



CHAPTER IV RESULTS AND DISCUSSION

4.1 Standard Analysis Chromatogram

The reference standard substances are analyzed by a HP-6890 gas chromatograph equipped with a flame ionized detector (FID) and HP-5 column, with dimension of 30 m. x 0.32 mm. x 0.5 μm . Following the method for product analysis as described in Chapter 3, it was found that the retention times of dodecane, pentadecane, hexadecane, heptadecane, octadecane, and eicosane are 9, 22, 30, 38, 47, and 60 min, respectively as shown in Figure 4.2. In case of palmitic acid and oleic acid, both of them were esterified with 14wt% $\text{BF}_3\text{-CH}_3\text{OH}$ before injecting into the GC. The result shows that the retention time of palmitic acid is at 57 min; meanwhile, the retention time of oleic acid having 65-88 % purity is at 63.4, 63.6 and 64.3 min. Their chromatograms are shown in Figure 4.3 and 4.4, respectively.

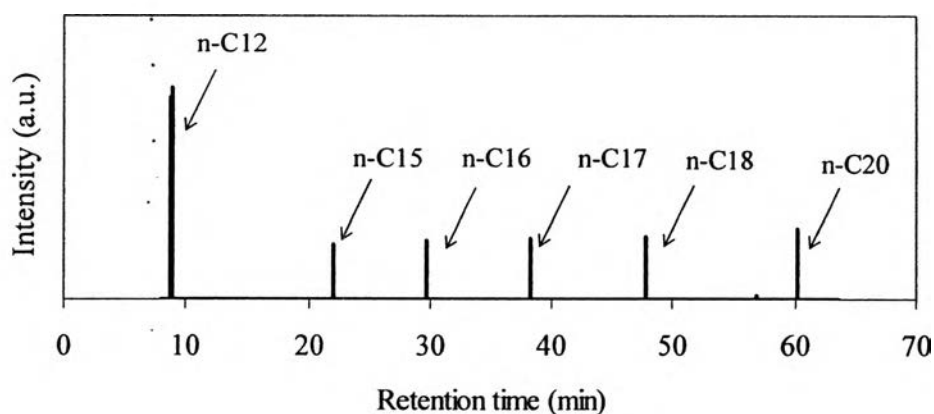


Figure 4.1 Standard chromatogram of the mixed substances; dodecane, pentadecane, hexadecane, heptadecane, octadecane, eicosane, palmitic acid, and oleic acid.

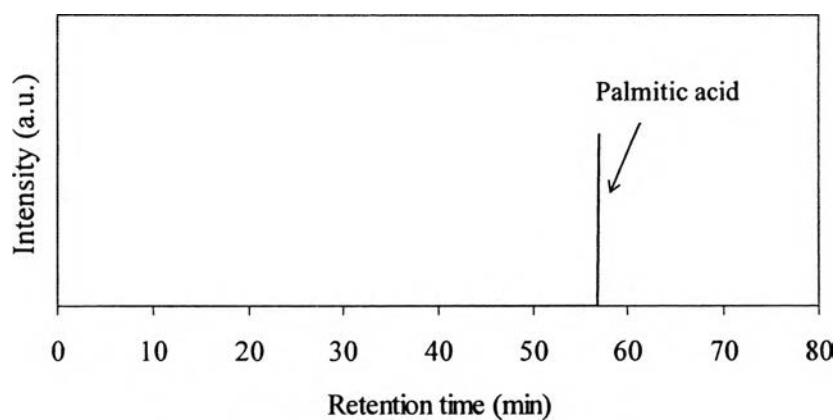


Figure 4.2 Standard chromatogram of palmitic acid

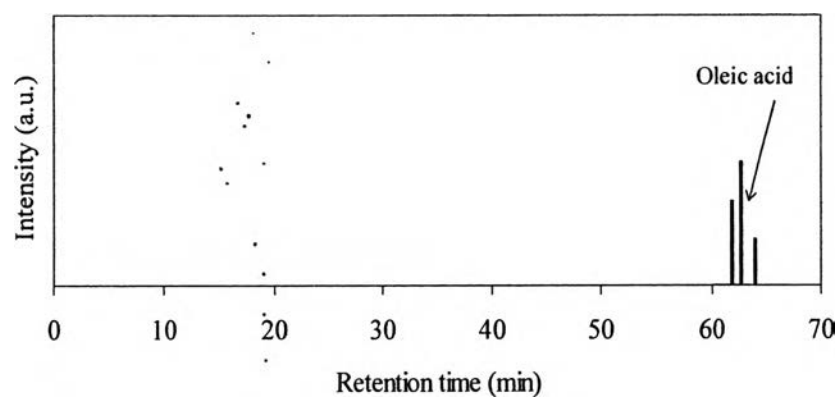


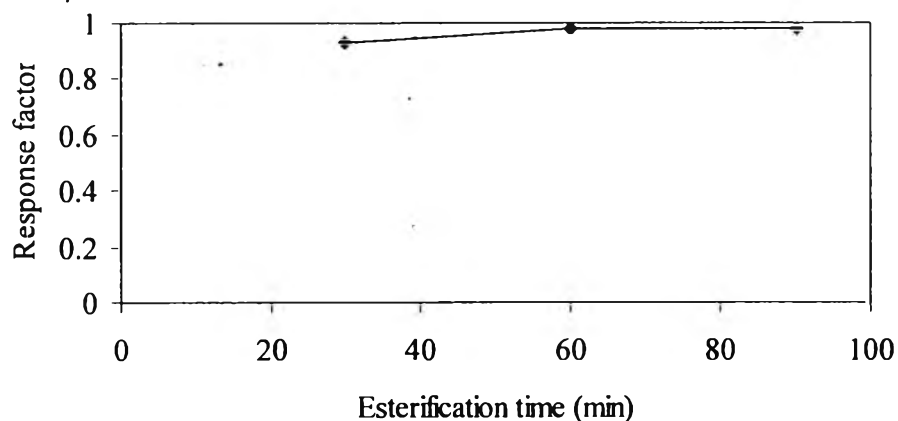
Figure 4.3 Standard chromatogram of oleic acid.

