



CHAPTER IV RESULTS AND DISCUSSION

4.1 Palm Oil Analysis Chromatogram

The chromatogram of palm oil (50 wt% crude palm oil in n-dodecane) analyzed by a GC/FID with cool-on column injector is shown in Figure 4.1. The chromatogram consists of 2 main peaks at 11, and 25 min which corresponding to n-dodecane (n-C12), and n-eicosane (n-C20) (internal standard), respectively. The peaks represent palm oil appear at 22, 28, and 32–46 min. The response factor value of palm oil is 1.0080.

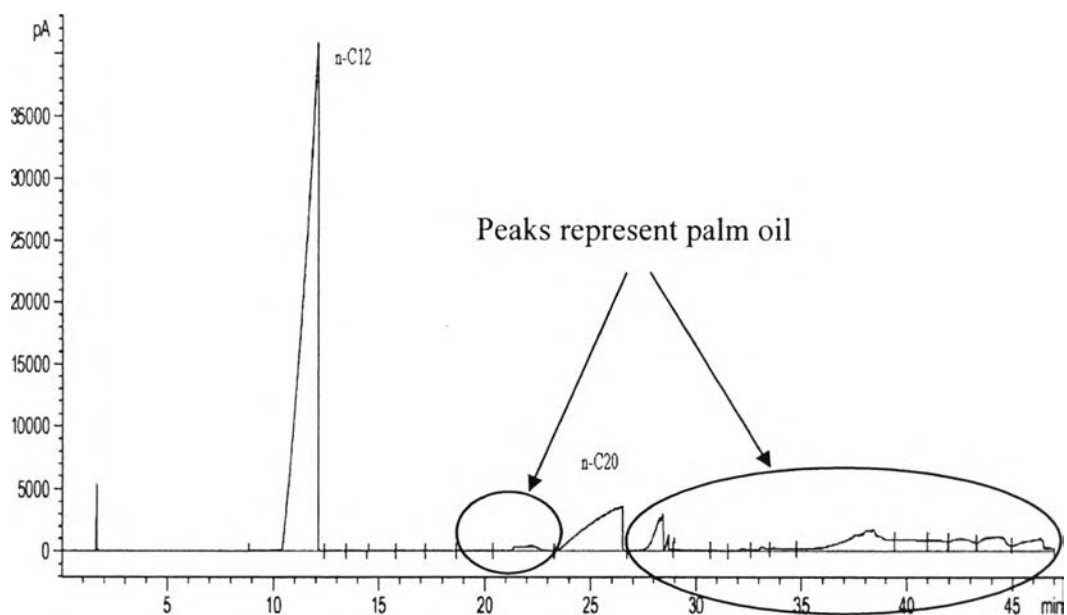


Figure 4.1 The chromatogram of 50 wt% palm oil in n-dodecane.

4.2 Standard Analysis Chromatogram

The chromatogram of the mixture of standard chemicals (24.97 wt% n-C15, 25.06 wt% n-C16, 25.94 wt% n-C17, 24.05 wt% n-C18, and 24.99 wt% n-C20 in n-dodecane) is shown in Figure 4.2. It shows that the retention times of n-dodecane (n-C12), n-pentadecane (n-C15), n-hexadecane (n-C16), n-heptadecane (n-C17), n-octadecane (n-C18), and n-eicosane (n-C20) are 11, 15, 16, 17, 19, and 25 min, respectively.

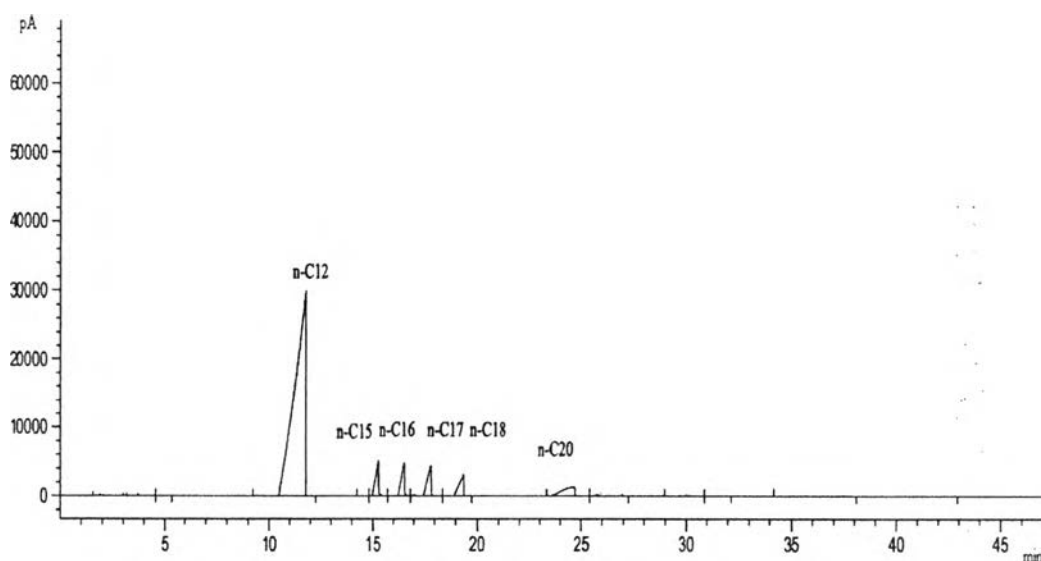


Figure 4.2 The chromatogram of the standard chemicals; dodecane, pentadecane, hexadecane, heptadecane, octadecane, and eicosane.

To find out the response factor value of each hydrocarbon compound, eicosane is used as the internal standard. Table 4.1 shows the response factor of each substance in mixture of standard chemicals.

Table 4.1 Response factor of each substance in the reference standard

Substances	Response factor
n-Pentadecane	1.0087
n-Hexadecane	1.0020
n-Heptadecane	1.0099
n-Octadecane	1.0051

4.3 Deoxygenation of Palm Oil over NiMo/Al₂O₃ Catalyst

4.3.1 Blank Test

The test run of 25 wt% palm oil in n-dodecane was conducted with a support: γ -Al₂O₃ (mesh size of 20/40, temperature of 325°C, pressure of 500 psig, H₂/feed molar ratio of 30, and liquid hourly space velocity (LHSV) of 0.05 h⁻¹). The result shows that alkane products (n-C15–n-C18) do not appear on the γ -Al₂O₃ support. This result is in agreement with a previous work done by Senol and co-workers, (2005). They reported that γ -Al₂O₃ could convert esters to corresponding alcohols and acids but γ -Al₂O₃ alone could not do the deoxygenation of molecules.

4.3.2 Effect of Reaction Parameters

The deoxygenation of palm oil over NiMo/Al₂O₃ catalyst was conducted at various parameters such as temperature, pressure, LHSV, and H₂/feed ratio as shown in Table 4.2.

