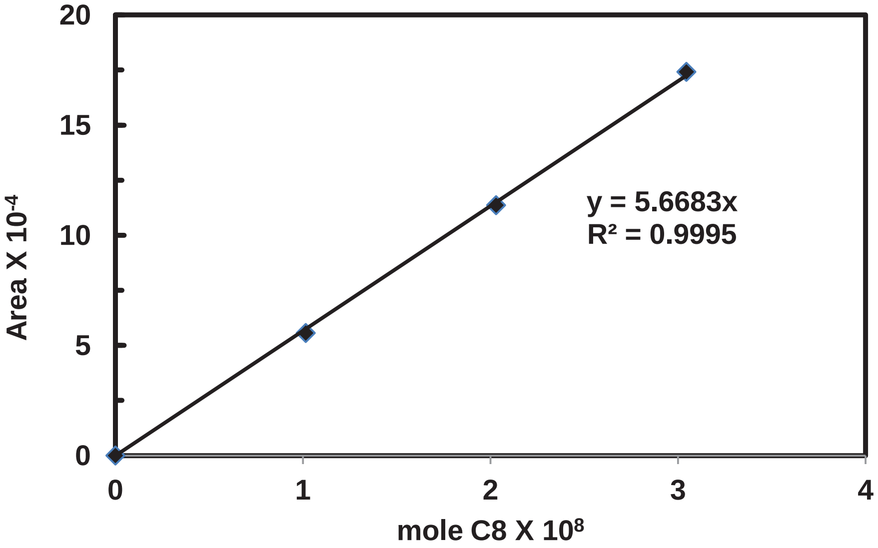


Figure B.7 Calibration curve of *n*-octane (C8).

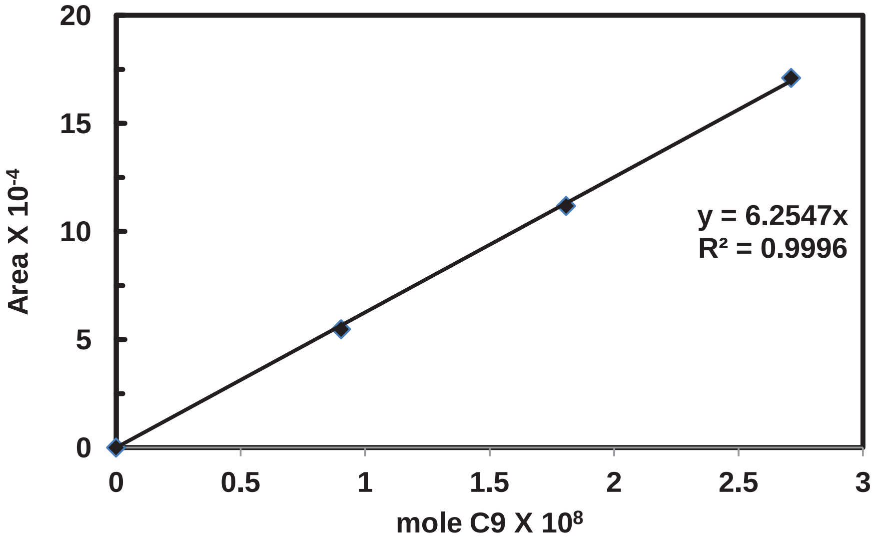


Figure B.8 Calibration curve of *n*-nonane (C9).

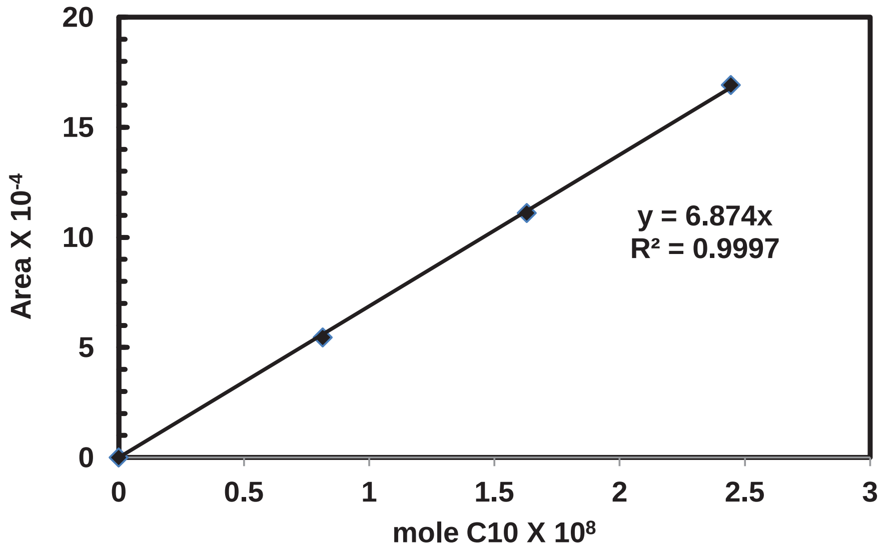


Figure B.9 Calibration curve of *n*-decane (C10).

