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รายงานวิจัยฉบับสมบูรณ์

โครงการ Second generation of biodiesel production from potential energy sources in Thailand
(การผลิตไบโอดีเซลในยุคที่ 2 จากแหล่งพลังงานที่มีศักยภาพในประเทศไทย)

โดย ผู้ช่วยศาสตราจารย์ ดร. วรพล เกียรติกิตติพงษ์ และคณะ

มิถุนายน 2555

สัญญาเลขที่ MRG5380143

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คณะผู้วิจัย	สังกัด
1 ผู้ช่วยศาสตราจารย์ ดร. วรพล เกียรติกิตติพงษ์	มหาวิทยาลัยศิลปากร
2 ศาสตราจารย์ ดร.สุทธิชัย อัสสะบำรุงรัตน์	จุฬาลงกรณ์มหาวิทยาลัย

สนับสนุนโดยสำนักงานคณะกรรมการการอุดมศึกษา สำนักงานกองทุนสนับสนุนการวิจัย
และมหาวิทยาลัยศิลปากร

กิตติกรรมประกาศ

ขอขอบคุณสำนักงานกองทุนสนับสนุนการวิจัย (สกว.) สำนักงานคณะกรรมการการอุดมศึกษา (สกอ.) และสถาบันวิจัยและพัฒนา มหาวิทยาลัยศิลปากร ที่ให้การสนับสนุนงานวิจัยนี้ ขอขอบคุณ ศาสตราจารย์ ดร.สุทธิชัย อัสสะบำรุงรัตน์ ที่ปรึกษาโครงการที่กรุณาให้คำแนะนำที่มีค่าเป็นอย่างยิ่งเสมอมา ขอขอบคุณ ศาสตราจารย์ ดร.ปิยะสาร ประเสริฐธรรม หัวหน้าศูนย์เชี่ยวชาญเฉพาะทางด้านคาตาไลซิสและวิศวกรรมปฏิกิริยาที่ใช้ตัวเร่งปฏิกิริยา ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย ที่ให้การสนับสนุนในการใช้เครื่องมือในการวิเคราะห์ต่างๆ และบริษัทน้ำมันพืชปทุม ที่ได้อนุเคราะห์สารตัวอย่างน้ำมันเพื่อใช้ในงานวิจัย ตลอดจนต้นสังกัดของผู้วิจัย ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์และเทคโนโลยีอุตสาหกรรม มหาวิทยาลัยศิลปากร ที่เอื้อเฟื้อสถานที่และให้เวลาผู้วิจัยในการทำวิจัยเป็นอย่างดี

Abstract

Project Code: MRG5380143

Project Title: Second generation of biodiesel production from potential energy sources in Thailand

Investigator: 1) Asst.Prof.Dr.Worapon Kiatkittipong, Silpakorn University (PI)

2) Prof.Dr.Suttichai Assabumrungrat, Chulalongkorn University (Mentor)

E-mail Address: kworapon@su.ac.th

Project Period: 24 months

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.

In addition, according to our previous works the wide range of ethers production by FCC self-etherification with ethanol catalyzed by beta zeolite could effectively enhance the RON, sustain the demand of oxygenated ethers and the amount of remaining olefinic compounds in the products are in compliance with the limiting values regulated by Euro IV standard (Kiatkittipong et al., 2008; 2009); however, converting the rest olefinic compounds would be beneficial both in terms of olefins reduction and enhanced ethanol substitution in gasoline. In this study, the influences of Si/Al ratio and the addition of copper (Cu) or magnesium (Mg) in the beta zeolite on the reaction performance were investigated. It was found that the beta zeolite with Si/Al ratio of 27 (beta27) can enhance higher ethanol conversion than those of 42 and 77. In addition, the modification of $beta_{27}$ by Cu (Cu- $beta_{27}$) can further improve the ethanol conversion from 38.2% ($beta_{27}$) to 55.1%, and the olefin content reduction from 46.2% ($beta_{27}$) to 62.4%.

Keywords: Bio-hydrogenated diesel, Hydroprocessing, Deoxygenation, Diesel-like hydrocarbon, Relevant palm oil.

บทคัดย่อ

รหัสโครงการ: MRG5380143

ชื่อโครงการ: การผลิตไบโอดีเซลในยุคที่ 2 จากแหล่งพลังงานที่มีศักยภาพในประเทศไทย

นักวิจัย: 1) ผู้ช่วยศาสตราจารย์ ดร. วรพล เกียรติกิตติพงษ์ มหาวิทยาลัยศิลปากร (หัวหน้าโครงการ)

2) ศาสตราจารย์ ดร.สุทธิชัย อัสสะบำรุงรัตน์ จุฬาลงกรณ์มหาวิทยาลัย (นักวิจัยที่ปรึกษา)

E-mail Address: kworapon@su.ac.th

ระยะเวลาโครงการ: 24 เดือน

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

นอกจากนี้จากงานวิจัยที่ผ่านมาของคณะผู้วิจัย (Kiatkittipong et al., 2008; 2009) ซึ่งได้ทำปฏิกิริยาอีเทอริฟิเคชันในตัวกับเอทานอลด้วยตัวเร่งปฏิกิริยาเบตาซีโอไลต์ สามารถเพิ่มค่าออกเทนด้วยสารประกอบออกซิจิเนตอีเทอร์ และปริมาณโอเลฟินส์ที่เหลืออยู่ผ่านเกณฑ์มาตรฐาน ยูโร 4 งานวิจัยนี้มุ่งเน้นพัฒนาตัวเร่งปฏิกิริยาให้สามารถลดปริมาณโอเลฟินส์ลงอีกพร้อมกับทดแทนน้ำมันด้วยเอทานอลได้มากขึ้น โดยได้ศึกษาผลของอัตราส่วนซิลิกอนต่ออลูมิเนียมและการเติมโลหะ พบว่าตัวเร่งปฏิกิริยาเบตาซีโอไลต์ที่มีค่าอัตราส่วนซิลิกอนต่ออลูมิเนียมเท่ากับ 27 (Beta_{27}) ให้ค่าการเปลี่ยนของเอทานอลที่สูงกว่าเบตาซีโอไลต์ที่มีค่าอัตราส่วนซิลิกอนต่ออลูมิเนียมเท่ากับ 42 และ 77 อีกทั้งเมื่อทำการปรับปรุง

Beta$_{27}$ ด้วยการเติมทองแดงพบว่าสามารถเพิ่มค่าเปลี่ยน (conversion) ของเอทานอลจาก 38.2% เป็น 55.1% และลดลงปริมาณโอเลฟินส์ลงได้ถึง 62.4% จาก 46.2%

คำหลัก: ไบโอไฮโดรจิเนตดีเซล ไฮโดรโปรเซสซิง ดีออกซิจิเนชัน ไฮโครคาร์บอนในช่วงดีเซล ส่วนที่เกี่ยวข้องกับการกลั่นน้ำมันปล์ม

Executive Summary

Introduction

Biodiesel is one of the promising alternative renewable fuels as it can reduce carbon dioxide (CO_2) in the carbon cycle and moreover particulate matter (PM), un-burnt hydrocarbon and carbon monoxide (CO) emissions. Typically, the triglycerides are converted via transesterification with methanol to produce fatty acid methyl esters (FAMEs) which are commonly referred to as 1st generation biodiesel. However, the use of FAMEs still have some drawbacks such as limited compatibility with conventional diesel engines, increase NO_x emissions, low oxidative stability, gum formation and possible engine problems due to their higher acid number than that of conventional diesel fuels. To overcome the disadvantageous of FAME, a hydroprocessing has been investigated as an alternative pathway of biodiesel production. In this process, triglycerides and fatty acids are converted to straight chain alkane ranging from n-C_{15}–n-C_{18} known as middle distillates, which are suitable to use as diesel fuels. It was reported that the obtained straight chain alkanes have a high cetane number above 98. Triglyceride of vegetable oil could be hydrogenated and broken down into various intermediates (i.e. monoglycerides, diglycerides and carboxylic acids) and the glycerol backbone of triglycerides is converted into propane. These intermediates are then converted into alkanes by three different pathways, decarboxylation, decarbonylation and hydrodeoxygenation, as shown in Eqs. (1)-(3), respectively.

$$R\text{-}CH_2\text{-}COOH \rightarrow R\text{-}CH_3 + CO_2 \quad (1)$$

$$R\text{-}CH_2\text{-}COOH + H_2 \rightarrow R\text{-}CH_3 + CO + H_2O \quad (2)$$

$$R\text{-}CH_2\text{-}COOH + 3H_2 \rightarrow R\text{-}CH_2\text{-}CH_3 + 2H_2O \quad (3)$$

Palm oil, the most potential feedstock for biodiesel production in Thailand, is mainly utilized in this study. The suitable operating conditions for the hydroprocessing of different palm oil feedstocks i.e. crude palm oil (CPO), degummed crude palm oil (DPO) and palm fatty acid distillate (PFAD) over commercial 5 wt% Pd/C was investigated.

Experimental

Reactor and operational details

For routine experiments, hydroprocessing of CPO, DPO and PFAD were performed in small shaking batch reactors. Prior to the experiments, the catalyst was reduced by hydrogen flow with the rate of 10 ml/min at 200 ºC for 2 h. After the reduction, the catalyst was cooled to 30 ºC under nitrogen flow. 0.1 g of reduced catalyst and 2 ml of the reactant were then loaded into the reactor, sealed, and purged by hydrogen gas for several times. The reactors were placed in the furnace at desired temperature with shaking at the maximum speed. After reaction was preceded at desired reaction time, the reactors were removed from the furnace and immersed in a water bath at ambient temperature to stop the reaction.

Analysis of hydroprocessed product

The gaseous products from each experiment was analyzed by gas chromatography (GC 14-B, Shimadzu Corporation) equipped with thermal conductivity detector (TCD). The liquid products were 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). Liquid samples of 0.1 µl were injected into the column inlet, where the injector and detector temperature were maintained at 350 ºC. The GC oven used temperature programmed by heating from 40 to 350 ºC with ramp rate of 15ºC/min and hold at 350 °C for 20 min. Simulated distillation (according to ASTM 2887) was used in this work to examine product distribution. The effectiveness of hydrotreating reactions was measured in term of diesel yields. The conversion and diesel selectivity of the products is determined by simulated distillation data as follows:

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

where Feed_{360+} is weight percent of the feed which have boiling point higher than 360 °C. Product_{360+} is weight percent of the product which have boiling point higher than 360 ºC.

As diesel is the desired product, diesel selectivity is determined based on the boiling point range, defined as

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

where $\text{Feed}_{180\text{-}360}$ and $\text{Product}_{180\text{-}360}$ are weight percent of the feed and products, respectively, which have a boiling point between 180 and 360 ºC (diesel molecules).

The liquid hydrocarbon product distribution are classified into four fractions i.e. the 65–150 ºC fraction is most likely alkanes ranging from C_5 to C_8, the 150–250 ºC fraction is most likely alkanes ranging from C_9 to C_{14}, the 250–380 ºC fraction is most likely alkanes ranging from C_{15} to C_{18} (known as middle distillate) and the 380-520 ºC fraction is defined as those compounds have high boiling point above the boiling point of n-heptadecane including unconverted triglyceride starting material, as well as oxygenated products [16].

Results and discussion

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.

Firstly, the optimum reaction time was determined at the point that diesel-range yield is obtained as shown in Figure 1A. It can be seen that CPO conversion increases with increasing residence time (from 0.25 to 5 h), the conversion increases rapidly at the beginning of the reaction up to 3 h after that it gradually increases. However, maximum diesel yield can be observed at reaction time of 3 h. This is due to the decrease of diesel selectivity after 3 h. As depicted in Figure 1B, lighter hydrocarbon, i.e. 65-150 °C and 150-250 °C, obviously increases with increasing residence time.

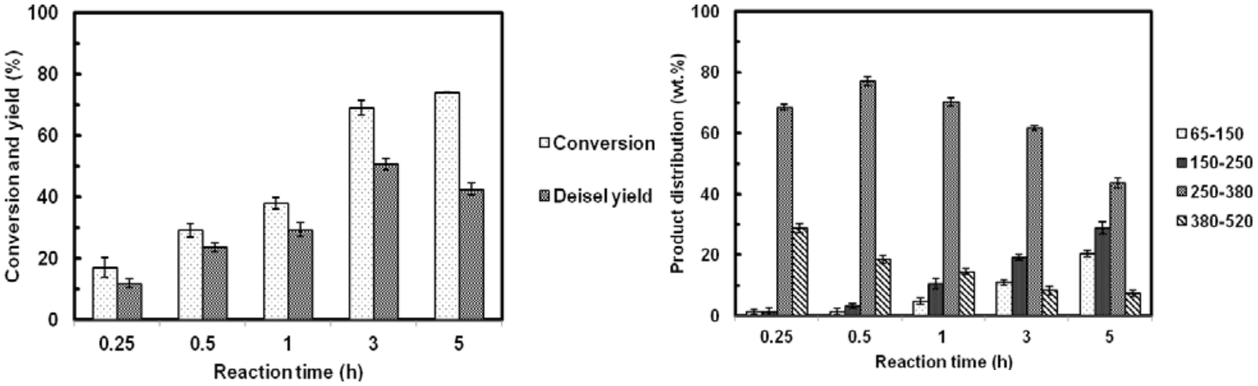

Fig. 1. The effect of reaction time on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of CPO feedstock (operating temperature = 400 °C, operating pressure = 40 bar).

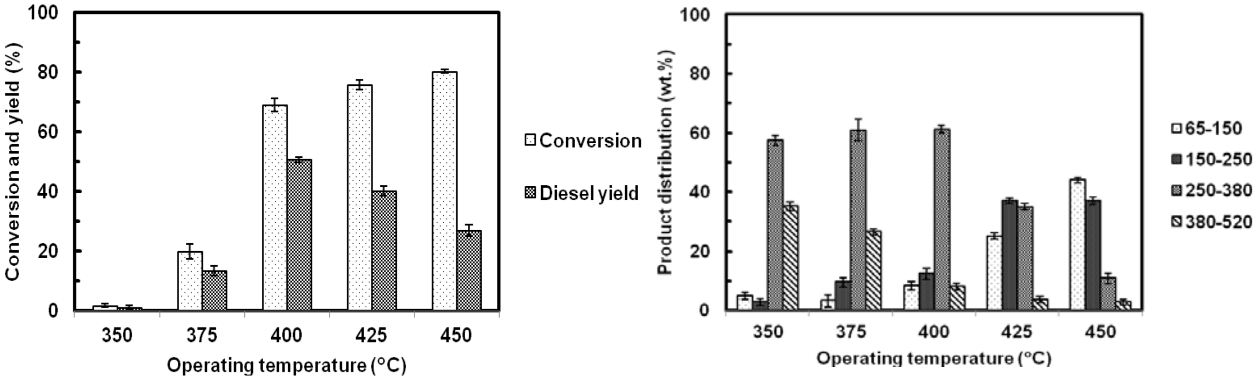

Fig. 2. The effect of operating temperature on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of CPO feedstock (reaction time = 3 h, operating pressure = 40 bar).

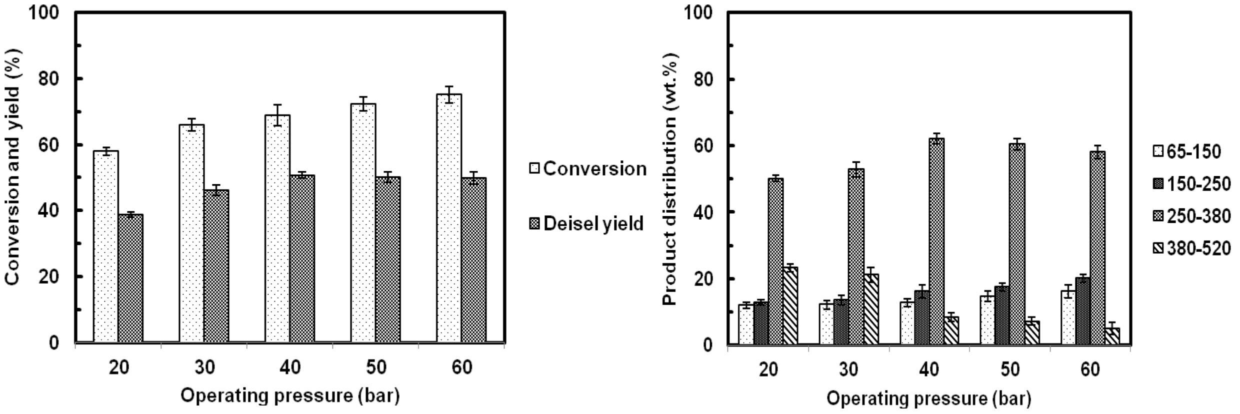

Fig. 3. The effect of operating pressure on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of CPO feedstock (reaction time = 3 h, operating temperature = 400 °C).

Products obtained from hydroprocessing of CPO at 3 h was found to be composed mainly of middle distillate in the range of 250-380 °C (Figure 1B), which are mostly C_{15}-C_{18} hydrocarbon. Particularly, the major liquid products are *n*-pentadecane (C_{15}) and *n*-heptadecane (C_{17}) (result not shown here), which contain one carbon atom shorter ($C_{(n-1)}$) than the total length of corresponding fatty acid i.e. palmitic and oleic acid. Theoretically, the $C_{(n-1)}$ can be produced by two parallel pathways via decarboxylation/decarbonylation whereas the hydrocarbon contain carbon atom same number as the fatty acid ($C_{(n)}$) are insignificantly formed (less than 5wt.%).

The effect of operating temperature was then investigated in the range of 350-450°C. The results shown in Figure 2A revealed that no conversion was observed at temperature of 350°C and 375°C since these temperatures are not high enough to give reasonable conversion and diesel yield. However, when temperature was increased to 400°C, conversion of CPO and yield increased significantly to 70% and 51%, respectively; this could be due to an increase of the rate of decarboxylation/decarbonylation. At higher temperature, CPO conversion increases as a function of temperature but diesel yield starts to decrease. As demonstrated in Figure 2B, 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 remain low but slightly increase with increasing temperature due to the converting of heavier hydrocarbon. Beyond this temperature range, the middle distillate decreases suddenly as it may crack to lighter fraction.

The effect of pressure on conversion and diesel yield is shown in Figure 3. By increasing the pressure 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, the most suitable operating conditions are at temperature of 400°C, pressure of 40 bar and with the reaction time of 3 h.

The optimal operating condition of different feedstock can be summarized in Table 1. 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 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.

Table 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

Conclusion

Catalytic hydroprocessing of three relevant palm oil products i.e. CPO, DPO and PFAD, was investigated using commercial 5 wt% Pd/C. The effects of reaction time, temperature, and pressure were determined to examine optimal operating condition for each feedstock. From the study, the highest diesel range product yield of 81% can be obtained from PFAD with less severe operating condition (lower operating temperature and pressure, shorter residence time) required. It was also revealed that the hydroprocessed products contains one carbon less hydrocarbon (C(n-1)) than the corresponding acid i.e. n-pentadecane and n-heptadecane, which indicates that decarboxylation/decarbonylation are the major reaction pathways. The findings would be an initiative for illustrating the use of relevant refining palm oil for biodiesel production via hydroprocessing and would be useful to manage cultivated palm oil to produce edible oil and biodiesel. For further implementation, the study on techno-economic analysis is recommended.

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). 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

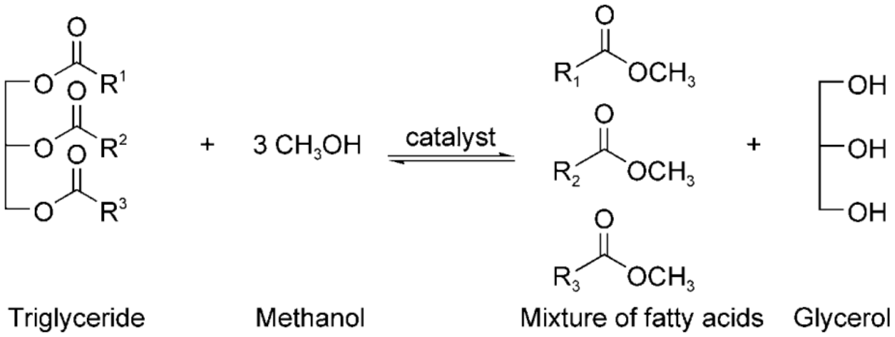

Figure 1.1 Transesterification reaction (Lestari et al., 2009).

(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 and physical refining process for palm oil production**.**

2.1 Hydroprocessing of vegetable oil for biodiesel production

The overall reaction pathway for conversion of triglycerides into alkanes is shown in Figure 2.1

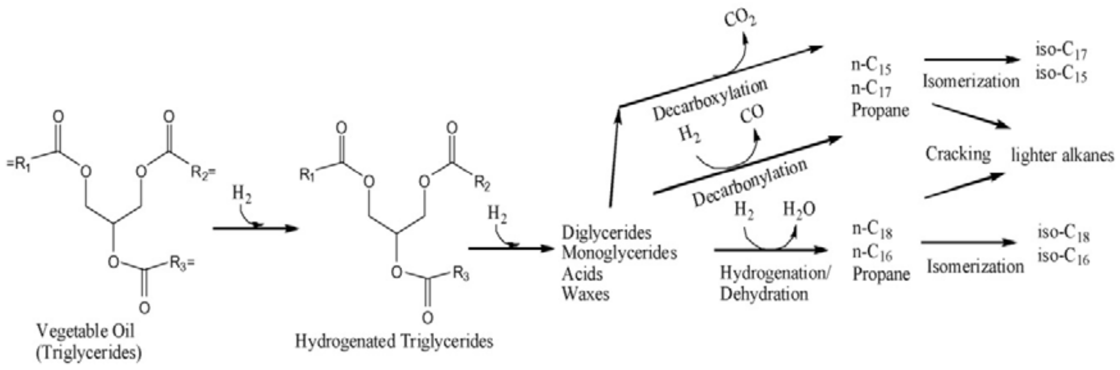

Figure 2.1 Reaction pathways for conversion of tri-glycerides to alkanes.

Triglyceride of vegetable oil could be hydrogenated and broken down into various intermediates (i.e. monoglycerides, diglycerides and carboxylic acids) and the glycerol backbone of triglycerides is converted into propane. These intermediates are then converted into alkanes by three different pathways, decarboxylation, decarbonylation and hydrodeoxygenation, as shown in Eqs. (1)-(3), respectively.

$$R\text{-}CH_2\text{-}COOH \rightarrow R\text{-}CH_3 + CO_2 \quad (1)$$

$$R\text{-}CH_2\text{-}COOH + H_2 \rightarrow R\text{-}CH_3 + CO + H_2O \quad (2)$$

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

As seen in Eqs.(1) and (2), the co-products from decarboxylation and decarbonylation are carbon dioxide (CO_2) and carbon monoxide (CO), respectively. Therefore, hydrocarbons resulting from decarboxylation and decarbonylation contain one carbon atom shorter than the total length of the fatty acid ($C_{(n-1)}$). The benefit of decarboxylation pathway is no hydrogen required to convert a carboxylic acid into a methyl group and CO_2 (as shown in Eq. (1)). For a decarbonylation pathway, carboxylic group is reacted with hydrogen to produce a methyl group, CO, and water (as shown in Eq. (2)). On the other hand, hydrodeoxygenation (HDO) pathway yields generally a hydrocarbon containing the same number of carbon atoms in the molecule as the corresponding fatty acid chain ($C_{(n)}$) and water as shown in Eq. (3). It is noted that two additional reactions, water gas shift (Eq. (4)) and methanation (Eqs. (5-6)) are also needed to be considered due to the formation of CO_2 and CO.

2.2 Physical refining process for palm oil production

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. Currently, palm oil in Thailand produced by extraction process and physical refining process, shown as Figure 2.2.

2.2.1 Degumming: The CPO is pumped through a plate heat exchanger and steam heater to increase the CPO temperature to 90 – 130 $^{\circ}$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)

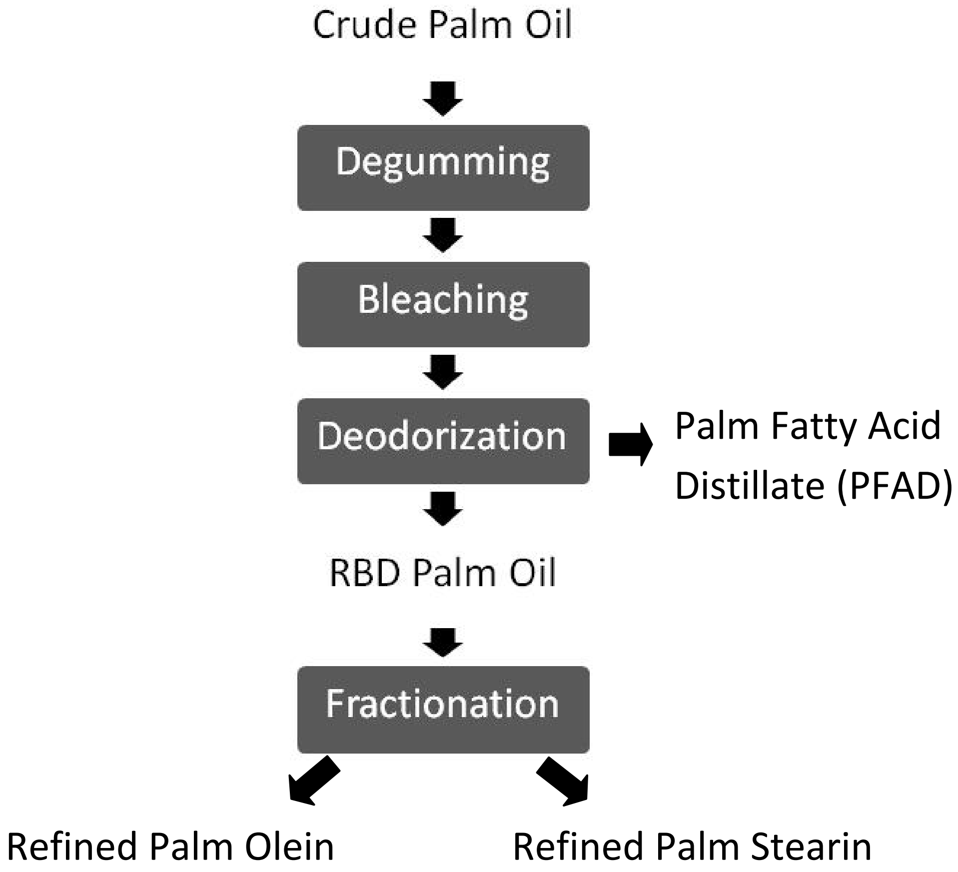

Figure 2.4 Physical refining process of crude palm oil

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)

CHAPTER 3

Literature Review

3.1 Hydroprocessing with conventional NiMo and CoMo sulfided catalysts

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).