To find out the response factor value of each hydrocarbon compound, the eicosane was used as the internal standard. Table 4.1 shows the response factor of each substance in the reference standard which contains pentadecane, hexadecane, heptadecane, and octadecane.

Table 4.1 Response factors of each substance in the reference standard

Substances	Response factor
n-Pentadecane	0.78
n-Hexadecane	0.81
n-Heptadecane	0.85
n-Octadecane	0.89

However, prior to calculate the response factor of palmitic acid and oleic acid, the optimum condition for esterification of palmitic acid and oleic acid was investigated by the method recommended from Sigma-Aldrich company. The palmitic acid was esterified at 100°C for 30, 60, and 90 min; whereas, the oleic acid was esterified at 64°C for 90 and 180 min. The response factor was measured by using the eicosane as the internal standard. The results show that response factor of palmitic acid is constant even though the esterification time was increased from 60 to 90 min as depicted in Figure 4.5. As a result, the palmitic acid is esterified completely with 14wt%BF₃-CH₃OH at 100 °C for 60 min.

**Figure 4.4** Plot of response factor versus esterification time for palmitic acid at 100°C.

In the case of esterification of oleic acid, it was found that response factor of oleic acid is constant even though the esterification time was increased from 90 to 180 min as depicted in Figure 4.6. As a result, the oleic acid is esterified completely with 14wt%BF₃-CH₃OH at 64 °C for 90 min. Furthermore, their response factors are shown in Table 4.2

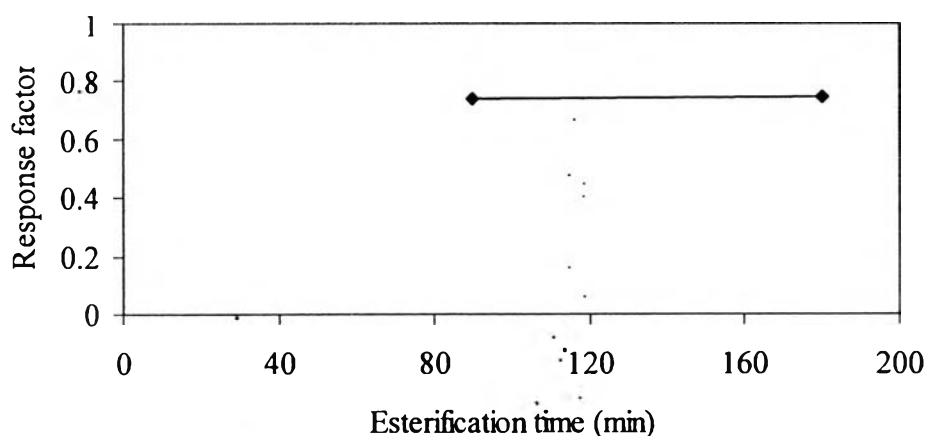


Figure 4.5 Plot of response factor versus esterification time for oleic acid at 64°C.

Table 4.2 Response factors of palmitic acid and oleic acid

Substances	Response factor
Palmitic acid	0.99
Oleic acid	0.74

4.2 Deoxygenation Experiment

4.2.1 Mass Transfer Limitation

To avoid the effect of mass transfer limitation on the deoxygenation of fatty acid (palmitic acid and oleic acid), the internal and external mass transfer limitation were investigated. In this part, the deoxygenation of 5 wt% oleic acid dissolved in n-dodecane was carried out at 350°C, 500 psig, WHSV= 1.5 hr⁻¹, and H₂/oleic acid= 70. In order to check the internal mass transfer limitation, two different mesh sizes of NiMo/γ-Al₂O₃ catalysts (20/40 and 40/60) were used and the oleic acid conversion was measured at constant condition. The result showed that no change in the oleic conversion even though the catalyst sizes were changed from 20/40 mesh to 40/60 mesh as shown in Figure 4.7.

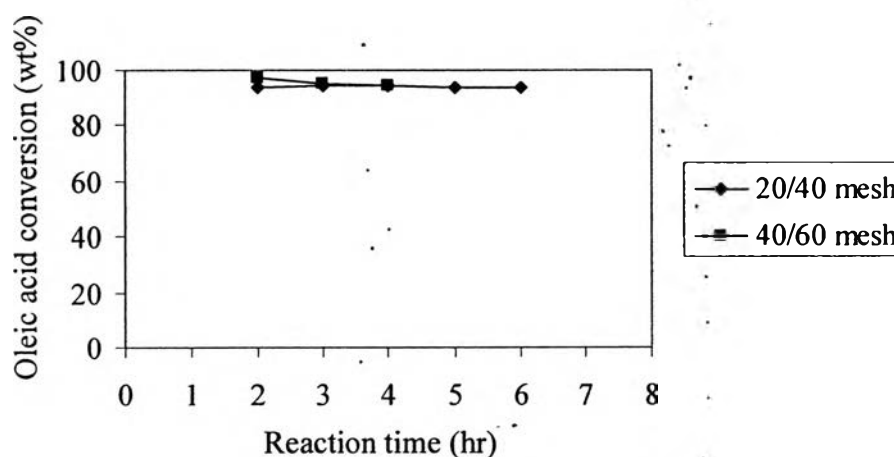


Figure 4.6 Plot of oleic acid conversion versus reaction time for various mesh size of NiMo/γ-Al₂O₃ at a constant WHSV of 1.5 hr⁻¹ (temperature: 325°C, pressure: 500 psig, feed flow rate: 0.47 ml/min, and H₂/oleic acid: 70).