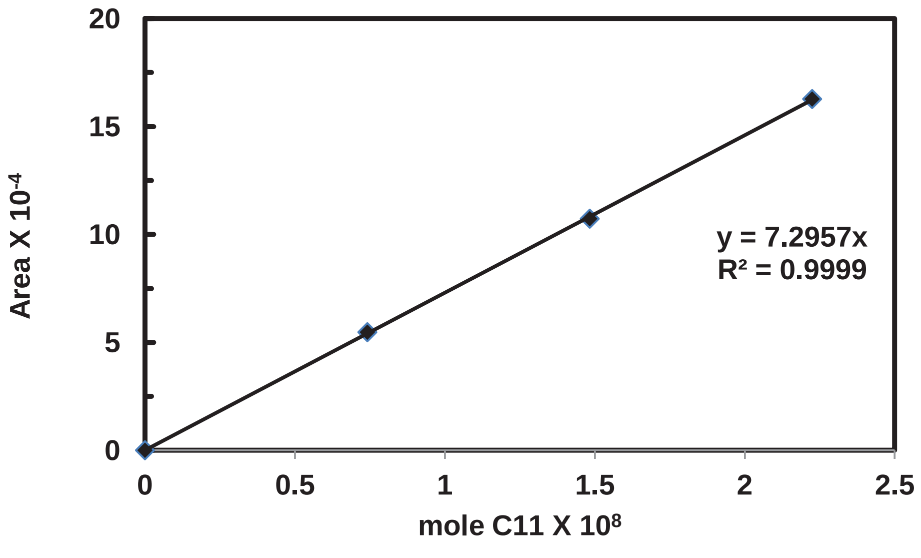


Figure B.10 Calibration curve of *n*-undecane (C11).

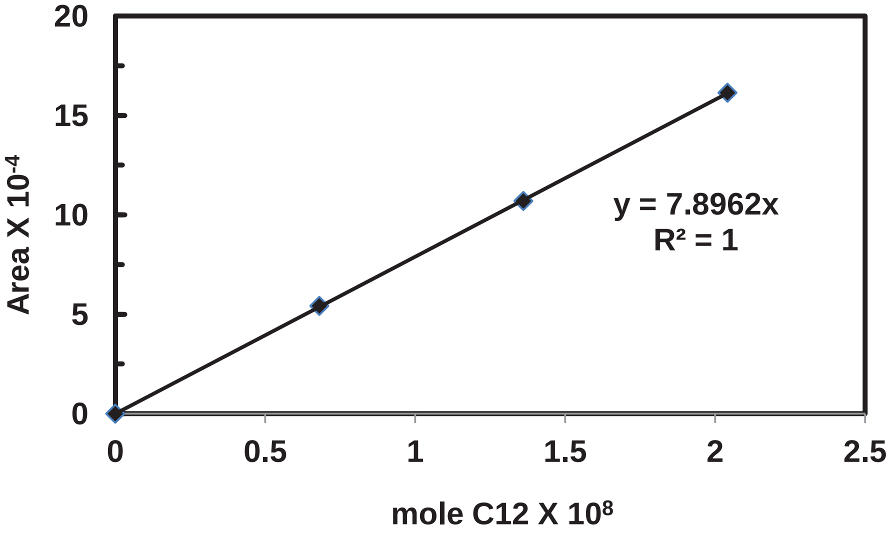


Figure B.11 Calibration curve of *n*-dodecane (C12).

