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Production of bio-hydrogenated diesel by catalytic hydrotreating of palm oil over NiMoS₂/γ-Al₂O₃ catalyst



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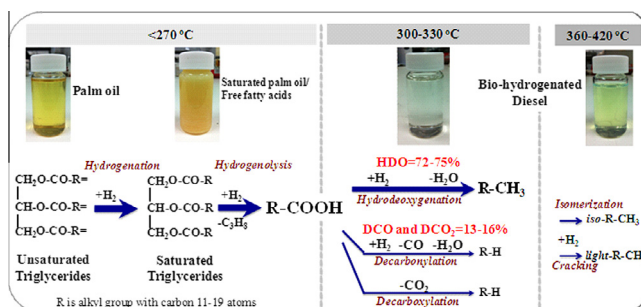
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HIGHLIGHTS

- Catalytic hydrotreating of palm oil to bio-hydrogenated diesel over NiMoS₂/Al₂O₃.
- Optimized reaction conditions (temperature, pressure, LHSV, and H₂/oil ratio).
- Three major pathways of hydrodeoxygenation, decarboxylation and decarbonylation.
- Major contribution of 65–80% from hydrodeoxygenation.
- Isomerization and cracking as minor pathways above 360 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

Catalytic hydrotreating of palm oil (refined palm olein type) to produce bio-hydrogenated diesel (BHD) was carried out in a continuous-flow fixed-bed reactor over NiMoS₂/γ-Al₂O₃ catalyst. Effects of dominant hydrotreating parameters: temperature: 270–420 °C; H₂ pressure: 15–80 bar; LHSV: 0.25–5.0 h^{−1}; and H₂/oil ratio: 250–2000 N(cm³/cm³) on the conversion, product yield, and a contribution of hydrodeoxygenation (HDO) and decarbonylation/decarboxylation (DCO/DCO₂) were investigated to find the optimal hydrotreating conditions. All calculations including product yield and the contribution of HDO and DCO/DCO₂ were extremely estimated based on mole balance corresponding to the fatty acid composition in feed to fully understand deoxygenation behaviors at different conditions. These analyses demonstrated that HDO, DCO, and DCO₂ reactions competitively occurred at each condition, and had different optimal and limiting conditions. The differences in the hydrotreating reactions, liquid product compositions, and gas product composition were also discussed.

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1. Introduction

The development of renewable fuel from bioresources has been an important key to the future energy due to the depletion of

petroleum fuels. Currently, there are two main catalytic conversion processes of triglycerides and/or free fatty acids to biofuels for diesel engines; (1) transesterification/esterification to produce bio-diesel and (2) hydrotreating process to produce renewable diesel, so-called bio-hydrogenated diesel (BHD) or green diesel. Typically, produced by transesterification of triglycerides and esterification of fatty acids with methanol in a temperature range of

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65–100 °C, fatty acid methyl esters (FAMES) or biodiesel has been used as a component in diesel blending (Chen et al., 2013). However, some downsides of biodiesel compared to petroleum diesel are the C=C bonds and C=O bonds remaining in the molecules of FAMES, resulting in low thermal and oxidation stability because of its high oxygen content, high viscosity, and low heating value (Liu et al., 2011).

Due to these disadvantages, BHD which has similar molecular structure as petroleum diesel and provides better diesel properties has attracted much attention for last decades. BHD can be produced by hydrotreating of triglycerides through 3 major reaction pathways including decarbonylation, decarboxylation, and hydrodeoxygenation (Faungnawakij and Suriye, 2013; Kubička and Kaluža, 2010), thus producing straight-chain alkanes ranging from C₁₅ to C₁₈ at 350–450 °C in the presence of H₂ at 50–150 bar (Choudhary and Phillips, 2011; Donnis et al., 2009). First, the reaction proceeds via hydrogenation of unsaturated triglycerides (C=C double bond) to form saturated triglycerides (Ochoa-Hernández et al., 2013), followed by hydrogenolysis of saturated triglycerides resulting in fatty acids and propane. Finally, the fatty acid undergoes through following reactions: (1) hydrodeoxygenation (HDO), an exothermic reaction, removes oxygen in the form of water and yields n-alkane with same carbon number as the corresponding fatty acid, (2) decarbonylation (DCO) and (3) decarboxylation (DCO₂), endothermic reactions, lead to elimination of oxygen in form of CO and water or CO₂, respectively. The consequent n-alkane has one carbon atom loss compared to the original fatty acid (Gong et al., 2012a; Mathias Snåre et al., 2006).

There are two types of catalyst mostly use in hydrotreating of triglycerides: (1) metal catalysts, such as Ni, Pd, Pt, Rh, Ru (Mathias Snåre et al., 2006; Morgan et al., 2012; Onyestyák et al., 2012; Santillan-Jimenez et al., 2013) and (2) bimetallic sulfide catalysts e.g. NiMoS₂, CoMoS₂, and NiWS₂ supported on Al₂O₃ (Hancsók et al., 2012; Kubička and Kaluža, 2010; Liu et al., 2011; Yang et al., 2013). The metal catalysts are favorable to DCO and DCO₂, while HDO is dominant in bimetallic sulfide catalysts, except NiWS₂. Some metal catalysts such as Ni, Pd, and Pt strongly promoted methanation reaction, consuming large amount of hydrogen. Moreover, using NiMoS₂ and CoMoS₂ as catalysts with good selectivity to HDO can be operated at lower temperature due to the nature of exothermic reaction. The formation of CO and CO₂ could affect product yield, catalyst deactivation, and downstream process for recycle gas (Donnis et al., 2009). Therefore, using bimetallic sulfide catalysts as NiMoS₂, which was high activity (Toba et al., 2011) and selective to HDO, was very attractive for hydrotreating process.

The effects of hydrotreating parameters when using bimetallic sulfide catalysts were explored in various literatures. The results indicated the temperature, WHSV/LHSV, hydrogen pressure, and H₂/oil ratio as significant operating parameters that could alter reaction pathways in hydrotreating process (Bezergianni et al., 2011, 2010a,b Bezergianni and Kalogianni, 2009). Furthermore, the relative activities of the DCO/DCO₂ and HDO reactions, as the most important key in hydrotreating process, were considered to evaluate hydrogen consumption, product yield, heat balance, and catalyst deactivation (Donnis et al., 2009; Satyarthi et al., 2013). However, many researchers estimated the relative activities of the DCO/DCO₂ and HDO reactions using the ratio of the amounts of n-alkanes with odd numbers of carbon atoms, to n-alkanes with even numbers of carbon atoms in the liquid product (Gong et al., 2012b; Kim et al., 2013; Liu et al., 2012). These estimations could not provide an actual relative contribution of HDO and DCO/DCO₂ reactions compared to mole balance analysis. Consequently, a comprehensive understanding the influence of reaction parameters on 3 major reaction pathways by using mole balance analysis is crucial.