Table 4.2 Examined parameters for deoxygenation of palm oil

Run	Temperature (°C)	Pressure (psig)	LHSV (h ⁻¹)	H ₂ /Feed molar ratio
1	300	500	3	30
2	325	500	3	30
3	350	500	3	30
4	375	500	3	30
5	325	400	3	30
6	325	600	3	30
7	325	700	3	30
8	325	500	5	30
9	325	500	0.5	30
10	325	500	0.1	30
11	325	500	0.05	30
12	325	500	3	15
13	325	500	3	22.5

4.3.2.1 Effect of Liquid Hourly Space Velocity (LHSV)

To study the effect of the liquid hourly space velocity, the deoxygenation of 25 wt% palm oil in n-dodecane was conducted at 325°C, 500 psig, and H₂/feed molar ratio of 30. The liquid hourly space velocity was varied from 0.05 to 5 h⁻¹. Figure 4.3 shows that the palm oil conversion was increased with contact time and it was completely converted after equivalent contact time of 10 h. In addition, intermediate products, white solid appearance, are observed at low contact time and they are decreased when the equivalent LHSV contact time is further increased. In term of total paraffinic hydrocarbons that are n-C15, n-C16, n-C17, and n-C18, Table 4.3 shows that selectivity to total paraffinic hydrocarbons increased with equivalent contact time. Moreover, n-C16 and n-C18 were obtained as two main products at all condition tested. Therefore, it can be reported that the production of renewable diesel

from deoxygenation of palm oil over the NiMo/Al₂O₃ catalyst prefers to occur via hydrodeoxygenation path.

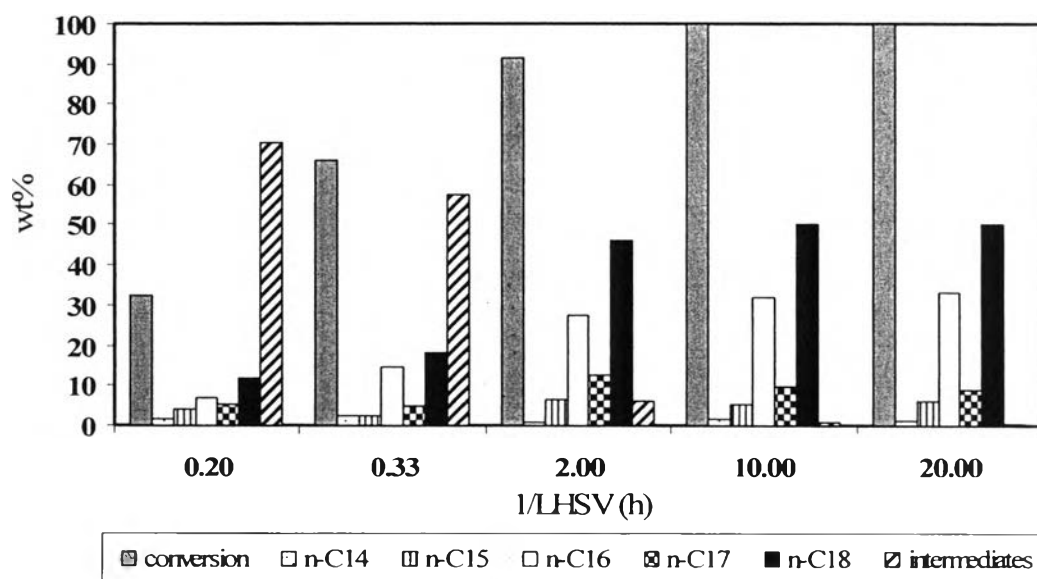
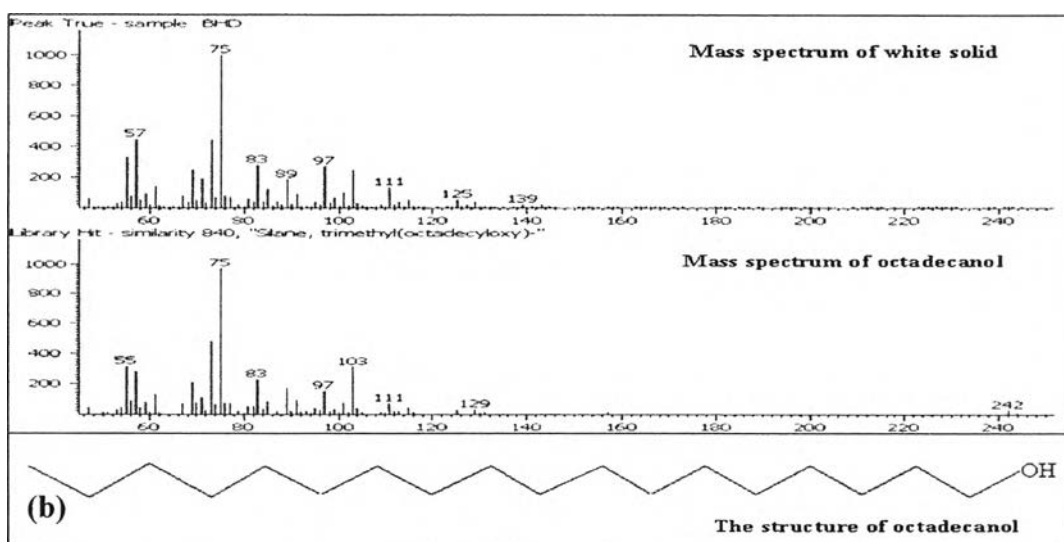
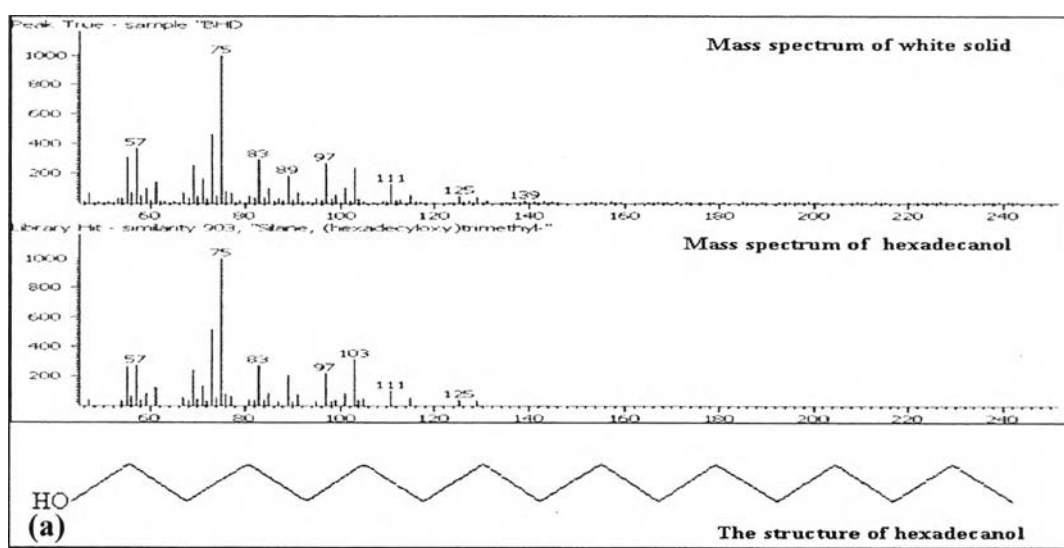


Figure 4.3 Conversion and product selectivity as a function of contact time, 1/LHSV (h), over NiMo/Al₂O₃ (temperature: 325°C, pressure: 500 psig, H₂/feed molar ratio: 30, and TOS: 4 h).