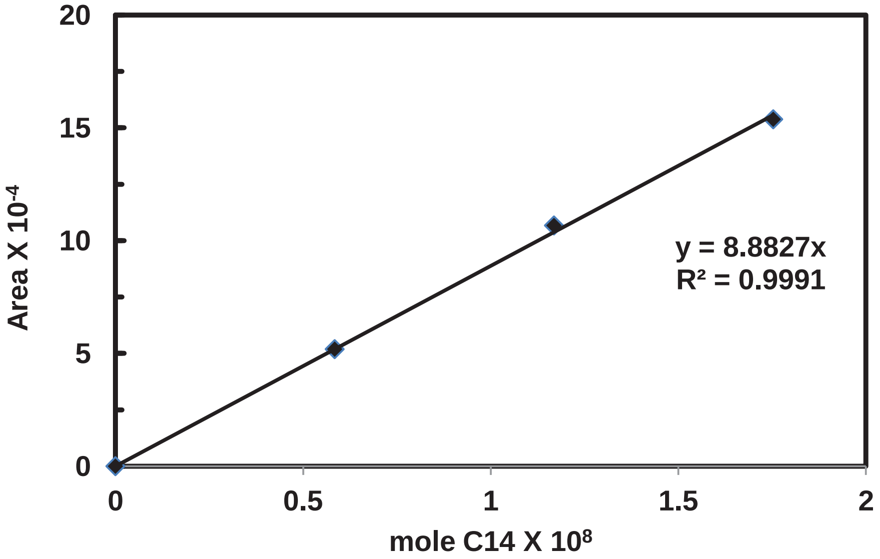


Figure B.12 Calibration curve of *n*-tetradecane (C14).

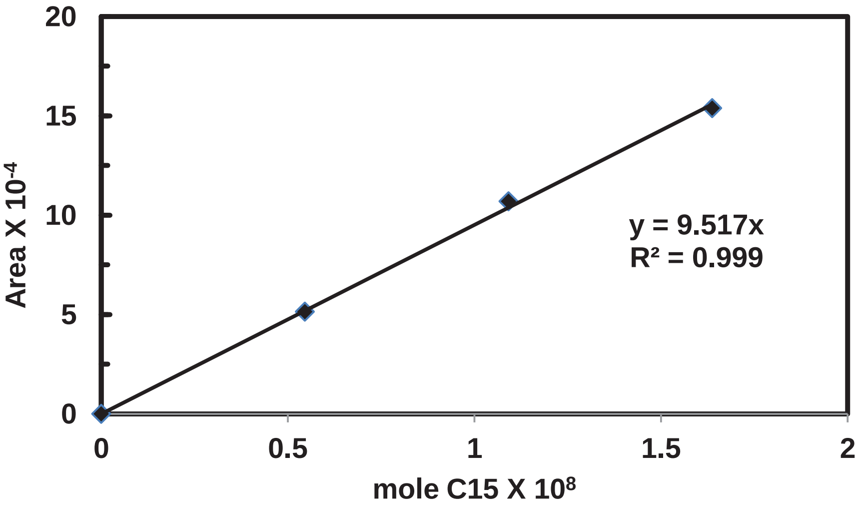


Figure B.13 Calibration curve of *n*-pentadecane (C15).

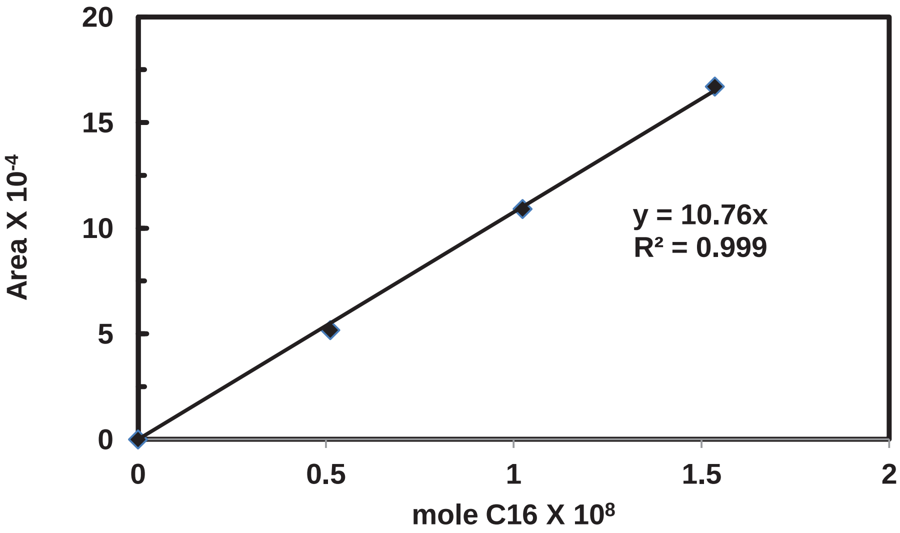


Figure B.14 Calibration curve of *n*-hexadecane (C16).