In this work, the effect of important operating parameters in hydrotreating of triglyceride in palm oil to bio-hydrogenated diesel catalyzed by bimetallic sulfide NiMoS₂/γ-Al₂O₃ in a fixed-bed reactor including temperature (270–420 °C), H₂ pressure (15–80 bar), liquid hourly space velocity (LHSV, 0.25–1.0 h^{−1}), and H₂/oil ratio (250–2000 N(cm³/cm³)) was investigated. Indeed, the understanding of these parameters on the contributions of HDO, DCO, and DCO₂ reactions is important to obtain the optimal operating and limiting conditions.

2. Experimental

2.1. Catalyst preparations

The γ-Al₂O₃ support (1.8 mm diameter, Sasol Company, Germany) was crushed and sieved to 0.5–1.0 mm diameter. The γ-Al₂O₃ supported NiMo catalyst was prepared by sequential impregnation. First, Mo was supported on γ-Al₂O₃ by impregnating of an aqueous solution of ammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O) (Carlo Erba Reagent, Italy) after the sample was dried at 120 °C for 12 h to obtain Mo/γ-Al₂O₃. Then, impregnation of an aqueous solution of nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) (Sigma–Aldrich Chemical Co. LLC., Germany) onto Mo/γ-Al₂O₃ catalyst was carried out in similar fashion. The resultant sample was dried at 120 °C for 12 h and then calcined at 500 °C for 5 h to obtain NiMo/γ-Al₂O₃ catalyst with loading of MoO₃ and NiO at 14 wt.% and 3.5 wt.%, respectively.

2.2. Catalytic hydrotreating of refined palm olein

Catalytic hydrotreating of palm oil (refined palm olein type) was carried out in a custom-made down-flow fixed-bed reactor with an internal diameter of 7 mm, length of 300 mm, and volume of 12 cm³. A schematic diagram of the experimental apparatus is shown in Fig. S1. Refined palm olein was commercially obtained from a local market in Thailand. Fatty acid compositions of palm olein were as follows: lauric acid (C12:0) 0.4%; myristic acid (C14:0) 0.8%; palmitic acid (C16:0) 37.4%; palmitoleic acid (C16:1) 0.2%; stearic acid (C18:0) 3.6%; oleic acid (C18:1) 45.8%; linoleic acid (C18:2) 11.1%; linolenic acid (18:3) 0.3%; arachidic acid (C20:0) 0.3%; and eicosenoic acid (C20:1) 0.1% (Viriya-Empikul et al., 2010). The catalyst (8.5 g) was loaded into the reactor, and was presulfided using a mixture of 1 wt% carbon disulfide in hexane. The presulfidation conditions were conducted in H₂ flow rate of 200 cm³/min with pressure of 20 bar. The temperature was increased from 30 to 150 °C (10 °C/min) and then to a target temperature of 300 °C (1 °C/min), while the catalyst was held at 300 °C for 15.5 h. In the reaction testing, the reactor was heated to desired temperature, and was pressurized with H₂ to desired pressure controlled by back pressure regulator. A HPLC pump was used to introduce the oil feed, while H₂ feed was controlled by mass flow controllers. After presulfidation, the catalysts were stabilized by flowing feeds through the reactor for 24 h before actual experiments was implemented. The reaction conditions were as follows: hydrotreating temperature of 270–420 °C, H₂ pressure of 15–80 bar, H₂/oil ratio, liquid hourly space velocity (LHSV) of 0.25–5.0 h^{−1}, and H₂/oil ratio of 250–2000 N(cm³/cm³). Each reaction parameter was evaluated by the use of fresh catalysts to eliminate the effect of catalysts deactivate during the experiments. Duplicate experiment with fresh catalyst was done in some cases with less than 5% error of repeated results while triplicate experiment with same catalyst was also done for all cases with less than 3% error of repeated results. The liquid product was collected every 3-h interval time for analysis.

2.3. Product analysis

The liquid products after separation of water phase were analyzed offline by gas chromatography equipped with capillary column (DB-1HT, 30 m × 0.32 mm × 0.1 μm) and a flame ionization detector (FID). The calibration curve of standards was used to quantify a composition of *n*-alkanes (*n*-C₈ to *n*-C₁₈) in liquid product. Briefly, 50 mg of sample was diluted with 1 ml of hexane and 1 μL of sample was injected into GC with the split ratio of 100. High injection and column temperature were used to direct analysis of triglyceride without chemical derivatization (Anand and Sinha, 2012; Peng et al., 2012). The injection and detector temperatures were 340 and 370 °C, respectively. The temperature program was increased from 40 to 270 °C at a rate of 8 °C/min, and held for 11 min, followed by an increase of 15 °C/min to 370 °C, and held for 15 min. The composition of gas products (C₃H₈, C₂H₆, CH₄, CO, CO₂, and H₂) were also analyzed by online gas chromatography with molecular sieve 5A and Porapak Q columns equipped with thermal conductivity detector (TCD) (GC-14B, Shimadzu).