Table 4.3 Conversion, n-C18/n-C17 ratio, selectivity to intermediate products, and total paraffinic hydrocarbon obtained from the deoxygenation of 25 wt% palm oil in dodecane over NiMo/Al₂O₃ at 325°C, 500 psig, H₂/feed molar ratio: 30, and TOS: 4 h

	Equivalent Contact Time, (1/LHSV) (h)				
	0.2	0.33	2	10	20
Conversion	32.46	66.14	91.53	100	100
Selectivity (wt%)					
Intermediate products	70.41	57.34	6.11	0.95	0.60
Total n-C15 to n-C18	28.09	40.28	92.88	97.33	98.23
C ₁₈ /C ₁₇ ratio	2.21	3.66	3.64	5.22	5.69

To further understand the structure of white solid, the white solid was dissolved in pyridine and silylated with BSTFA after that analyzed by GC/MS (Pegasus Mass Selective Detector equipped with 6890 Network GC system). The mass spectrum of white solid is shown in Figure 4.4. It was found that the mass spectrum of white solid corresponds to that of hexadecanol, octadecanol, hexadecanoic acid, and octadecanoic acid. Therefore, it is believed that hexadecanol, octadecanol, hexadecanoic acid, and octadecanoic acid are observed as intermediates in the deoxygenation of palm oil.



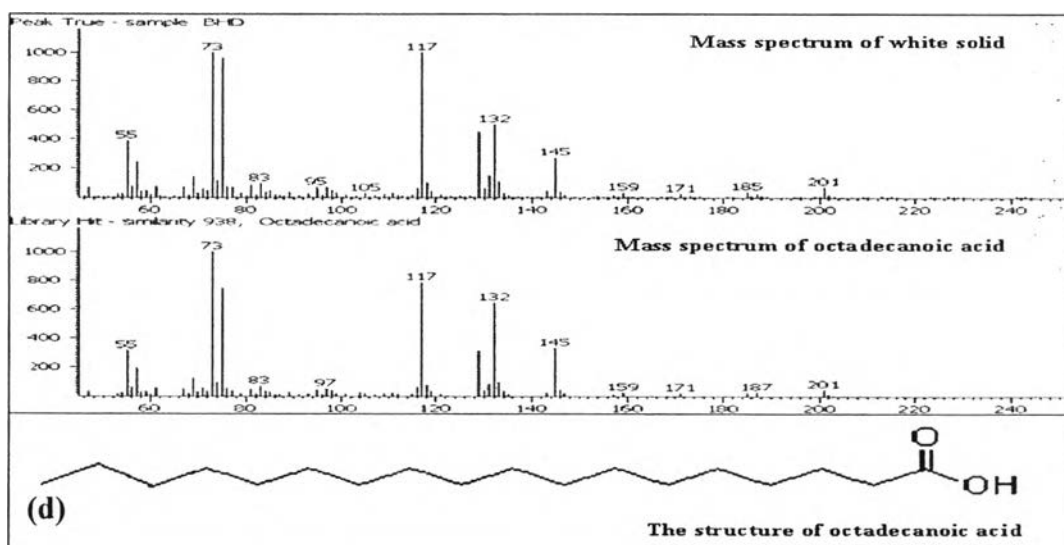
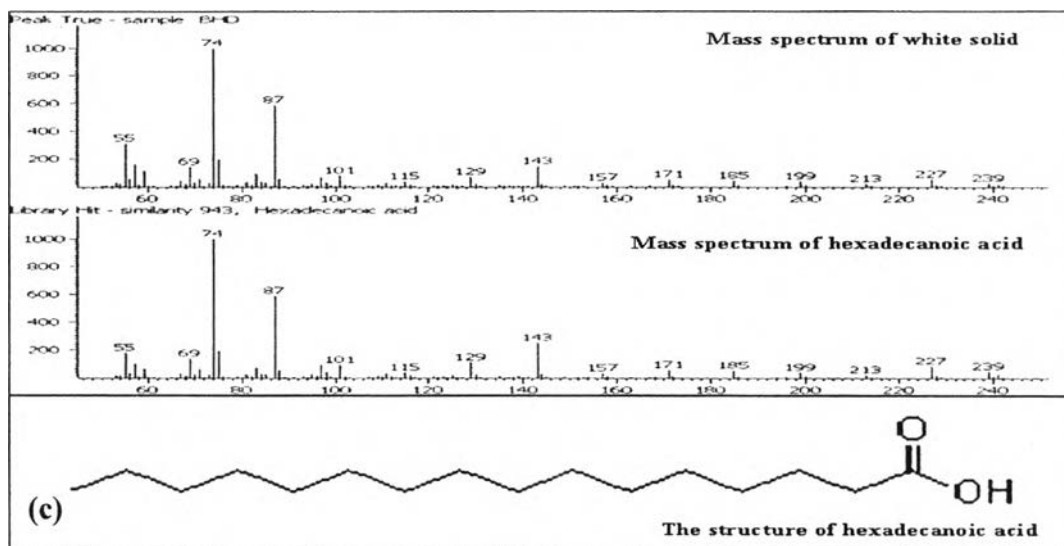


Figure 4.4 Mass spectrum of white solid obtained from GC/MS compared to that of (a) hexadecanol, (b) octadecanol, (C) hexadecanoic acid, and (d) octadecanoic acid from NIST Library.

4.3.2.2 Effect of Reaction Temperature

To study the effect of the reaction temperature, the deoxygenation of 25 wt% palm oil in n-dodecane was conducted at 500 psig, LHSV of 3 h^{-1} , and H_2/feed molar ratio of 30. The reaction temperature was varied from 300 to 375°C . The results are shown in Figure 4.5. Palm oil conversion was increased with reaction temperature while selectivity to intermediate products was decreased. At the temperature above 325°C , increasing the temperature caused an increased of the selectivity towards lighter products. It is probably due to thermal cracking at high temperature. In the consideration of n-C18/n-C17 ratio, Table 4.4 shows that the value of n-C18/n-C17 decreased when the reaction temperature was increased. Therefore, it can be reported that the deoxygenation of palm oil should be done at the temperature in the range of 300 to 325°C to inhibit the cracking reaction and the reaction via hydrodecarbonylation path is likely to occur at high temperature.