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 deoxygenation of methyl laurate and canola oil is discussed 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 ^oC 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).

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 $\underline{+}$ 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 $Mo_2N/\gamma\text{-}Al_2O_3$ 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. The reactor has the inner diameter of 2.35 mm and a length of 9 mm. 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.

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 and analyzed by gas chromatography (GC 14-B, Shimadzu Corporation) by injecting 10 µl pass Porapak Q column with a thermal conductivity detector (TCD). 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 $\text{Feed}_{180–360}$ and $\text{Product}_{180–360}$ are the weight percent of the feed and product, respectively, which have a boiling point between 180 and 360 ^{o}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 °C fraction is most likely alkanes ranging from C5 to C8, the 150–250 °C fraction is most likely alkanes ranging from C9 to C14, the 250–380 °C fraction is most likely alkanes ranging from C15 to C18 (desired product know as middle distillate) and the 380-520 °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

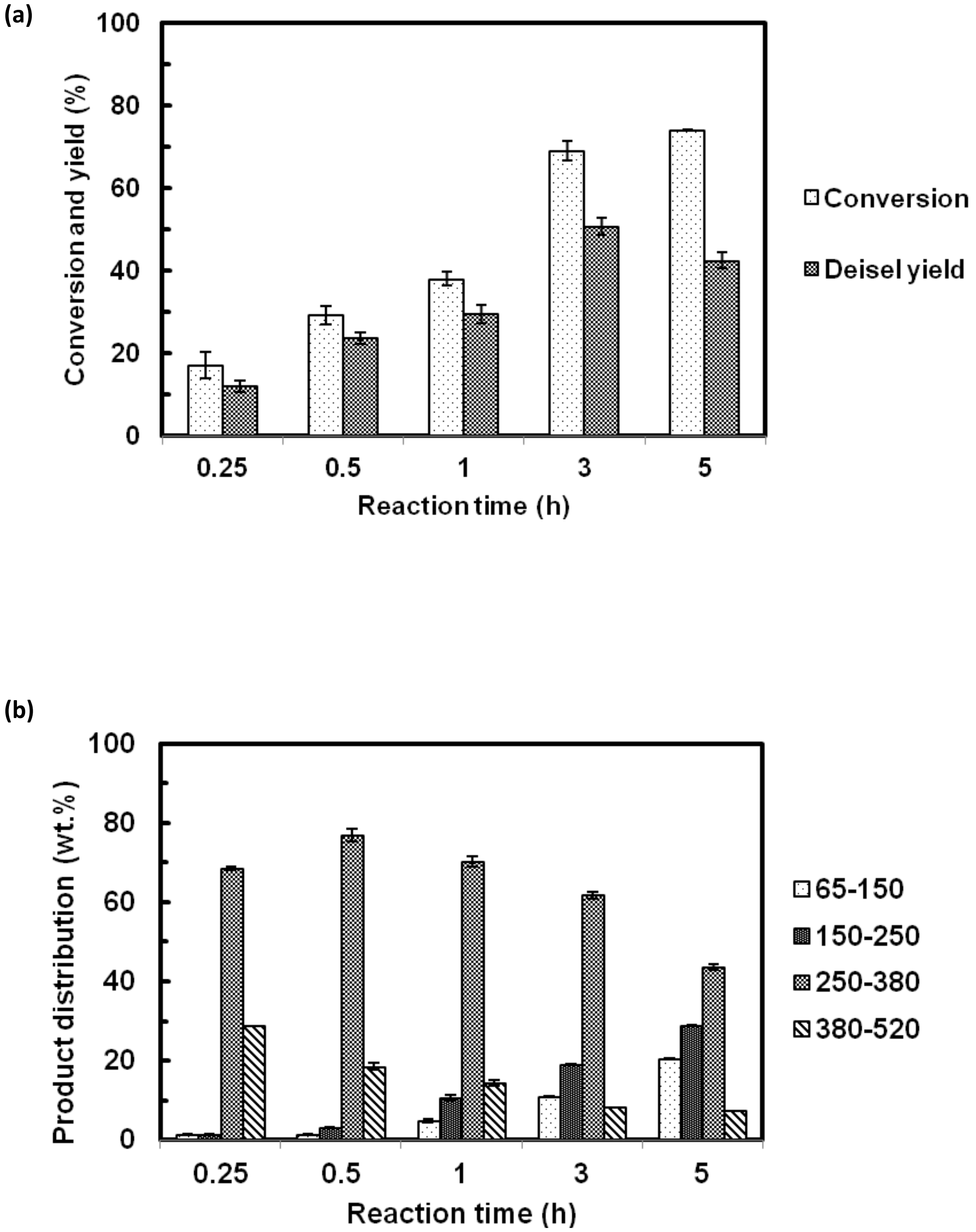

Figure 5.1 The effect of reaction time on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of CPO feedstock. (operating temperature = 400 °C, operating pressure = 40 bar).

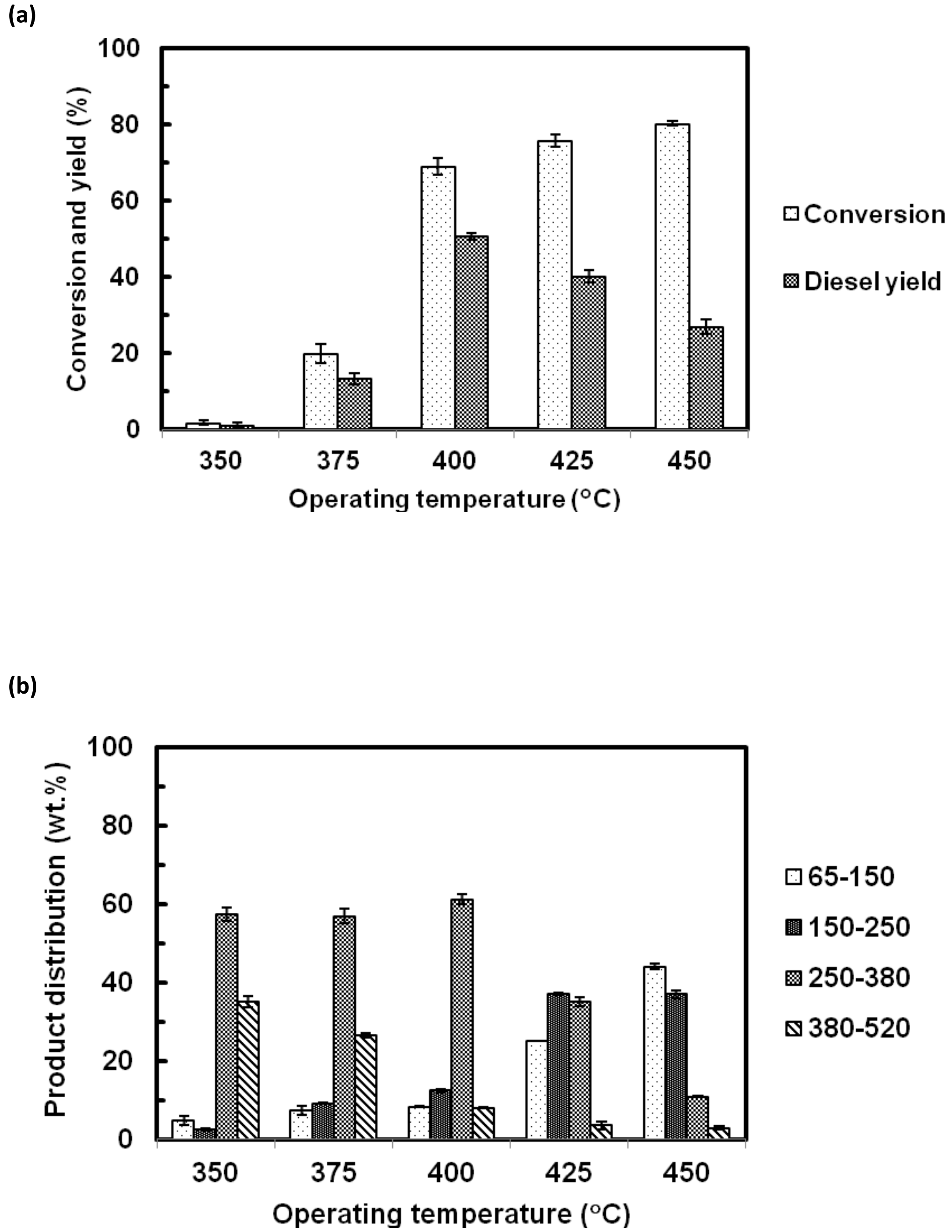

Figure 5.2 The effect of operating temperature on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of CPO feedstock. (reaction time = 3 h, operating pressure = 40 bar).

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)

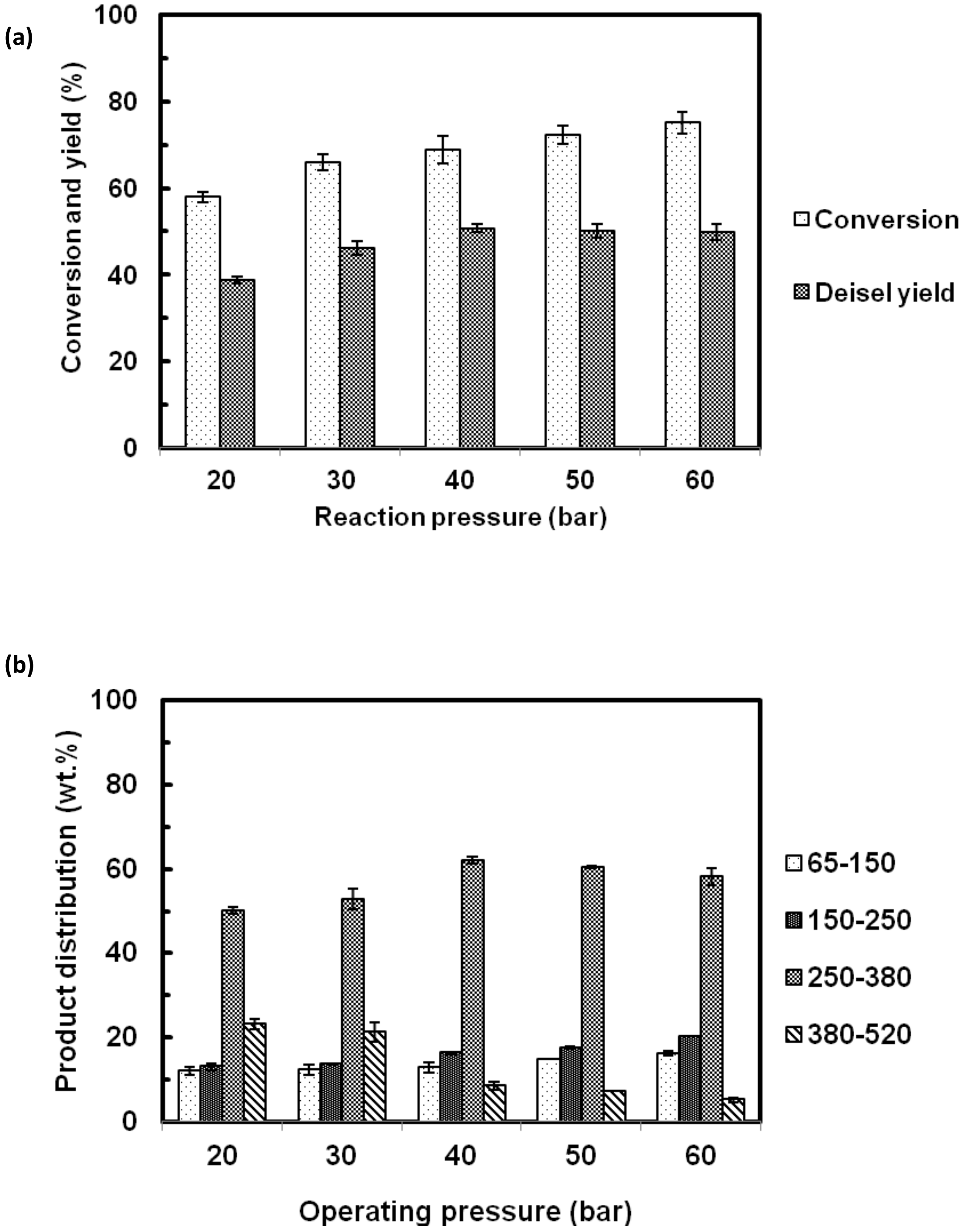

Figure 5.3 The effect of operating pressure on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of CPO feedstock. (reaction time = 3 h, operating temperature = 400 °C).

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.

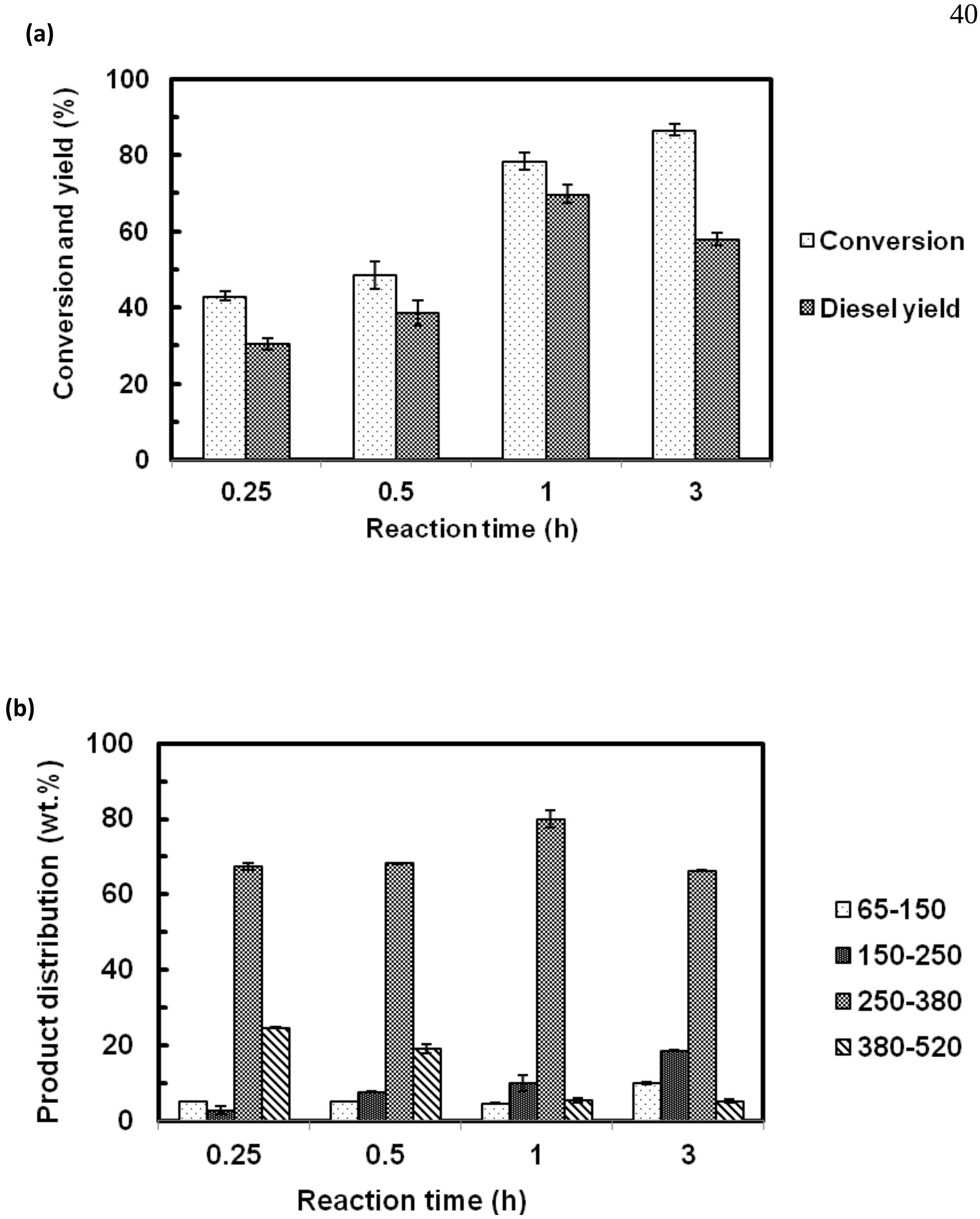

Figure 5.4 The effect of reaction time on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of DPO feedstock. (operating temperature = 400 °C, operating pressure = 40 bar).

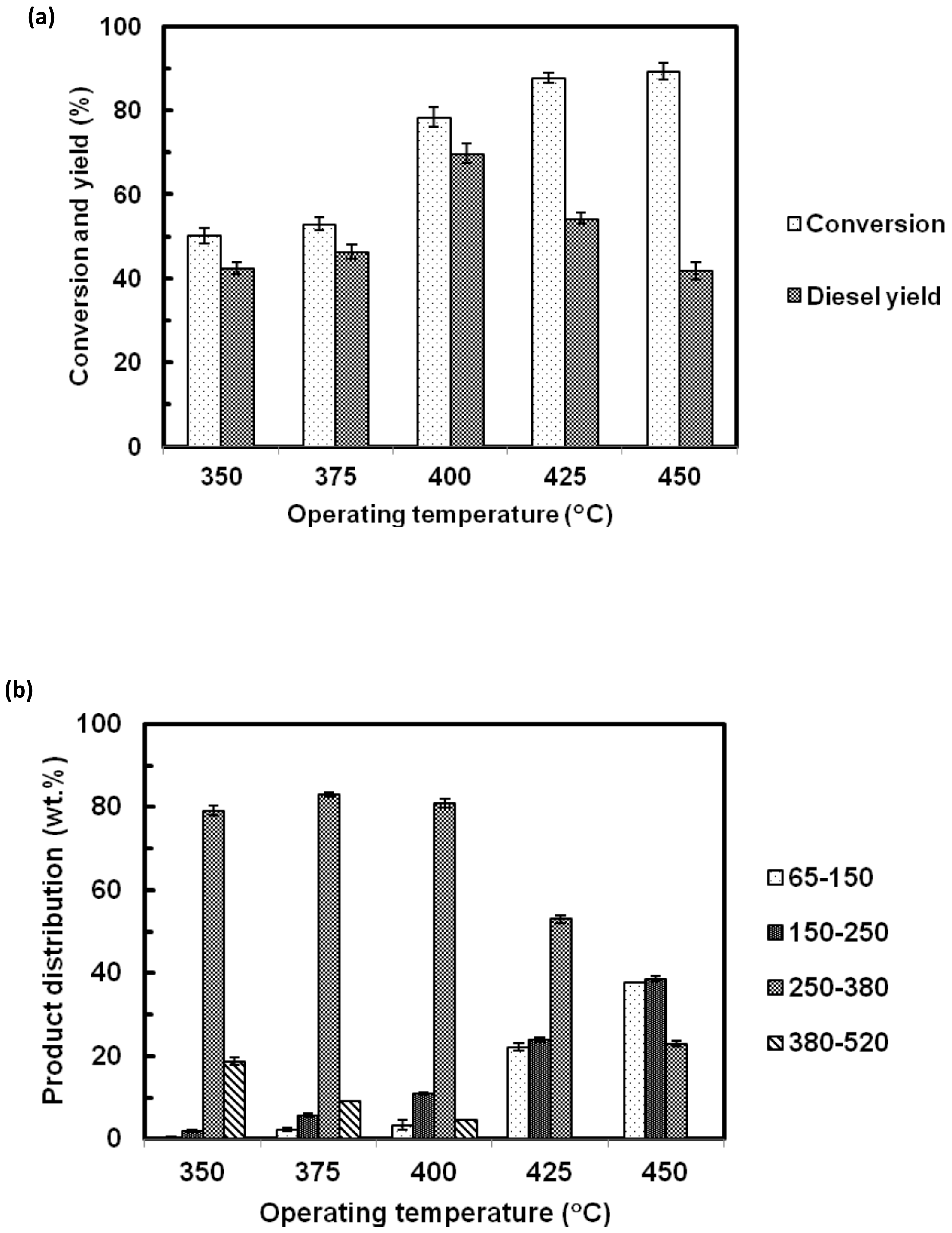

Figure 5.5 The effect of operating temperature on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of DPO feedstock. (reaction time = 1 h, operating pressure = 40 bar).

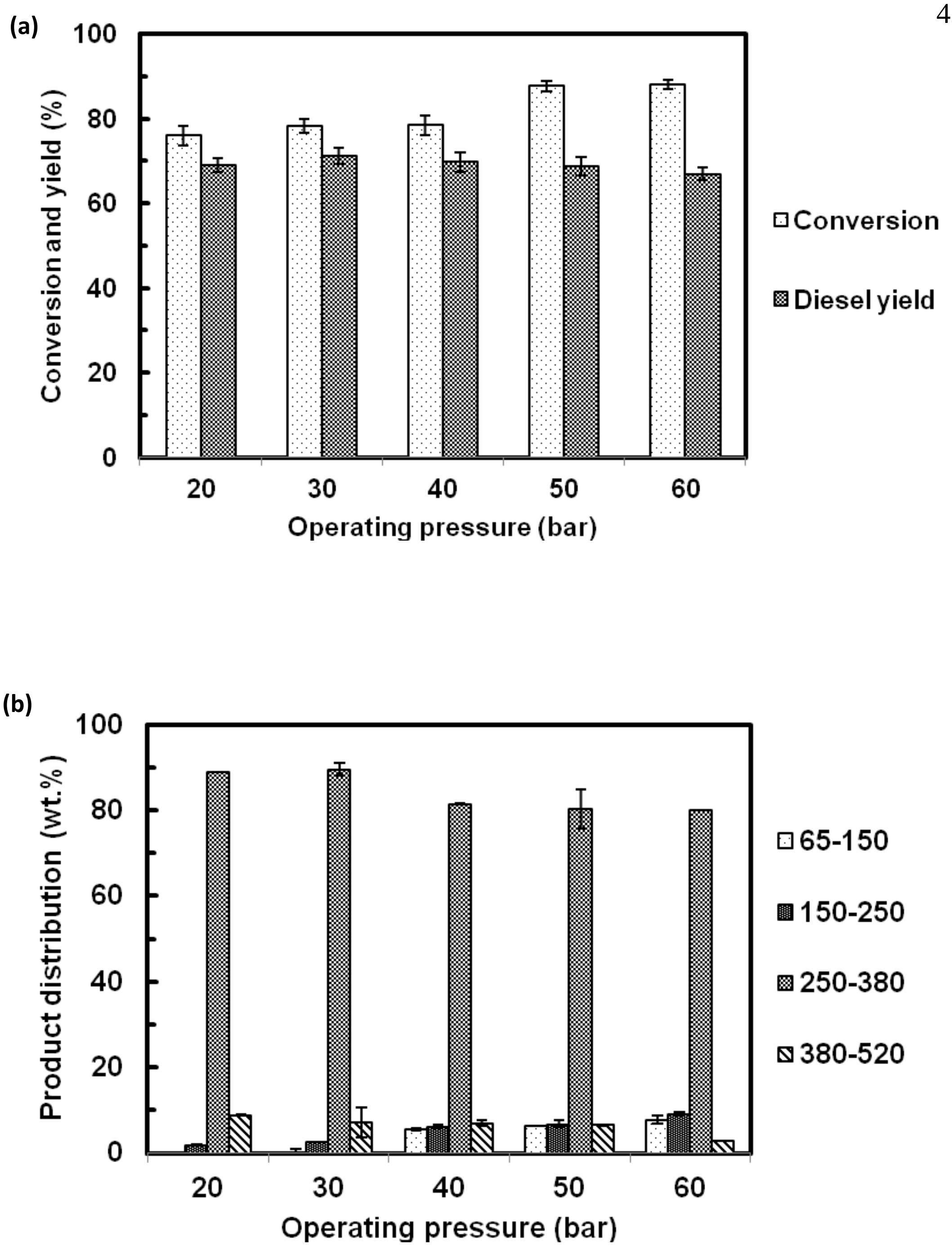

Figure 5.6 The effect of operating pressure on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of DPO feedstock. (reaction time = 1 h, operating temperature = 400 °C).

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).