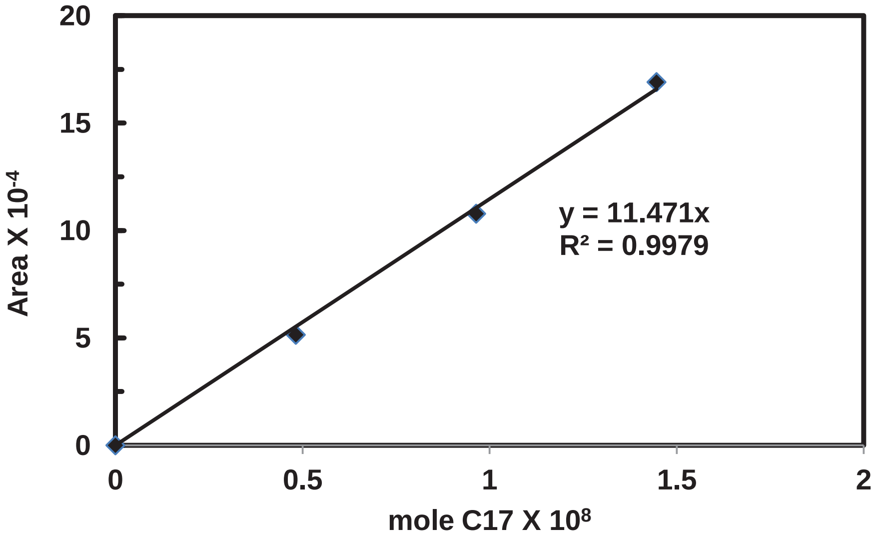


Figure B.15 Calibration curve of *n*-heptadecane (C17).

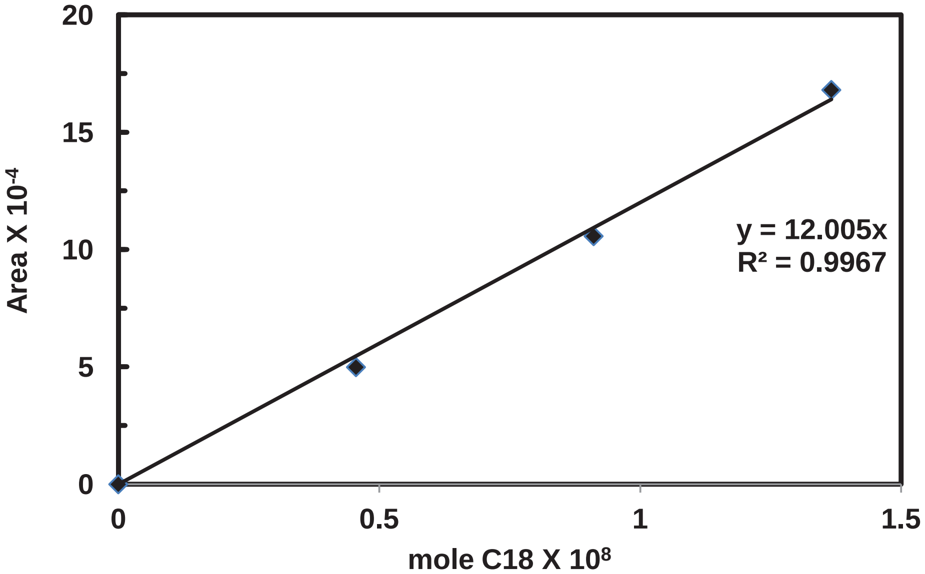


Figure B.16 Calibration curve of *n*-octadecane (C18).

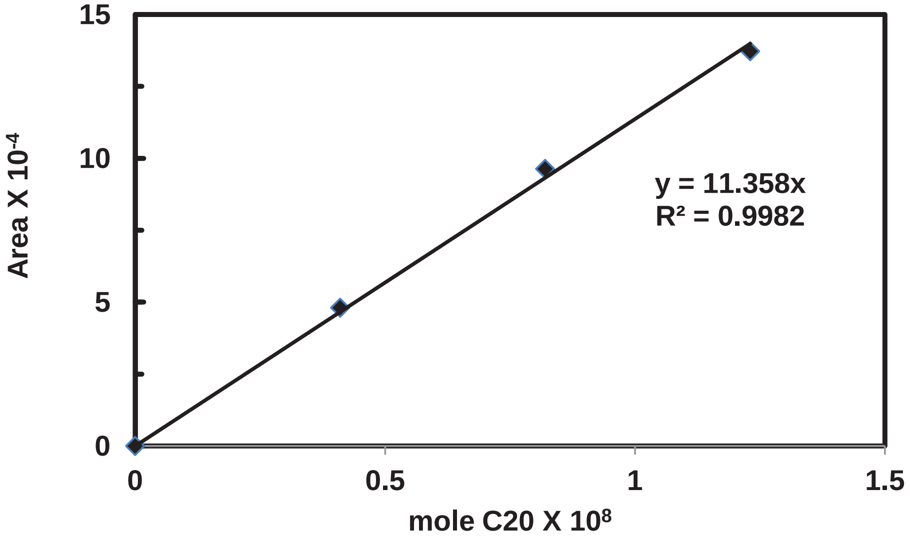


Figure B.17 Calibration curve of n-eicosane (C20).