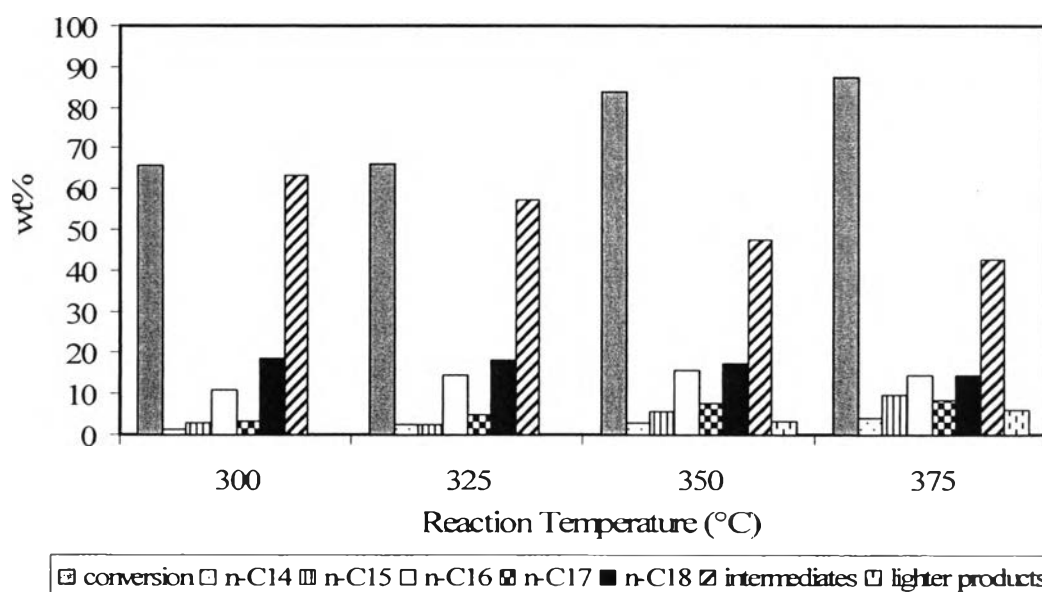


Figure 4.5 Conversion and product selectivity as a function of reaction temperature over NiMo/Al₂O₃ (pressure: 500 psig, LHSV: 3 h^{-1} , H_2/feed molar ratio: 30, and TOS: 4 h).

Table 4.4 Conversion, n-C18/n-C17 ratio, selectivity to intermediate products, and total paraffinic hydrocarbon obtained from deoxygenation of 25 wt% palm oil in dodecane over NiMo/Al₂O₃ at 500 psig, LHSV: 3 h⁻¹, H₂/feed molar ratio: 30, and TOS: 4 h

	Reaction Temperature (°C)			
	300	325	350	375
Conversion	65.71	66.14	83.77	87.53
Selectivity (wt%)				
Intermediate products	63.18	57.34	47.69	42.62
Lighter products	-	-	3.13	5.87
Total n-C15 to n-C18	35.44	40.28	46.34	47.57
C ₁₈ /C ₁₇ ratio	5.78	3.66	2.32	1.73

4.3.2.3 Effect of Reaction Pressure

To study the effect of the reaction pressure, the deoxygenation of 25 wt% palm oil in n-dodecane was conducted at 325°C, LHSV of 3 h⁻¹, and H₂/feed molar ratio of 30. The reaction pressure was varied from 400 to 700 psig. The result was shown in Figure 4.6. When the reaction pressure was increased, the palm oil conversion was also increased while selectivity to intermediate products was decreased. In term of total selectivity to paraffinic hydrocarbons, it was found that the total selectivity to paraffinic hydrocarbons was increased when increased the reaction pressure. It is probably due to increasing of hydrogen partial pressure drive the reaction go toward resulting in high paraffinic hydrocarbon products at high hydrogen partial pressure. Moreover, the result revealed that the n-C18/n-C17 ratio tends to increase with reaction pressure as shown in Table 4.5. It is due to the increasing in the production of n-C18 at high pressure. Therefore, it can be reported that the deoxygenation of palm oil over the NiMo/Al₂O₃ prefers to undergo hydrodeoxygenation especially at high pressure.

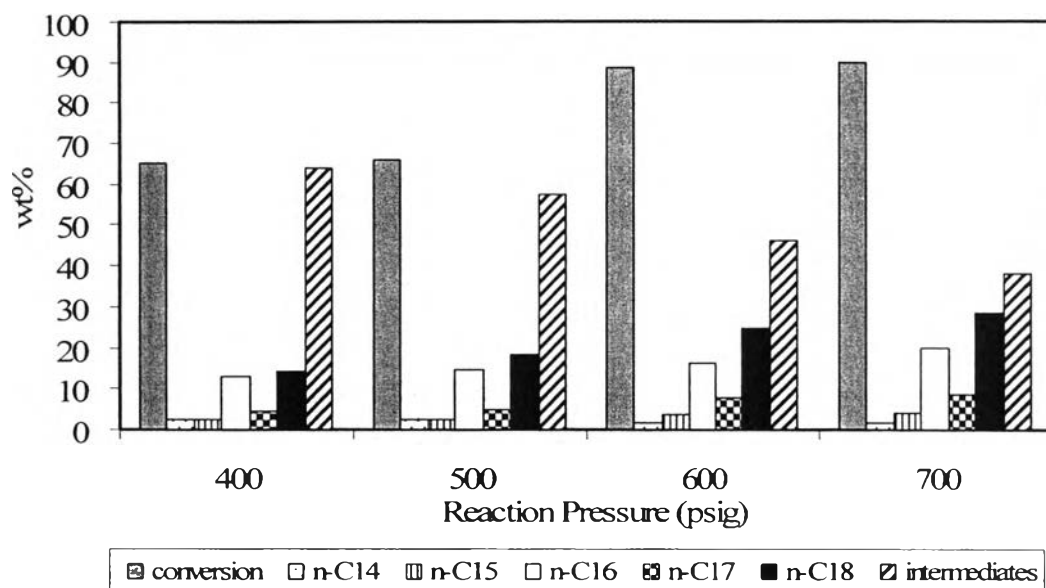


Figure 4.6 Conversion and product selectivity as a function of reaction pressure over NiMo/Al₂O₃ (temperature: 325°C, LHSV: 3 h⁻¹, H₂/feed molar ratio: 30, and TOS: 4 h).

Table 4.5 Conversion, n-C18/n-C17 ratio, selectivity to intermediate products, and total paraffinic hydrocarbon obtained from deoxygenation of 25 wt% palm oil in dodecane over NiMo/Al₂O₃ at 325°C, LHSV: 3 h⁻¹, H₂/feed molar ratio: 30, and TOS: 4 h

	Reaction Pressure (psig)			
	400	500	600	700
Conversion	65.34	66.14	88.50	89.87
Selectivity (wt%)				
Intermediate products	63.84	57.34	46.15	38.11
Total n-C15 to n-C18	33.73	40.28	52.31	60.46
C ₁₈ /C ₁₇ ratio	3.12	3.66	3.23	3.35

4.3.2.4 Effect of H_2 /Feed Ratio

To study the effect of H_2 /feed ratio, the deoxygenation of 25 wt% palm oil in n-dodecane was conducted at 325°C, 500 psig, and LHSV of 3 h⁻¹. The H_2 /feed molar ratio was investigated at 15, 22.5, and 30. Figure 4.7 shows that when the H_2 /feed molar ratio was increased, the palm oil conversion was slightly increased. Moreover, it was found that the selectivity to n-hexadecane (n-C16) and n-octadecane (n-C18) increased with the H_2 /feed molar ratio. Table 4.6 shows that the higher H_2 /feed molar ratio, the higher the n-C18/n-C17 is observed that is corresponds to the increasing of selectivity to n-C18 at high H_2 /feed molar ratio. Therefore, the deoxygenation of palm oil via hydrodeoxygenation path prefers to be occurred at higher H_2 /feed molar ratio, compared to hydrodecarbonylation path.