For the external mass transfer limitation, the experiment was conducted by varying the feed flow rates in accordance with the amount of catalyst at constant WHSV. It was observed that the oleic conversion is constant even though the feed flow rate was increased from 0.235 ml/min to 0.47 ml/min as shown in Figure 4.8. Therefore, the NiMo/γ-Al₂O₃ catalysts having mesh size of 20/40 and the feed flow rate of 0.47 ml/min are use to eliminate the mass transfer limitation on the deoxygenation. In addition, even though the palmitic acid was used as feed instead of

oleic acid, it should have no effect of mass transfer limitation on deoxygenation of palmitic acid since their molecular weights are not too different.

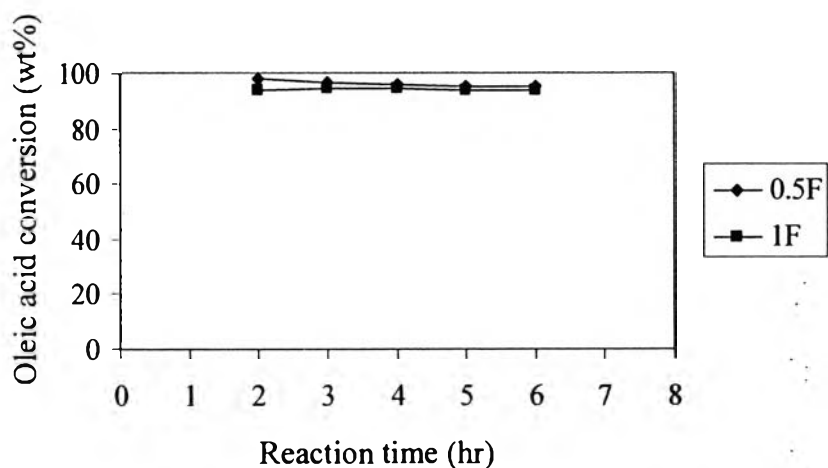


Figure 4.7 Plot of oleic acid conversion versus reaction time for various feed flow rate at a constant WHSV of 1.5 hr^{-1} (temperature: 325°C , pressure: 500 psig, feed flow rate (F): 0.47 ml/min, and $\text{H}_2/\text{oleic acid}$: 70).

4.2.2 Blank Test

Test run of pure dodecane was conducted with: NiMo/ $\gamma\text{-Al}_2\text{O}_3$ catalyst (mesh size of 20/40), $300\text{-}450^\circ\text{C}$, 500 psig, $\text{H}_2/\text{dodecane} = 8$, and WHSV = 0.64 hr^{-1} . It was found that dodecane is cracked at the temperature above 325°C as shown in Figure 4.9. Therefore, the deoxygenation of fatty acid is recommended to take place at the temperature below 325°C to avoid the cracking of the products.

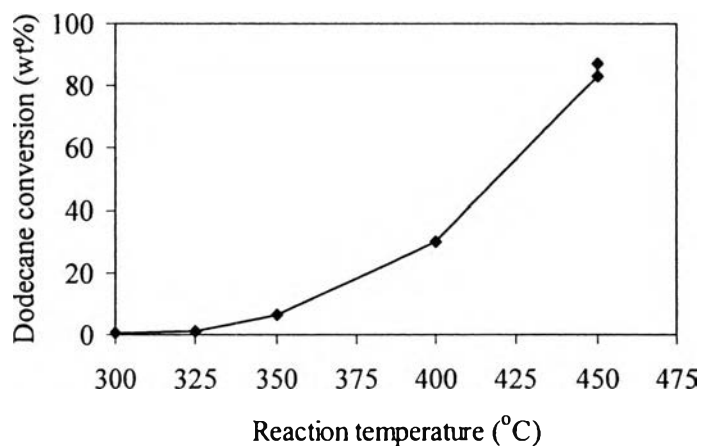


Figure 4.8 Plot of dodecane conversion versus reaction temperature using NiMo/ γ -Al₂O₃ as catalyst (temperature: 325°C, pressure: 500 psig, WHSV: 0.64 hr⁻¹, and H₂/dodecane: 8).

4.2.3 Effect of Reaction Parameters on the deoxygenation of fatty acid

The deoxygenation of fatty acid was done over NiMo/ γ -Al₂O₃ catalyst at various parameters such as temperature, pressure, WHSV, H₂/fatty acid ratio, and fatty acid concentration as shown in Table 4.3. Liquid products from the experiment was collected manually every 1 hr. After that, the liquid products were esterified with 14wt%BF₃-CH₃OH before injection into GC

Table 4.3 Examined parameters for deoxygenation of fatty acid (palmitic acid and oleic acid)

Run	Temperature (°C)	Pressure (psig)	H ₂ /fatty acid	WHSV (hr ⁻¹)	[fatty acid] wt%
1	275	500	70	0.5	5
2	300	500	70	0.5	5
2	325	500	70	0.5	5
3	325	250	70	0.5	5
4	325	350	70	0.5	5
5	325	600	70	0.5	5
6	325	500	35	0.5	5
7	325	500	140	0.5	5
8	325	500	210	0.5	5
9	325	500	70	0.25	5
10	325	500	70	0.1	5
11	325	500	70	0.05	5
12	325	500	70	0.5	20
13	325	500	70	0.5	50
14	325	500	70	0.5	100