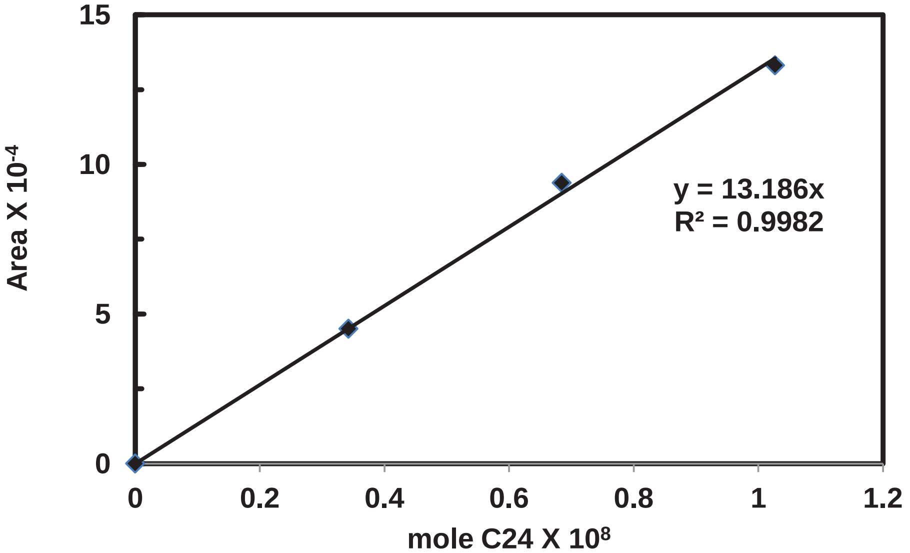


Figure B.18 Calibration curve of *n*-tetracosane (C24).

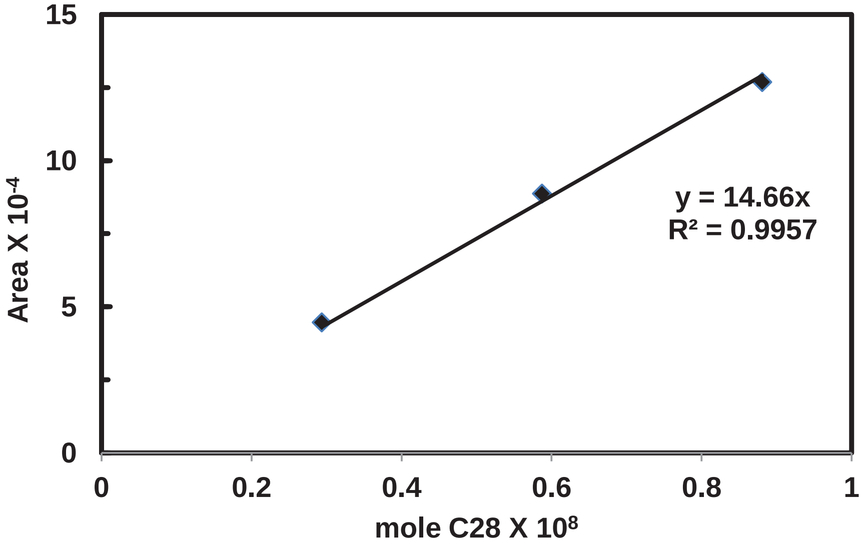


Figure B.19 Calibration curve of *n*-octacosane (C28).