In-depth analysis, the mole balance of organic liquid product was used to determine the conversion and product yields; the mole balance was always 90–95% accurate for all conditions before and after reaction. The conversion of triglyceride was defined as mole of triglyceride converted to others (intermediates and hydrocarbon). The product yields were theoretically determined base on mole balance of *n*-alkanes (*n*-C₁₅–*n*-C₁₈) in product corresponding to mole of fatty acids (C₁₆ and C₁₈ fatty acids) in oil feed. Product yield to *n*-C₁₅–*n*-C₁₈ fraction and conversion were calculated using the following equations:

$$\text{Conversion of TG (\%)} = \left(\frac{\text{mol TG in feed} - \text{mol TG in product}}{\text{mol TG in feed}} \right) \times 100 \quad (1)$$

$$\text{Product yield (\%)} = \left(\frac{\text{Total mol of } n\text{-alkane (} n\text{-C}_{15} \text{ to } n\text{-C}_{18} \text{) in product}}{\text{Total mol of fatty acid (C}_{15} \text{ to C}_{18} \text{) in feed}} \right) \times 100 \quad (2)$$

The % contribution of hydrodeoxygenation (HDO) and decarbonylation/decarboxylation (DCO/DCO₂) reactions were also calculated based on mole balance, using the total mole of *n*-alkanes with odd numbers (HDO) or even numbers (DCO/DCO₂) of carbon atoms in product, to mole of fatty acid in oil feed using the following equations:

$$\text{HDO (\%)} = \left(\frac{\text{Total mol of } n\text{-alkane (} n\text{-C}_{16} \text{ and } n\text{-C}_{18} \text{ in product)}}{\text{Total mol of fatty acid (C}_{15} \text{ to C}_{18} \text{) in feed}} \right) \times 100 \quad (3)$$

$$\text{DCO/DCO}_2 (\%) = \left(\frac{\text{Total mol of } n\text{-alkane (} n\text{-C}_{15} \text{ and } n\text{-C}_{17} \text{ in product)}}{\text{Total mol of fatty acid (C}_{15} \text{ to C}_{18} \text{) in feed}} \right) \times 100 \quad (4)$$

3. Results and discussions

The effects of hydrotreating temperature, hydrogen pressure, liquid hourly space velocity (LHSV), and hydrogen to oil ratio on the *n*-alkane composition of the liquid product are represented in Table 1. The palm oil used in this study was composed mainly of C₁₆ and C₁₈ fatty acids (>98.4 wt.%), thus the main composition of liquid product was *n*-alkane of C₁₆ and C₁₈ due to high selective HDO reaction of NiMoS₂/γ-Al₂O₃ catalyst. As demonstrated in Table 1, the increase in hydrotreating temperature enhances the cracking reaction, where the light hydrocarbon compositions, *n*-C₈ to *n*-C₁₄, were observed. Hydrotreating temperature and hydrogen pressure also affected to % contribution of hydrotreating

product (HDO and DCO/DCO₂) for each *n*-alkane product, exhibited in Table 2.

3.1. Effect of hydrotreating temperature

Reaction temperature has been identified as one of dominant parameters on the catalyst deactivation and catalyst performance (Yang et al., 2013). In this section, effect of hydrotreating temperature was conducted in the range of 270–420 °C with fixed operating conditions: 50 bar of H₂ Pressure, 1.0 h^{−1} of LHSV, and 1000 Ncm³/cm³ of H₂/Oil ratio, and the results are shown in Fig. 1. It should be first noted that the hydrotreating reaction over pure γ-Al₂O₃ resulted in 56% conversion of triglyceride without BHD product yield. The results indicated that only the saturated triglyceride scission to free fatty acids and propane occurred. Interestingly, the BHD product yield were obtained when the reaction was catalyzed by NiMoS₂/γ-Al₂O₃ catalyst, suggesting the hydrotreating activity of NiMoS₂ species.

The organic liquid product obtained from hydrotreating temperature of 270 °C became solidified at room temperature and consisted of palmitic acid and stearic acid with small amount of triglyceride. Our results were consistent to those of Šimáček et al. (2009), at hydrotreating temperature lower than 310 °C, the liquid product also contained reactant and intermediates including triglyceride, free fatty acids, and *n*-octadecanol (Šimáček et al., 2009). These results suggested that the reaction proceeded through the hydrogenation of C=C bond in unsaturated triglyceride, followed by C–O bond cleavage via hydrogenolysis of saturated triglyceride to produced free fatty acids and propane (Peng et al., 2012; Zhao et al., 2013). As illustrated in Fig. 1a, the reactants underwent to HDO, DCO, and DCO₂ reactions with product yield of 26.7% (270 °C). Based on our operating condition obtained from 330–420 °C of hydrotreating temperature, the triglyceride and fatty acids were not detected in organic liquid product, resulting in 100% conversion of triglyceride. Interestingly, as shown in Fig. 1a, the product yield increased from 26.7% to 89.8% with increasing temperature from 270 to 300 °C. The results confirmed that hydrotreating temperature of 300 °C was successful to convert triglyceride to *n*-alkane for palm oil over NiMoS₂ catalyst. On the other hand, the decrease in product yield from 88.9% to 37.9% with increasing temperature from 330 to 420 °C could be related to the promotion of isomerization, cracking, and cyclization reactions because the light-hydrocarbons, iso-paraffins, cycloparaffins and some aromatics were found in liquid product at high reaction temperature (420 °C). The detected iso-paraffins were iso-C₁₅ and iso-C₁₇ such as 1-methylpentadecane 1-methylpentadecane 3-methylpentadecane, and 3-methylheptadecane, thus causing by isomerization reaction of *n*-C₁₆ and C₁₈. However, the formation of *n*-alkanes possibly undergo through the thermal cracking of triglyceride rather than went through the deoxygenation reaction at higher temperature (Kim et al., 2013; Yang et al., 2013). Fortunately, the iso-paraffins are favorable in liquid product, thus improving the cold flow properties including cloud point and pour point.

To fully understand deoxygenation behavior at difference conditions, % contribution of HDO and DCO/DCO₂ was considered and represented in Fig. 1b. The hydrodeoxygenation (HDO) is dominant through catalyzed by NiMoS₂ catalyst (Kiatkittipong et al., 2013; Veriansyah et al., 2012). The DCO/DCO₂ moderately increased from 4.6% to 16.8% with raising temperature from 270 to 300 °C, whereas, an increase in temperature from 270 to 330 °C greatly enhanced HDO from 21.9% to 74.9%. At the temperature higher than 330 °C, DCO/DCO₂ slightly decreased and the dramatically decrease in HDO was observed at the temperature higher than 360 °C due to the enhancement of cracking and isomerization reactions in good agreement with thermodynamic point of view.

Table 1
Effect of operating parameters on liquid product composition.