4.2.3.1 Deoxygenation of Oleic Acid over NiMo/Al₂O₃

4.2.3.1.1 Effect of Temperature

To study the effect of the reaction temperature, the deoxygenation of 5wt% oleic acid in n-dodecane was conducted at 500 psig, WHSV of 0.5 hr⁻¹, and H₂/oleic acid ratio of 70. The reaction temperature was varied from 275, 300, to 325°C. The liquid product was collected and analyzed by GC. The results showed that the oleic acid conversion was 98% when the reaction was carried out at 275°C for 3 hr time on stream; however, less selectivity to n-octadecane (C18) and no n-heptadecane (C17) were obtained at this temperature, leading to the high intermediate product selectivity. As the reaction temperature increased, the oleic acid was completely converted after 3 hr time on stream. Furthermore, it was observed that the selectivity to n-heptadecane (C17) and n-octadecane (C18) increased with the reaction temperature as shown in Figure 4.13. Simultaneously, the selectivity to intermediate product decreases with the reaction temperature. Therefore, the deoxygenation is favorable to occur at temperature higher than 275°C and lower than 325°C to inhibit the cracking reaction as reported in the effect of solvent. Furthermore, the gas phase product was collected and analyzed by TCD detector; it was found that CO and H₂ are present in the gas product.

To further understand the structure of white solid as shown in Figure 4.10 (a), the white solid was dissolved in ethanol and analyzed by GC-MS (Agilent 5973 Network Mass Selective Detector equipped with 6890N Network GC system). The chromatogram and mass spectrum of white solid are shown in Figure 4.10 (b) and 4.11. It was found that the mass spectrum of white solid was corresponded to that of octadecanol as depicted in Figure 4.11. Therefore, it is believed that the white solid is 1-octadecanol.

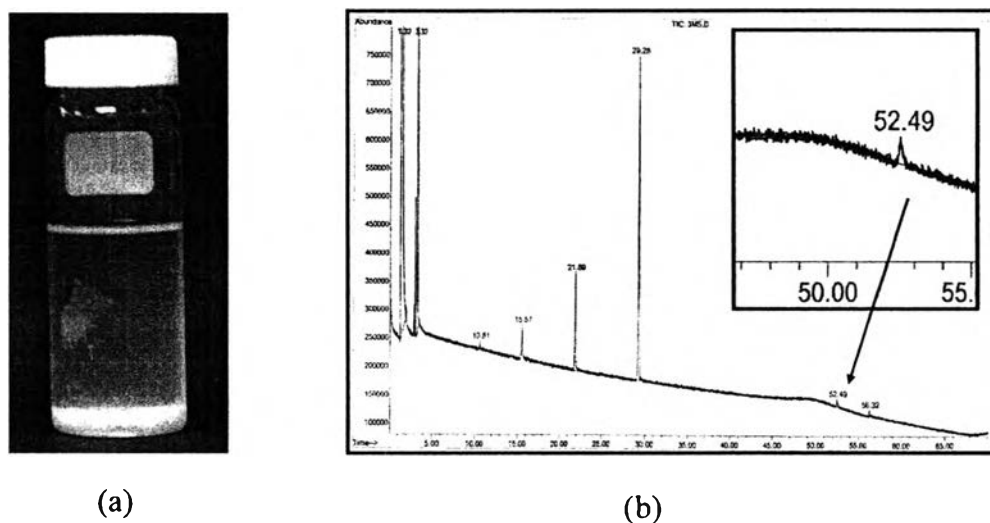


Figure 4.9 The pictures of (a) product with white solid and (b) its chromatogram analyzed by GC-MS.

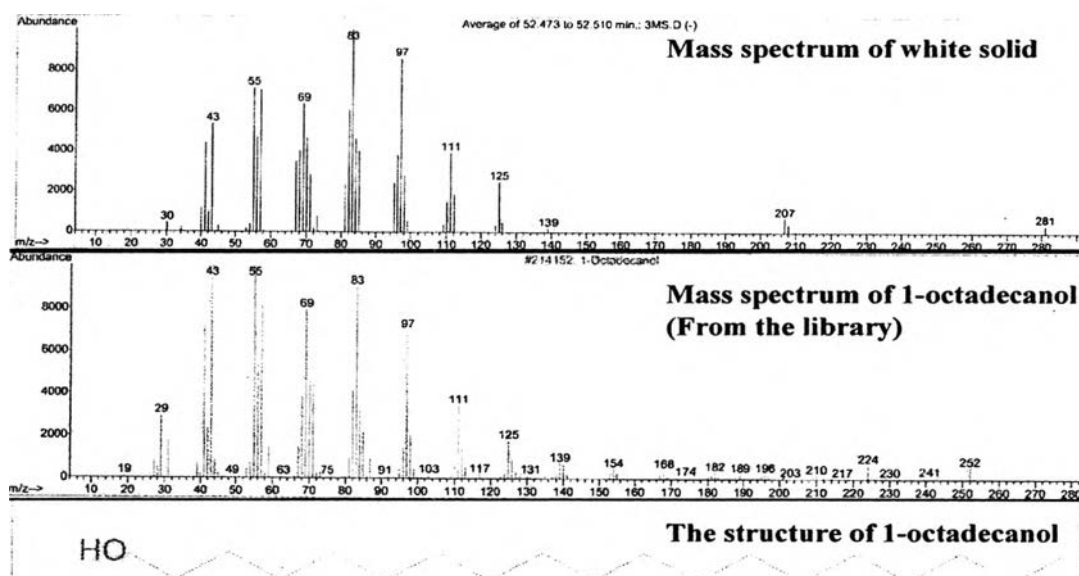


Figure 4.10 The mass spectrum of white solid obtained from GC/MS compared to that of 1-octadecanol from NIST Library.