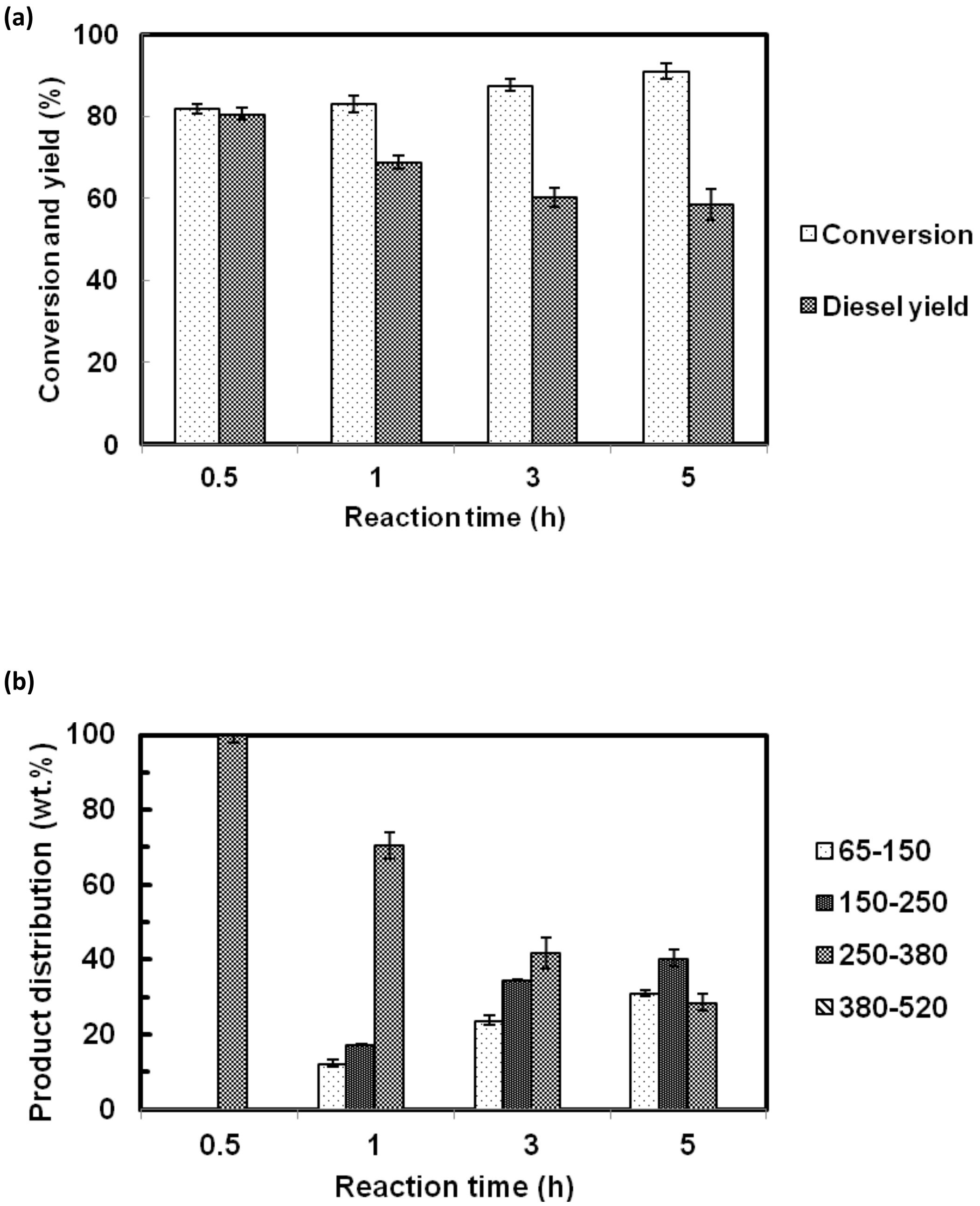

Figure 5.7 The effect of reaction time on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of PFAD feedstock. (reaction time = 0.5 h, operating temperature = 375 °C).

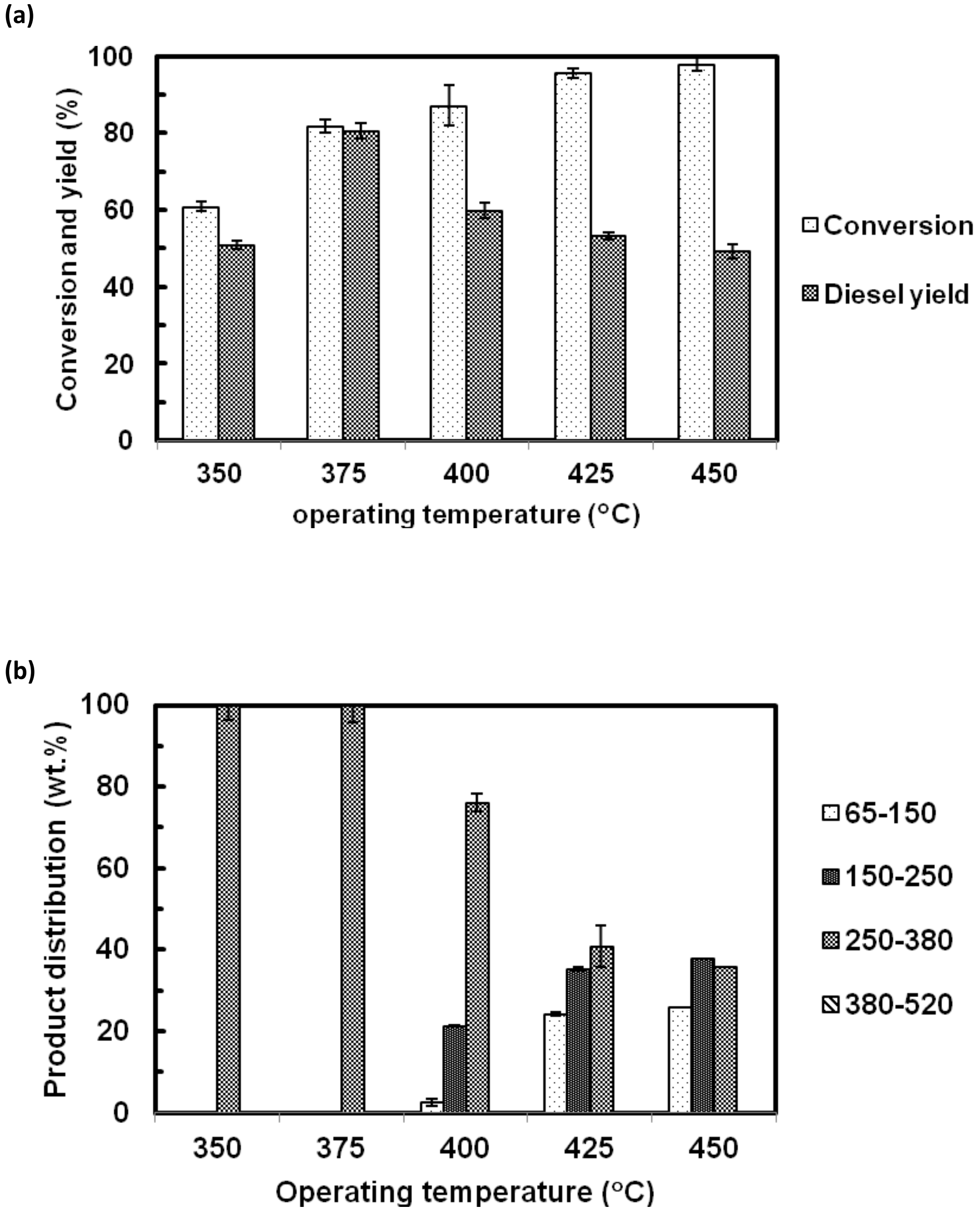

Figure 5.8 The effect of operating temperature on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of PFAD feedstock. (reaction time = 0.5 h, operating pressure = 40 bar).

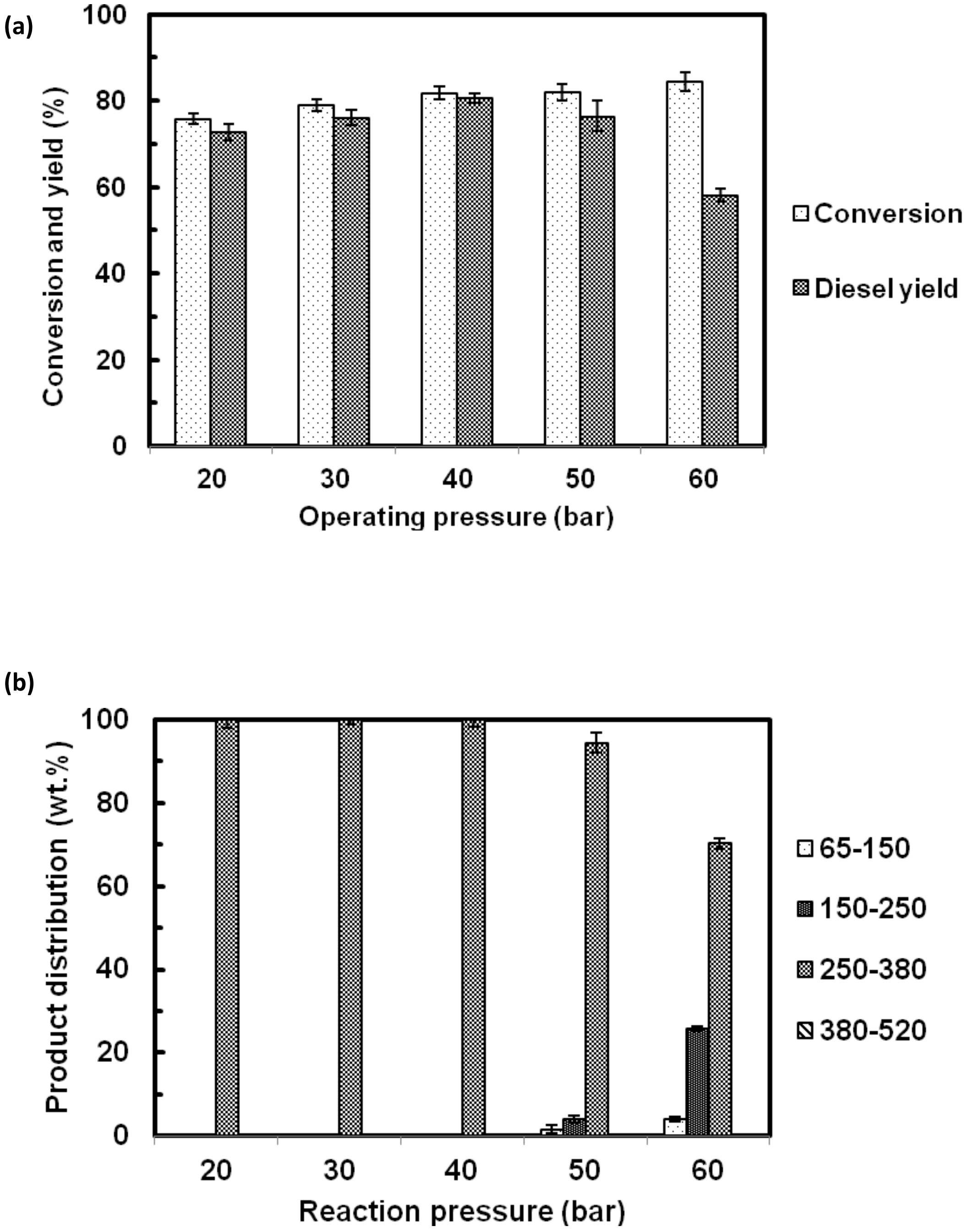

Figure 5.9 The effect of operating pressure on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of PFAD feedstock. (reaction temperature = 375 °C, reaction time = 0.5 h).

As can be seen, deoxygenation of free fatty acids: palmitic acid, stearic, oleic, and linoleic, can 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

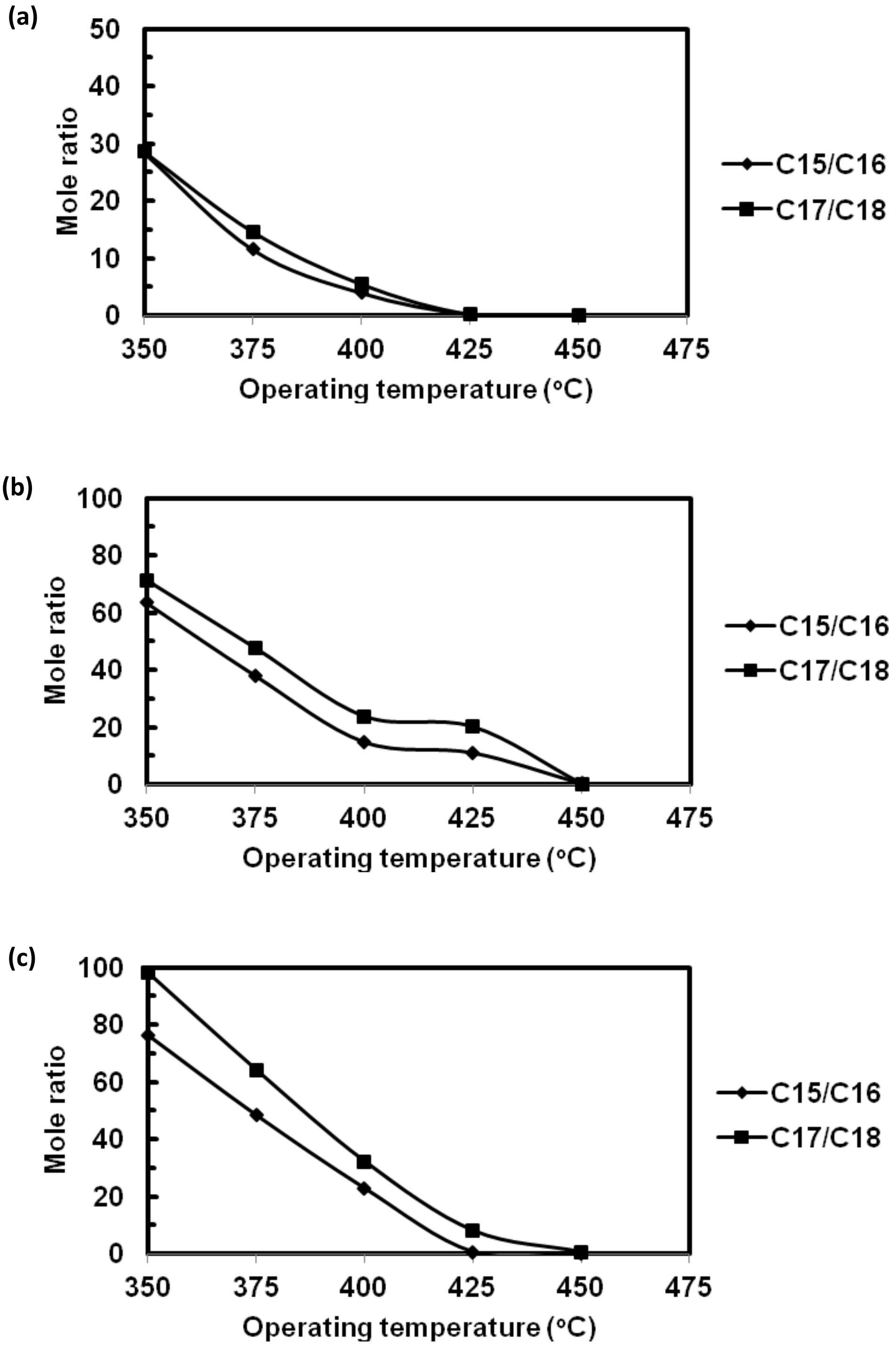

Figure 5.10 The ratio of C(n-1)/C(n) paraffins as a function of the operating temperature a) used CPO as feedstock b) used DPO as feedstock and c) used PFAD as feedstock.

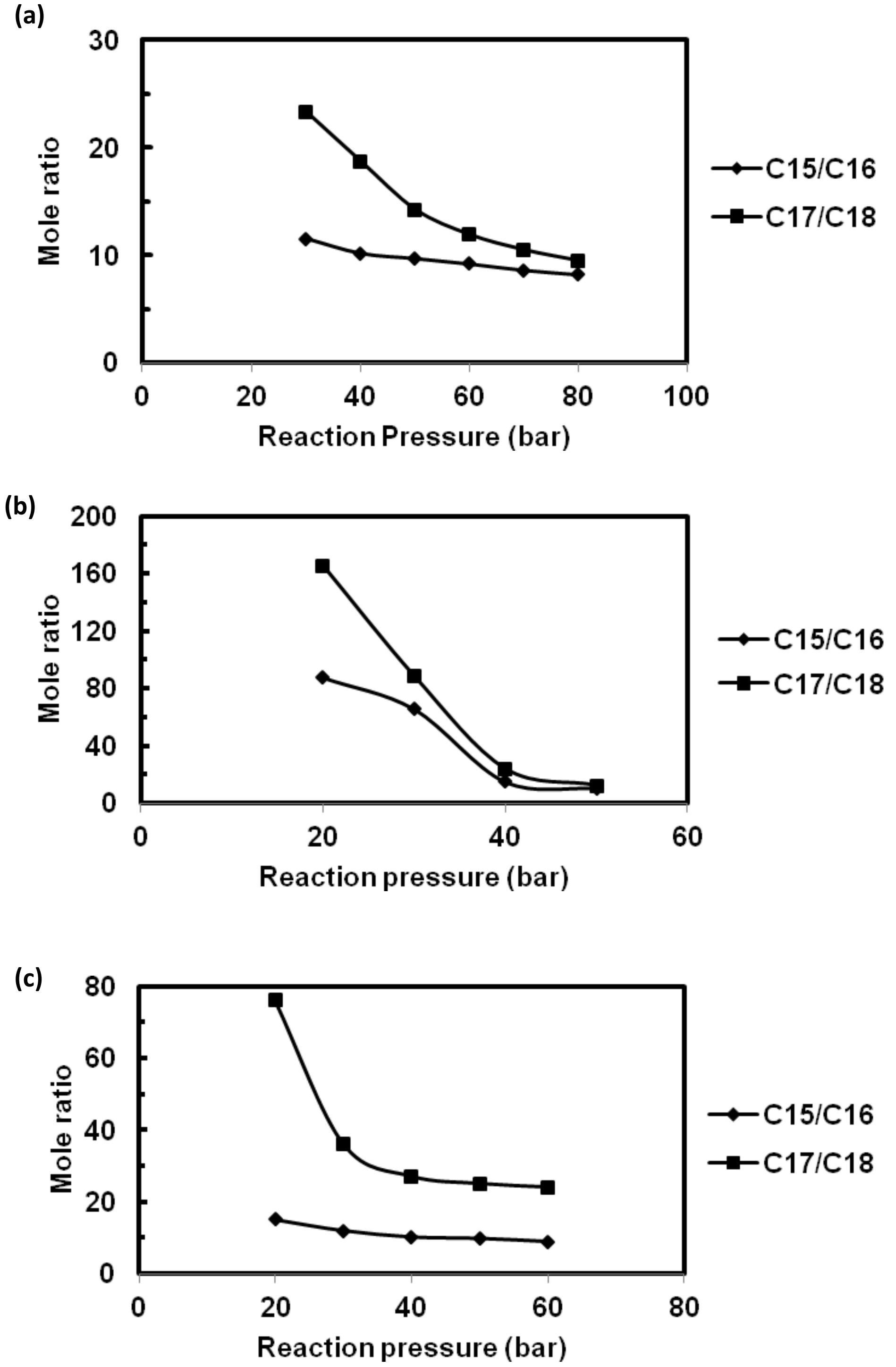

Figure 5.11 The ratio of C(n-1)/C(n) paraffins as a function of the reaction pressure a) used CPO as feedstock b) used DPO as feedstock and c) used PFAD as feedstock.

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. 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.

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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Output ที่ได้จากโครงการ

1.ผลงานตีพิมพ์ในวารสารวิชาการระดับนานาชาติที่มีค่า Impact factor

1) **Worapon Kiatkittipong***, Suwimol Wongsakulphasatch, Nattapon Tintan, Navadol Laosiripojana, Piyasan Praserthdam and Suttichai Assabumrungrat, "Gasoline upgrading by self-etherification with ethanol on modified beta-zeolite" Fuel Processing Technology 92 (10) 1999-2004 (2011) (Impact factor 2011 = 2.945)

2) **Worapon Kiatkittipong***, Songphon Phimsen, Suwimol Wongsakulphasatch, Navadol Laosiripojana, Suttichai Assabumrungrat, "Diesel-like hydrocarbons production from hydroprocessing of relevant refining palm oil" อยู่ระหว่างการพิจารณาเพื่อตีพิมพ์ในวารสาร Fuel Processing Technology (Impact factor 2011 = 2.945)

2. การนำผลงานวิจัยไปใช้ประโยชน์

ได้นำผลงานวิจัยไปใช้ประโยชน์ในเชิงวิชาการโดยมีการพัฒนาการเรียนการสอนในรายวิชาหัวข้อพิเศษในแขนงวิศวกรรมการเร่งปฏิกิริยาเคมี ของภาควิชาวิศวกรรมเคมี ม.ศิลปากร รวมถึงการสร้างนักวิจัยใหม่ระดับปริญญาโทในหัวข้อดังกล่าวในจำนวน 2 คนโดยนายทรงพล พิมเสนได้ศึกษาต่อในระดับปริญญาเอกด้วยทุนปริญญาเอกกาญจนาภิเษก และนายชัยยศ คงวัฒนกุลได้ทำงานที่บริษัท SCG Chemicals

3. การนำเสนอผลงานในการประชุมวิชาการระดับนานาชาติ

1) Worapon Kiatkittipong*, Chaiyod Kongwattanakul, Suwimol Wongsakulphasatch, Navadol Laosiripojana, Piyasan Praserthdam, Suttichai Assabumrungrat International, Sulphide vs carbide catalysts for hydroprocessing of waste cooking oil for biodiesel production, Symposium on Chemical Reaction Engineering 23 (ISCRE 23)

2) The hydroprocessing of waste cooking palm oil for diesel like hydrocarbons production over Ni-Mo/Al_2O_3 carbide catalyst, Narisara Rodboon, Chaiyod Kongwattanakul, Worapon Kiatkittipong*, Piyasan Praserthdam and Suttichai

Assabumrungrat, Pure and Applied Chemistry International Conference 2012 (PACCON 2012)

3) Songphon Phimsen, Worapon Kiatkittipong*, Suwimol Wongsakulphasatch, Navadol Laosiripojana, Suttichai Assabumrungrat, Diesel-like hydrocarbons production from hydroprocessing of different palm-oil feedstocks, 6th Asia Pacific Chemical Reaction Engineering Symposium (APCRE'11), 18-21 September 2011, Beijing, China

4) Worapon Kiatkittipong*, Parinya Intaracharoen, Navadol Laosiripojana and Suttichai Assabumrungrat, Utilization of glycerol as transportation fuel, 22nd North American Catalysis Society Meeting (NAM), Detroit, Michigan, USA, 5-10 June 2011.

5) C. Kongwattanakul, W. Kiatkittipong* and S. Assabumrungrat, Hydroprocessing of waste cooking palm oil over Pd/C catalyst, Pure and Applied Chemistry International Conference 5-7 Jan (2011)

ภาคผนวก

Appendices

Fuel Processing Technology 92 (2011) 1999–2004

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Gasoline upgrading by self-etherification with ethanol on modified beta-zeolite

Worapon Kiatkittipong [a,*], Suwimol Wongsakulphasatch [a], Nattapon Tintan [a], Navadol Laosiripojana [b], Piyasan Praserthdam [c], Suttichai Assabumrungrat [c]

[a] Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom 73000, Thailand
[b] The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand
[c] Center of Excellence in Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

ARTICLE INFO

Article history:
Received 19 March 2011
Received in revised form 21 May 2011
Accepted 31 May 2011
Available online 25 June 2011

Keywords:
Modified beta zeolite
Renewable energy
Olefins reduction
Etherification
FCC gasoline

ABSTRACT

This research studied the modification of beta-zeolite for self-etherification process of fluidized catalytic cracking (FCC) gasoline and ethanol. The catalytic activity of reducing olefins in FCC gasoline accompanied with higher ethanol substitution was evaluated; moreover, the influences of Si/Al ratio in beta zeolite and the addition of copper (Cu) or magnesium (Mg) in the beta zeolite on the reaction performance were also investigated. It was found that the beta zeolite with Si/Al ratio of 27 (beta$_{27}$) can enhance higher ethanol conversion than those of 42 and 77. In addition, the modification of beta$_{27}$ by Cu (Cu-beta$_{27}$) can further improve the ethanol conversion from 38.2% (beta$_{27}$) to 55.1%, and the olefin content reduction from 46.2% (beta$_{27}$) to 62.4%. The improvement of the catalytic activity also enhances the obtained gasoline properties i.e. lower blending Reid vapor pressure (bRvp) and higher research octane number (RON).

1. Introduction

Fluid catalytic cracking (FCC) of gasoline is the main contribution of olefins when it is blended with gasoline pool. Such olefinic compounds usually present in an unstable form, which are easily oxidized by photochemical reaction, leading to an increase of ground ozone level. Hence the amounts of olefinic compounds are enforced to have a limiting upper value of 18 vol.% as regulated by Europe IV vehicle standard of unleaded gasoline. Several studies on selective hydrogenation for olefins reduction have been proposed and some of them have already been performed the pilot-scale operations; however, this technique is still facing problems with low gasoline yield and loss in research octane number (RON) [1,2]. Converting olefins in FCC gasoline by hydroisomerization and aromatization was therefore developed and was succeeded in reducing the loss of octane number from olefin reduction due to compensation by the formation of iso-paraffins and aromatics [1,3–5]. However, this process has to be operated at a high temperature between 270 and 370 °C with pure hydrogen at the pressure of 2.0–3.0 MPa. A catalyst modification for non-hydrogenation reduction of olefins, which is known as a process without hydrogen supply in feed, has been proposed as it is especially beneficial for the refineries where hydro-treating is limited or low-cost hydrogen could not be provided [6]. The products from the non-hydrogenation provide similar RON or slightly higher than those obtained from the original FCC gasoline [6–8]. The operating temperatures of non-hydrogenation reduction of olefins in this operation are normally in the range of 170–400 °C.

Since most conventional techniques are usually operated at relatively high temperatures and it is difficult to achieve higher RON as well as the process does not increase a renewability of gasoline, etherification reaction is proposed as an alternative way for upgrading FCC gasoline [9]. By etherifying the entire FCC gasoline, the olefin content and bRvp of the gasoline could be reduced with an increase of gasoline yield, octane number and oxygen content. The etherification of the entire FCC gasoline has been successfully experimented with methanol [10–13]. Rihko and Krause [11] employed Amberlyst 16 for etherification of light FCC gasoline with methanol. Tert-amyl methyl ether (TAME), producing from iso-amylene (C_5-olefinic compounds), was observed to be the main ether products. Hu et al. [13] investigated various catalysts i.e. beta-, MOR-, ZSM5-zeolite and D005 cationic exchange resin for FCC etherification with methanol. They reported that beta-zeolite provides the highest conversion and catalytic stability. In addition, instead of methanol, the FCC process could also employ the renewable reagents i.e. ethanol [9,14] and glycerol [15]. An advantage of using such renewable reagents is that they are more environmentally friendly, which can partially reduce the global warming from gasoline utilization. Kiatkittipong et al. [9] studied FCC gasoline upgrading by etherification with ethanol. The use of ethanol in the etherification process can overcome the constraint of using ethanol as fuel extender by direct blending method (as well known as “gasohol”) which is limited at ca. 10–20 vol.% for non-flex fuel engine. Moreover, this process can decrease evaporative loss by reducing gasoline volatility. Considering the catalytic performance, beta-zeolite was found to enhance better catalytic activity than Amberlyst 16 since it provides not only higher

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[*] Corresponding author. Tel./fax: +66 3421 9368.
E-mail address: kworapon@su.ac.th (W. Kiatkittipong).