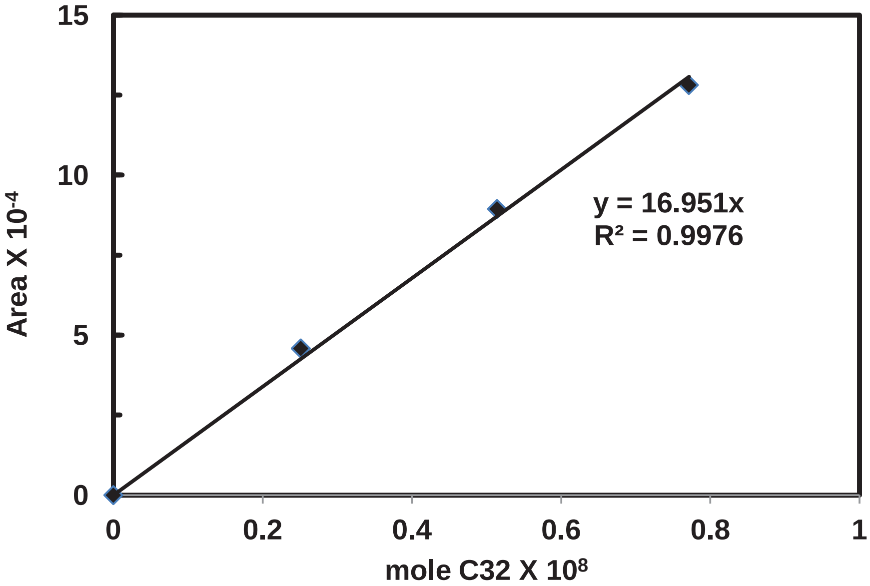


Figure B.20 Calibration curve of n-dotriacontane (C32).

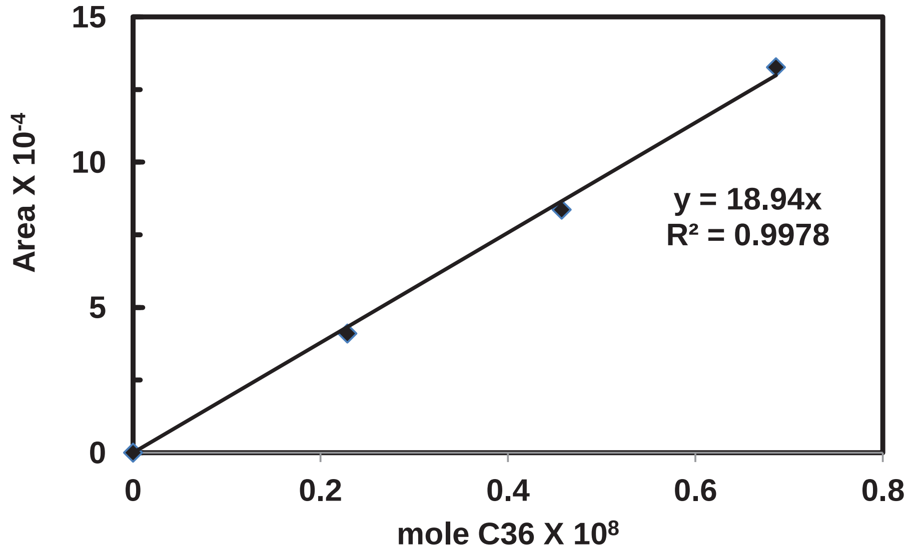


Figure B.21 Calibration curve of *n*-hexatriacontane (C36).

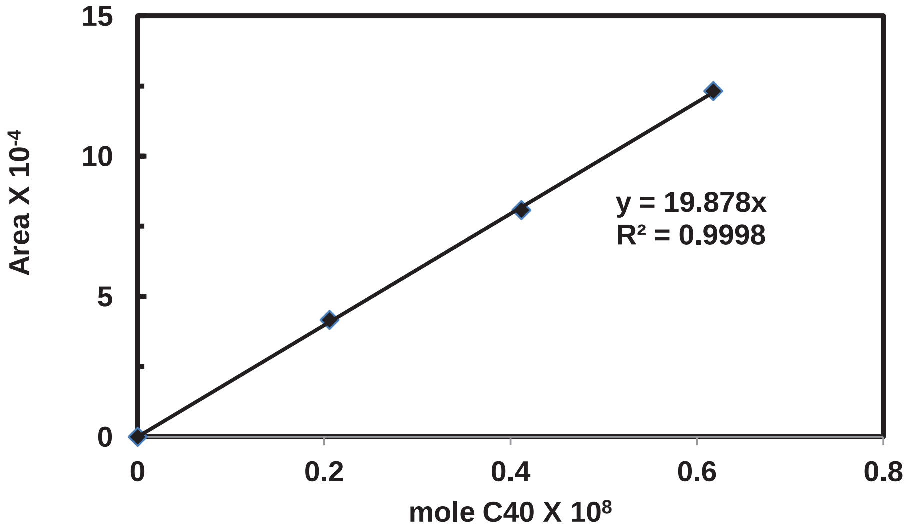


Figure B.22 Calibration curve of *n*-tetracontane (C40).

APPENDIX C

APPENDIX C

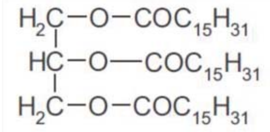
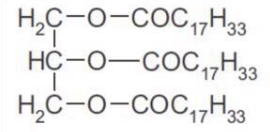
CALCULATION H_2 TO FEED RATIO

C.1 In case of DPO.