From the literature reviews (Snare *et al.*, 2007), it was proposed that under inert atmosphere, deoxygenation of unsaturated fatty acid over Pd catalyst was occurred via hydrogenation of double bond and further deoxygenation of saturated fatty acid to produce n-heptadecane (C17). Moreover, the reaction pathway of deoxygenation of methyl ester over sulphided NiMo/ γ -Al₂O₃ proposed by Senol *et al.* (2005) was generated by hydrogenation of methyl ester to produce alcohol molecules. Then, alcohols were dehydrated to alkene and followed by hydrogenation of alkene to yield alkane. However, alcohol can be cracked to alkene and further hydrogenated to alkane product having one carbon atom less than the original ester. Based on these propose pathways of deoxygenation of unsaturated fatty acid and methyl ester, the reaction pathway of deoxygenation of oleic acid over NiMo/ γ -Al₂O₃ under hydrogen flow is proposed as depicted in Figure 4.12, that is, oleic acid is hydrogenated to stearic acid, followed by hydrogenation of carbonyl group of stearic acid into 1-octadecanol. After that, 1-octadecanol is dehydrated to octadecene and followed by hydrogenation of octadecene to n-octadecane having H₂O as by product. This pathway is called hydrodeoxygenation. However, 1-octadecanol can be cracked to 1-heptadecene and further hydrogenated to 1-heptadecane having CO as a by-product. This path is called hydrodecarbonylation. The ratio of C18 to C17 is used to explain what reaction pathway of fatty acid deoxygenation is preferable to occur. When the C18/C17 ratio is higher than one, the deoxygenation of fatty acid is likely to take place via hydrodeoxygenation path. In contrast, the C18/C17 below one indicates that the deoxygenation of fatty acid prefers to occur through hydrodecarbonylation way.

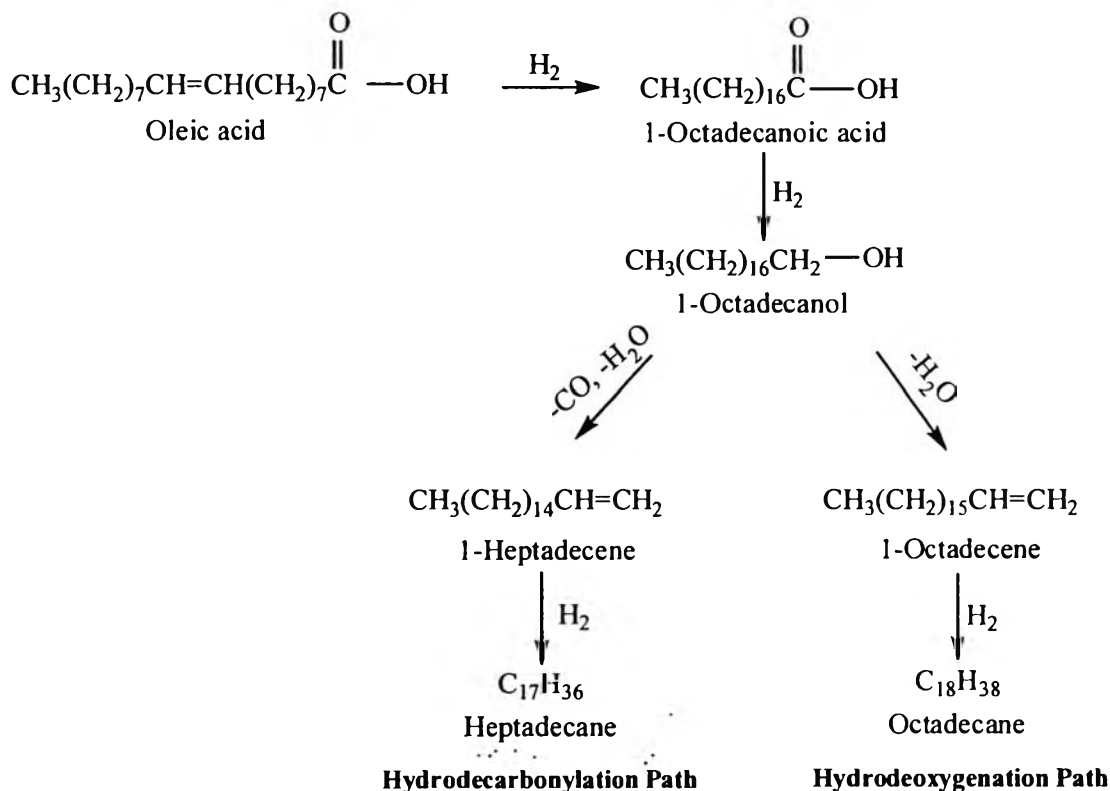


Figure 4.11 Reaction pathway of deoxygenation of oleic acid over NiMo/ γ -Al₂O₃ under hydrogen atmosphere.

In the consideration of the hydrocarbon products, Figure 4.11 shows that n-octadecane is favorable to be produced compared to n-heptadecane at all reaction temperature. It clearly indicates that deoxygenation of oleic acid over NiMo/Al₂O₃ is preferably occurred via hydrodeoxygenation compared to hydrodecarbonylation; consequently, the ratio of C18 to C17 is higher than unity as shown in Table 4.4. Moreover, as observed that the oleic acid conversion is almost 100% when the reaction was operated at 275°C; however, the main products are intermediates, white solid appearance, which are not dissolved in dodecane. It is assumed that that oleic acid is rapidly hydrogenated to stearic acid, leading to 100wt% conversion of oleic acid.