Parameters	T (°C)	P (bar)	LHSV (h^{-1})	$\text{H}_2/\text{oil ratio}$ $\text{N}(\text{cm}^3/\text{cm}^3)$	Liquid product composition (wt%)					Product phase	Product color
					$n\text{-C}_8\text{--}n\text{-C}_{14}$	$n\text{-C}_{15}$	$n\text{-C}_{16}$	$n\text{-C}_{17}$	$n\text{-C}_{18}$		
Temperature	270	50	1	1000	0.2	1.7	9.1	2.9	14.1	Solid	Yellow
	300	50	1	1000	0.8	6.3	30.3	10.7	47.7	Liquid	Clear
	330	50	1	1000	1.0	4.9	32.1	8.0	48.7	Liquid	Clear
	360	50	1	1000	2.5	3.2	33.5	4.6	44.6	Liquid	Light green
	390	50	1	1000	5.7	3.1	31.8	3.5	33.0	Liquid	Light green
	420	50	1	1000	12.8	3.8	22.3	2.8	12.7	Liquid	Green
Pressure	300	15	1	1000	0.9	6.0	29.3	10.3	43.9	Liquid	Green
	300	30	1	1000	0.9	7.6	29.3	12.8	45.5	Liquid	Clear
	300	50	1	1000	0.8	6.3	30.3	10.7	47.7	Liquid	Clear
	300	80	1	1000	0.8	5.9	31.7	10.3	50.4	Liquid	Clear
LHSV	300	50	0.25	1000	0.6	3.4	34.3	6.1	54.7	Liquid	Clear
	300	50	0.5	1000	0.6	5.6	31.9	10.0	49.4	Liquid	Clear
	300	50	1	1000	0.6	6.3	30.7	10.9	47.4	Liquid	Clear
	300	50	1.5	1000	0.6	5.8	30.7	9.7	46.0	Liquid	Clear
	300	50	2	1000	0.6	5.6	31.2	9.2	46.1	Liquid	Clear
	300	50	3	1000	0.6	5.3	30.6	8.8	45.3	Liquid	Clear
	300	50	5	1000	0.6	5.3	29.9	8.8	44.5	Liquid	Clear
$\text{H}_2/\text{oil ratio}$	300	50	1	250	0.3	4.3	12.9	7.3	20.1	Solid	Yellow
	300	50	1	500	1.0	7.2	29.0	12.2	46.3	Liquid	Clear
	300	50	1	750	0.8	6.6	30.2	11.3	47.9	Liquid	Clear
	300	50	1	1000	0.6	6.6	30.9	11.1	48.2	Liquid	Clear
	300	50	1	1500	0.8	7.1	31.1	12.1	48.3	Liquid	Clear
	300	50	1	2000	0.8	6.0	31.9	10.1	49.4	Liquid	Clear

Table 2
Effect of hydrotreating temperature and hydrogen pressure on% contribution of each n-alkane.

Parameters	T (°C)	P (bar)	HDO (%) ($n\text{-C}_{16}$)	HDO (%) ($n\text{-C}_{18}$)	DCO/DCO ₂ (%) ($n\text{-C}_{15}$)	DCO/DCO ₂ (%) ($n\text{-C}_{17}$)
Temperature	270	50	22.7	21.4	4.4	4.7
	300	50	74.1	71.0	16.4	17.1
	330	50	78.5	72.4	12.9	12.8
	360	50	83.3	66.4	8.1	6.9
	390	50	78.4	49.6	8.1	5.6
	240	50	51.9	17.0	9.5	4.2
	300	15	72.6	66.4	15.8	16.5
Pressure	300	30	72.6	68.7	19.8	20.3
	300	50	74.1	71.0	16.4	17.1
	300	80	79.1	76.4	15.6	16.5

The % contributions of HDO and DCO/DCO₂ for each n-alkane ($n\text{-C}_{15}$, $n\text{-C}_{16}$, $n\text{-C}_{17}$, and $n\text{-C}_{18}$) were calculated based on mole balance using the total mole of n-alkanes with odd numbers (HDO) or even numbers (DCO/DCO₂) of carbon atoms in the product.

The exothermic HDO is unfavorable at higher temperature (Mathias Snåre et al., 2006); however, endothermic DCO and DCO₂ are not followed the trend. Therefore, it should be noted there are competitive reactions between HDO and DCO/DCO₂, occurring at each temperature.

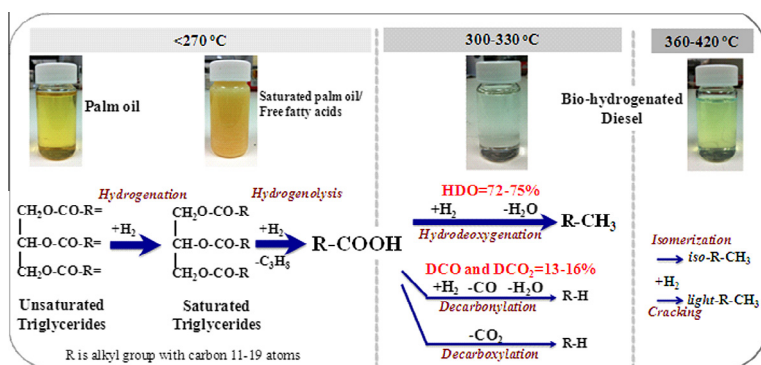
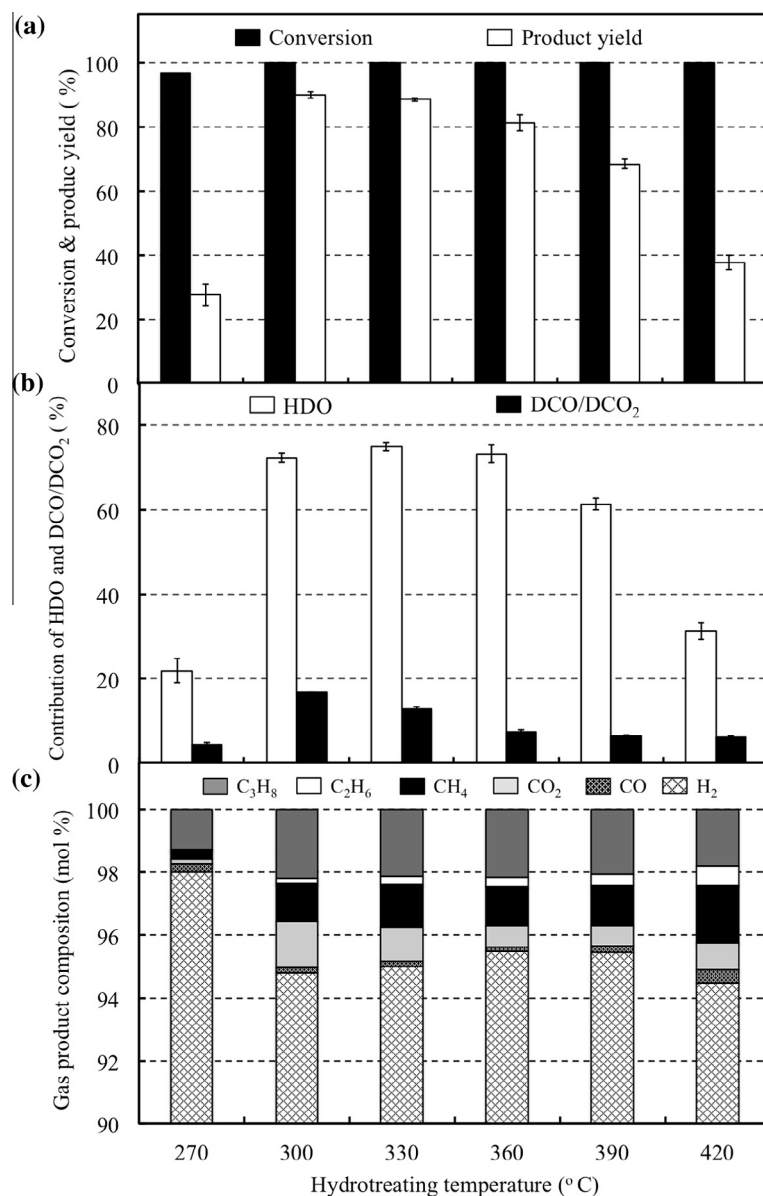
According to the results discussed in previous section, HDO (72–75%) was a major reaction pathway, whereas DCO and DCO₂ (13–16%) were minor reaction pathways. Illustrated in Schematic 1, the double bonds in saturated triglycerides were hydrogenated to unsaturated triglycerides, subsequently cleaved to free fatty acids and propane (270 °C). The free fatty acid, as the major oxygenated intermediates, could undergo to yield a fatty acid alcohol and subsequently hydrocarbons at temperature higher than 300 °C through HDO reaction, leading to elimination of water from palm oil (12–15 wt.% of total liquid product). Some free fatty acids could directly be converted to hydrocarbons via DCO and DCO₂ reactions, thus releasing oxygen in form of CO, H₂O, and CO₂, respectively. Furthermore, the cracking and isomerization reactions could proceed at temperature above 360 °C.