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doi:10.1016/j.fuproc.2011.05.024

Table 1
Compositions of FCC gasoline (vol.%).

Carbon number	n-Paraffins	i-Paraffins	Olefins	Naphtenes	Aromatics	Total
C4	0.215	0.111	1.208	0	0	1.534
C5	0.996	7.691	6.693	0	0	15.380
C6	1.102	11.764	7.053	1.631	0.323	21.874
C7	0.794	7.146	7.246	2.564	2.230	19.980
C8	1.059	5.953	0.688	2.230	4.608	14.538
C9	0.391	3.030	1.937	2.827	5.079	14.264
C10	0.257	2.620	0	0.137	5.563	8.577
C11	0.281	0.829	0	0.087	0.766	1.864
C12	0.077	0.446	0	0.205	0.909	1.637
Total	5.072	39.591	24.825	9.681	20.478	99.647

ethanol and olefin conversion but also gives higher RON with lower blending Reid vapor pressure (bRvp). A satisfied drivability index showed that no cold start problem occurs even at low bRvp [14]. However, it is worth to note that in the case of FCC etherified with glycerol, Amberlyst 16 expresses much higher catalytic activity than that of beta-zeolite. The explanation is possibly due to the fact that the glycerol derived ethers products are larger and more obstructed than ethanol derived ether, which may not suit to the pore structure of zeolite [15]. The demand of oxygenated ethers is usually limited by the reaction of C_4 and C_5 reactive olefins. Recently, several studies have been investigating the synthesis of these ethers in different routes i.e. ethanol derived ethers such as ethyl *tert*-butyl ether (ETBE) and *tert*-amyl ethyl ether (TAEE) [17–20], and glycerol derived ethers [16]. When employing the whole FCC gasoline as olefins sources for etherification, so called “self-etherification”, the wide range of ethers production by FCC self-etherification with ethanol [9,14] and glycerol [15] could effectively enhance the RON and sustain the demand of oxygenated ethers.

According to our previous works on the etherified FCC gasoline with ethanol, the amount of remaining olefinic compounds in the products are in compliance with the limiting values regulated by Euro IV standard [9,14]; however, converting the rest olefinic compounds would be beneficial both in terms of olefins reduction and enhanced ethanol substitution in gasoline. It is known from previous studies that only tertiary olefins (double bond attached to a tertiary carbon) are reactive for etherification [21–23]. Moreover, the etherification reactions are strongly limited by the thermodynamics. Many studies on the thermodynamics of various ethanol etherification reactions with e.g. C_4-isobutene [24,25], C_5-isoamylene [21] and various C_6 reactive olefins [23,26] have been published. The equilibrium conversion from the experiments [27] agrees well with their theoretical calculation [23], where ETBE formation is substantially higher than that of 2-ethoxy-2-methylpentane and TAEE, respectively. Therefore, higher demand of ethanol to substitute in gasoline by converting to ethers cannot be implemented by only etherification. The idea of this study is to combine the catalytic isomerization of non-reactive olefins to produce a surplus reactive olefins and etherification with ethanol as a synergy for ethanol supplementary in gasoline with olefin reduction. Many researchers have studied on skeletal isomerization especially n-butenes to isobutene, in which various metals e.g. magnesium [28] and copper [29] were loaded on silica-alumina or zeolite supported for skeletal isomerization enhancement. In this study, we focus on the modification of beta-zeolite to achieve higher ethanol and olefin conversions with preferable gasoline properties for enhancing renewability and environmental friendliness of gasoline.

2. Materials and method

2.1. Chemicals

FCC gasoline was obtained from the catalytic cracking unit of an oil refinery; its compositions are given in Table 1. Chemical precursors employed in the study for modifying beta-zeolite are copper nitrate ($Cu(NO_3)_2.2.5H_2O$) and magnesium chloride ($MgCl_2.6H_2O$) supplied from Ajax Finechem Ltd. Commercial beta-zeolite with Si/Al = 27 in the form of Na^+ (mean particle size of 3–6 µm) was purchased from Tosoh company, Japan.

2.2. Catalyst modification

2.2.1. Removal of Na^+ from beta-zeolite

Beta-zeolite was exchanged into H^+ form by dissolving 10 g of beta-zeolite in 150 ml of 1 M NH_4Cl aqueous solution at 80 °C for 5 h. The exchanged process was performed for 3 times. After that beta-zeolite was washed with deionized water for 3 times. The beta-zeolite was separated by centrifugation and dried at 110 °C for 3 h. At this stage, the obtained crystals were in the NH_4^+ form. Then, the sample was calcined at a temperature of 550 °C under air stream for 6 h to dissociate the ammonium into H^+ form, as NH_3 escapes to the atmosphere and H^+ stays on the catalyst to balance the ionic charge [17].

2.2.2. Dealumination of beta-zeolite

Beta-zeolite was dealuminated by following the procedure reported by Collignon et al. [30], from which 10 g of beta-zeolite was dissolved in 200 ml of 0.5 M HNO_3 solution and stirred at 80 °C for a desired period. The zeolite was then washed with deionized water for several times and dried at 110 °C for 3 h.

2.2.3. Modification by ion exchanging with metal cation

After exchanged beta-zeolite to H^+ form, Hbeta-zeolite was then back exchanged with cations Cu and Mg. The procedure of the back exchange is similar to that reported by Nieminen et al. [29] and Canizares et al. [31], in which 10 g of Hbeta-zeolite was mixed with 150 ml aqueous solution of 0.1 M copper nitrate or 0.5 M aqueous magnesium chloride at 80 °C. Metal-Hbeta-zeolite was then washed

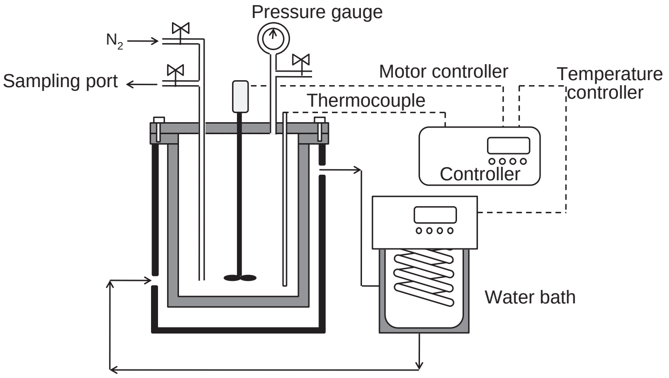

Fig. 1. Schematic diagram of the reactor apparatus.

with deionized water, dried at 110 °C for 12 h and calcined under air flow at 500 °C for 3 h.

2.3. Experimental technique

Etherification of FCC gasoline with glycerol was carried out in a cylindrical shape autoclave reactor as shown in Fig. 1. A valve for liquid sampling and a port for the thermocouple were installed at the top of the reactor. For all experiments, the mixture was stirred by using a turbine at the maximum speed of 1163 rpm since the effect of external mass transfer resistance could be negligible at this stirring speed [9]. The reactor was maintained at a constant temperature by circulating hot water in jackets. The ratio of FCC gasoline:ethanol was varied in vol.% (with total volume of 100 cm^3) and 10 g of catalyst was carried out at 70 °C for 10 h under a pressure of 0.8 MPa. It should be noted that although it is not practical in industrial application, high ratio of catalyst to reactant was applied in this study in order to reach reaction equilibrium within 10 h. After reaction, the reactor was cooled down to room temperature before collecting the sample from the reactor in order to prevent evaporation loss.

2.4. Catalyst characterizations

Structural characteristics of the catalysts were investigated by powder X-ray diffraction (XRD) analysis using a Siemens D5000 diffractometer equipped with CuKα radiation and Ni filter. Its surface area and mean pore diameter were determined by N_2 adsorption (BET method) using a BEL-SORP automated system. Chemical analysis was determined by inductive couple plasma (ICP), Varian: liberty 220. Acidity of catalyst was investigated by Micromeritics 2000 TPD/TPR ammonia-temperature programmed desorption (NH_3-TPD).

2.5. Product analysis

The standard analysis of research octane number (RON), blending Reid vapor pressure (bRvp) and distillation temperature was carried out following the standard methods of ASTM D-2699, ASTM D-5191 and ASTM D-86, respectively.

3. Results and discussion

3.1. Catalyst characterization

The surface area and mean pore diameter of the catalysts with Cu and Mg loading and dealumination are illustrated in Table 2. It can be seen that the catalyst surface area and mean pore diameter decrease with metal loading. The chemical composition of the catalysts is shown in Table 2 in terms of Si/Al molar ratio and metal content (Cu, Mg). Beta-zeolite starting material with Si/Al = 27 was dealuminated to two levels (i.e., Si/Al of 42 and 77) and Cu and Mg were exchanged with H^+ in similar level at approximately 1 wt.%.

Fig. 2 shows the XRD patterns of beta-zeolite with different Si/Al ratios and metal loadings. The spectrum of beta-zeolite has characteristic peaks similar to those previously reported in the literature [17]. It is noted that these peaks are also observed in all catalyst samples indicating that the incorporation of metal does not change crystalline structure of the modified beta-zeolite. In addition, no significant peaks of Cu and Mg are observed from the XRD due to low amount of metal loading.

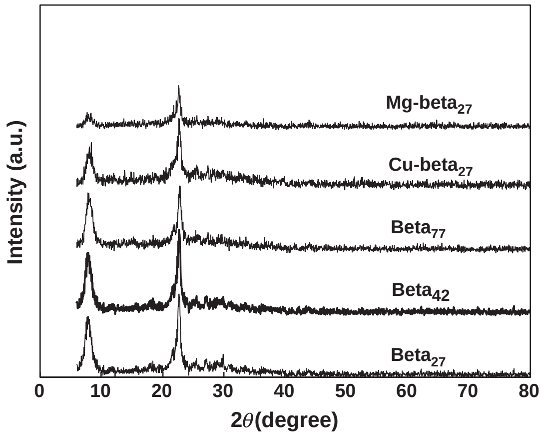

Fig. 2. XRD patterns of beta-zeolite catalyst.

3.2. Catalyst performance

The catalyst performance for etherification of FCC gasoline with ethanol is presented in terms of ethanol conversion as shown in Fig. 3. It can be seen that beta-zeolite with Si/Al of 27 shows a greater activity toward the FCC etherification with ethanol compared to beta-zeolite with Si/Al of 42 and 77. It is noted that ethanol conversion slightly decreases (from 38.0% to 36.3%) with increasing Si/Al ratio from 27 to 42; however, it drastically decreases (from 38% to 21% when Si/Al ratio is increased to 77. The role of copper and magnesium on the reaction performance was investigated as shown in Fig. 3. It was found that the addition of both copper and magnesium into beta-zeolite with Si/Al ratio of 27 (denoted as Cu-beta$_{27}$ and Mg-beta$_{27}$) can significantly enhance the etherification of FCC gasoline with ethanol. The highest ethanol conversion of 55.1% could be obtained with Cu-beta$_{27}$ catalyst at 20 vol.% ethanol. With increasing ethanol substitution ratio up to 30 vol.%, higher amount of ethanol was converted with a conversion of 49.6% as shown in Table 3. The characterization of obtained gasoline products is provided in the next section.

3.3. Characterization of gasoline products

The composition of FCC gasoline (as shown in Table 1) illustrates that the main components of olefins are C_5–C_7 hydrocarbons and about 25 vol.% of olefins are found in gasoline. Table 3 presents the gasoline properties, olefins conversion, and ethanol conversion of FCC gasoline for FCC:ethanol initial feed ratios of 80:20 and 70:30, respectively. It can be seen that the original FCC gasoline has RON of 88 and bRvp of 6.5. The RON increases to 94.8 and 97.9 with ethanol direct blending at 20 and 30 vol.%, respectively; however, bRvp increases up to 7.42 and 8.0. An increase of bRvp induces higher

Table 2
Properties of catalysts.

Catalysts	Si/Al [−][a]	Metal content (Cu, Mg) [wt.%][a]	Surface area [$m^2\ g^{-1}$][b]	Mean pore diameter [nm][b]
Beta$_{27}$	27	–	667	0.59
Beta$_{42}$	42	–	625	0.58
Beta$_{77}$	77	–	563	0.59
Cu-beta$_{27}$	27	0.92	550	0.57
Mg-beta$_{27}$	27	1.04	535	0.53

[a] Determined by ICP.
[b] Determined by BET.

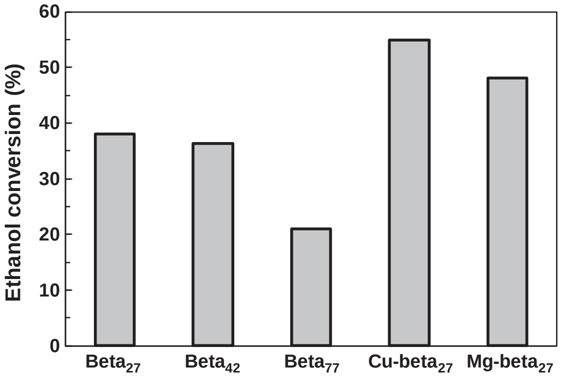

Fig. 3. Ethanol conversion from etherification with FCC gasoline catalyzed by various beta-zeolite based catalysts (FCC gasoline:ethanol = 80:20 by volume).

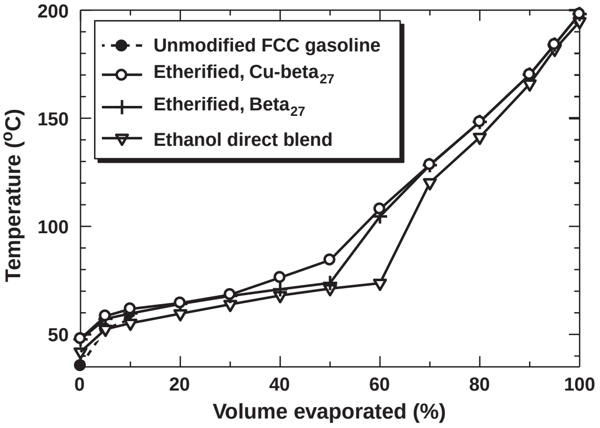

Fig. 4. Distillation temperatures (following the ASTM D-86 standard method).

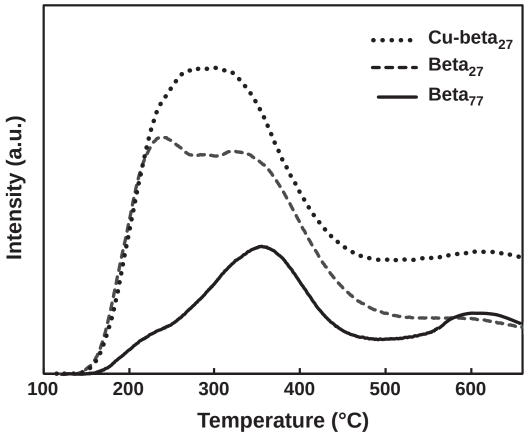

Fig. 5. NH_3-TPD results of different catalysts.

evaporative loss and leads to vapor lock which is not favorable especially in summer or in tropical countries. It is worthy to note that recently more restriction on gasoline volatility is enforced i.e. California Reformulated Gasoline Phase 3 (CaRFG3) regulation with the cap limit of bRvp at 6.4–7.2 seasonally (http://www.arb.ca.gov/fuels/gasoline/carfg3/carfg3.htm). As presented in Table 3, FCC etherified with ethanol by using either $beta_{27}$ or Cu-$beta_{27}$ could effectively decrease the values of bRvp because the olefins in FCC gasoline and ethanol are converted to ethers which have lower bRvp. The main ether product obtained in this study is TAEE, which is similar to the case of etherification of FCC gasoline with methanol as reported by Rihko and Krause [11], where TAME is obtained as a main ether product. The concentration of ethers and some free ethanol remaining in the final products is provided in Table 3. The less free ethanol left in gasoline indicates a higher possibility of using the gasoline in a non-flex fuel engine. The oxygen contents determined from ethanol and ethers left in final product are approximately 6.7–7.0 and 9.6–10.0 wt.% in cases of etherification with 20 and 30 vol.% ethanol, respectively. By incorporating copper in $beta_{27}$ (Cu-$beta_{27}$), the etherification reaction is enhanced as indicated by an increase of ethanol conversion and olefins reduction. It is worthy to note that from the analysis of the olefin distribution, both the amounts of tertiary olefins and non-reactive branched olefins decreased. This will be discussed in more details in the next paragraph. For other gasoline properties, density and viscosity of the etherified gasoline are found to be close to those of the commercial gasohol. When ethanol is increased to 30 vol.%, similar trend to those of 20 vol.% ethanol is observed for all properties studied.

The results of distillation temperatures carried out following the ASTM D-86 standard method are shown in Fig. 4. The direct blending of ethanol significantly changes the distillation curve compared to that of the original FCC gasoline as the distillation temperature is drastically affected at the temperature of 50–60 evaporated volume (T_{50} and T_{60}). Apart from the initial boiling point (IBP), the distillation temperature of direct blending ethanol decreases throughout the percent volume of evaporated gasoline.

In case of FCC gasoline etherified with ethanol using catalyst either Cu-$beta_{27}$ or $beta_{27}$, the gasoline products showed higher values of IBP, T_5, and T_{10} than those of the original FCC gasoline. The higher values of these front end distillation temperatures support the results of lower value of the bRvp, which are in the order of Cu-$beta_{27}$ < $beta_{27}$ < original FCC gasoline < ethanol direct blending. The least remaining of ethanol from unconverted in etherified gasoline with Cu-$beta_{27}$ makes the most similar distillation curve compared to the original FCC gasoline as shown by the closer distillation temperature in the range of T_{30}–T_{60}. From the

Table 3
Comparison of gasoline properties.

Properties	FCC gasoline	Gasoline E10	20 vol.% Ethanol			30 vol.% Ethanol		
			Direct blend	Etherified gasoline		Direct blend	Etherified gasoline	
				$Beta_{27}$	Cu-$beta_{27}$		$Beta_{27}$	Cu-$beta_{27}$
RON	88	95	94.8	94.2	94.8	97.9	98.2	98.5
bRvP (psi)	6.5	< 9.0	7.42	5.64	5.22	8.0	6.47	6.08
Density (g cm^{-3})	0.683	0.749	0.735	0.745	0.748	0.735	0.745	0.749
Viscosity (Pa s)	6.09×10^{-4}	5.05×10^{-4}	6.20×10^{-4}	6.19×10^{-4}	6.17×10^{-4}	6.03×10^{-4}	5.09×10^{-4}	5.14×10^{-4}
Ethanol conversion (%)			0	38.2	55.1	0	40.3	49.6
Olefins reduction (%)			0	46.2	62.4	0	60.1	68.7
Free ethanol left (wt.%)		Approx .11%	22.4	13.9	10.1	33.1	19.8	16.7
Ethers conc. (wt.%)			0	16.2	22.4	0	22.8	26.2

Table 4
Comparison of olefin reduction techniques.

Reaction	References	Catalyst, operating *T* and *P*	Olefins (vol.%)			Aromatics (vol.%)			RON		
			Initial	Final	Change (%)	Initial	Final	Change (%)	Initial	Final	Change
Hydroisomerization	Fan et al. [1]	β/ZSM-5 composite, 315 °C, 2.0 MPa	41.1	9.9	−75.9	17.4	29.3	+68.4	91.7	92.1	+0.4
	Fan et al. [2]	SAPO-11/MOR/β/ZSM, 300 °C, 2.0 MPa	41.7	6.3	−84.9	17.1	21.4	+25.1	91.7	86.3	−5.4
Non-hydrogenation	Zubin et al. [36]	BPyC-$AlCl_3$ ionic liquid[1], 25 °C, N.A.[2]	42.5	28.0	−34.1	15.7	18.1	+15.3	91.3	90.5	−0.8
	Ding et al. [6]	kaolin/γ-Al_2O_3/ZSM-5, 400 °C, 0.1 MPa	43.5	18.7[3]	−56.8	14.4	33.7[3]	+134.0	92.1	~92 [4]	~0 [4]
	Li et al. [7]	Ni/W/SiO_2.Al_2O_3, 170 °C, 2.5 MPa	51.0	25.6	−49.8	19.1	37.1	+94.2	88.6	89.1	+0.5
	Lihua and Jinshen [8]	Ni,Mo/β-zeolite, 140 °C, 2.0 MPa	60.9	33.0	−45.8	12.2	29.1	+138.5	92.0	95.0	+3.0
Etherification with ethanol (20 vol.%)	Kiatkittipong et al. [9]	β-zeolite (Si/Al = 40), 70 °C, 0.8 MPa	25.7	13.9	−45.9	17.0	16.9	−0.6	88.0	94.1	+6.1
	Kiatkittipong et al. (this study)	Cu-β-zeolite (Si/Al = 27), 70 °C, 0.8 MPa	24.8	9.3	−62.4	20.5	20.7	+1.0	88.0	94.8	+6.8

[1] BPyC = 1-butylpyrinium chloride.
[2] N.A. = not available.
[3] Determined from Fig. 2 of Ding et al. [6] with optimal kaolin/γ-Al_2O_3 ratio of 1.5.
[4] Ding et al. [6] reported preserving of gasoline RON.

results, we could presume that higher olefin consumption, which are mostly in C_5–C_7 range, might mainly contribute to higher front end distillation temperature while higher ethanol conversion mainly contribute to higher middle range distillation temperature.

The NH_3-TPD profiles of Cu-beta$_{27}$, beta$_{27}$, and beta$_{77}$ are shown in Fig. 5. Comparing the NH_3-TPD profiles between beta$_{77}$ and beta$_{27}$, it can be revealed that the total acidity (determined by total area of the graph) decreases with increasing Si/Al. This manner is as expected since the acid site in zeolite is generally formed on the Si–O–A1 linkage of the zeolite framework. In addition, a decrease of weak acidity is more pronounced compared with the strong acidity. It is worth to note that both the weak and strong acid sites are active for etherification reaction; however weak acid is more stable due to less carbon formation [32]. The Cu-beta$_{27}$ catalyst can increase both weak and strong acid sites. It is found that the reaction that requires strong acid (over 400 °C) rather than weak acid is the skeletal isomerization as observed by Woo et al. [33] and Escalante et al. [34] for skeletal of n-butene to iso-butene. However, in this study, the major decreased olefins are reactive and non-reactive branched olefins rather than linear olefins. It is known that the reaction involving positional isomerization is faster than skeletal isomerization [35]. Stronger acid catalyst and/or higher operating temperature would be needed for skeletal isomerization compared to those for positional or double bond shift isomerization. The increase of olefins conversion could therefore be presumably arisen from isomerization among branched olefin to reactive olefins, which could be further reacted by etherification with ethanol.

3.4. Comparison of olefin reduction techniques

Since operating condition among various techniques is different and the amount of olefins in the FCC gasoline feedstock among various studies is varied in a wide range ca. 25–61 vol.% as shown in Table 4, therefore, comparison performances of olefin reduction among different techniques might be difficult. As a consequence, it is worth to provide the necessary data, such as operating temperature and pressure, catalyst, feed and product composition, to give an overall idea in order to clarify characteristics and advantages of each process. The ability of etherification with ethanol for reducing olefins in FCC gasoline is compared with current techniques of hydroisomerization and non-hydrogenation as summarized in Table 4. It can be seen that hydroisomerization, which is usually accompanied with aromatization, can diminish the olefins at the highest extent (84.9% of olefins reduction). However, the process would suffer from the loss of RON if compensation by an increase of aromatics compound is not enough.

Non-hydrogenation was proposed instead of hydroisomerization in case when low-cost hydrogen is unavailable. However, as presented in Table 4, non-hydrogenation shows a much lower degree of olefin reduction than that of hydroisomerization process. In addition, the RON obtained from hydroisomerization or non-hydrogenation strongly depends upon the degree of olefins reduction and aromatization. Therefore, to compromise the olefins and aromatic content under the restriction limit (18 vol.% for olefins and 35 vol.% for aromatics) it is necessary to consider the RON value preserved in the gasoline as well.

From the study, it is summarized that etherification with ethanol shows an intermediate performance between hydroisomerization and non-hydrogenation process as indicated by reduction of olefin. Moreover, the change of aromatic compounds can be negligible. It is worth to note that the change in vol.% of olefin and aromatic compounds in the case of etherification shown here was calculated by excluding from the dilution effect of ethanol substitution. In addition, the process shows the improvement of RON which is obtained from generated ether compounds and unreacted ethanol remaining in the gasoline. Therefore we could claim here that self-etherification of FCC gasoline with ethanol catalyzed by Cu-beta$_{27}$ catalyst is one of promising processes for reducing olefins with effective increasing RON and renewability of the gasoline.

Conclusion

The etherification of FCC gasoline with ethanol is a promising technology for gasoline upgrading by efficient reduction of olefin content accompanying with quality improvement. The beta-zeolite with Si/Al of 27 modified by ion-exchanged with Cu shows an outstanding performance; it provides high ethanol conversion and olefin consumption e.g. 55.1 and 62.4%, respectively, in case of 20% ethanol in feed. By increasing the ethanol fraction in feed up to 30 vol.%, the reaction could be further enhanced. Higher ethanol conversion means ethanol could be higher supplemented into gasoline and less free ethanol remaining. Lower ethanol left in gasoline results in lower blending Reid vapor pressure (bRvp). Comparison to other techniques for reducing olefin content in FCC gasoline, etherification with ethanol catalyzed by Cu-beta catalyst provides intermediate values of olefin reduction between the hydroisomerization and non-hydrogenation process. However, our proposed technique could effectively improve RON without an increase of aromatic content.

Acknowledgments

Financial supports from Silpakorn University Research and Development Institute, the Thailand Research Fund and Commission on Higher Education are gratefully acknowledged.