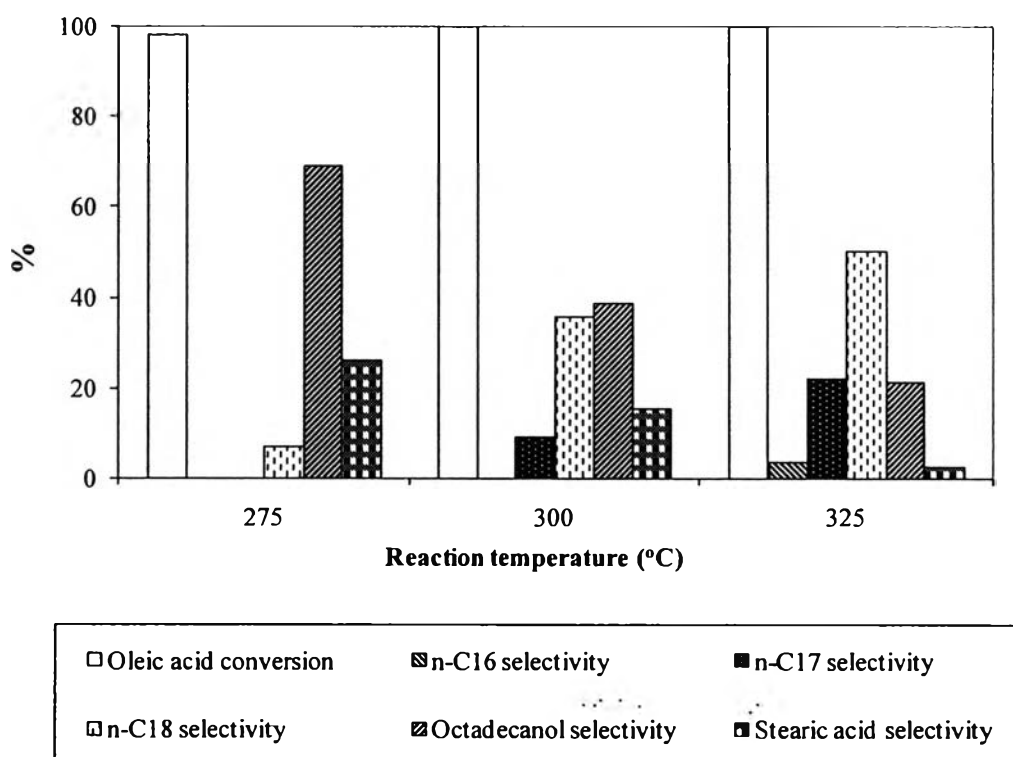


Figure 4.12 Plot of oleic acid conversion and product selectivity obtained after 3 hr versus reaction temperature using NiMo/Al₂O₃ as catalyst (pressure: 500 psig, WHSV: 0.5 hr⁻¹, H₂/oleic acid: 70, and feed flow rate: 0.235 ml/min).

Table 4.4 The hydrocarbon product selectivity and C18/C17 ratio obtained after 3 hr of deoxygenation of 5wt% oleic acid in dodecane over NiMo/ Al₂O₃ catalyst at 500 psig, WHSV 0.5 hr⁻¹, H₂/oleic acid 70

Temperature (°C)	Hydrocarbon product selectivity (wt%)				C18/C17 ratio
	C16	C17	C18	C17+C18	
275	0	0	7	7	
300	0	10	35	45	3.7
325	3	20	45	65	2.3

4.2.3.1.2 Effect of Reaction Pressure

The deoxygenation of 5wt% oleic acid in n-dodecane was done over NiMo/Al₂O₃ catalyst at temperature of 325 °C, WHSV of 0.5 hr⁻¹, and H₂/feed ratio of 70. The reaction pressure was varied at 250, 350, 500 and 600 psig. It was found that the oleic acid conversion was reached 100% when the reaction was done at 350, 500, and 600 psig after 3 hr compared to the reaction operated at 250 psig as shown in Figure 4.14. In term of product selectivity, it was found the selectivity to n-heptadecane and n-octadecane were lower when the reaction was operated at 250 psig; leading to enhancement in intermediate selectivity. However, it was observed that n-octadecane is favorable to produce at higher pressure; meanwhile, the production of n-heptadecane is decreased with the reaction pressure as shown in Figure 4.14. In term of total selectivity to C17 and C18, it was found the reaction operated at 350 psig and 500 psig exhibited the same value but significant difference in the C18/C17 ratio. That is, the C18/C17 ratio at low pressure (350 psig) is lower than that at high pressure (500psig) due to the increasing in the production of n-heptadecane at low pressure as shown in Table 4.5. Therefore, it can be reported that deoxygenation of oleic acid via hydrodecarbonylation is likely to occur at low pressure, while, the deoxygenation of oleic acid by way of hydrogenation is preferred to carry out at high pressure as shown in Table 4.5.