The activity of decarbonylation and decarboxylation reaction can be compared to amount of CO and CO₂. As discussed in previous section, the decline in DCO/DCO₂ yield was observed at the temperature higher than 330 °C, thus causing in decrease of CO

and CO₂ with the similar trend (Fig. 1c). These results could be noted that the rate of two reactions is similar and these reactions occur with the same mechanism. By comparison amount CO and CO₂, the results showed that DCO₂ has higher activity than DCO. Moreover, the decrease in amount of CO and CO₂ could be related to methanation, exothermic reaction, between CO or CO₂ with H₂. Consequently, the higher amount of CO and CO₂ production at 420 °C reaction temperature was also observed. Perhaps, the slightly increase in amount of C₂H₆ between 360–420 °C was due to the cracking of liquid product or direct cracking of triglyceride rather than cracking of C₃H₈ to CH₄ and C₂H₆ as same as the methanation reaction. In Table 2, the results of increase in HDO of $n\text{-C}_{16}$ and decrease in HDO of $n\text{-C}_{18}$ suggested that the cracking of $n\text{-C}_{18}$ to $n\text{-C}_{16}$ and C₂H₆ would be occurred at temperature higher than 360 °C.

3.2. Effect of hydrogen pressure

Hydrogen pressure, strong effect to deoxygenation, isomerization, and cracking reactions, is an important parameter of hydrotreating reaction of triglycerides to hydrocarbons. Moreover, the H₂ consumption must be taken account of the economical evolution of operating conditions. In this experiment, hydrogen pres-



tures were investigated in the range of 15–80 bar at hydrotreating temperature of 300 °C, while the other parameters were retained as same as those discussed in Section 3.1, to avoid the catalyst

deactivation and cracking reaction. At the pressure of 15 bar, the liquid product remained small amount of palmitic acid and stearic acid, thus indicating the incomplete transformation of free fatty