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Submitted to Fuel Processing Technology
Type of Contribution: Research article

Diesel-like hydrocarbons production from hydroprocessing of relevant refining palm oil

Worapon Kiatkittipong [a,*], Songphon Phimsen [a], Suwimol Wongsakulphasatch [a],
Navadol Laosiripojana [b], Suttichai Assabumrungrat [c]

[a] Department of Chemical Engineering , Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom 73000, Thailand
[b] The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand
[c] Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
*Corresponding author: kworapon@su.ac.th
* To whom all correspondence should be addressed.
Tel./Fax: +66 3421 9368
E-mail address: kworapon@su.ac.th

Abstract: The conversion of crude palm oil (CPO) and its physical refining including degummed palm oil (DPO) and palm fatty acid distillate (PFAD) to diesel fuel by hydroprocessing with 5 wt% Pd/C catalyst was studied in this work. The effects of operating parameters (i.e. reaction time, operating temperature, and pressure) were examined in order to determine suitable operating condition for each feedstock. It was found that the hydroprocessing of CPO at 400°C and 40 bar with reaction time of 3 h achieves highest diesel yield of 51%. When gum is removed from CPO, namely DPO, the highest diesel yield of 70% can be obtained at the shorter reaction time (1 h). In case of PFAD, which contains mainly of free fatty acids, maximum diesel yield of 81% could be enhanced at milder conditions (375°C with the reaction time of 0.5 h). From the study, 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. It is revealed that these compounds are generated via decarboxylation/decarbonylation pathways.

Keywords: Bio-hydrogenated diesel, Hydroprocessing, Deoxygenation, Diesel-like hydrocarbon, Relevant palm oil.

1. Introduction

Due to an increase of the world's energy demand and petroleum-oil as well as concern on global warming problem [1-3], the production of renewable fuels is growing much interest. Biodiesel is one of the promising alternative renewable fuels as it can reduce carbon dioxide (CO_2) in the carbon cycle and moreover particulate matter (PM), un-burnt hydrocarbon and carbon monoxide (CO) emissions. Typically, the triglycerides are converted via transesterification with methanol to produce fatty acid methyl esters (FAMEs) which are commonly referred to as 1st generation biodiesel. However, the use of FAMEs still have some drawbacks such as limited compatibility with conventional diesel engines [4], increase NO_x emissions, low oxidative stability, gum formation and possible engine problems due to their higher acid number than that of conventional diesel fuels [5]. Moreover glycerol, a byproduct of this process, is needed to utilize to alleviate a glut of glycerol [6-12]. To overcome the disadvantageous of FAME, a hydroprocessing has been investigated as an alternative pathway of biodiesel production. In this process, triglycerides and fatty acids are converted to straight chain alkane ranging from n-C_{15}–n-C_{18} known as middle distillates, which are suitable to use as diesel fuels. It was reported that the obtained straight chain alkanes have a high cetane number above 98 [13]. These processes are divided into two main types, which are hydrotreating of pure vegetable oil [4, 14-19] and co-processing of vegetable oil with crude-oil-based refinery fractions [16, 20, 21]. Normally, hydroprocessing are included in a large group of reactions such as hydrotreating (heteroatom removal e.g. sulfur and nitrpgen as called hydrodesulfurization and hydrodenitrogenation respectively), hydrocracking, hydrogenation, isomerization and deoxygenation. Conventional hydroprocessing catalyst e.g. NiMo and CoMo have been used for many decades as hydrodesulfurization (HDS) catalysts for sulfur removal from petroleum product. Moreover, it has been found that conventional hydrotreating catalysts are suitable for deoxygenation of triglycerides. However, the deactivation of catalyst is the main problem because high oxygen content in triglyceride causes leaching of sulfur from the catalyst surface [22]. To conserve catalyst activity, the sulfiding agents, such as H_2S [23] and dimethyl disulfide [20, 24, 25] are added in reaction system but the amount of sulfiding agent needs to be optimized for the desired activity of the catalyst and the target product quality. In addition, these compounds are very toxic and could easily poison many systems in the human, especially the nervous system. Therefore, non-sulfided catalysts, such as nitride catalysts, Pd and Pt are interested for the production of biofuels because they eliminate the need to add a sulfiding agent to a biomass-derived feedstock in order to prevent the deactivation of sulfided metal catalysts [26]. Previously, many metal catalysts such as Pd, Ni, Ru, Ir, Os, Rh loaded on alumina or silica or activated carbon as well as some alloys and bimetallic catalysts have been studied in stearic acid deoxygenation. Among these catalysts, it is revealed that Pd/C shows the highest catalyst activity at 300 °C under 17 bar of helium in a semibatch reactor with selectivity of 95% to heptadecane at complete conversion [27]. A wide range of oxygenated molecules are used as starting material for hydroprocessing, such as fatty acids and their esters [28-32] or directly triglycerides [33, 34]. Triglyceride of vegetable oil could be hydrogenated and broken down into various intermediates (i.e. monoglycerides, diglycerides and carboxylic acids) and the glycerol backbone of triglycerides is converted into propane. These intermediates are then converted into alkanes by three different pathways, decarboxylation, decarbonylation and hydrodeoxygenation, as shown in Eqs. (1)-(3), respectively.

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

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

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

As seen in Eqs.(1) and (2), the co-products from decarboxylation and decarbonylation are carbon dioxide (CO_2) and carbon monoxide (CO), respectively. Therefore, hydrocarbons resulting from decarboxylation and decarbonylation contain one carbon atom shorter than the total length of the fatty acid ($C_{(n-1)}$). The benefit of decarboxylation pathway is no hydrogen required to convert a carboxylic acid into a methyl group and CO_2 (as shown in Eq. (1)). For a decarbonylation pathway, carboxylic group is reacted with hydrogen to produce a methyl group, CO, and water (as shown in Eq. (2)). On the other hand, hydrodeoxygenation (HDO) pathway yields generally a hydrocarbon containing the same number of carbon atoms in the molecule as the corresponding fatty acid chain ($C_{(n)}$) and water as shown in Eq. (3). It is noted that two additional reactions, water gas shift (Eq. (4)) and methanation (Eqs. (5-6)) are also needed to be considered due to the formation of CO_2 and CO [35].

$$CO + H_2O \leftrightarrows CO_2 + H_2 \qquad (4)$$

$$CO + 3H_2 \leftrightarrows CH_4 + H_2O \qquad (5)$$

$$CO_2 + 4H_2 \leftrightarrows CH_4 + 2H_2O \qquad (6)$$

The reaction performed in different atmospheric gas strongly affects the reaction performance. Comparison between the reactions performed under inert gas and hydrogen gas using Pd/C catalyst revealed that the reaction under hydrogen atmosphere faster than the case of inert atmosphere or lower concentration of H_2 [36]. In addition, the presence of hydrogen can reduce the aromatization reaction, which is undesirable because aromatics probably form coke leading to deactivation of catalyst [13]. Moreover, aromatization reaction depends on reaction pressure and amount of unsaturated fatty acid [24]. Aromatic compound can increase with increasing an amount of unsaturated fatty acid but opposite trend is observed when reaction pressure is increased. When comparing amount of aromatic compound in deoxygenated product between the use of palm oil and maracuja, soybean oil as starting material, Guzman et al. [24] found that in case of palm oil, aromatic compounds could not be found even at low pressure (25 bar) but very high amount of aromatic compounds were observed at high pressure (90 bar) in case of maracuja and soybean oil. This is due to palm oil consist of polyunsaturated fatty acid, i.e linoleic (C18:2) and linolenic (C18:3), about 12 wt.% while in maracuya and soya is 71 and 64 wt.%, respectively. However, hydroprocessing of palm oil has been scarcely studied and limited to the use only crude palm oil as starting material.

For edible oil production, crude palm oil (CPO) is physically refined by removing impurities to the acceptable levels. Fig. 1 is demonstrated the refinery process of palm oil. Firstly, an impurity called gum (phospholipids, phosphotides) in CPO was removed by precipitation process. This process usually occurs at 90-130 °C and use phosphoric acid as a precipitant. At this state, we will obtain degummed palm oil (DPO). The DPO is then bleached to remove any undesirable impurities such as pigments and trace metals giving a bleached palm oil (BPO). Next, the BPO is deodorized to eliminate free fatty acid content. This step gives refined, bleached, deodorized palm oil (RBDPO) and palm fatty acid distillate (PFAD) as a by-product. Finally, the RBDPO is fractionated to yield refined palm olein and refined palm stearin. It should be noted that PFAD was successfully employed as a starting material for the production of H_2 via steam reforming [37] and methyl ester in near-critical methanol condition [38].

Typically, using of inedible oil and waste cooking oil are focused for biodiesel production to alleviate food vs. fuel debate. However, palm oil shows the advantage of the efficient planting, harvesting and collecting. In this study, the suitable operating conditions for the hydroprocessing of different palm oil feedstocks i.e. crude palm oil (CPO), degummed crude palm oil (DPO) and palm fatty acid distillate (PFAD) over commercial 5 wt% Pd/C was investigated.

2. Experimental

2.1 Chemicals and catalysts

5 wt% Pd/C (Aldrich Chemical Co) was employed as a catalyst. The surface area of the catalyst determined by N_2 adsorption (BET method) using a BEL-SORP automated system is 1026 m^2/g. The starting raw materials i.e. CPO, DPO and PFAD were obtained from Pathum Vegetable Oil, Co. Ltd. (Thailand). The distribution of fatty acids in these feedstocks is presented in Table 1. It is noted that CPO consists of triglyceride higher than 95 wt%, while PFAD consists of 93.2 wt% free fatty acid (FFA). The composition of CPO is similar to DPO (only the gum in CPO is removed). Calibration mixture for ASTM-2887 was purchased from Restex Co.

2.2 Reactor and operational details

For routine experiments, hydroprocessing of CPO, DPO and PFAD were performed in small shaking batch reactors. Prior to the experiments, the catalyst was reduced by hydrogen flow with the rate of 10 ml/min at 200 ºC for 2 h (with the ramp rate of 5 ºC/min). After the reduction, the catalyst was cooled to 30 ºC under nitrogen flow. 0.1 g of reduced catalyst and 2 ml of the reactant were then loaded into the reactor, sealed, and purged by hydrogen gas for several times. The reactors were placed in the furnace at desired temperature with shaking at the maximum speed. After reaction was preceded at desired reaction time, the reactors were removed from the furnace and immersed in a water bath at ambient temperature to stop the reaction.

2.3 Analysis of hydroprocessed product

The gaseous products from each experiment was analyzed by gas chromatography (GC 14-B, Shimadzu Corporation) equipped with thermal conductivity detector (TCD). The liquid products were 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). Liquid samples of 0.1 μl were injected into the column inlet, where the injector and detector temperature were maintained at 350 ºC. The GC oven used temperature programmed by heating from 40 to 350 ºC with ramp rate of 15ºC/min and hold at 350 °C for 20 min. Simulated distillation (according to ASTM 2887) was used in this work to examine product distribution.

The effectiveness of hydrotreating reactions was measured in term of diesel yields. The conversion and diesel selectivity of the products is determined by simulated distillation data as follows [14]:

$$\text{Conversion (\%)} = \frac{\text{Feed}_{360+} - \text{Product}_{360+}}{\text{Feed}_{360+}} \times 100 \qquad (7)$$

where Feed_{360+} is weight percent of the feed which have boiling point higher than 360 °C. Product_{360+} is weight percent of the product which have boiling point higher than 360 ºC.

As diesel is the desired product, diesel selectivity is determined based on the boiling point range, defined as

$$\text{Diesel selectivity (\%)} = \frac{\text{Product}_{180\text{-}360} - \text{Feed}_{180\text{-}360}}{\text{Feed}_{360+} - \text{Product}_{360+}} \times 100 \qquad (8)$$

where $\text{Feed}_{180\text{-}360}$ and $\text{Product}_{180\text{-}360}$ are weight percent of the feed and products, respectively, which have a boiling point between 180 and 360 ºC (diesel molecules) [14].

The liquid hydrocarbon product distribution are classified into four fractions i.e. the 65–150 ºC fraction is most likely alkanes ranging from C_5 to C_8, the 150–250 ºC fraction is most likely alkanes ranging from C_9 to C_{14}, the 250–380 ºC fraction is most likely alkanes ranging from C_{15} to C_{18} (known as middle distillate) and the 380-520 ºC fraction is defined as those compounds have high boiling point above the boiling point of n-heptadecane including unconverted triglyceride starting material, as well as oxygenated products [16].

3 Results and discussion

3.1 CPO

Firstly, the optimum reaction time was determined at the point that diesel-range yield is obtained as shown in Figure 2A. It can be seen that CPO conversion increases with increasing residence time (from 0.25 to 5 h), the conversion increases rapidly at the beginning of the reaction up to 3 h after that it gradually increases. However, maximum diesel yield can be observed at reaction time of 3 h. This is due to the decrease of diesel selectivity after 3 h. As depicted in Figure 2B, lighter hydrocarbon, i.e. 65-150 °C and 150-250 °C, obviously increases with increasing residence time.

Products obtained from hydroprocessing of CPO at 3 h was found to be composed mainly of middle distillate in the range of 250-380 °C (Figure 3B), which are mostly C_{15}-C_{18} hydrocarbon. Particularly, the major liquid products are *n*-pentadecane (C_{15}) and *n*-heptadecane (C_{17}) (result not shown here), which contain one carbon atom shorter ($C_{(n-1)}$) than the total length of corresponding fatty acid i.e. palmitic and oleic acid. Theoretically, the $C_{(n-1)}$ can be produced by two parallel pathways via decarboxylation/decarbonylation whereas the hydrocarbon contain carbon atom same number as the fatty acid ($C_{(n)}$) are insignificantly formed (less than 5wt.%). In contrast, C_{16} and C_{18} are obtained as the main products from the hydroprocessing of CPO catalyzed by NiMo/γ-Al_2O_3 catalyst [24]. For Pd/C catalysts, similar reaction pathway was observed by Kubickova and co-worker who investigated the hydroprocessing of ethyl stearate (C_{18} ester compound) and found the main product is n-heptadecane [39]. These results are also in consistent with Veriansyah et. al. [40], who found that decarboxylation/decarbonylation was the main reaction pathways when Ru, Ni, and Pd catalysts were used, while hydrodeoxygenation was more important when NiMo, CoMo and Pt catalysts were used. It is worthy to note that due to the presence of CO, CO_2, water and hydrogen, the reactions such as water gas shift and methanation could also take place. Therefore identifying the reaction between decarboxylation and decarbonylation is difficult. However, the gaseous products of CO_2 and CO confirm the results of liquid products which contain one shortage of carbon atom, $C_{(n-1)}$. The beneficial of decarboxylation/decarbonylation over hydrodeoxygenation is less demand of hydrogen consumption as shown in Eqs. 1-3, respectively.

The effect of operating temperature was then investigated in the range of 350-450°C. The results shown in Figure 3A revealed that no conversion was observed at temperature of 350°C and 375°C since these temperatures are not high enough to give reasonable conversion and diesel yield. However, when temperature was increased to 400°C, conversion of CPO and yield increased significantly to 70% and 51%, respectively; this could be due to an increase of the rate of decarboxylation/decarbonylation. At higher temperature, CPO conversion increases as a function of temperature but diesel yield starts to decrease. As demonstrated in Figure 3B, 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 remain low but slightly increase with increasing temperature due to the converting of heavier hydrocarbon. Beyond this temperature range, the middle distillate decreases suddenly as it may crack to lighter fraction.

The effect of pressure on conversion and diesel yield is shown in Figure 4. By increasing the pressure 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, the most suitable operating conditions are at temperature of 400°C, pressure of 40 bar and with the reaction time of 3 h.

3.2 DPO

Figure 5 shows the conversion and diesel yield as a function of residence time for DPO feedstock. Similar tendency to the case of CPO was observed, from which the 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 as maximum diesel yield of 70% can be obtained in 1 h. Regarding the effect of temperature, moderate conversion (ca.50%) and diesel yield (ca.45%) can be achieved at low temperature of 350 and 375°C (Figure 6A) while these were not observed in case of CPO. As demonstrated in Figure 6B, 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 6A. For the effect of pressure, it was observed that the operating pressure slightly affects the conversion but not the diesel yield as shown in Figure 7A. By considering the view point of diesel yield, the suitable operating pressure is at 20 bar.

When compared to CPO, higher diesel yield can be obtained from DPO at less severe operating condition since the purity of DPO is higher than CPO as the contaminations of phospholipid compounds are removed. It should be noted that although DPO offers higher diesel yield with milder operating condition than CPO, for further development to industrial scale, the energy consumption during degummed process must also be taken into account and the energy saving during the hydroprecessing period must be compared.

3.3 PFAD

As shown in Figure 8A, 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%. Figure 8B demonstrates the decrease of middle distillate selectivity as a function of residence time. This observed phenomenon could be due to the cracking of middle distillate molecules into light hydrocarbons (C_6-C_{14}). The PFAD conversion in all residence times are found to be higher than DPO and CPO since the compositions of PFAD are mainly free fatty acid, i.e. palmitic acid, oleic acid, and linoleic, which could be easily converted to aliphatic alkane compared to triglyceride. From the study, it is obvious that the operating temperature of 375°C is the best condition as the maximum diesel yield of 81% can be obtained. In case of pressure, increasing pressure can increase conversion as depicted in Figure 10. The operating pressure suggested for PFAD is 40 bar since the maximum diesel yield can be obtained at this condition. It is worthy to note that for DPO and CPO, the operating pressure does not influence the diesel yield. However, with too high pressure, the adverse effect of pressure is observed for PFAD.

From the literature, Immer and co-worker [41] studied deoxygenation of stearic, oleic and linoleic acids over a 5wt.% Pd/C catalyst at 300 ºC, 15 bar, 1.6 g reactant, 23 g dodecane solvent and 350 mg 5% Pd/C catalyst under 10% H_2 and reported that 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 C_{18} free fatty acids, oleic and linoleic, are hydrogenated to stearic acid before decarboxylation. However, since the hydrogenation of the unsaturated C_{18} 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. Moreover, Lestari and co-worker [42] 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 can be concluded that the deoxygenation rates of different saturated fatty acids are independent of carbon chain length of its fatty acids [42]. According to the previous literatures, the deoxygenation of free fatty acids (i.e. palmitic, stearic, oleic, and linoleic acids) can mostly proceed at temperature around 300°C. In this study, higher operating temperature (375 °C) is required for PFAD conversion, which could be due to the containing of mono-, di-, and tri-glycerides. Moreover, others impurities in PFAD can also lead to the decrease of the deoxygenation rates [43]. 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.

4. Conclusion

Catalytic hydroprocessing of three relevant palm oil products i.e. CPO, DPO and PFAD, was investigated using commercial 5 wt% Pd/C. The effects of reaction time, temperature, and pressure were determined to examine optimal operating condition for each feedstock. From the study, the highest diesel range product yield of 81% can be obtained from PFAD with less severe operating condition (lower operating temperature and pressure, shorter residence time) required. It was also revealed that the hydroprocessed products contains one carbon less hydrocarbon ($C_{(n-1)}$) than the corresponding acid i.e. *n*-pentadecane and *n*-heptadecane, which indicates that decarboxylation/decarbonylation are the major reaction pathways. The findings would be an initiative for illustrating the use of relevant refining palm oil for biodiesel production via hydroprocessing and would be useful to manage cultivated palm oil to produce edible oil and biodiesel. For further implementation, the study on techno-economic analysis is recommended.

Acknowledgment

Financial supports from the Thailand Research Fund and Office of the Higher Education Commission are gratefully acknowledged.

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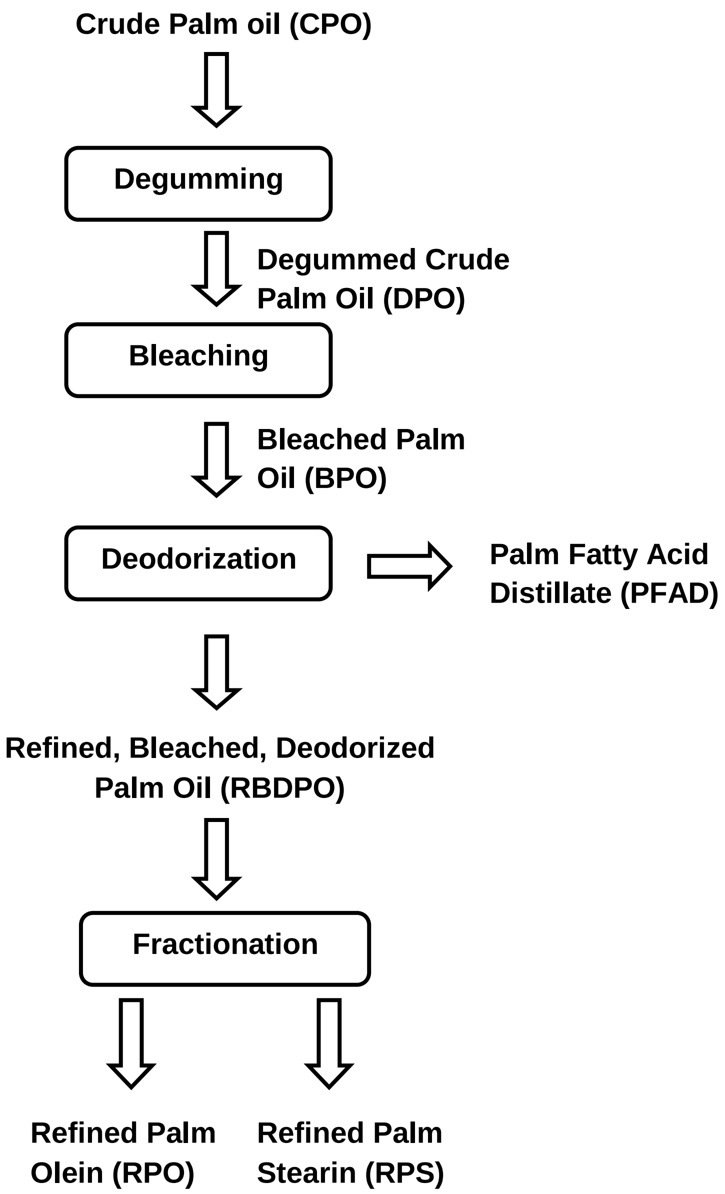

Fig. 1. Physical refining process of crude palm oil.

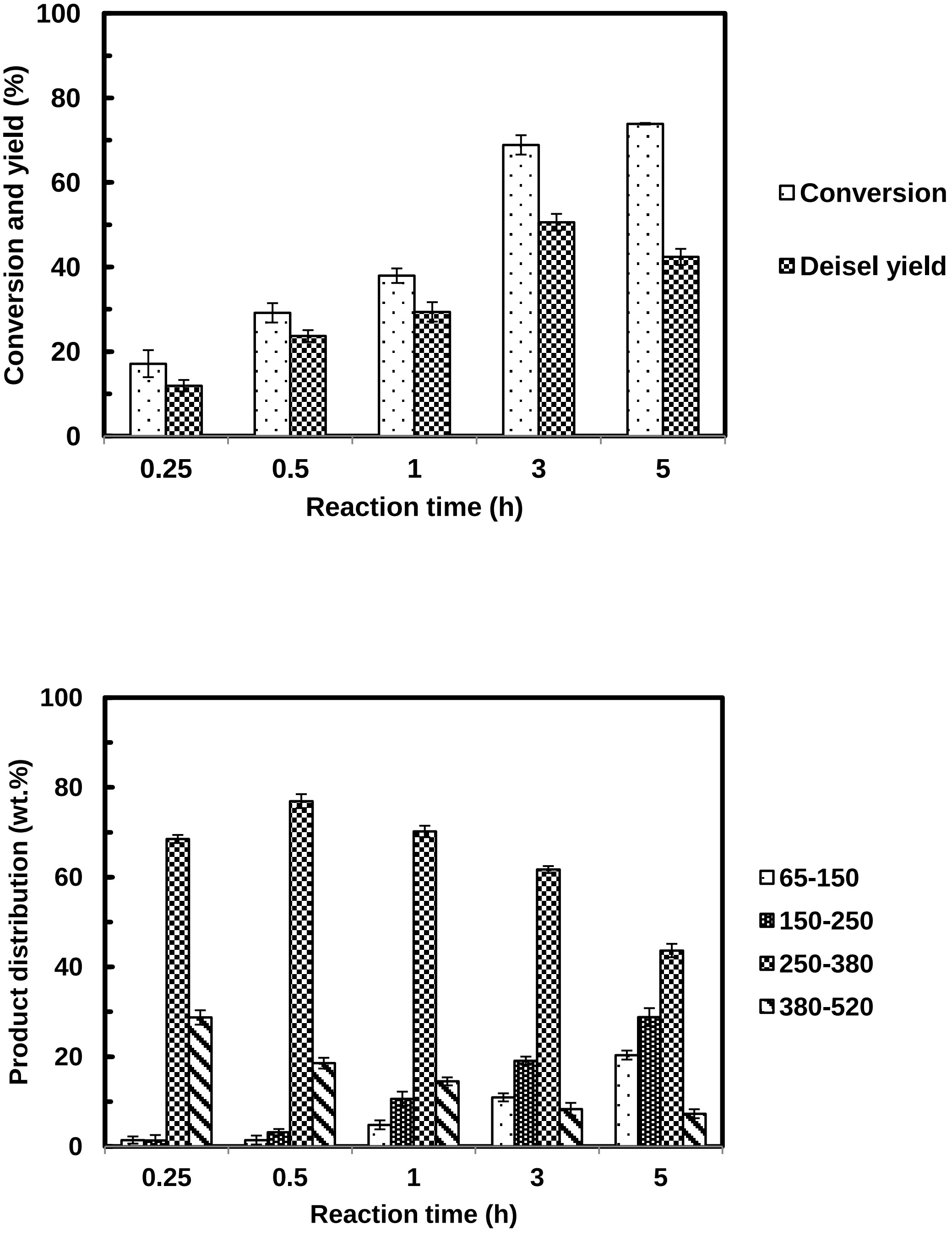

Fig. 2. The effect of reaction time on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of CPO feedstock (operating temperature = 400 °C, operating pressure = 40 bar).