Table C.1 Fatty acid composition of DPO.

Fatty acids	Structure	Formular	Wt.% in DPO	Normalization (Wt.%)	Mass Fraction
Palmitic	16:0	$C_{16}H_{32}O_2$	45.4	54	0.54
Oleic	18:1	$C_{18}H_{34}O_2$	39	46	0.46

Table C.2 Properties of tristearin and trioleate.

Property	Tripalmitin	Trioleate
Chemical structure	 $\begin{array}{l} H_2C-O-COC_{15}H_{31} \\ HC-O-COC_{15}H_{31} \\ H_2C-O-COC_{15}H_{31} \end{array}$	 $\begin{array}{l} H_2C-O-COC_{17}H_{33} \\ HC-O-COC_{17}H_{33} \\ H_2C-O-COC_{17}H_{33} \end{array}$
Molecular weight	807.32	885.43

Molecular weight of DPO = (0.54 X 807.32) + (0.46 X 885.43) = 841.25 g/mole$_{DPO}$

In each experiment, the volume of feedstock was fixed at 2 ml.

The density of DPO at room temperature (30 °C) is 0.9 g/cm^3.

The weight of feedstock = 0.9 X 2 = 1.8 g

Mole of DPO in feedstock = 1.8 /841.25 = 0.002140 mole

Mole of hydrogen required for convert triglyceride into linear hydrocarbon are illustrated in Figure C.1. Theoretically, in case of triglyceride containing three molecules of unsaturated fatty acid, 3 mole of hydrogen for hydrogenated to hydrogenated triglyceride are required. Consequently, hydrogenated triglycerides breakdown to produce one 1 mole of propane and 3 mole of saturated fatty acid, this step require 3 mole of hydrogen. Finally, the saturated fatty acid are converted to linear alkane via 3 different pathways i.e. decarboxylation, decarbonylation, and hydrogenation. The deoxygenation pathway requires the highest hydrogen consumption of 3 mole per one mole of free fatty acid. Therefore, minimum mole of hydrogen to mole of unsaturated triglyceride in feed ratio is 15:1. However, our DPO contained approximately 50:50 of unsaturated and saturated fatty acid so the first step of hydrogenated triglyceride required about 1.5 mole of hydrogen per mole of triglyceride in DPO. Therefore, minimum mole of hydrogen to mole of triglyceride in DPO and CPO feed ratio is approximately 13.5:1.

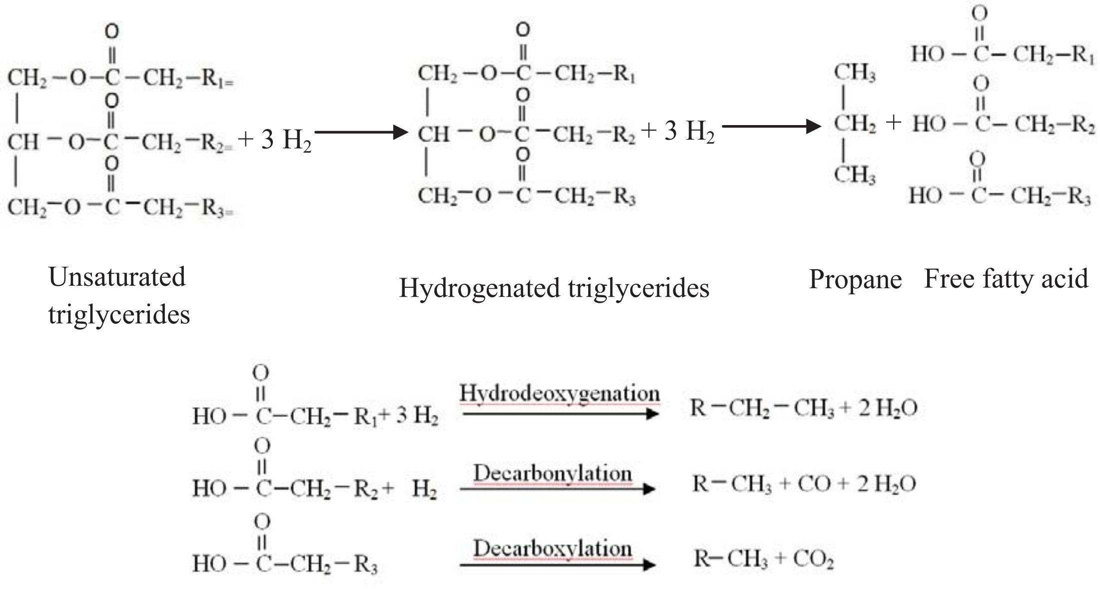


Fig C.1 The hydrogen consumption in hydroprocessing process of DPO.