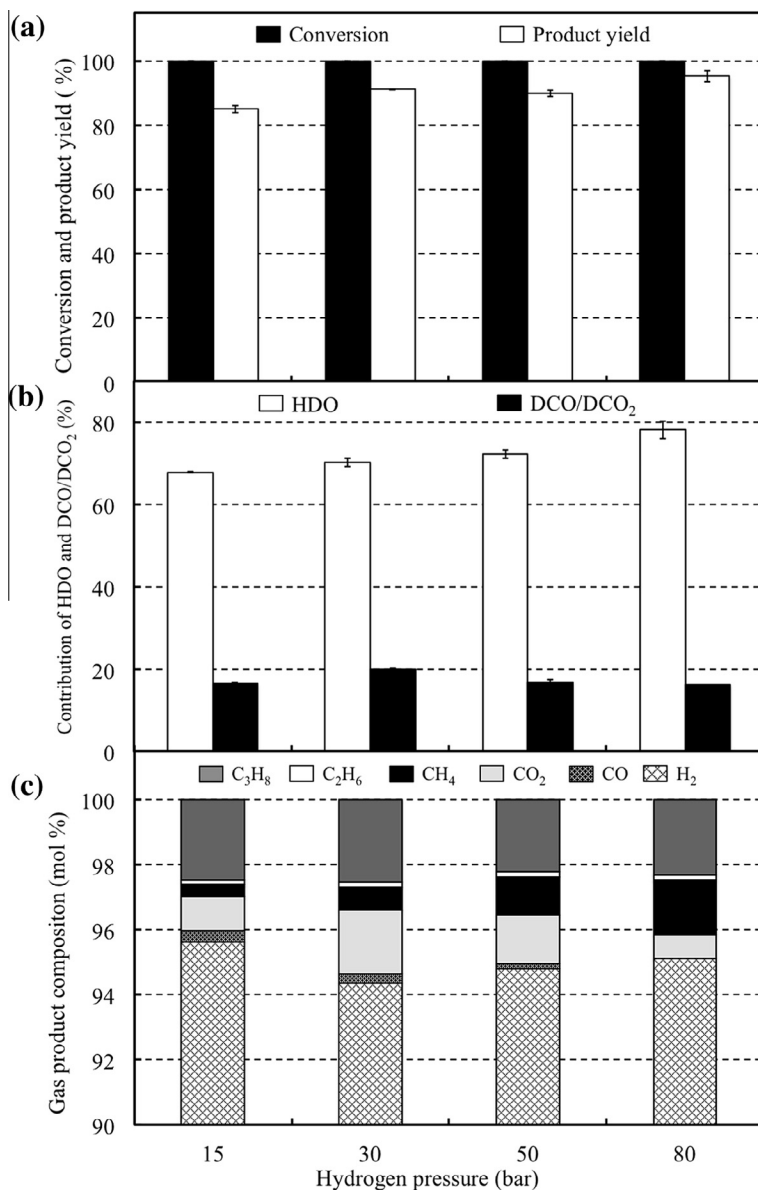


Fig. 2. Effect of H₂ pressure on (a) conversion and product yield, (b) % contribution of HDO and DCO/DCO₂, and (c) gas product composition. All experiments were performed at a H₂ pressure in the range of 15–80 bar, hydrotreating temperature of 300 °C, H₂/oil ratio of 1000 N(cm³/cm³), and LHSV of 1 h⁻¹.

acids to n-alkane due to the insufficient H₂ pressure. Similarly to Anand and Sinha (2012) and Kubička et al. (2009), low conversion was observed at hydrogen pressure of 20 bar and the reduced partial pressures of hydrogen led hydrogen mass transfer limitations on the catalyst surface. As shown in Fig. 2a, the hydrogen pressure did not significant effect on the conversion of triglyceride (100% conversion was obtained at 15–80 bar). The product yield slightly increased up to 95.2% with increasing hydrogen pressure from 15 to 80 bar. Since, the H₂ pressure is the function of adsorbed hydrogen on the surface of catalyst active sites, increase in hydrogen pressure raised the solubility of hydrogen in the vegetable oil across the catalyst surface. As presented in Fig. 2b, the HDO activity enhanced from 67.8% to 78.1% with increasing H₂ pressure from 15 to 80 bar, but slightly decreased the DCO/DCO₂ from 20.1% to 16.3% when increase H₂ pressure from 30 to 80 bar. The HDO dominated the total process under pressures because of more H₂ consumption in comparison to DCO and DCO₂ (Liu et al., 2011). Consequently, HDO pathway was favorer than DCO/DCO₂ due to the larger amount of hydrogen at active sites. On the other hand, DCO/

DCO₂ increased with decreasing hydrogen pressure as the results of lowering amount of hydrogen at the catalyst surface (Kubička and Kaluža, 2010). In proposed in various works, the fatty acids obtained from hydrogenolysis of triglyceride leads to aldehyde production with rate determining step, followed by either (1) decarboxylation of octadecanal to n-heptadecane and carbon monoxide or (2) hydrogenation of octadecanal to octadecanol. Subsequently, the octadecanol undergoes dehydration and hydrogenation to the n-octadecane (hydrodeoxygenation) (Peng et al., 2012; Zhao et al., 2013). It should be note that increase of the H₂ pressure from 15 to 80 bar led to reaction shifts from octadecanal to 1-octadecanol, followed by octadecane and decarboxylation rate was suppressed at high H₂ pressure.

As discussed in the previous section, large amounts of CO and CO₂ were observed due to the increasing of DCO and DCO₂ reactions at low H₂ pressure of 30 bar (Fig. 2c). The increase in H₂ pressure led to the decreasing in composition of CO and CO₂ and increasing of CH₄ contents. Perhaps, the increase in CH₄ composition with increasing H₂ pressure was attributed to the charac-

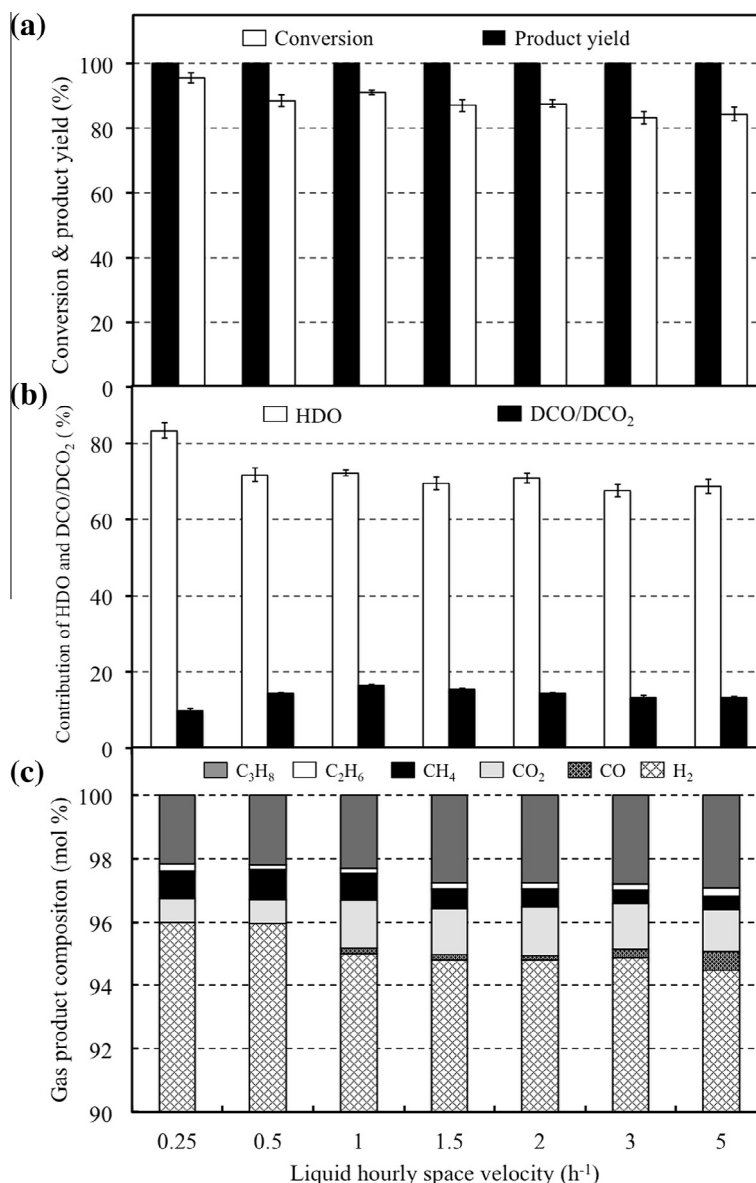


Fig. 3. Effect of LHSV on (a) conversion and product yield, (b) % contribution of HDO and DCO/DCO₂, and (c) gas product composition. All experiments were performed at LHSV in the range of 0.25–5 h^{-1} , hydrotreating temperature of 300 °C, H₂ pressure of 50 bar, and H₂/oil ratio of 1000 $\text{N}(\text{cm}^3/\text{cm}^3)$.

teristic of methanation reactions with favor at high H₂ pressure (Gao et al., 2012). Moreover, the slightly decrease in C₃H₈ and increase in C₂H₆ would be due to the cracking of C₃H₈ to CH₄ and C₃H₆ at high H₂ pressure.