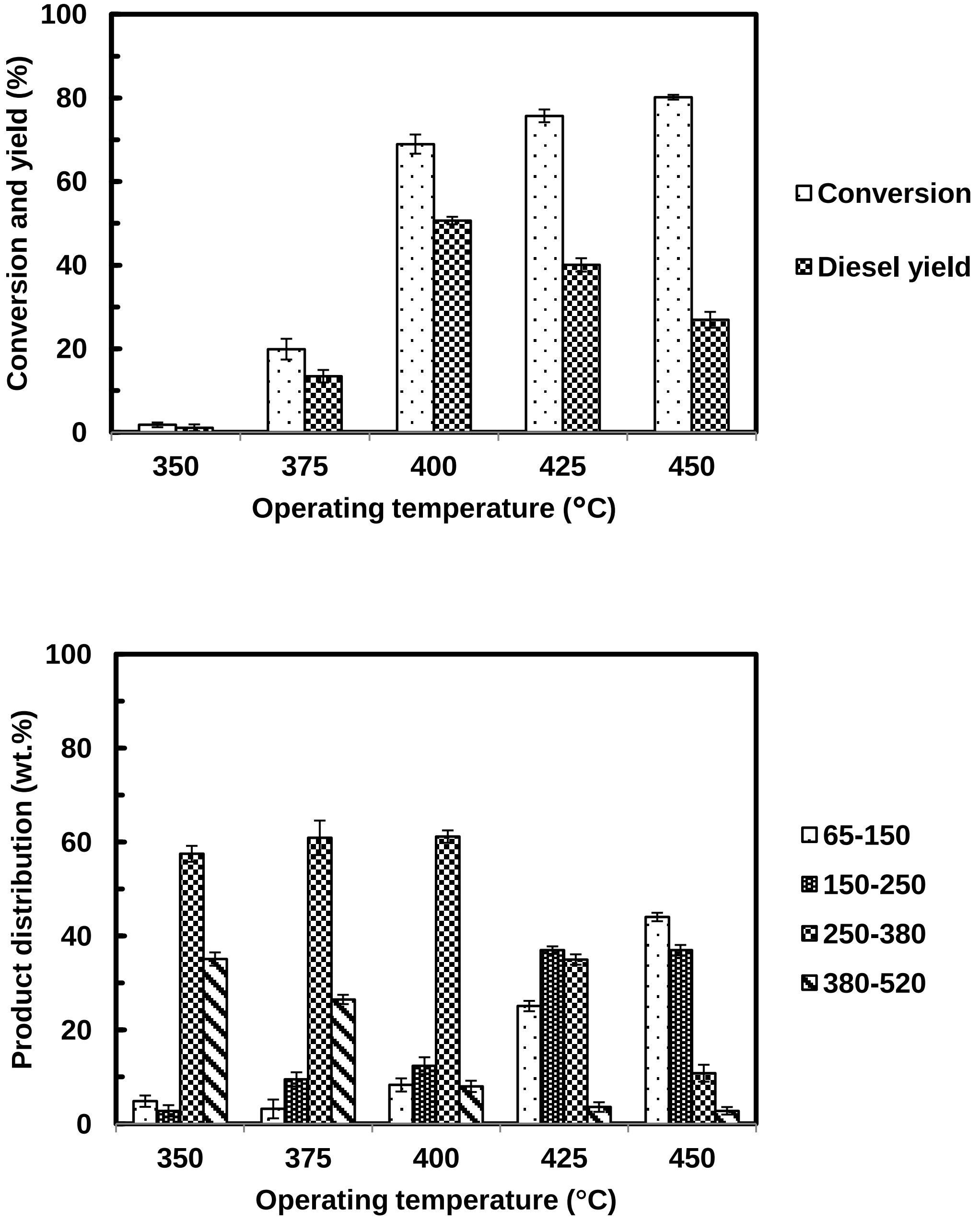

Fig. 3. The effect of operating temperature on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of CPO feedstock (reaction time = 3 h, operating pressure = 40 bar).

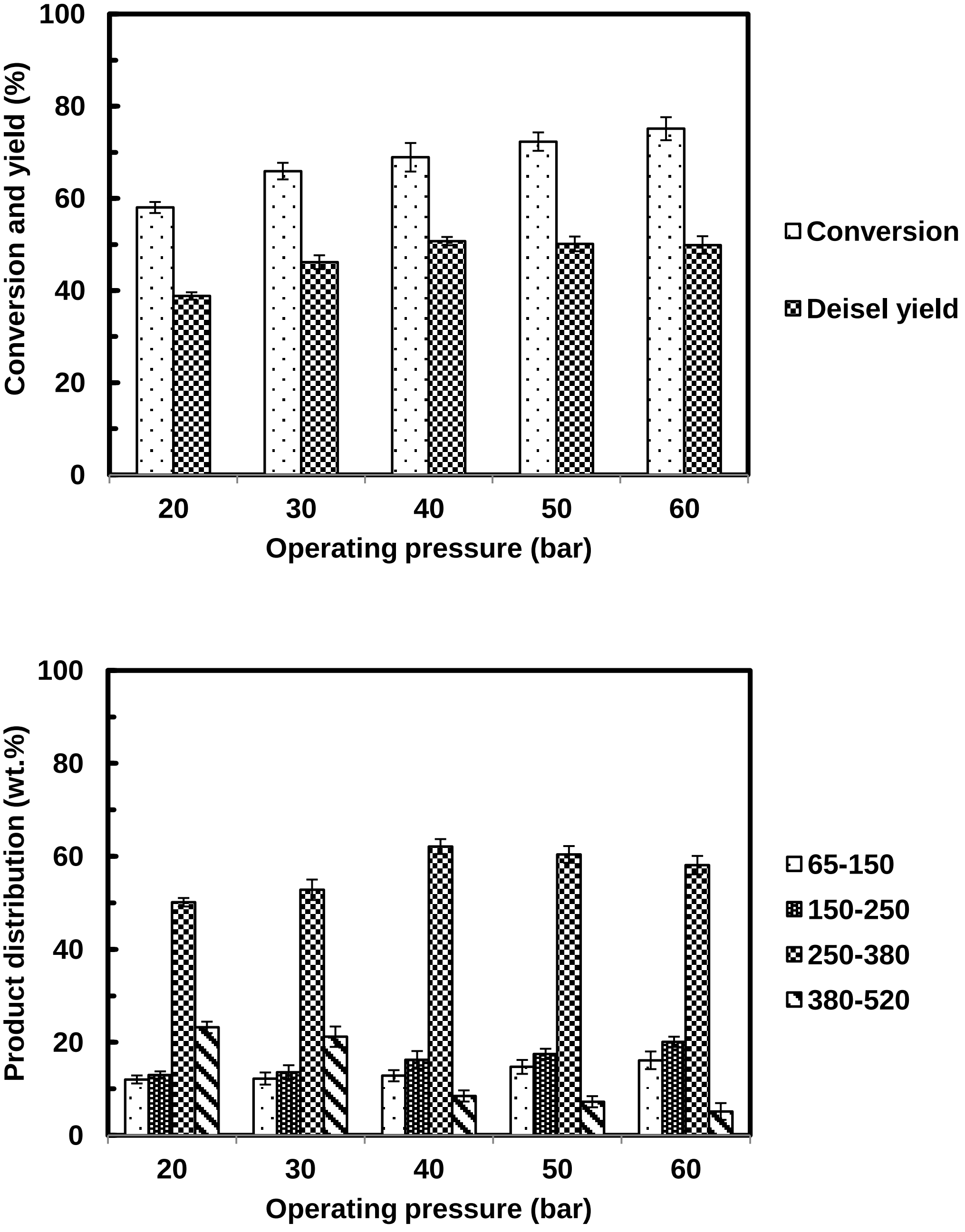

Fig. 4. The effect of operating pressure on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of CPO feedstock (reaction time = 3 h, operating temperature = 400 °C).

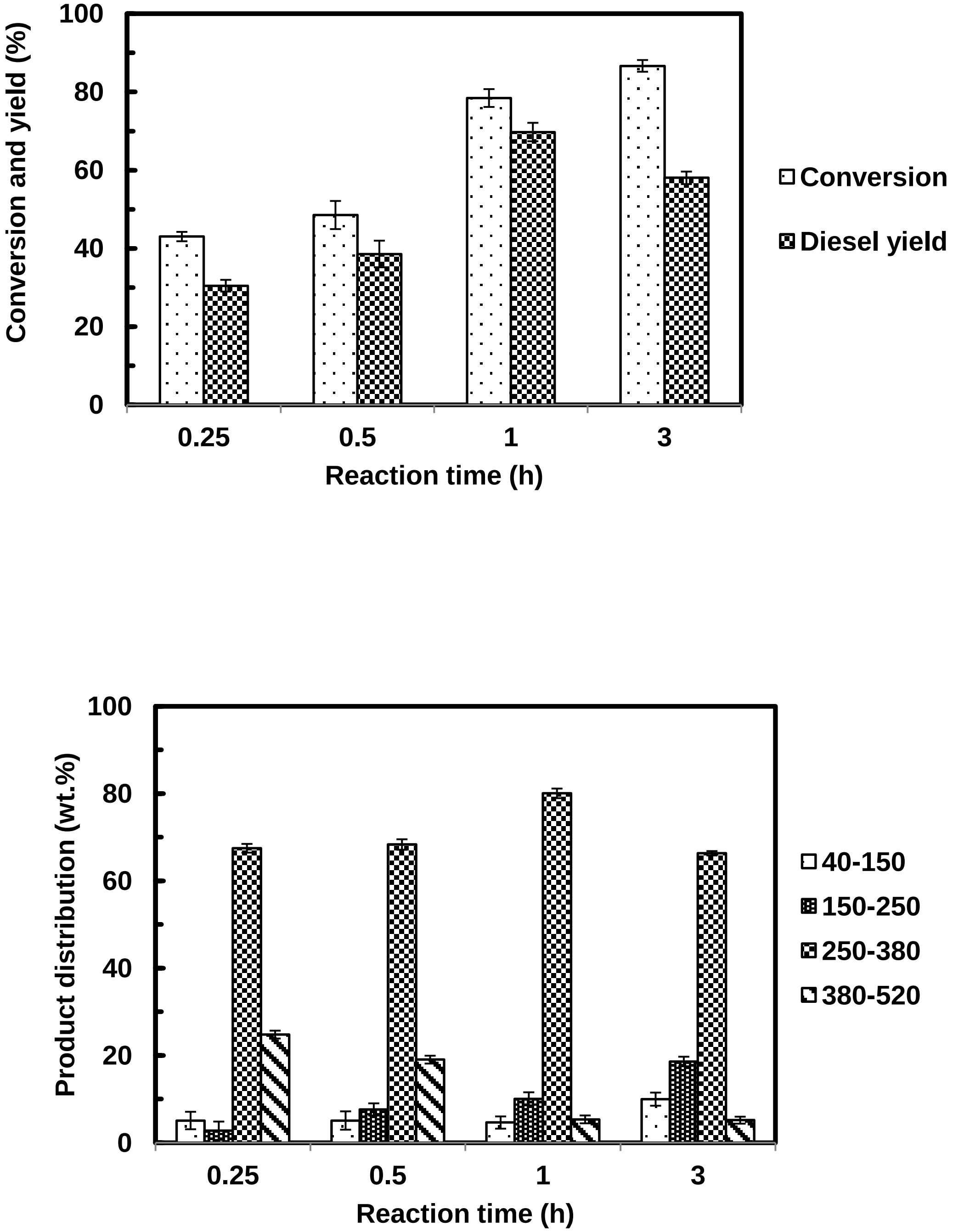

Fig. 5. The effect of reaction time on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of DPO feedstock (operating temperature = 400 °C, operating pressure = 40 bar).

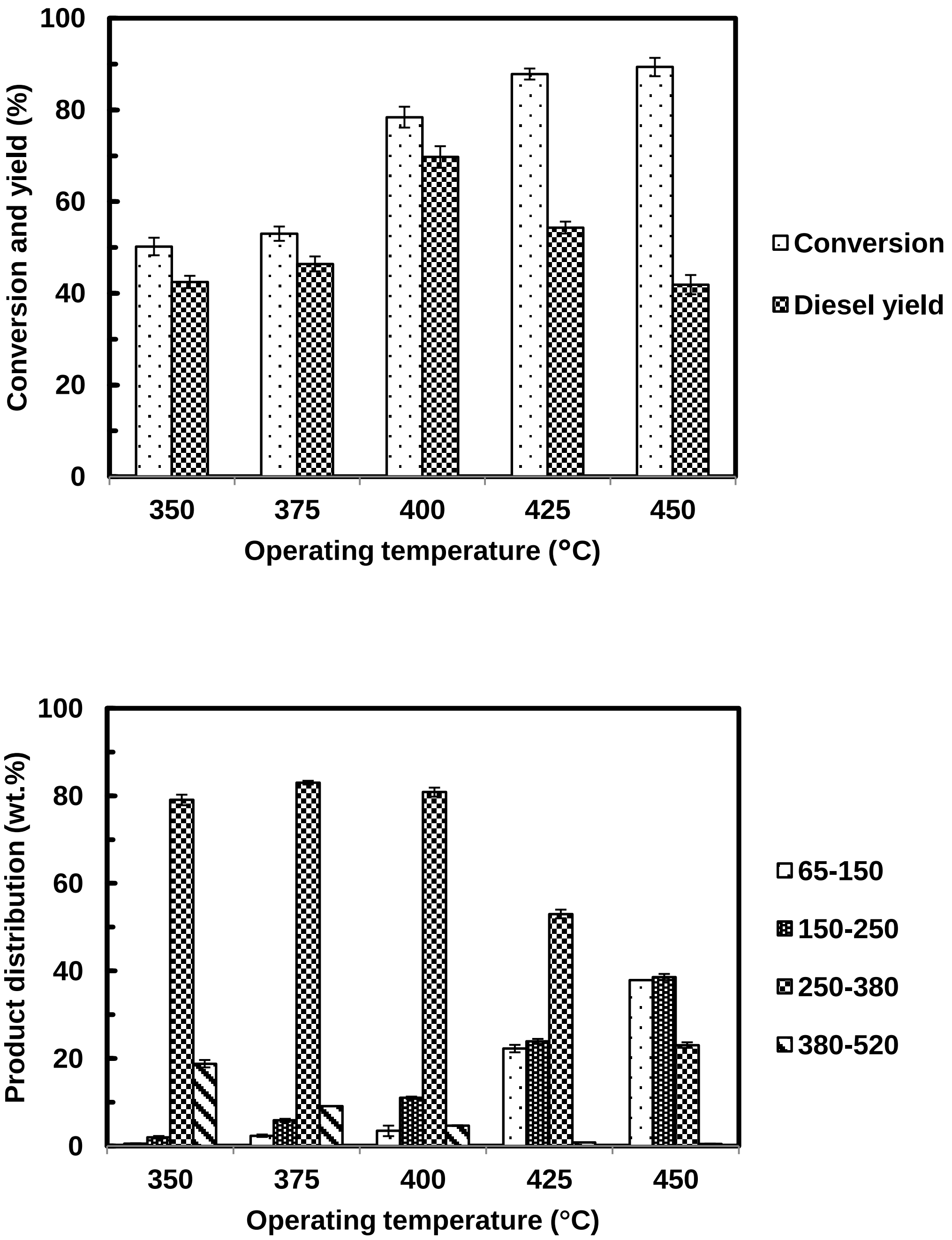

Fig. 6. The effect of operating temperature on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of DPO feedstock (reaction time = 1 h, operating pressure = 40 bar).

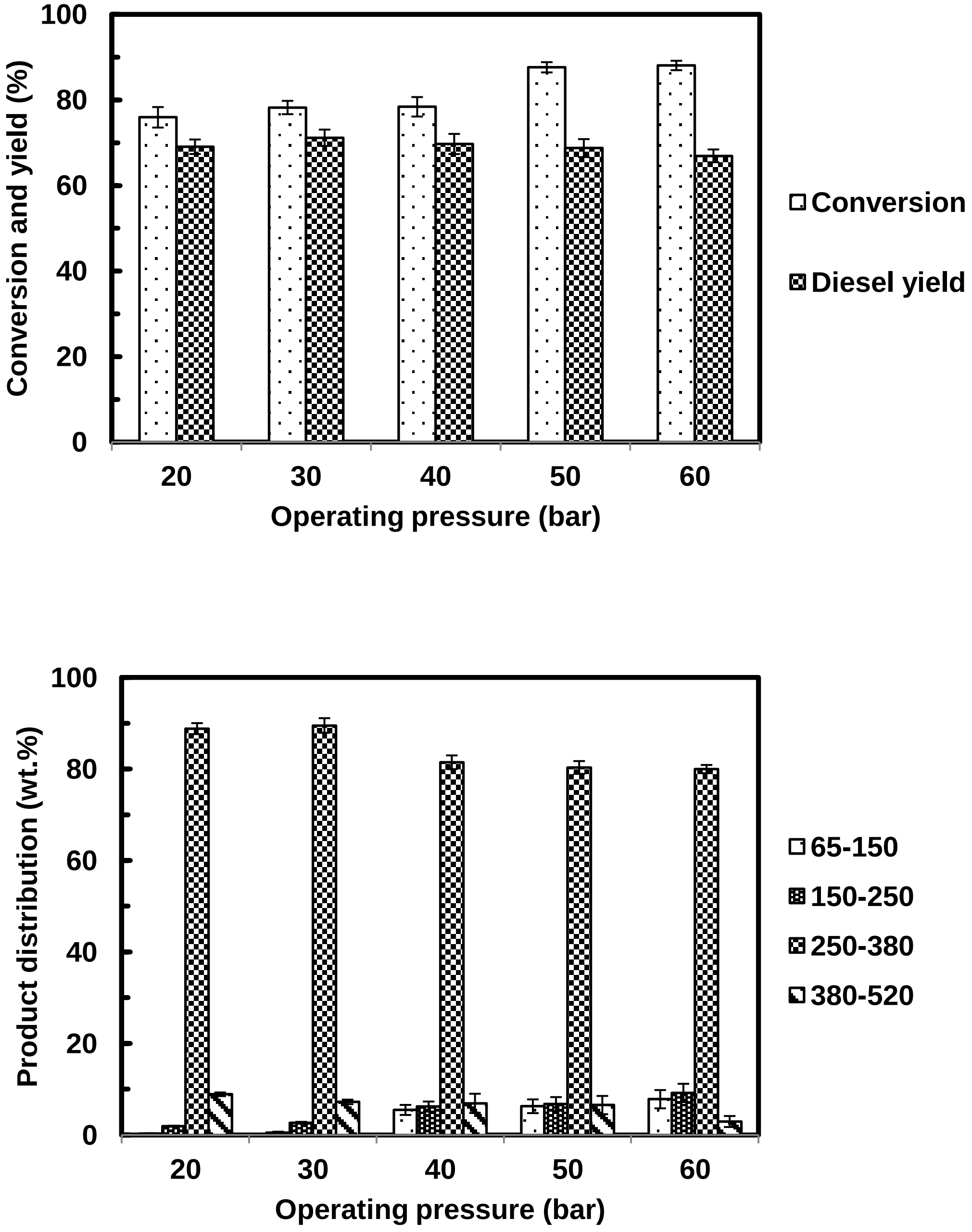

Fig. 7. The effect of operating pressure on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of DPO feedstock (reaction time = 1 h, operating temperature = 400 °C).

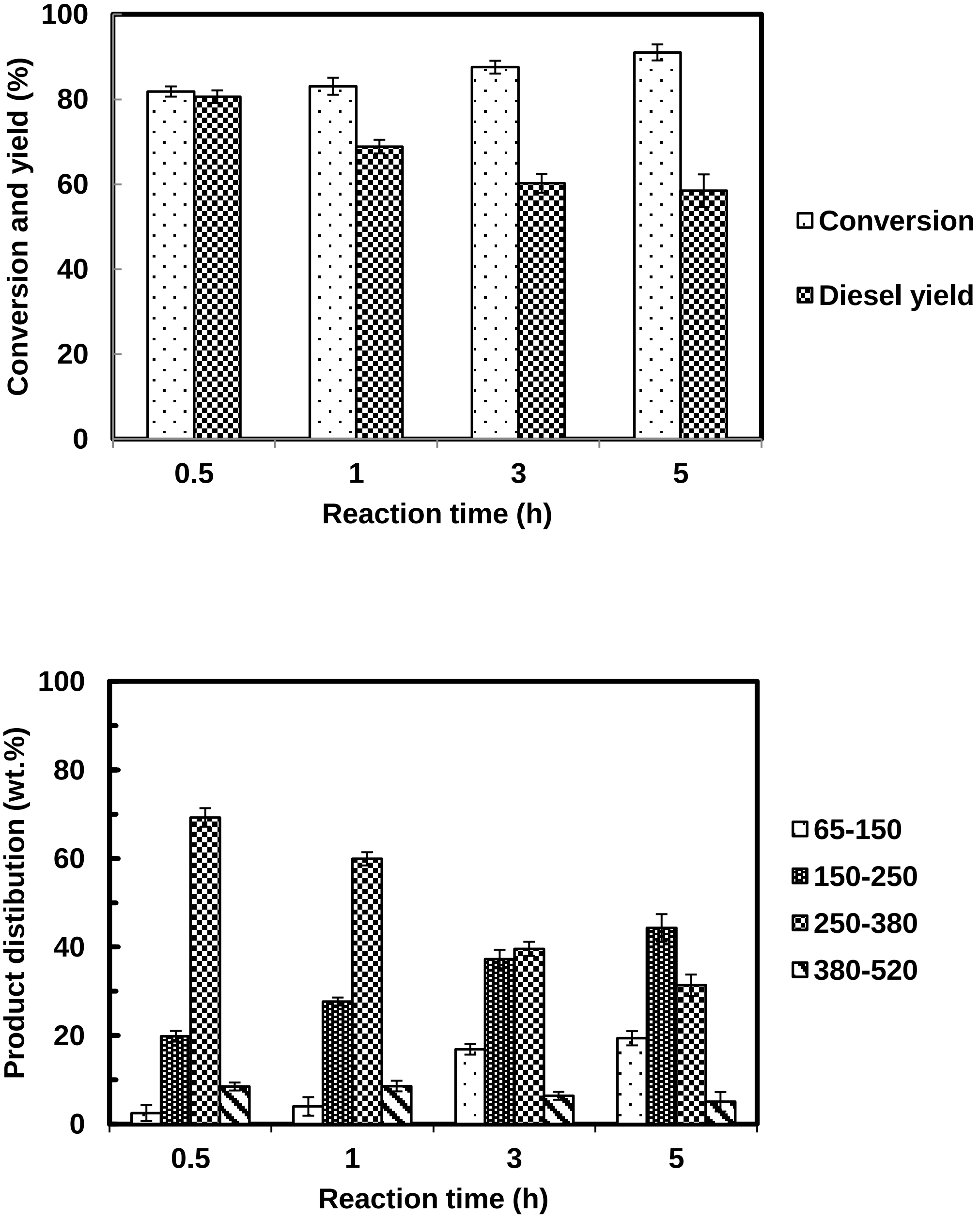

Fig. 8. The effect of reaction time on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of PFAD feedstock (operating temperature = 375 °C, operating pressure = 40 bar).

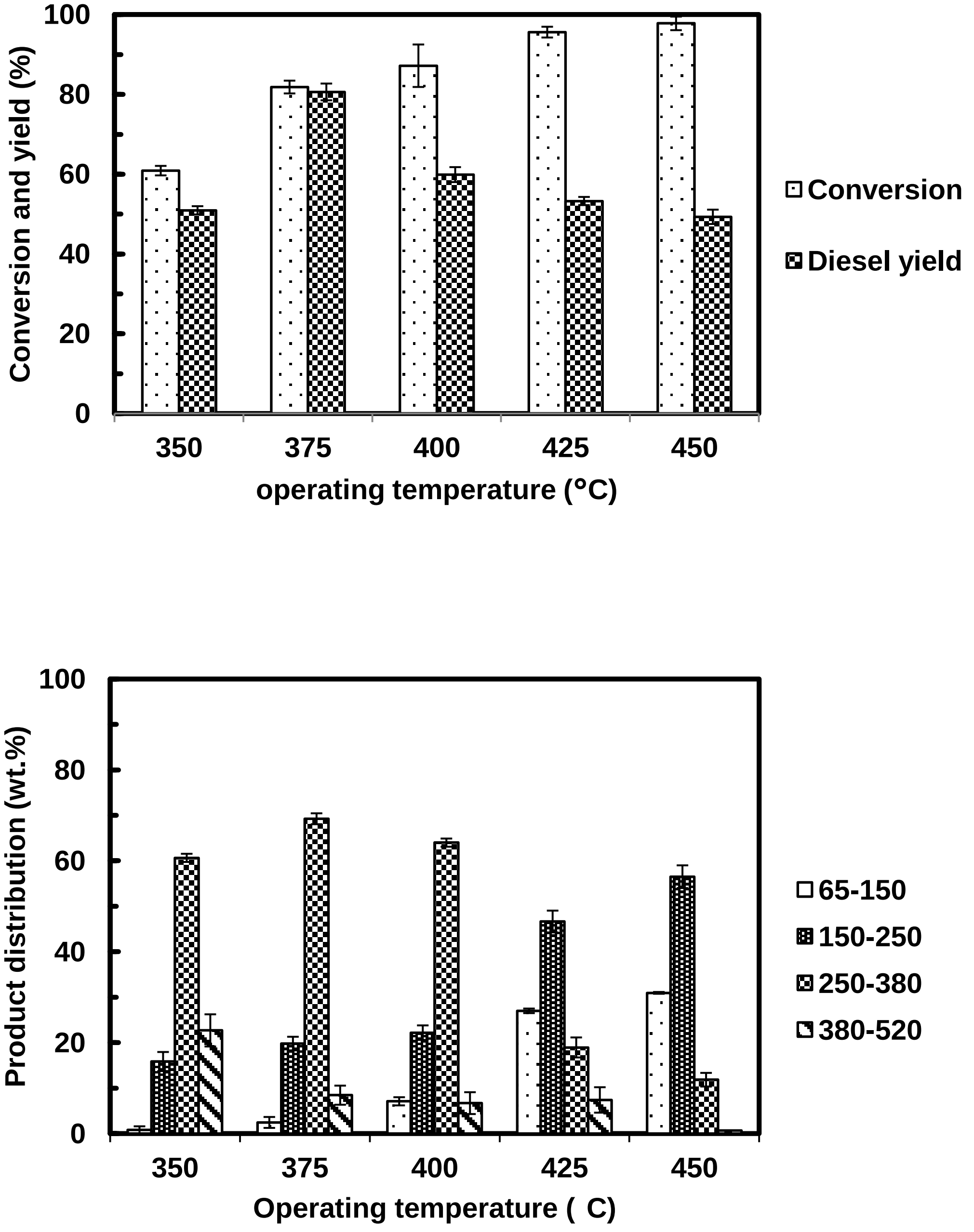

Fig. 9. The effect of operating temperature on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of PFAD feedstock (reaction time = 0.5 h, operating pressure = 40 bar).