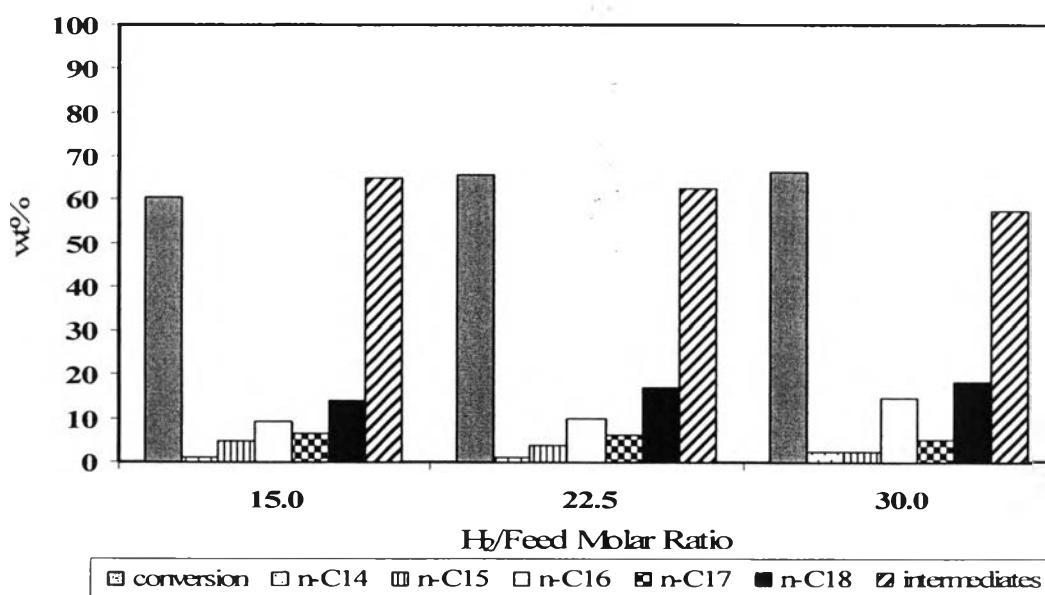


Figure 4.7 Conversion and product selectivity as a function of H_2 /feed molar ratio over NiMo/ Al_2O_3 (temperature: 325°C, pressure: 500 psig, LHSV: 3 h⁻¹, and TOS: 4 h).

Table 4.6 Conversion, n-C18/n-C17 ratio, selectivity to intermediate products, and total paraffinic hydrocarbon obtained from deoxygenation of 25 wt% palm oil in dodecane over NiMo/Al₂O₃ at 325°C, 500 psig, LHSV: 3 h⁻¹, and TOS: 4 h

	H₂/Feed Molar Ratio		
	15	22.5	30
Conversion	60.35	65.61	100
Selectivity (wt%)			
Intermediate products	64.76	62.40	57.34
Total n-C15 to n-C18	34.28	36.65	40.28
C ₁₈ /C ₁₇ ratio	2.18	2.81	3.66

4.4 Deoxygenation of Palm Oil over Pd/C Catalyst

4.4.1 Effect of Reaction Parameters

The deoxygenation of palm oil over Pd/C catalyst was conducted at various parameters such as temperature, pressure, LHSV, and H₂/feed ratio as shown in Table 4.7.

Table 4.7 Examined parameters for deoxygenation of palm oil

Run	Temperature (°C)	Pressure (psig)	LHSV (h ⁻¹)	H ₂ /Feed molar ratio
1	300	500	3	30
2	325	500	3	30
3	350	500	3	30
4	375	500	3	30
5	325	400	3	30
6	325	600	3	30
7	325	700	3	30
8	325	500	5	30
9	325	500	0.5	30
10	325	500	0.1	30
11	325	500	0.05	30
12	325	500	0.1	15
13	325	500	0.1	22.5

4.4.1.1 Effect of Liquid Hourly Space Velocity (LHSV)

To study the effect of the liquid hourly space velocity, the deoxygenation of 25 wt% palm oil in n-dodecane was conducted at 325°C, 500 psig, and H₂/feed molar ratio of 30. The liquid hourly space velocity was varied from 0.05 to 5 h⁻¹. Figure 4.8 shows that the palm oil conversion approached 100% as the equivalent contact time increased and it was completely converted after equivalent contact time of 10 h. In addition, it was found that there are a lot of intermediate products (hexadecanol, octadecanol, hexadecanoic acid, and octadecanoic acid) were observed at low contact time and they are decreased when the contact time is further increased. In consideration of total paraffinic hydrocarbons, Table 4.8 shows that the selectivity to total paraffinic hydrocarbons increased with contact time that is corresponds to decreasing of selectivity to intermediate products. At all condition

tested, the result showed that n-pentadecane (n-C15) and n-heptadecane (n-C17) were observed as two main products in liquid phase. Therefore, it can be reported that the production of renewable diesel from the deoxygenation of palm oil over the Pd/C catalyst prefers hydrodecarbonylation path.

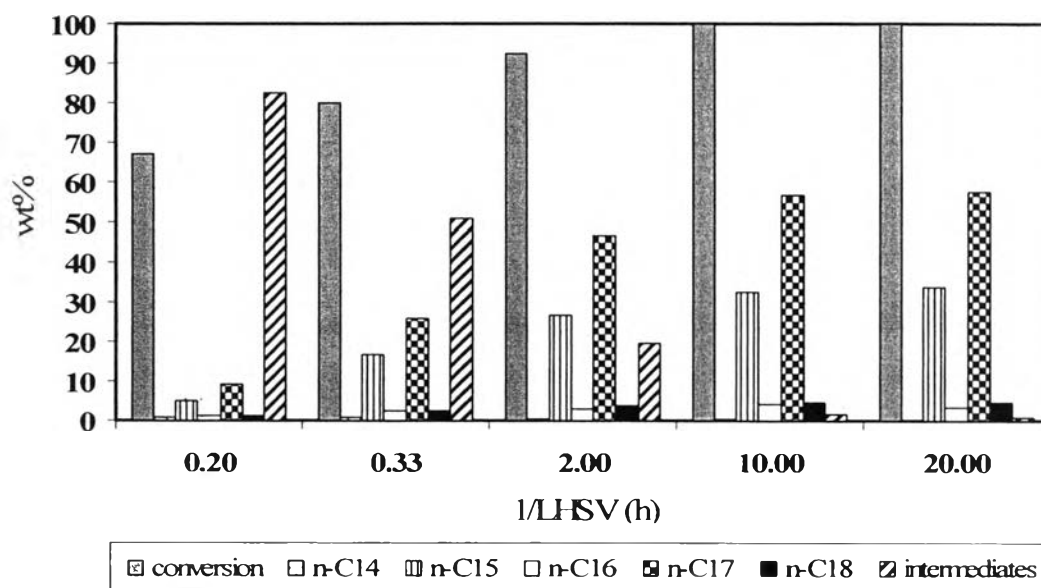


Figure 4.8 Conversion and product selectivity as a function of contact time, 1/LHSV (h), over Pd/C (temperature: 325°C, pressure: 500 psig, H₂/feed molar ratio: 30, and TOS: 5 h).