3.3. Effect of liquid hourly space velocity

Liquid hourly space velocity (LHSV) which, defines as the ratio of feed volume flow rate with volume of packed catalyst is used to determine the contact time between feed and catalyst. LHSV plays an important role for regulating catalyst effectiveness and catalyst life expectancy (Bezergianni et al., 2011; Bezergianni and Kalogianni, 2009; Yang et al., 2013). According to previous work, high space time (around 8–17 h^{-1}), the formation of white waxy oxygenated intermediates, mainly free fatty acids and esters are observed (Anand and Sinha, 2012; Huber et al., 2007; Kubička et al., 2009) and rapidly plugged the reactor. Therefore, the effect of LHSV on conversion and product yield with % contribution of HDO and DCO/DCO₂ was conducted in the wide range of LHSV

(0.25–5 h^{-1}) with fixed the operating condition: hydrotreating temperature: 300 °C; H₂ Pressure: 50 bar; and H₂/Oil ratio: 1000 $\text{N}(\text{cm}^3/\text{cm}^3)$.

Demonstrated in Fig. 3a, LHSV did not significantly effect on the conversion of triglyceride; 100% conversion was obtained at 0.25–5 h^{-1} , at hydrotreating temperature of 300 °C without wax precipitation of liquid product at higher LHSV (5 h^{-1}) and zero acid value. However, the increase in LHSV from 0.25 to 5 h^{-1} slightly dropped in the product yield from 95% to 84.3%, indicating the insufficient contact time of reactants and catalysts. Furthermore, the decrease in contact time suppressed the deoxygenation, cracking, and isomerization reactions (Chen et al., 2013). Nevertheless, the increase in contact time (at low LHSV) would promote the cracking and isomerization reactions; thereby the effect of LHSV is demonstrated at low temperature (300 °C) to avoid this situation. The decrease in LHSV from 0.5 to 0.25 h^{-1} raised the product yield up to 95% because allowing longer contact time between reactant and catalyst in low LHSV

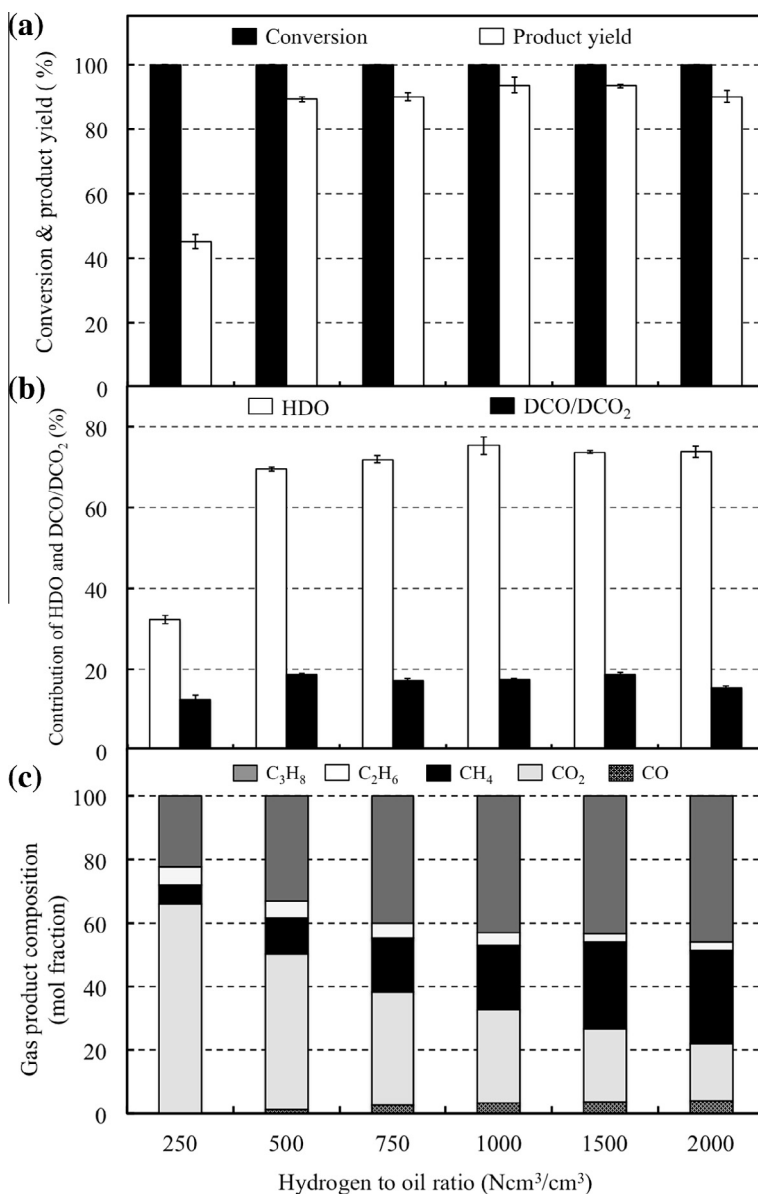


Fig. 4. Effect of H_2 /oil ratio on (a) conversion and product yield, (b) % contribution of HDO and DCO/DCO₂, and (c) gas product composition. All experiments were performed at H_2 /oil ratio in the range of 250–2000 Ncm³/cm³, hydrotreating temperature of 300 °C, H_2 pressure of 50 bar, and LHSV of 1 h⁻¹.

would enhance the product yield at low hydrotreating temperature (300 °C).