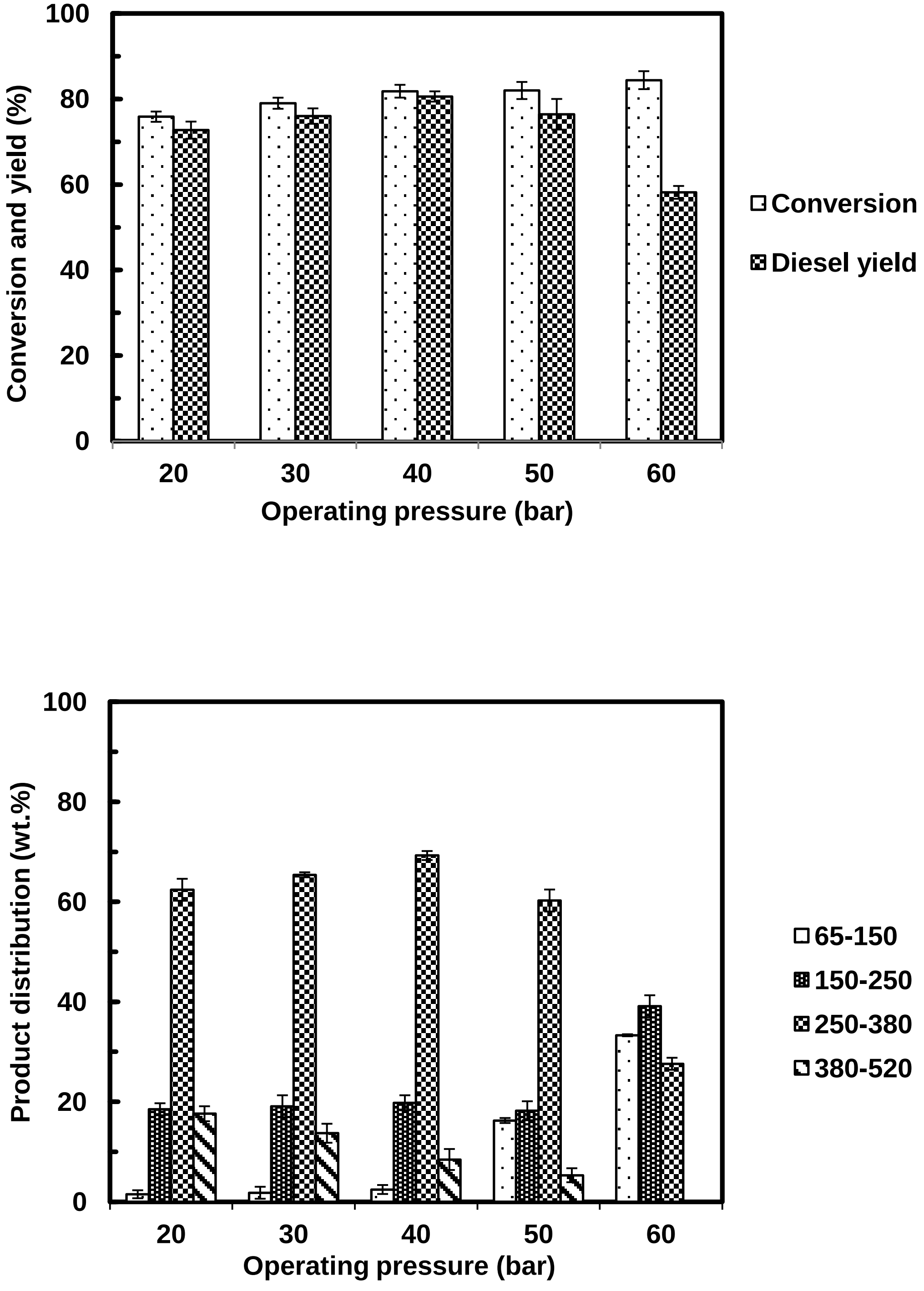

Fig. 10. The effect of operating pressure on (a) conversion and diesel yield and (b) product distribution of liquid hydrocarbon from hydroprocessing of PFAD feedstock (reaction temperature = 375 °C, reaction time = 0.5 h).

Table

Table 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.

SULPHIDE VS CARBIDE CATALYSTS FOR HYDROPROCESSING OF WASTE COOKING OIL FOR BIODIESEL PRODUCTION

Worapon Kiatkittipong[1,*], Chaiyod Kongwattanakul[2],
Suwimol Wongsakulphasatch[1], Navadol Laosiripojana[3],
Piyasan Praserthdam[2], Suttichai Assabumrungrat[2]
[1]Department of Chemical Engineering, Faculty of Engineering and
Industrial Technology, Silpakorn University,
Nakhon Pathom 73000, Thailand
[2] Center of Excellence in Catalysis and Catalytic Reaction Engineering,
Department of Chemical Engineering, Faculty of Engineering,
Chulalongkorn University, Bangkok 10330, Thailand
[3]The Joint Graduate School of Energy and Environment, King Mongkut's
University of Technology Thonburi, Bangkok 10140, Thailand
*Corresponding author: kworapon@su.ac.th

Summary

Waste cooking palm oil is used as a starting feedstock for hydrotreated biodiesel production. Ni- and Co-Mo/γ-Al_2O_3 were pretreated by sulphidation or carburization. The operating temperature of 380°C, hydrogen pressure of 50 bar and reaction time of 6 h were found to be suitable to maximize the diesel yield. Sulphide catalyst provides slightly higher diesel yield than carbide catalyst; however, the carbide catalyst is more promising than the sulphide catalyst in term of reusability. Catalytic performance of the used carbide catalyst after pretreatment is still comparable to the fresh one whereas the regenerated sulphide catalyst is still suffered from activity loss.

Keywords

Hydrotreated biodiesel; Waste cooking palm oil; Sulphidation; Carburization.

Introduction

Hydroprocessing of vegetable oil has been known as a process for biodiesel production. Their advantages over fatty acid methyl ester (FAME) from trans-esterification are such as higher diesel-like, more compatibility to diesel engine, higher cetane number, more stability than that of FAME, and no glycerol formation as a by-product [1, 2].

Palm oil is one of the most potential feedstock for biodiesel production. Guzman et al. [3] investigated hydroprocessing of crude palm oil (CPO) at pilot plant scale using NiMo/γ-Al_2O_3 sulphide catalyst. CPO can be deeply converted into paraffins in the diesel range under operating temperature of 350°C and hydrogen pressure of 40–90 bar.

Since lower cost of raw material leads to lower cost of biodiesel production, many attempts have been focused on using waste cooking oil as a feedstock. For example, Bezergianni et al. [4] investigated hydrocracking of fresh and used cooking oil for biofuels production. Commercial hydrocracking catalyst was pre-sulphided before experiment. The results showed that both feedstocks are suitable for high diesel yields with smaller kerosene and gasoline yields.

In this study, waste cooking palm oil (WCPO) is used as a starting feedstock. The catalytic activity of carburization of Ni- and Co-Mo/γ-Al_2O_3 is compared to conventional sulphide Ni- and Co-Mo/γ-Al_2O_3 hydrotreating catalyst.

Experimental

Catalyst preparation

The catalysts were prepared by incipient wetness co-impregnation. The γ-Al_2O_3 with a surface area of 113.8 m^2/g was used as support. The metal salts used to provide the required metals including ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}.4H_2O$ (99.99%, Merck), nickel nitrate hexahydrate $Ni(NO_3)_2.6H_2O$ (99.99%, Aldrich) and cobalt nitrate hexahydrate $Co(NO_3)_2.6H_2O$ (99.99%, Aldrich). After calcination, the $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ oxide catalysts were activated either sulphidation or carbunization before using.

Pretreatment of feedstock

The general process of pretreatment consists of two steps: filtration and dehydration. Initially, suspended solid impurity was removed by filtration and then the WCPO was repeatedly water-washed and shaken for extraction of water soluble impurities as well as phospholipids. After that the waste cooking palm oil was heated to above 105°C for 1 h to get rid of the water by evaporation.

Reaction performance test

The WCPO and catalyst were loaded into parallel batch reactor under H_2 pressurized.

Organic liquid products were collected and analyzed by gas-chromatography equipped with flame ionization detector (GC-14B, Shimadzu). Distillation temperature was determined by simulated distillation according to the ASTM-2887-D86 procedure.

Results and discussion

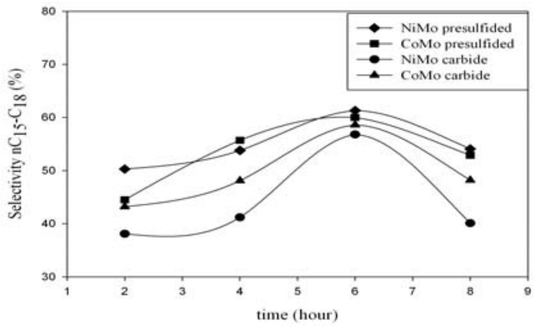

Fig.1 Effect of reaction time on selectivity of n-C_{15}-C_{18} alkanes products in different catalysts. (Operating temperature of 380 °C and hydrogen pressure of 50 bar)

The selectivity of n-C_{15}-C_{18} alkanes increases with increasing reaction time and shows optimum at 6 h in all catalysts as shown in Fig.1. The increase of reaction time leads to an increase in conversion of tri-glycerides and fatty acids to n-C_{15}-C_{18} alkanes (results are not shown here). However, too long reaction time may lead to an increase of lighter hydrocarbons ($< C_{15}$) from cracking. It is worth to note that the complete conversion can be obtained from all catalysts within 6 h; hence the selectivity of n-C_{15}-C_{18} at 6 and 8 h also represent their yield. Sulphide catalysts (both NiMo and CoMo) gave slightly higher diesel range yield than that of carbide catalysts. Among these four catalysts, NiMo sulphide gave the highest n-C_{15}-C_{18} yield of 61.3%.

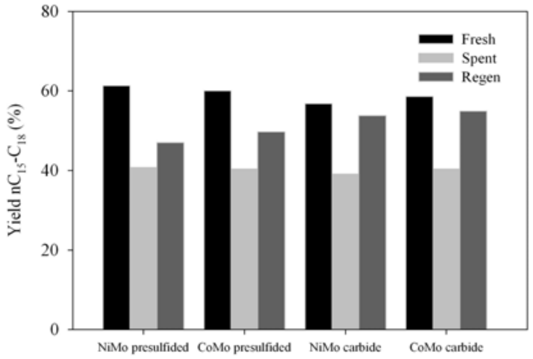

Fig.2 The yield of n-C_{15}-C_{18} with fresh, spent and regenerated catalysts in hydroprocessing (Operating temperature of 380 °C and hydrogen pressure of 50 bar).

The activity of the fresh, spent and regenerated catalysts are shown in Fig. 2. The activity of all spent catalysts dramatically decreased compared with the fresh ones. The spent catalysts were regenerated in fixed bed using air at temperature of 400°C. After pretreatment the catalytic performance of the used carbide catalyst is comparable to the fresh carbide catalyst while the regenerated sulphide catalysts are suffered from activity loss.

Acknowledgments

Financial supports from the Higher Education Research Promotion and National Research University Project of Thailand, Office of the Higher Education Commission (EN278A) and the Thailand Research Fund are gratefully acknowledged.

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THE 6th PURE AND APPLIED CHEMISTRY INTERNATIONAL CONFERENCE 2012

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& THE CHEMICAL SOCIETY OF THAILAND UNDER THE PATRONAGE OF
HER ROYAL HIGHNESS PRINCESS CHULABHORN MAHIDOL

THE HYDROPROCESSING OF WASTE COOKING PALM OIL FOR DIESEL LIKE HYDROCARBONS PRODUCTION OVER Ni-Mo/Al_2O_3 CARBIDE CATALYST

Narisara Rodboon[1], Chaiyod Kongwattanakul[1], Worapon Kiatkittipong[2,*], Piyasan Praserthdam[1] and Suttichai Assabumrungrat[1]

[1] Center of Excellence in Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
[2] Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom 73000, Thailand

*Author for correspondence; E-Mail:kworapon@su.ac.th, Tel.&Fax. +66 34 219 368

Abstract: This work focuses on a utilization of waste cooking palm oil (WCPO) as an alternative feedstock for hydrotreated biodiesel (HBD) production. The reaction was performed in a batch reactor under elevated temperature and pressure. NiMo/Al_2O_3in carbided form was employed as a catalyst. Liquid products are hydrocarbons which mainly identified as C15 - C18 alkanes. The maximum yield of n-C15-C18 alkanes of 61.5% could be obtained at a reaction temperature of 380°C, hydrogen pressure of 50 bar and reaction time of 6 h.

1. Introduction

Energy and environmental crisis are become a crucial problem of the world. Biodiesel is one of the most potential to alleviate the problem especially in transportation sector. However, fatty acid methyl esters from trans-esterification, the first generation of biodiesel, have several limitations. Hydrotreated biodiesel (HBD) nowadays becomes an interest touse as renewable energy for diesel engine. Palm oil is the most potential feedstock for biodiesel production in Thailand; however, as the food vs. fuel debate, many researches are turning to focus on using inedible or waste oil.Waste cooking palm oil (WCPO) is used as a starting feedstock instead of fresh palm oil in order to reduce cost of raw material and environmental burden to treat it. WCPO has thetriglycerides or fatty acids ranging from C_{16}-C_{18}which may suitable for producing diesel fuel.

Several researchers have tried to develop new catalysts for hydroprocessing because waste cooking crude oil feedstocks contain amounts of sulfur, nitrogen, and oxygen, which form to heteroatom compounds. The activity of Mo_2C/Al_2O_3 had over two times greater than commercial sulfides Mo-Ni-S/Al_2O_3catalyst [9]. Moreover, the bimetallic compounds showed high activity and stability compared with the corresponding monometallic carbides [8].

In this study, hydroprocessing of WCPO was performed in a batch reactor under operating temperature of 360, 380, 400 and 420 ˚C, hydrogen pressure of 50 bar, reaction time 2-8 h catalyzed by NiMo/Al_2O_3 carbide in-house prepared catalysts. The yield of C15 - C18 alkanes is calculated from simulated distillation following by ASTM-2887-D86 procedure.

2. Materials and Methods

2.1 Chemicals

All chemical used as catalyst precursors were ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}.4H_2O$ (99.99%, March) and nickel nitrate hexahydrate Ni $(NO_3)_2.6H_2O$ (99.99%, Aldrich).γ-Al_2O_3 with surface area of 113.8 m^2/gwas used as a support. The gas employed were air (T.I.G), N_2 (T.I.G, 99.99%), He (T.I.G, 99.999%), CH_4 (T.I.G, 99.999%), H_2 (T.I.G, 99.999%) and 1% (v/v) O_2/He (T.I.G, 99.999%).

WCPO was obtained from Sarmyarn restaurant in Bangkok. The WCPO contains some food particles, phospholipids, grease, and wax. The general process of pretreatment consists of two steps including filtration and dehydration. Initially, suspended solid impurity was removed by filtration and then the WCPO was repeatedly water washed and shaken for extraction of water soluble impurities as well as phospholipids. After that the waste cooking palm oil was heated to above 105˚C for 1 h to get rid of water by evaporation [1].

2.2 Preparation of catalysts

NiMo/$Al_2O_3$was prepared by the incipiant wetness impregnation method.A heated aqueous solution of a mixture of $(NH_4)_6Mo_7O_{24}.4H_2O$ and $Ni(NO_3)_2.6H_2O$ was added dropwise to γ-Al_2O_3 support. Thepreparation of the carbide catalysts was carried out by converting the oxide precursor material into carbides in a reactive gas flow of 20% CH_4/H_2.

2.3 Catalyst characterizations

XRD was performed to determine the bulk phase of catalysts by SIEMENS D 5000 X-ray diffractometer connected to a computer with Diffract ZT programs version 3.3 for fully control of the XRD analyzer.

The BET apparatus for the multiple point method consisted of two feed lines for helium and nitrogen

(Micromeritics ASAP 2020). Temperature programmed reduction (TPR) was performed to determine the reduction behaviors of the samples by using a Micrometritics Chemisorb 2750.

2.4 Experimental

The 2 ml of WCPO and 0.01 grams of catalyst were loaded into a tubular reactor and place into a batch reactor. The reaction for hydroprocessing experiments were performed under elevated temperature and pressure. The reactor was purged for several times to remove air in the reactor. The reactor was compressed to desired hydrogen pressure and then put into the furnace for desired temperature.

2.5 Analysis products

After the reaction run, aqueous phase and organic liquid phase were physically separated and analyzed by gas-chromatography equipped with flame ionization detector (GC-14B, Shimadzu). In addition, The fraction distilled from 250 to 380°C was the major distillated fraction, the diesel range (n-C_{15}-C_{18}) were determined by program simulated distillation curve according to the ASTM-2887-D86 procedure. Theyields of n-C_{15}-C_{18} alkanes products of base on a the total liquid products basis as shown in equation (1) and (2) [2].

$$\text{Conversion (\%)} = \frac{\text{Feed}_{360+} - \text{Product}_{360+}}{\text{Feed}_{360+}}.100 \qquad (1)$$

$$\text{Product selectivity (\%)} = \frac{\text{Product}_{A\text{-}B} - \text{Feed}_{A\text{-}B}}{\text{Feed}_{360+} - \text{Product}_{360+}}.100 \qquad (2)$$

In equation (1), Feed_{360+} and Product_{360+} are wt% of the feed and product respectively, which have a boiling point higher than 360ºC. In equation (2), $\text{Feed}_{A\text{-}B}$ and $\text{Product}_{A\text{-}B}$ are the wt% of the feed and product respectively, which have a boiling point range between A and B degrees Celsius.

Huber et al., 2007 and Mikulec et al., 2010 used yield of diesel range instead of selectivity by assuming triglyceride and free fatty acid are completely converted (100% conversion). In this study, selectivity are defined selectivities of nC15-C18 alkanes products (which corresponding to distillation temperature in the range of 250-380ºC) based on the total yield of organic liquid products. Yield can be used only complete conversion which no observe triglyceride and fatty acid in the products.

3. Results and Discussion

3.1 Catalyst characterizations

The BET surface area, pore volume and diameter of all catalyst samples are given in Table 1.The BET surface area further decreased when NiMo/Al_2O_3 oxide catalyst was converted into NiMo/Al_2O_3 carbide catalyst. Nevertheless, the decreasing in surface area sustained by supported carbides can be attributed to the increase of the metallic concentration in the form of carbon fiber on the surface [6]. The presence of carbon fiber in prepared NiMo/Al_2O_3 and CoMo/Al_2O_3 carbide are illustrated by H_2-TPR which will be discussed later. The properties of the carbide catalysts were changed from slab structure to the hexagonal close-packed structure [3]. Moreover, the pore volume and pore diameter slightly increased because sintering of support in carburization.

Table 1: The BET surface area, pore volume and pore diameter of support and various catalysts

Catalyst	A_{BET} (m^2/g)	V_p (cm^3/g)	D_{BJH} (nm)
γ-Al_2O_3 support	113.8	0.2382	5.20
NiMo/Al_2O_3 oxide	97.24	0.1770	5.11
NiMo/Al_2O_3 carbide	70.62	0.1863	5.87

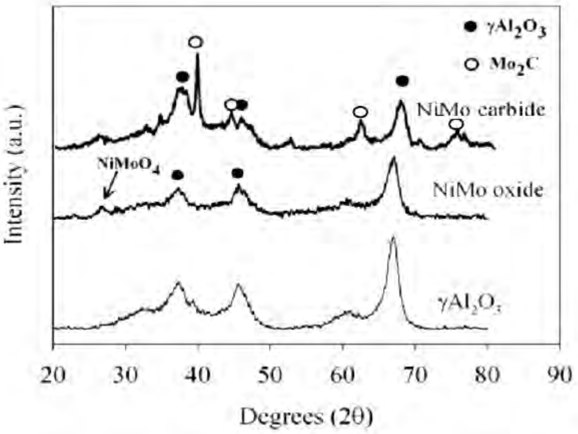
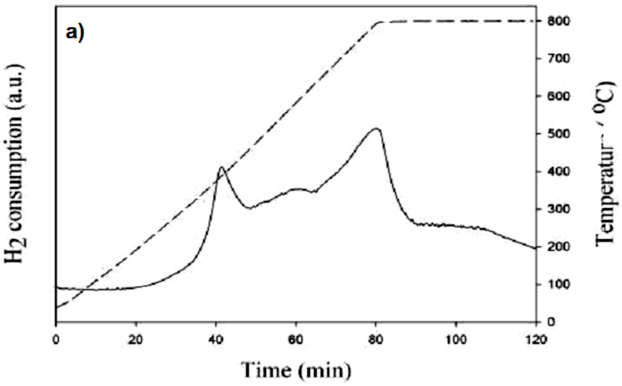


Figure 1. XRD patterns of γ-Al_2O_3 supports, NiMo/Al_2O_3oxide and carbide catalysts.



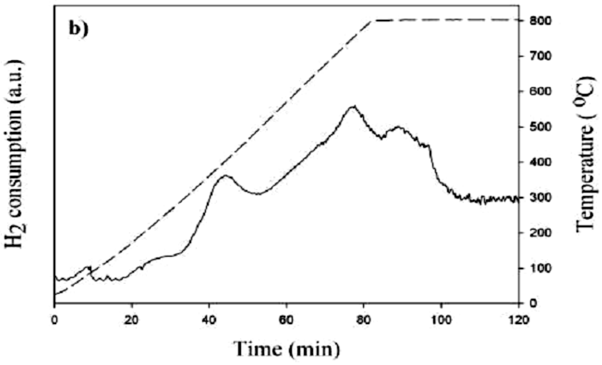


Figure 2. TPR profiles of a) NiMo/Al_2O_3 oxide catalyst b) NiMo/Al_2O_3 carbide catalyst.

The XRD spectra for γ-Al_2O_3 supports and NiMo/Al_2O_3 oxide catalysts are shown in Figure 1. Three peaks at 38°, 46° and 67° were observed for all catalysts. These three peaks were assigned to the γ-Al_2O_3 phase [10]. For the NiMo/Al_2O_3 oxide catalyst exhibits slight diffraction peak located at 26.48 and 26.56 respectively. This can beassigned the XRD peak of $NiMoO_4$ which corresponding with Vallejo et at., 2005.In contrast, the characteristic peak of nickel oxide (37.3°, 43.3°, 62.8° and 75.5°) and molybdenum oxide (MoO4 at 27°, 34°, 49°, 53°, and 55°) [11] are not appearance in our sample. The absence was due to the XRD pattern of γ-Al_2O_3 overlap with in the 2θ interval. For the XRD patterns of NiMo/Al_2O_3 carbidedid not exhibit significant peaks of Ni since its low loading. The XRD peak of identical β-Mo_2C crystals was observed at 38.9°, 44°, 64.5° and 74.3° [6,11].

Temperature-programmed reduction of hydrogen (H_2-TPR) was performed in order to determine the reduction behaviours. The H_2-TPR profiles of the NiMo/Al_2O_3 oxide catalyst and NiMo/Al_2O_3 carbides catalystare shown in Figure 2 a) and 2 b) respectively. The peak of the NiMo/Al_2O_3 oxide catalyst reduction located at temperature lower than 400°C could be assigned to the reduction of surface oxygen bonded of MoO_3 in the oxide precursor[12]. The reduction temperature for NiMo/Al_2O_3 oxide was observed first peak at temperature 400°C [13]. TPR profile of nickel supported on γ-Al_2O_3 has three ranges of the reduction process. Only reduction process of NiO (not interacted with γ-Al_2O_3) were located between temperature 240-260 °C and two ranges of NiO-interacted with γ-Al_2O_3were located between temperature 420-440 °C and 520-540 °C.The NiMo/Al_2O_3 carbide catalyst has peak maximam at around 400 °C. This peak is due to the reduction of surface oxygen on passivated carbided Mo[11]and Ni metal promoter. The absence of above peak at lower temperature in carbide catalysts show that MoO_3 is completely converted into carbide during carburization.

3.2 The yields of n-C_{15}-C_{18} alkane products

The effect of reaction temperature and reaction time on yield of n-C_{15}-C_{18} alkanes products are shown in Figure 3. The results shown that the yield of n-C_{15}-C_{18} alkanes products wereinitially increased with reaction time. However, too long of reaction time lead to lower yield of the n-C_{15}–C_{18} alkanes. The yield of the n-C_{15}–C_{18} alkanes decrease as the reaction temperature increases to 420˚C. Due to cracking of normal alkanes to lighter hydrocarbonswith long reaction period and operating temperatureas shown in the Figure 3, the maximum yield of n-C_{15}-C_{18} alkanes products reach at reaction time of 6 hours. The maximum yield of n-C_{15}-C_{18} alkanes products is 61.5% and 100% conversionunder the temperature 380˚C and hydrogen pressure 50 bar and reaction time of 6 hours.The performance of NiMo/Al_2O_3 oxide catalyst are not proceed because this form not react for this reaction.

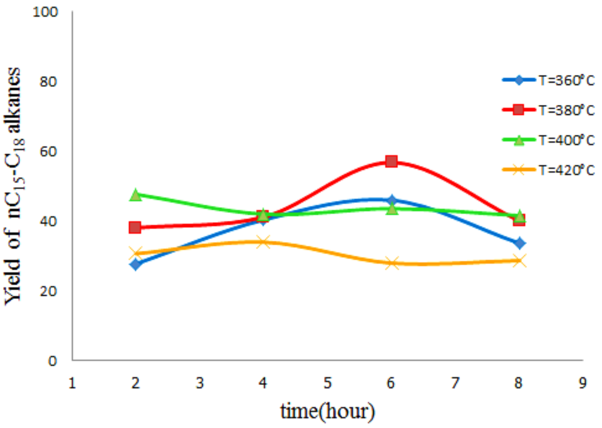


Figure 3. Yield of nC15-C18 alkane products over NiMo/Al_2O_3 carbide catalyst. (hydrogen pressure of 50 bar)

4. Conclusions

In this work, the hydrotreated process of WCPO gives the biodiesel production over NiMo/Al_2O_3 carbide catalyst. The maximum yield of of n-C_{15}-C_{18} alkane productswas 61.5% under the temperature 380˚C and hydrogen pressure 50 bar and reaction time of 6 hours.