Table 4.8 Conversion, n-C18/n-C17 ratio, selectivity to intermediate products, and total paraffinic hydrocarbon obtained from deoxygenation of 25 wt% palm oil in dodecane over Pd/C at 325°C, 500 psig, and H₂/feed molar ratio: 30, and TOS: 5 h

	Equivalent Contact Time, (1/LHSV) (h)				
	0.2	0.33	2	10	20
Conversion	67.21	79.98	92.65	100	100
Selectivity (wt%)					
Intermediate products	82.55	50.94	19.58	1.64	1.03
Total n-C15 to n-C18	16.82	48.10	79.86	97.85	98.77
C ₁₈ /C ₁₇ ratio	0.16	0.10	0.08	0.08	0.08

4.4.1.2 Effect of Reaction Temperature

To study the effect of the reaction temperature, the deoxygenation of 25 wt% palm oil in n-dodecane was conducted at 500 psig, LHSV of 3 h^{-1} , and H_2/feed molar ratio of 30. The reaction temperature was varied from 300 to 375°C . The results is shown in Figure 4.9. When the reaction temperature was increased, palm oil conversion was also increased while the selectivity to intermediate products was decreased. Moreover, it was observed that the selectivity to lighter products— nonane (C_9H_{20}), decane ($\text{C}_{10}\text{H}_{22}$), and undecane ($\text{C}_{11}\text{H}_{24}$)— increased at the temperature above 325°C . It is probably due to cracking reaction. In the consideration of n-C18/n-C17 ratio, Table 4.9 shows that the value of n-C18/n-C17 decreased when the reaction temperature is increased. Therefore, it can be reported that the deoxygenation of palm oil over Pd/C catalyst should be done at the temperature lower than 350°C to inhibit the cracking reaction and the reaction prefers to undergo hydrodecarbonylation especially at high temperature.

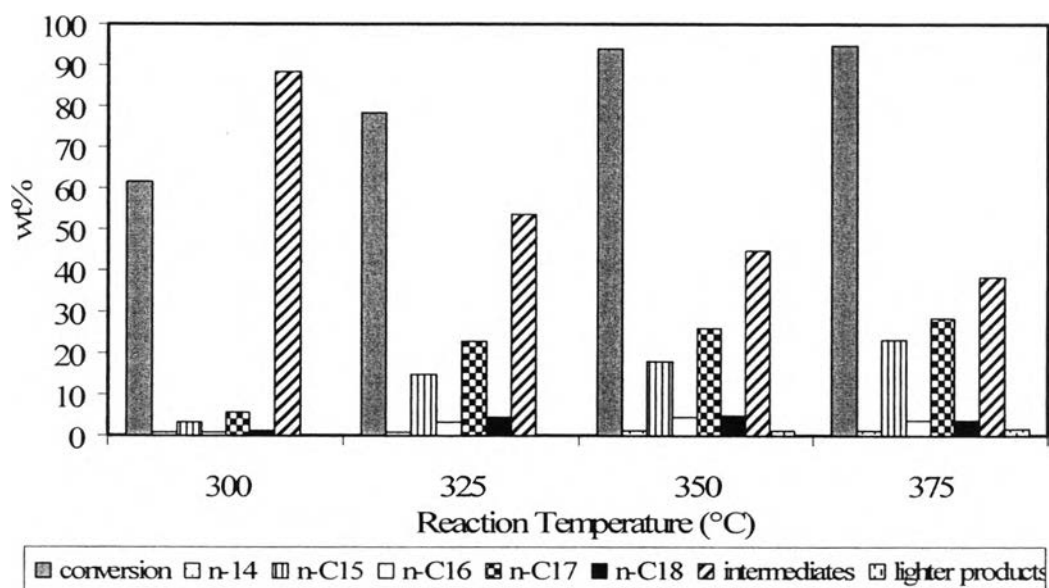


Figure 4.9 Conversion and product selectivity as a function of reaction temperature over Pd/C (pressure: 500 psig, LHSV: 3 h^{-1} , H_2/feed molar ratio: 30, and TOS: 4 h).

Table 4.9 Conversion, n-C18/n-C17 ratio, selectivity to intermediate products, and total paraffinic hydrocarbon obtained from deoxygenation of 25wt% palm oil in dodecane over Pd/C at 500 psig, LHSV: 3 h⁻¹, and H₂/feed molar ratio: 30, and TOS: 4 h

	Reaction Temperature (°C)			
	300	325	350	375
Conversion	61.64	78.53	94.00	94.69
Selectivity (wt%)				
Intermediate products	88.44	53.68	44.87	38.57
Lighter products	-	-	1.01	1.42
Total n-C15 to n-C18	10.93	45.50	53.10	58.99
C ₁₈ /C ₁₇ ratio	0.23	0.19	0.18	0.13

4.4.1.3 Effect of Reaction Pressure

To study the effect of the reaction pressure, the deoxygenation of 25 wt% palm oil in n-dodecane was conducted at 325°C, LHSV of 3 h⁻¹, and H₂/feed molar ratio of 30. The reaction pressure was varied at 400, 500, 600, and 700 psig. The result is shown in Figure 4.10. The palm oil conversion was increased when the reaction pressure was increased. In term of total selectivity to paraffinic hydrocarbons, Table 4.10 shows that total selectivity to paraffinic hydrocarbons increased with the reaction pressure resulting in decreasing of intermediate products. In term of n-C18/n-C17 ratio, this ratio slightly decreased with reaction pressure. Therefore, it can be reported that the deoxygenation of palm oil over the Pd/C catalyst prefers to undergo hydrodecarbonylation at all condition tested.