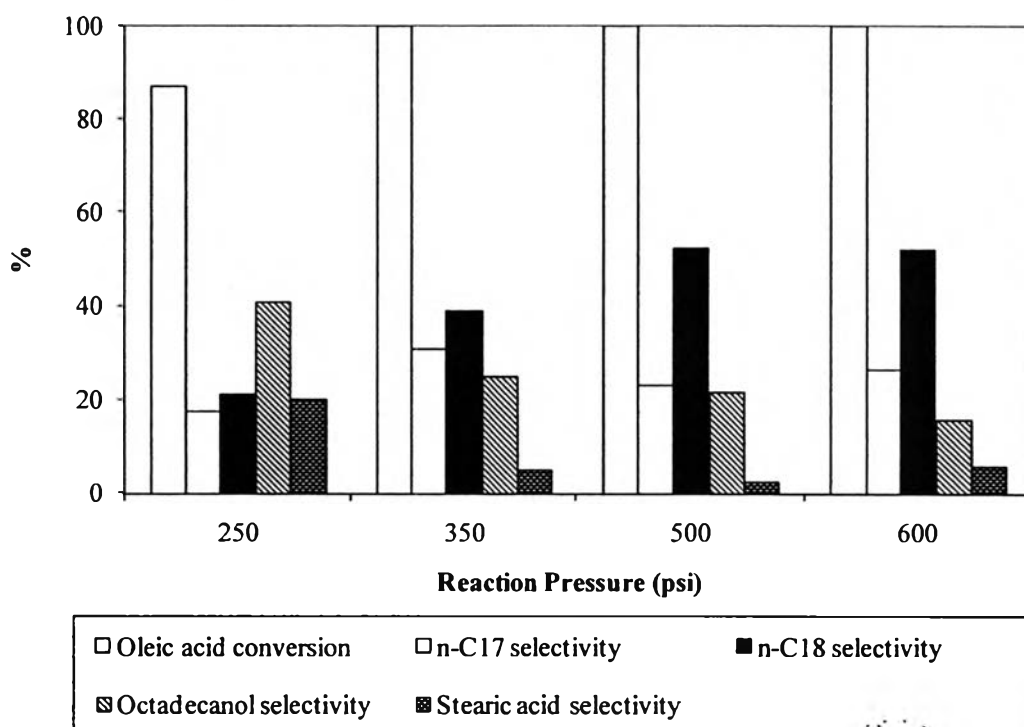


Figure 4.13 Plot of oleic acid conversion and product selectivity versus reaction pressure using NiMo/Al₂O₃ as catalyst (temperature: 325°C, WHSV: 0.5 hr⁻¹, H₂/oleic acid: 70, and feed flow rate: 0.235 ml/min).

Table 4.5 The hydrocarbon product selectivity and C18/C17 ratio obtained after 3 hr of deoxygenation of 5wt% oleic acid in n-dodecane over NiMo/Al₂O₃ catalyst at 325°C, WHSV 0.5 hr⁻¹, and H₂/oleic acid 70

Pressure (psig)	Hydrocarbon product selectivity (wt%)				C18/C17 ratio
	C16	C17	C18	C17+C18	
250		17	20	37	1.2
350		30	35	65	1.2
500	3	20	45	65	2.3
600		18	43	61	2.3

4.2.3.1.3 Effect of H₂/Oleic acid ratio

The deoxygenation of 5wt% oleic acid in n-dodecane was done over NiMo/ Al₂O₃ catalyst at temperature of 325 °C, pressure of 500 psig, WHSV of 0.5 hr⁻¹. The H₂/oleic acid ratios were investigated at 35, 70, 140, and 210. The results show that although the H₂/oleic acid ratios are varied, the oleic acid conversion was 100%. However, as observed previously, even though the oleic conversion is completely converted, the liquid products are not only consisted of C17 and C18, but also intermediate products, especially at H₂/oleic acid ratio of 35 as show in Figure 4.15. Moreover, it was found that the selectivity to intermediate products decreases with the H₂/oleic acid ratio. In term of C17 selectivity, this value is higher when the reaction is operated under higher H₂/oleic acid ratio. On the contrary, the enhancement in H₂/oleic acid ratio does not have influence on C18 selectivity. Table 4.6 reported that the higher the H₂/oleic acid ratio, the lower the C18/C17 is observed. Therefore, the deoxygenation reaction of oleic acid via hydrodecarbonylation path is prefer to be occurred at higher H₂/oleic acid ratio, compared to hydrodeoxygenation path.

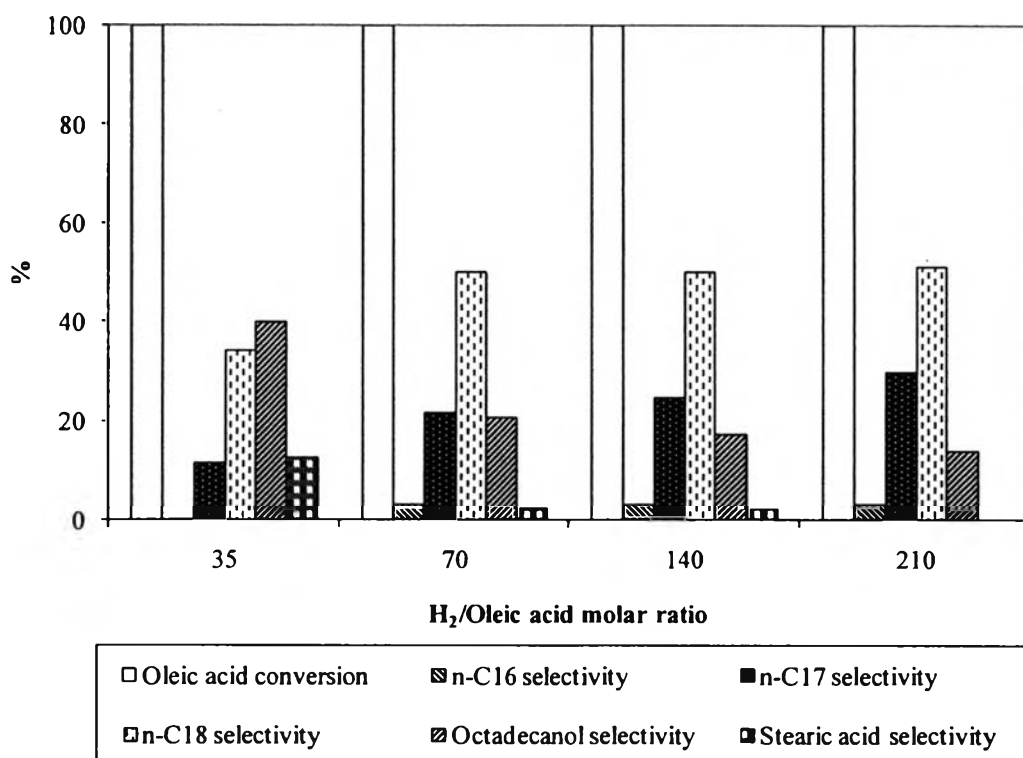


Figure 4.14 Plot of oleic acid conversion and product selectivity versus H₂/oleic acid ratio using NiMo/Al₂O₃ as catalyst (temperature: 325°C, pressure: 500 psig, WHSV: 0.5 hr⁻¹, and feed flow rate: 0.235 ml/min).