The space volume in reactor is 5.5 cm^3.

The mole of hydrogen in reaction was calculated, as follow:

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

For example, if the initial cold hydrogen pressure is 20 bar and room temperature is 303 K, we can calculate mole of initial hydrogen:

$$\mathrm{n} = \frac{20\ \mathrm{bar} \times (5.5 \times 10^{-6}\mathrm{m}^3)}{(8.314 \times 10^{-5}\frac{\mathrm{m}^3\mathrm{bar}}{\mathrm{K.mole}}) \times 303\mathrm{K}} = 0.0044\ \mathrm{mole}$$

Table C.3 Calculation of H_2 to feed ratio.

P (bar)	**n (mole H_2)**	**H_2:feed (mol/mol)**
20	0.0044	2.0406
30	0.0065	3.0610
40	0.0087	4.0813
50	0.0109	5.1016
60	0.0131	6.1219

As shown in Table , even the pressure is 60 bar, the H_2 to triglyceride is 6.12 which is less than 13.5 as minimum required until hydrodeoxygenation as illustrated above.

C.2 In case of PFAD.

Table C.4 Fatty acid distribution of PFAD.

Fatty acids	**Formular**	**Molecular weight (g/mole)**	**Wt.% in DPO**	**Normalization (Wt.%)**	**Mass Fraction**
Palmitic	$C_{16}H_{32}O_2$	256.42	49	57.8	0.58
Oleic	$C_{18}H_{34}O_2$	282.46	35.8	42.2	0.42

Molecular weight of PFAD = (0.58 X 256.42) + (0.42 X 282.46) = 267.36 g/mol_{PFAD}

In each experiment, the volume of feedstock was fixed at 2 ml.

The density of PFAD at room temperature (30 °C) is 0.9 g/cm^3.

The weight of feedstock = 0.9 X 2 = 1.8 ml

Mole of PFAD in feedstock = 1.8 g/267.36 = 0.00673 mole

Free fatty acid is the main composition of PFAD feedstock so the hydrogen consumption per mole of free fatty acid to produce linear alkane is less than that of triglyceride (CPO and DPO). Theoretically, unsaturated free fatty acid requires one mole of hydrogen for hydrogenated to saturated free fatty acid. Consequently, 3 mole of hydrogen is required for deoxygenation. Therefore, minimum mole of hydrogen to mole of unsaturated triglyceride in feed ratio is 4:1. However, our PFAD contained approximately 50:50 of unsaturated and saturated fatty acid so the first step of hydrogenated triglyceride required about 0.5 mole of hydrogen per mole of fatty acid in PFAD. Therefore, minimum mole of hydrogen to mole of triglyceride in DPO and CPO feed ratio is approximately 3.5:1.

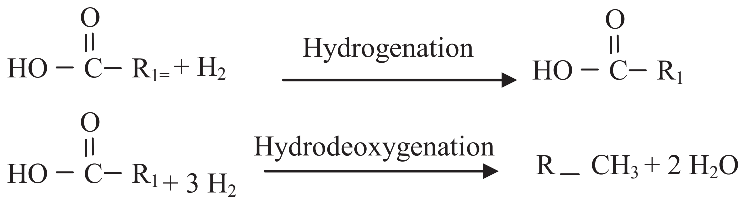


Fig C.2 The hydrogen consumption in hydroprocessing process of PFAD.

Table C.5 Calculation of hydrogen excess in case of PFAD.

P (bar)	n (mole H_2)	H_2:feed (mol/mol)
20	0.0044	0.6534
30	0.0065	0.9800
40	0.0087	1.3067
50	0.0109	1.6334
60	0.0131	1.9600

As shown in Table C.5, even the pressure is 60 bar, the H_2 to triglyceride is 1.96 which is less than 3.5 as minimum required until hydrodeoxygenation as illustrated above.

APPENDIX D

International Proceeding

Songphon Phimsen, Worapon Kiatkittipong, Suwimol Wongsakulphasatch, Navadol Laosiripojana, Suttichai Assabumrungrat, “Diesel-like hydrocarbons production from hydroprocessing of different palm-oil feedstocks”, The 6th Asia Pacific Chemical Reaction Engineering (APCRE) Symposium, Beijing, China, 18-21 Sep, 2011 (oral presentation)

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2008	received the bachelor degree of Biotechnology, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Phathom, Thailand.
2004	High school certificate from Wat nuaunoradit School, Bangkok.

Special Interest	Biofuels/Hydroprocessing/Renewable energy