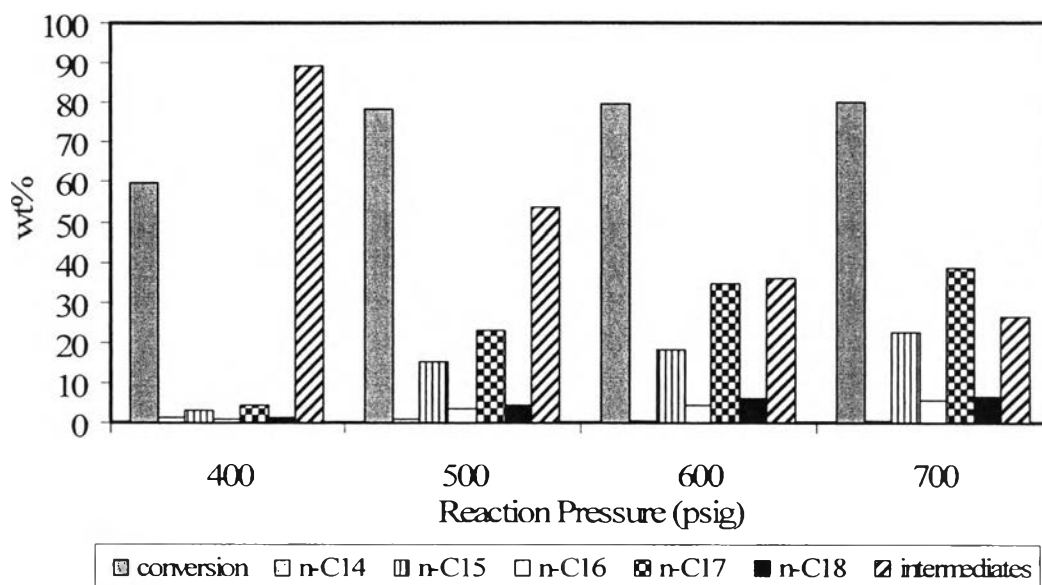


Figure 4.10 Conversion and product selectivity as a function of reaction pressure over Pd/C (temperature: 325°C, LHSV: 3 h⁻¹, H₂/feed molar ratio: 30, and TOS: 4 h).

Table 4.10 Conversion, n-C18/n-C17 ratio, selectivity to intermediate products, and total paraffinic hydrocarbon obtained from deoxygenation of 25 wt% palm oil in dodecane over Pd/C catalyst at 325°C, H₂/feed molar ratio: 30, LHSV: 3 h⁻¹, and TOS: 4 h

	Reaction Pressure (psig)			
	400	500	600	700
Conversion	59.92	78.53	79.64	80.03
Selectivity (wt%)				
Intermediate products	89.28	53.68	36.06	26.59
Total n-C15 to n-C18	9.60	45.49	63.33	72.81
C ₁₈ /C ₁₇ ratio	0.31	0.19	0.17	0.17

4.4.1.4 Effect of H₂/Feed Ratio

To study the effect of H₂/feed ratio, the deoxygenation of 25 wt% palm oil in n-dodecane was conducted at 325°C, 500 psig, and LHSV of 3 h⁻¹. The H₂/feed molar ratio was investigated at 15, 22.5, and 30 molar ratio. Figure 4.11 shows that the palm oil conversion increased with H₂/feed molar ratio.

Moreover, Table 4.11 reveals that the selectivity to hydrocarbon products increased with the H_2 /feed molar ratio especially n-hexadecane (n-C16) and n-octadecane (n-C18) which leads to the higher n-C18/n-C17 at high H_2 /feed molar ratio. Therefore, the deoxygenation of palm oil via hydrodeoxygenation path is preferred to be occurred at higher H_2 /feed molar ratio, compared to hydrodecarbonylation path.

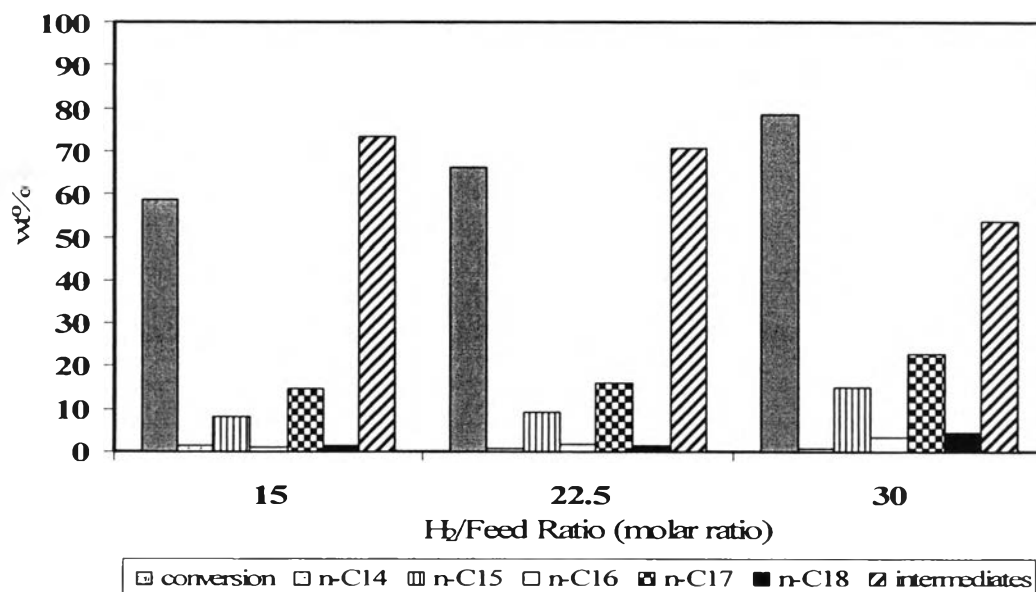


Figure 4.11 Conversion and product selectivity as a function of H_2 /feed molar ratio over Pd/C (temperature: 325°C, pressure: 500 psig, LHSV: 3 h⁻¹, and TOS: 4 h).

Table 4.11 Conversion, n-C18/n-C17 ratio, selectivity to intermediate products, and total paraffinic hydrocarbon obtained from deoxygenation of 25 wt% palm oil in dodecane over Pd/C at 325°C, 500 psig, LHSV: 3 h⁻¹, and TOS: 4 h

	H_2/Feed Molar Ratio		
	15	22.5	30
Conversion	58.81	66.08	78.53
Selectivity (wt%)			
Intermediate products	73.41	70.79	53.68
Total n-C15 to n-C18	25.26	28.39	45.49
C_{18}/C_{17} ratio	0.09	0.10	0.19

4.5 Proposed Reaction Pathways of the Deoxygenation of Palm Oil

From the literature reviews (Huber *et al.*, 2007), it was proposed a reaction pathway for conversion of triglycerides into alkanes. In the first step of this reaction pathway the triglyceride is hydrogenated and broken down into various intermediates which they suppose are monoglycerides, diglycerides and carboxylic acids. These intermediates are then converted into alkanes by three different pathways: decarboxylation, decarbonylation and hydrodeoxygenation. Based on these proposed pathways, the reaction pathway of deoxygenation of palm oil under hydrogen flow can be proposed in the same manner. First of all, palm oil is hydrogenated and broken down into corresponding acids that are hexadecanoic acid and octadecanoic acid, followed by hydrogenation of carbonyl group into hexadecanol and octadecanol. After that, hexadecanol and octadecanol are dehydrated and hydrogenated to long chain alkanes with carbon atoms equivalent to the carbon atoms of fatty acids in each oil molecule that are n-hexadecane (n-C16) and n-octadecane (n-C18) having H₂O as by product. This pathway is called hydrodeoxygenation. However, hexadecanoic acid and octadecanoic acid can be decarbonylated and further hydrogenated to alkane products that have one carbon atom less than the original fatty acids in each oil molecule that are n-pentadecane (n-C15) and n-heptadecane (n-C17) having CO and H₂O as a by-product. This path is called hydrodecarbonylation.