Acknowledgment

Financial supports from the Thailand Research Fund and Office of the Higher Education Commission are gratefully acknowledged.

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P-Mo-13 **Preparation and Activity Evaluation of Hydrotreating Catalysts Based on Coke Derived Activated Carbon**
Yu Shi, Song Chen and Jinwen Chen, *Natural Resources Canada, CanmetENERGY, Devon, AB, Canada*

In this study, the catalyst support effect was evaluated by conducting pilot plant comparative performance tests with two activated carbon–based catalysts, an alumina-supported catalyst, and two commercial hydrotreating catalysts. Under the same test conditions, the activated carbon–supported catalysts give better hydrotreating performance than the commercial catalysts.

P-Mo-14 **Biojet Fuel Production from Catalytic Cracking and Hydrocracking of Vegetable Oil**
Huali Wang(K), Craig DiMaggio, Manhoe Kim, Shuli Yan, Steven Salley and Simon Ng, *Chemical Engineering and Material Science, Wayne State University, Detroit, MI*

This study is to synthesize, characterize and test zeolite supported noble metal, transition metal nitride and carbide catalysts for their activities in hydrocracking of vegetable oils to produce jet fuel products.

P-Mo-15 **Production of Green Diesel from Brown Grease via a Two-Step Catalytic Hydrogenation/Decarboxylation**
Elvan Sari[1], Craig DiMaggio[2], Manhoe Kim[2], Steven O Salley[1] and Simon Ng[2], *(1)Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, MI, (2)Chemical Engineering and Material Science, Wayne State University, Detroit, MI*

Brown grease as a potential low cost and non-food competing feedstock was converted to green diesel via two-step reaction; double bond hydrogenation and decarboxylation under low pressure with minimum hydrogen consumption. The product was comprised of mainly n-pentadecane and n-heptadecane.

P-Mo-16 **Adsorption of Pyrolysis Oil Compounds on Oxide Catalysts**
Chandramouli Vaddepalli(K) and Friederike C Jentoft, *Chemical, Biological and Materials Engineering, University of Oklahoma, Norman, OK*

The adsorption and reaction of hydroxyacetone, an important and representative pyrolysis oil constituent, on a variety of oxides (SiO_2, Al_2O_3, TiO_2, ZrO_2, CeO_2) was investigated using IR spectroscopy as the primary method. Hydroxyacetone interacts strongly with all oxide surfaces and cannot be desorbed without residues remaining on the surface.

P-Mo-17 **Reaction Network and Kinetics of the Conversion of Triglycerides on Supported Pt Catalysts**
Kyle W Elam, Lance L Lobban and **Rolf E Jentoft**, *Chemical, Biological and Materials Engineering, University of Oklahoma, Norman, OK*

We have investigated the reaction network and kinetics for the conversion of triglycerides to hydrocarbons on supported Pt catalysts in batch reaction with and without the addition of hydrogen. Both the metal and the support are active for triglyceride conversion with competitive surface adsorption influencing the reaction rate.

P-Mo-18 **Utilization of Glycerol as Transportation Fuel**
Worapon Kiatkittipong[1], Parinya Intaracharoen[1], Navadol Laosiripojana[2] and Suttichai Assabumrungrat[3], *(1)Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom, Thailand, (2)The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Bangkok, Thailand, (3)Center of Excellence in Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand*

Tert-butyl alcohol was employed to replace isobutylene in the reaction with glycerol to produce glycerol ethers cetane enhancer. A reactive distillation was applied to remove water from the reaction zone. FCC gasoline self-etherification with glycerol showed great environmental benefits. Ethers produced renewably from glycerol could extend the transportation fuel volume.

P-Mo-19 **The Effect of CO_2 and Coke Precursors on the Catalytic Partial Oxidation of Methane**
McKenzie P Kohn[1], **Amanda Simson**[1](K), Marco J Castaldi[2] and Robert J Farrauto[3], *(1)Department of Earth and Environmental Engineering, Columbia University, New York, NY, (2)Earth and Environmental Engineering, Columbia University, New York, NY, (3)BASF Corporation, Iselin, NJ*

This research investigates the effect of CO_2 and higher-order hydrocarbons that are found in CH_4 sources such as landfill gas and real natural gas on the performance of a Rh/Al_2O_3 monolithic catalyst.

Utilization of glycerol as transportation fuel

Worapon Kiatkittipong [1*], Parinya Intaracharoen[1], Navadol Laosiripojana[2]
and Suttichai Assabumrungrat[3]
[1] *Department of Chemical Engineering, Faculty of Engineering and Industrial Technology,*
Silpakorn University, Nakhon Pathom 73000, THAILAND
[2] *The Joint Graduate School of Energy and Environment,*
King Mongkut's University of Technology Thonburi, Bangkok 10140, THAILAND
[3] *Center of Excellence in Catalysis and Catalytic Reaction Engineering,*
Department of Chemical Engineering, Faculty of Engineering,
Chulalongkorn University, Bangkok10330, THAILAND
*kworapon@su.ac.th

Introduction

Glycerol, a major by-product from biodiesel production, is expected to be oversupplied in the near future. Di- and tri-*tert*-butyl ethers of glycerol (DTBG, TTBG) are usable as a potential cetane enhancer for diesel [1]. Karinen and Krause [2] studied the etherification of glycerol with iso-butylene (IB) over Amberlyst 35 catalyst. Due to the shortage of IB, tert-butyl alcohol (TBA) was employed to replace IB in the reaction with glycerol; however water formation inhibited the catalyst activity [3]. Therefore, as the first approach, we suggested the use of reactive distillation (RD) to remove water from the reaction zone in this study. Moreover, in our previous study, fluidized catalytic cracking (FCC) gasoline was used for broad range of ethers production by self-etherification with ethanol. The process showed beneficial over "gasohol" by enhancement of ethanol supplement simultaneous with its quality improvement [4-5]. Hence, for the second approach, glycerol was expected to supplement in gasoline by etherification with entire FCC gasoline [6].

Experimental

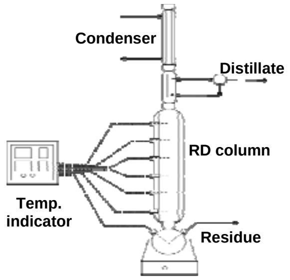
The reactive distillation set-up consists of a four-neck round bottom flask with a mantle heater served as the reboiler, the vacuum-insulated column and the condenser (Fig. 1).

For FCC self-etherification, the reaction was carried out in an autoclave reactor at 70 °C for 10 h under a N_2 pressure of 2.6 MPa. The initial reaction mixture contained 84 cm^3 of FCC gasoline, 16 cm^3 of glycerol and 10 g of catalyst.

Results and Discussion

From the simulations (not shown here), the optimum design for the RD column is 6 rectifying stages and 6 reaction stages without stripping stage. A set of experiments was carried out at the suitable configuration obtained from the simulation. The liquid mole fraction profile of each component and temperature profile along the reactive distillation column were shown in Fig. 2. The vapor-liquid equilibrium stages ensure that water is produced and excess TBA exists in the top of the column. The products i.e. MTBG, DTBG and TTBG are in the bottom stream. The simulations are in good agreement with the experimental results.

As shown in Fig. 3, etherified FCC gasoline with glycerol shows higher distillation temperature than that of original FCC gasoline and the shape of distillation curve is more similar to that of original FCC gasoline than that etherified with ethanol. The olefin content decreased opposing with increasing of octane number (from 88.0 to 90.1) due to the formation of glycerol-derived ethers, and the etherified gasoline product has lower bRvp than that of original FCC gasoline (decrease from 6.6 to 4.5 psi).



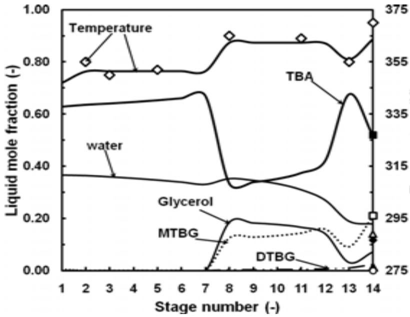


Fig. 1 Schematic diagram of reactive distillation **Fig. 2**. Mole fraction and temperature profiles along the column

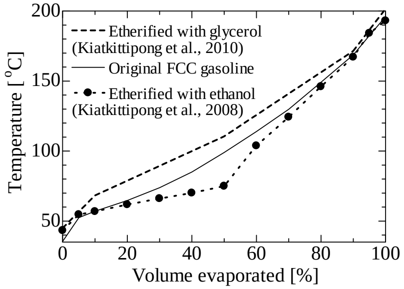


Fig. 3. Distillation curve follows ASTM D-86 [6]

Significance

FCC gasoline self-etherification with glycerol showed great environmental benefits. Ethers produced renewably from glycerol could extend the transportation fuel volume.

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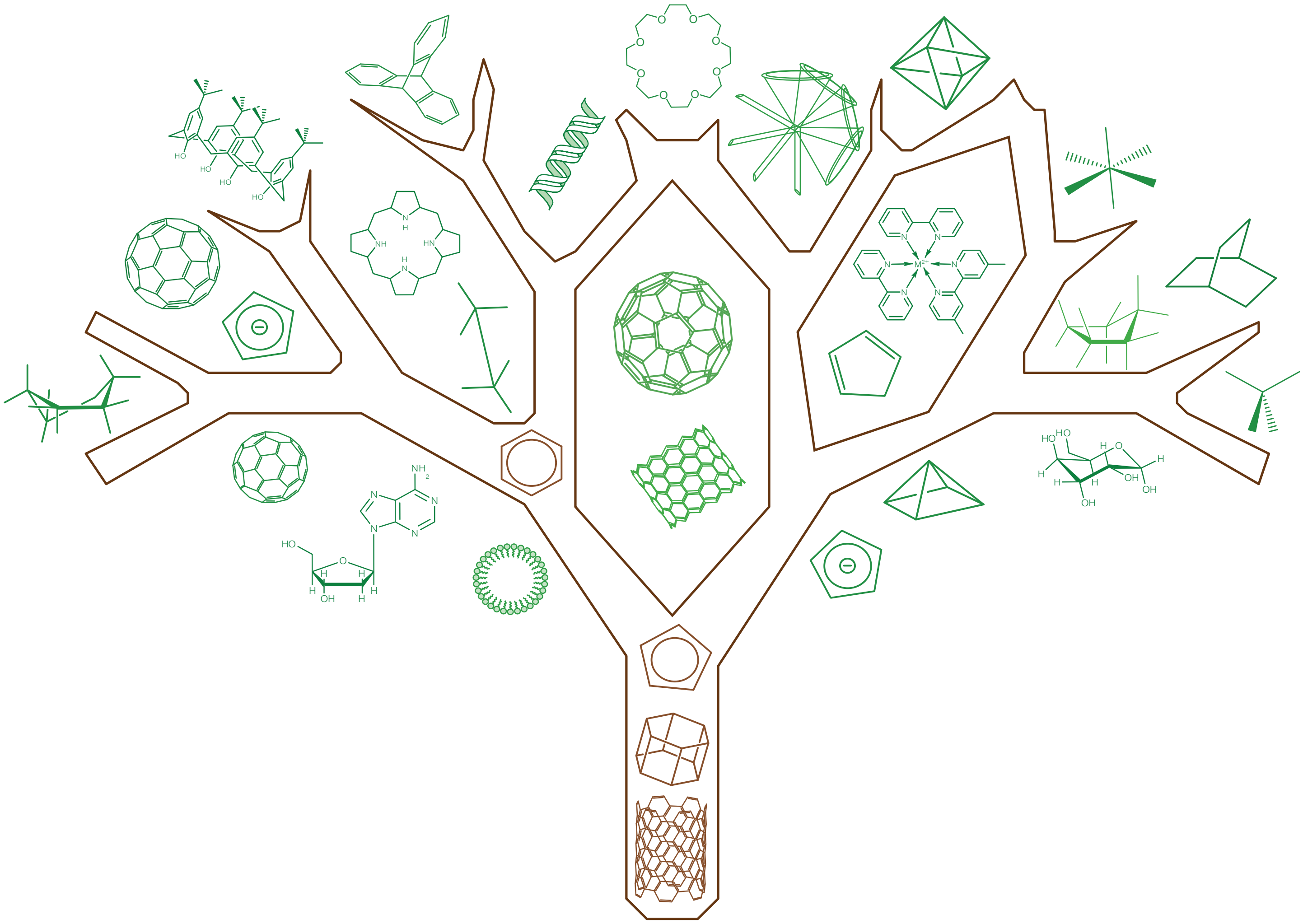

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Hydroprocessing of waste cooking palm oil over Pd/C catalyst

C. Kongwattanakul[1], W. Kiatkittipong[2,*] and S. Assabumrungrat[1]

[1] Center of Excellence on Catalysis and Catalytic Reaction Engineering,
Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University,
Bangkok 10330, Thailand
[2] Department of Chemical Engineering, Faculty of Engineering and Industrial Technology,
Silpakorn University, Nakhon Pathom 73000, Thailand

*E-mail: kworapon@su.ac.th

Abstract: The research focuses on hydroprocessing of waste cooking palm oil (WCPO) for biodiesel production. The obtained product is expected to replace the fatty acid methyl ester (FAME) from trans-esterification known as 1st generation of biodiesel. The WCPO contains 33 wt% palmitic acid. The reaction was performed in a shaking batch reactor under operating temperature of 280 – 420°C, hydrogen pressure of 30 – 50 bar, reaction time 2-8 h and catalyzed by Pd/C commercial catalyst. Reaction products were analyzed using gas-chromatography methods. Gas products contain carbon monoxide, carbon dioxide, methane and hydrogen-rich gas. Liquid reaction products are hydrocarbons whose main components are identified as C_{15} - C_{18} alkanes. The maximum yield of n-C_{15}-C_{18} alkanes of 70.9% could be obtained at a reaction temperature of 400°C, hydrogen pressure of 50 bar and reaction time of 6 h.

Introduction

Presently, the production of renewable fuels has been expanding worldwide for energy and environmental securities. Biodiesel is a promising alternative in renewable fuels production because it decreases amounts of carbon dioxide; moreover, it also helps decrease dependence on fossil fuels, and improve the rural economics and so on [1–3]. A conventional method for producing biodiesel is trans-esterification of vegetable oils. Triglycerides of vegetable oils are reacted with an alcohol mostly methanol or ethanol, from which fatty acid methyl esters (FAME) is obtained as a main product while glycerol is obtained as a by-product. However, the obtained glycerol is in excess of demand thus alternative ways to utilize glycerol have been recently suggested [4]. However, the stability and cetane number of FAME has been mainly an obstacle for being mixed with mineral diesel fuels [2]. In generally, limitation of FAME is at 7 wt% because the car manufactures observed filter plugging from the tank to the engine [5–6]. Therefore the use of FAME as "1st generation biodiesel" still has a limitation to substitute fossil diesel.

Recently, hydroprocessing of vegetable oil has been known as a process for biodiesel production to replace FAME from trans-esterification, it is so called "2nd generation biodiesel. The primary advantages of this biodiesel production over 1st generation biodiesel technology are: the obtained hydrocarbon fuels are similar to fossil diesel fuel, the propane byproduct is preferable over glycerol byproduct, the cetane number is greater and capital costs and operating costs are lower [7–8].

The overall reaction pathway for conversion of triglycerides into alkanes is shown in Figure 1. Double bonds of triglycerides is hydrogenated and preceded by other reactions which are broken down into various intermediates by hydroprocessing process [5].

There are mainly three pathways for hydroprocessing of triglycerides [1, 6] including hydrodeoxygenation (hydrogenation/dehydration), decarboxylation, and decarbonylation.

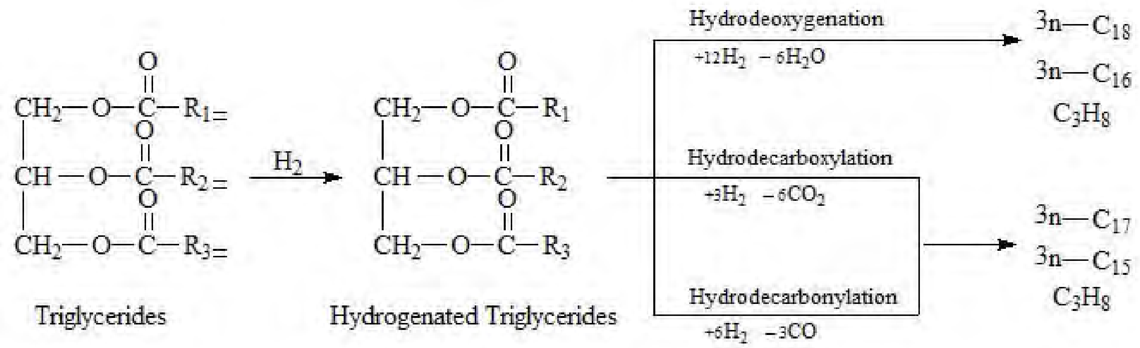

Figure 1. The reaction pathway overall of triglycerides to alkanes.

Palm oil, the most potential feedstock in Thailand, was considered in this study. The lower cost of raw material led to the low production cost of biodiesel production. Therefore, in this study, waste cooking palm oil (WCPO) is used a starting feedstock instead of fresh palm oil in order to reduce cost of raw-material and environmental burden to treat it.

Materials and Methods

The waste cooking palm oil (WCPO) was obtained from Sarmyarn restaurant in Bangkok. The WCPO contains some food particles, phospholipids, grease, and wax and so on. The general process of pretreatment consists of two steps including filtration and dehydration. Initially, suspended solid impurity was removed by filtration and then the WCPO was repeatedly water washed and shaken for extraction of water soluble impurities as well as phospholipids. After that the waste cooking palm oil was heated to above 105°C for 1 h to get rid of the water by evaporation [3, 9–10].

The compositions of WCPO analyzed by GC-MS are presented in Table 1.

Table 1: Chemical compositions of pretreated waste cooking palm feedstock.

Fatty acid composition	**wt%**
Palmitic acid (C16:0)	33.11
Stearic acid (C18:0)	13.01
Oleic acid (C18:1)	17.12
Others	
Octadecanol ($C_{18}H_{38}O$)	7.92
Eicosane ($C_{20}H_{42}$)	14.04
Hexanedioic ($C_{22}H_{42}O_4$)	14.8

The catalyst employed in this study is 5 wt% Pd loaded on activated carbon support (Pd/C), (Aldrich). Before the reaction was performed, the catalyst was reduced under H_2 flow rate of 50 ml/min at a temperature of 350°C for 2 h. The reaction tests- were performed under operating temperatures of 280–420°C, hydrogen pressure of 30–50 bar and reaction times of 2–8 h. After the reaction run, aqueous and organic liquid phase were physically separated and, analyzed using several gas-chromatography methods. Gas products (carbon monoxide, carbon dioxide, methane, propane) was analyzed by gas-chromatography with 4 m molecular sieve 5A and a 2 m porapak Q column and thermal conductivity detector (GC-8A, Shimadzu). Organic liquid products were analyzed by gas-chromatography with flame ionization detector (GC-14B, Shimadzu).

Results and Discussion

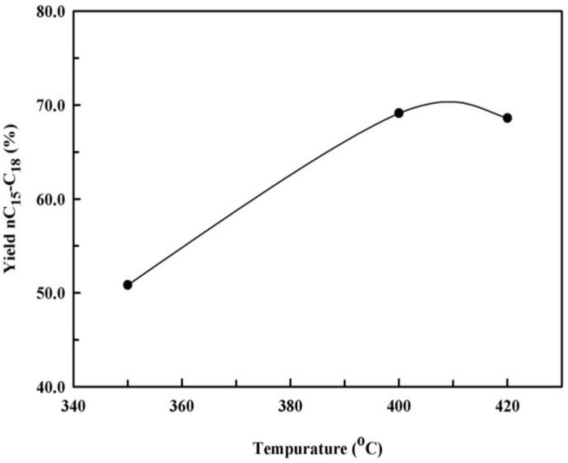

Figure 2. Effect of operating temperature on yield of n-C_{15}–C_{18} alkanes (H_2 pressure = 50 bar).

The reaction could not be taken place at reaction temperatures below 280°C as no desired product of n-C_{15}–C_{18} alkanes and no gaseous products can be detected as shown in Figures 2 and 3 respectively.With increasing temperature at a constant hydrogen pressure, reaction towards the hydrodecarboxylation and hydrodecarbonylation were enhanced, and therefore the yield of n-C_{15}–C_{18} alkanes increased (Figure 2) accompanying with increasing of all gaseous products i.e. CO_2, CO and CH_4 increases (Figure 3). However, n-C_{15}–C_{18} alkanes slightly decreased with increasing the temperature from 400 to 420°C. Cracking reaction could also enhanced with increasing temperature as observed by increasing of lighter hydrocarbons (data is not show here) and some gas products. The effect of H_2 pressure on product yields of n-C_{15}–C_{18} alkanes is illustrated in Figure 4. Yield of n-C_{15}–C_{18} alkanes significantly increased with increasing hydrogen pressure from 30 to 50 bar. The maximum yield of 69.1% could be obtained with hydrogen pressure of 50 bar and reaction temperature from 400°C. However, it should be noted that no improvement of n-C_{15}–C_{18} alkanes yield could be observed with increasing hydrogen from 30 to 40 bar.

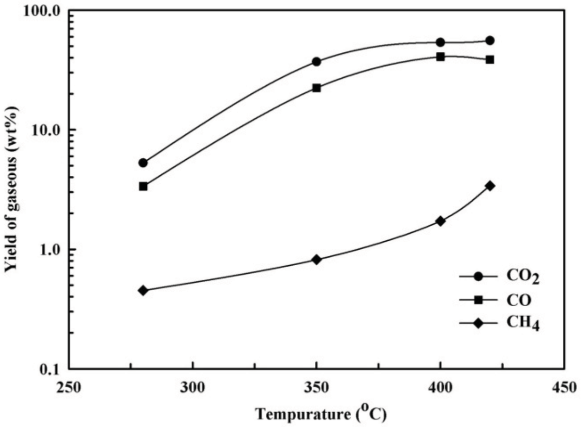

Figure 3. Effect of operating temperature on gaseous products yield (H_2 pressure = 50 bar).

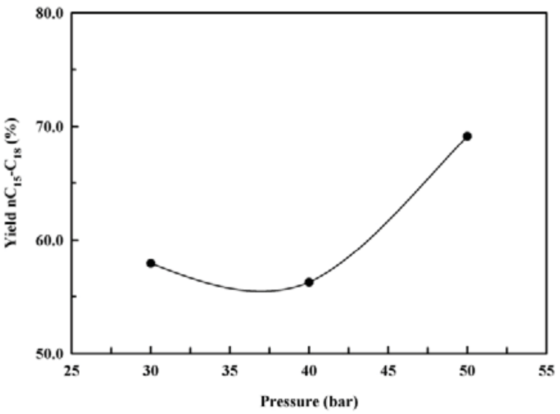

Figure 4. Effect of operating pressure on yield of n-C_{15}–C_{18} alkanes (operating temperature = 400˚C).

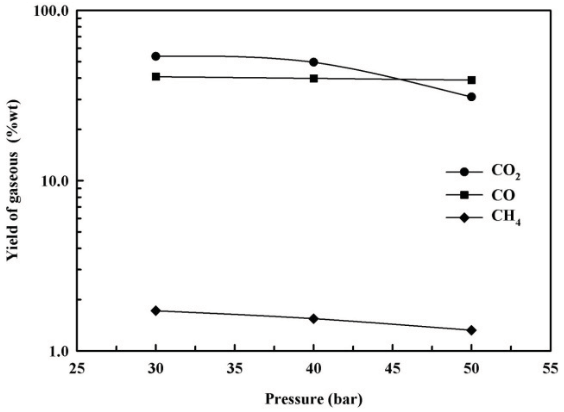

Figure 5. Effect of operating pressure on gaseous products yield (operating temperature = 400°C).

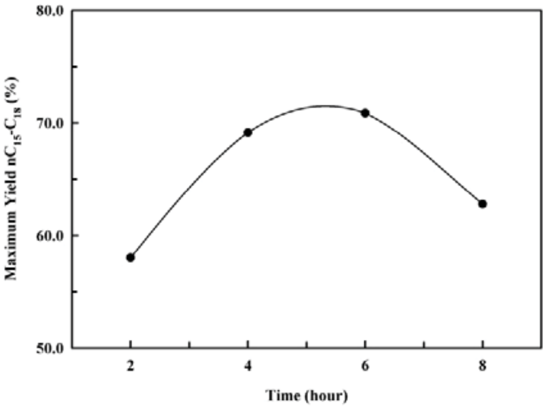

Figure 6. The maximum yield of n-C_{15}-C_{18} alkanes products varying time of reaction.

The explanation of this phenomenon could not be given yet in this study. Considering gas product (Figure 5), CO_2 formation from the hydrodecarboxylation reaction was decelerated by increasing the reaction pressure (as the number of moles of the products is higher than that of the reactants).

The yield of the n-C_{15}–C_{18} alkanes increases from 58.0 to 69.1 and 70.9% with reaction time 2, 4 and 6 h respectively as shown in Figure 6. This increase is due to an increase in conversion of tri-glycerides and fatty acids to alkanes. The yield of the n-C_{15}–C_{18} alkanes decreases to 62.78% as the reaction time increases to 8 h, which is due to cracking of normal alkanes to lighter hydrocarbons.

Conclusion

The hydroprocessing of WCPO is a prominent process for the biodiesel production. The maximum yield of the n-C_{15}–C_{18} alkanes was 70.87% under at a reaction conditions temperature of 400°C, hydrogen pressure of 50 bar and reaction time of 6 h. The reaction pathway involves hydrogenation of the double bonds followed by alkane production by three different pathways: hydrodeoxygenation, hydrodecarboxylation and hydrodecarbonylation. The selectivity to the hydrodecarboxylation plus hydrodecarbonylation products increases with increasing temperature and increasing the pressure of hydrogen favors reactions of hydrodeoxygenation.

Acknowledgement

Financial supports from the Thailand Research Fund and Commission on Higher Education are gratefully acknowledged.

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