In Fig. 3b, an overall similarly decline trend on % contribution of HDO from 83.1% to 68.7% was observed when increasing the LHSV from 0.25 to 5 h⁻¹. On the other hand, the increase in LHSV from 0.25 to 1 h⁻¹ increased the % contribution of DCO/DCO₂ from 9.7% to 16.4%, while there is slightly decrease in % contribution of DCO/DCO₂ from 16.4% to 13.4% with increasing LHSV from 1 to 5 h⁻¹. The results can be indicated that LHSV did not significant influence on reaction pathways including HDO and DCO/DCO₂ when increase the LHSV from 1 to 5 h⁻¹. At LHSV lower than 1 h⁻¹ (increase in contact time) the reactions seem to promote HDO than DCO/DCO₂. The rate of hydrogenolysis of the (H₂)C–O bonds in triglyceride to fatty acid alcohols (HDO) should be slower than the cracking of the –C(=O)–C₁₇ bonds (DCO₂); the former reaction required higher contact time between reactant and catalyst than the later (Sankaranarayanan et al., 2011). These results should be indicated that the decrease in LHSV with increase the

contact time was sufficient for HDO and suppressed DCO and DCO₂ reactions at low hydrotreating temperature.

Effects of LHSV on gas product composition, illustrated in Fig. 3c, suggested that LHSV had strongly influence the methanation reaction, which was favorable when decrease in LHSV i.e., higher LHSV, the more CO and CO₂ but the less CH₄ in the gas product. In addition, propane slightly increased due to cracking of propane to lighter hydrocarbon (mostly methane) was suppressed at higher LHSV.

3.4. Effect of hydrogen to oil ratio

The hydrogen to oil ratio, which defines to the ratio of hydrogen feed to the liquid feed, is another conventional parameter in economic feasibility and hydrotreating processes which has strong influence on hydrogenation, deoxygenation, and cracking efficiency. In this section, the effect of hydrogen to oil ratio was conducted in the range of 250–2000 Ncm³/cm³, while the other

parameters were retained as same as those discussed in Section 3.3. Illustrated in Fig. 4a, the H_2 /oil ratio showed small impact on the conversion; however, dramatically improvement in product yield from 45.2% up to 93.3% with the change of H_2 /oil ratio from 250 to 1500 $N(\text{cm}^3/\text{cm}^3)$ due to the improvement of deoxygenation reactions (HDO and DCO/DCO₂). Additionally, at H_2 /oil ratio of 250 $N(\text{cm}^3/\text{cm}^3)$, the product was separated into two layers at room temperature. The analysis suggested that the upper liquid phase was hydrocarbons and the bottom solid phase was fatty acids (mainly, palmitic acid and stearic acid) due to insufficient of hydrogen. However, the use of H_2 to oil ratio of 2000 $N(\text{cm}^3/\text{cm}^3)$ reduced the product yield to 90% due to the decreasing of DCO/DCO₂ reactions (Fig. 4b). The hydrogen consumption for converting 1 ml of palm oil to hydrocarbon could be estimated from fatty acid composition. It was assumed that the main composition of triglyceride in palm oil is tripalmitin and triolein, and assumed that the reaction was taken place through hydrodeoxygenation when using NiMoS₂ as catalyst. Therefore, 1 mol of tripalmitin, which contained six oxygen atoms will consume 12 mol of hydrogen to produce hexadecane, while 1 mol of triolein, which contained six oxygen atoms and 3 C=C double bonds will consume 15 mol of hydrogen to produce octadecane. By 50% of tripalmitin and 50% triolein, 1 mol of palm oil will consume 13.5 mol of hydrogen to produce hydrocarbons through hydrogenation and hydrodeoxygenation reactions. The density of palm oil was 0.903 g/ml, and the molecular weight was 838 g/mol. Finally, it was determined that 1 ml of palm oil will consume about 325 ml of hydrogen (at standard temperature and pressure (STP)) to form hydrocarbons through hydrogenation and hydrodeoxygenation reactions. In Fig. 4a, the highest production yield was obtained at H_2 /oil ratio of 1000 to 1500 $N(\text{cm}^3/\text{cm}^3)$, suggesting the hydrogen should be about 3–5 times as much as the ratio of consumed hydrogen to oil. Additionally, the larger amount of hydrogen supplied during hydrotreating process possibly retard coke deposition onto the catalyst (Kim et al., 2013) and also remove the water from the catalyst (Satyarthi et al., 2013), thus preventing the catalyst deactivation.

The contribution of HDO increased from 32.3% to 75.3% when increase H_2 /oil ratio from 250 to 1000 $N(\text{cm}^3/\text{cm}^3)$ and the trend was constant at H_2 /oil ratio in the range 1500 to 2000 $N(\text{cm}^3/\text{cm}^3)$ at 73.7%, represented in Fig. 4b. On the other hand, the increase in H_2 /oil ratio from 250 to 500 $N(\text{cm}^3/\text{cm}^3)$ enhanced the contribution of DCO/DCO₂ from 12.6% to 18.9%, while the increase in H_2 /oil ratio up to 2000 $N(\text{cm}^3/\text{cm}^3)$ decreased the DCO/DCO₂ to 15.5%. Similar fashion to those in the study of H_2 pressure was observed, that the large adsorption of H_2 at catalyst active sites is enhanced through the high H_2 /oil ratio used via promoted overall reaction pathway. Otherwise, the trend was constant due to the saturation of adsorbed H_2 on catalyst active sites.

For CO and CO₂, the H_2 /oil ratio strongly affected on the enhanced methanation reaction with high H_2 /oil ratio (Fig. 4c), in good agreement with Gao et al. (2012). As they analyzed the comprehensive thermodynamic of reactions occurring in the methanation of carbon oxides (CO and CO₂) using the Gibbs free energy minimization method, and found the enhancement of methanation due to the high H_2 /CO and H_2 /CO₂ ratio.

4. Conclusions

The effect of reaction parameters on hydrotreating of palm oil to BHD over NiMoS₂/γ-Al₂O₃ was investigated. The recommended conditions were as follows: temperature: 300 °C, Pressure: 30–50 bar, LHSV: 1–2 h^{−1}, and H_2 /oil ratio: 750–1000 $N(\text{cm}^3/\text{cm}^3)$ with the product yield of 90.0% and n-alkane content >95.5%. Temperature strongly affected to reaction pathways (DCO, DCO₂, HDO,

cracking, and isomerization), while higher pressure promoted HDO reaction. The increase in LHSV suppressed reactions due to the insufficient contact time. H_2 /oil ratio should be higher than 3–5 time of theoretical requirement. Furthermore, methanation reaction impacted on H_2 consumption at low temperature and high pressure.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2014.01.100>.

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