4.6 Stability Testing of Selected Catalyst

NiMo/Al₂O₃ was selected to test for its stability in the deoxygenation of palm oil for 9 days. The deoxygenation reaction was conducted at 325°C, 600 psig, LHSV 0.1 h⁻¹, and H₂/feed molar ratio of 30. From Figure 4.12, it was found that during 9 day-time-on-stream, the palm oil conversion slightly decreased with time on stream. n-Octadecane (n-C18) and n-hexadecane (n-C16) are favorable to be produced compared to n-heptadecane (n-C17) and n-pentadecane (n-C15). From the Figure 4.12, it can be reported that palm oil conversion and selectivity to alkane products quite stable under the condition tested. Moreover, trace amount of intermediate products were also observed. Furthermore, the gas phase product was collected and analyzed by TCD detector; it was found that CO is present in small amount in the gas product. It is indicate that the deoxygenation of palm oil over the NiMo/Al₂O₃ is preferable via hydrodeoxygenation path compared to hydrodecarbonylation path.

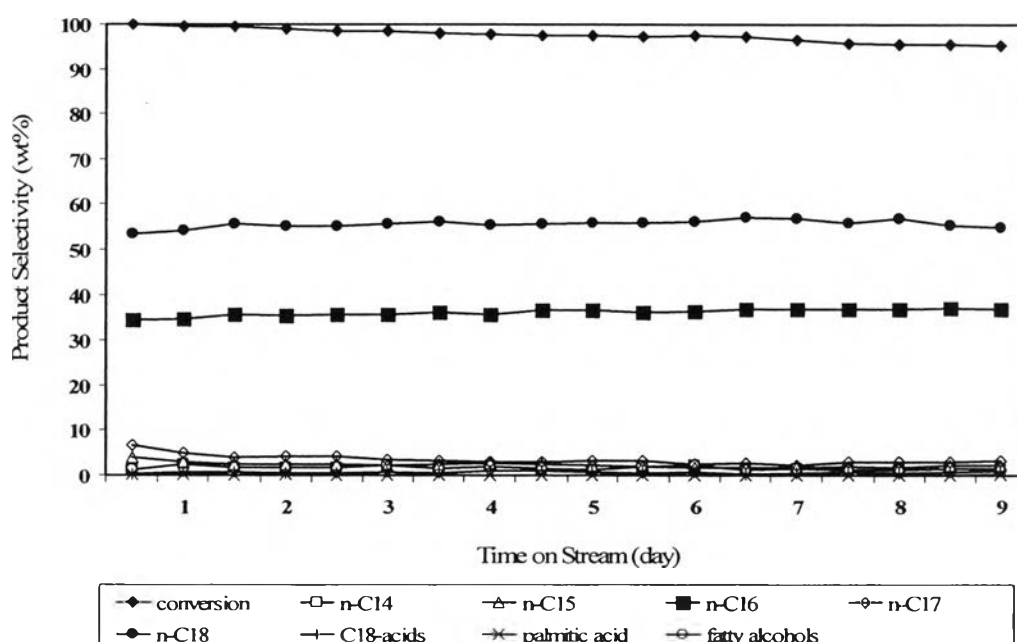


Figure 4.12 Long term stability testing of the NiMo/ γ -Al₂O₃ catalyst on the deoxygenation of 25 wt% palm oil (temperature: 325°C, pressure: 600 psig, H₂/feed molar ratio: 30, and LHSV: 0.1 h⁻¹).

4.7 Temperature Programmed Oxidation (TPO)

Temperature Programmed Oxidation (TPO) experiments were performed in order to investigate the amount of carbon formed (coke) on the NiMo/ γ -Al₂O₃ and Pd/C catalysts after the reaction was carried out at 325°C, 500 psig, LHSV 0.1 h⁻¹, and H₂/feed molar ratio 30 for 13.5 h. Figure 4.13 shows the oxidation temperature of these two catalysts. The results revealed that the amount of carbon formation on NiMo/ γ -Al₂O₃ and Pd/C were 5.48 and 9.91% weight, respectively. However, it can be suggested that these carbon formations had no effect on the performance of catalyst because the deactivation was not observed during 13.5 hours of testing.

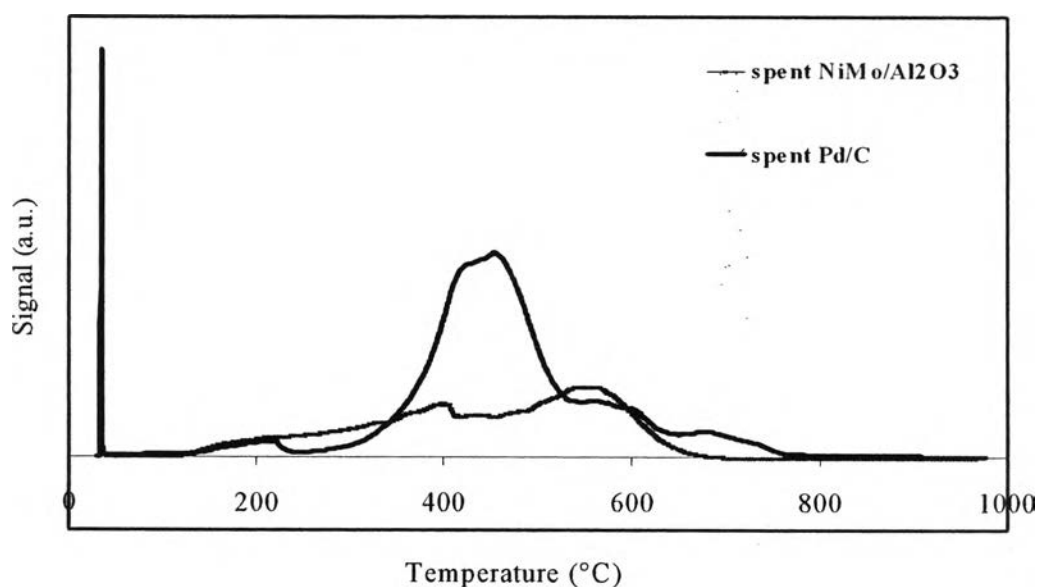


Figure 4.13 Temperature programmed oxidation profiles of the spent NiMo/Al₂O₃ and Pd/C catalysts for 13.5 h.