Table 4.6 The hydrocarbon product selectivity and C18/C17 ratio obtained after 3 hr of deoxygenation of 5wt% oleic acid in dodecane over NiMo/Al₂O₃ catalyst at 325°C, 500 psig, and WHSV 0.5 hr⁻¹

H ₂ /Oleic acid ratio	Hydrocarbon product selectivity (wt%)				C18/C17 ratio
	C16	C17	C18	C17+C18	
35		13	37	50	2.9
70	3	20	45	65	2.2
140	3	23	45	68	1.9
210	3	27	45	72	1.7

4.2.3.1.4 Effect of Weigh Hourly Space Velocity (WHSV)

The deoxygenation of 5wt% oleic acid in n-dodecane was done over NiMo/ γ -Al₂O₃ catalyst at temperature of 325°C, pressure of 500 psig, and H₂/oleic ratio of 70. The weigh hourly space velocity defined as the ratio of mass flow rate of oleic acid to weigh of the catalyst is varied from 0.05 to 1.5 hr⁻¹ as described in Table 4.3. Figure 4.16 showed that the oleic acid conversion approached 100% as the space time was increased from 0.67 hr to 2 hr. In addition, the intermediate products were completely converted to hydrocarbon compounds (C16, C17, and C18) when the space time was further increased. However, Table 4.7 showed that no significant change in total selectivity to C17 and C18 was observed although the space time is increased from 4 to 20 hr. The value of C18/C17 reveals that the production of diesel-fuel-like hydrocarbon from the deoxygenation of oleic acid prefers hydrodeoxygenation pathway to hydrodecarbonylation pathway, especially at higher space time.

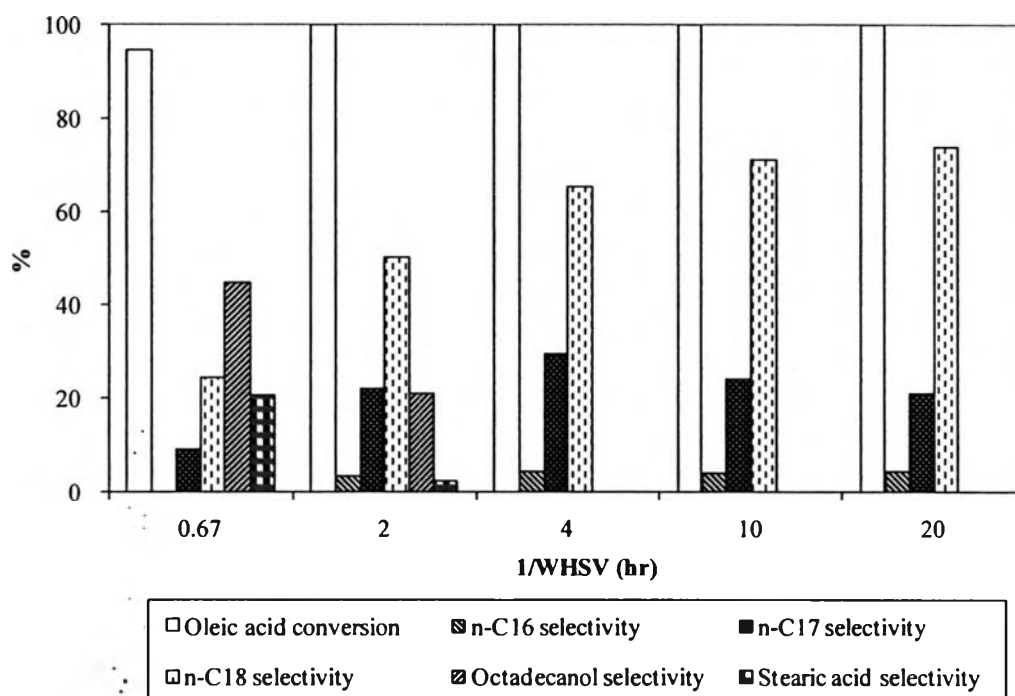


Figure 4.15 Plot of oleic acid conversion and product selectivity versus Weigh Hourly Space Velocity, WHSV (hr^{-1}), using NiMo/Al₂O₃ as catalyst (temperature: 325°C, Pressure: 500 psig, H₂/oleic acid: 70, and feed flow rate: 0.235 ml/min).

Table 4.7 The hydrocarbon product selectivity and C18/C17 ratio of deoxygenation of 5wt% oleic acid in dodecane over NiMo/Al₂O₃ catalyst at 325°C, 500 psig, and H₂/oleic acid 70

Contact time (hr)	Hydrocarbon product selectivity (wt%)				C18/C17 ratio
	C16	C17	C18	C17+C18	
0.67		9	25	34	2.6
2	4	22	50	72	2.2
4	5	30	65	95	2.2
10	4	24	72	96	3.0
20	5	21	74	95	3.5

4.2.3.2 Deoxygenation of Oleic Acid over Sulphided NiMo/Al₂O₃

To study the effect of sulphided NiMo/Al₂O₃ catalyst, the deoxygenation of 5wt% oleic acid in n-dodecane was conducted at temperature of 325°C, pressure of 500 psig, WHSV of 0.25 hr⁻¹, and H₂/oleic acid ratio of 70. The liquid product was collected and analyzed by GC. The result showed that the oleic acid was completely converted to hydrocarbon products (C17 and C18) when the reaction was carried out at this condition. As shown in Figure 4.16, the presulphided catalyst increased the catalytic activity of the hydrogenation catalyst when compared to the unsulphided NiMo/Al₂O₃. Furthermore, the reaction pathway of the sulphided NiMo/Al₂O₃ under hydrogen atmosphere still prefers hydrodeoxygenation to hydrodecarbonylation pathway.

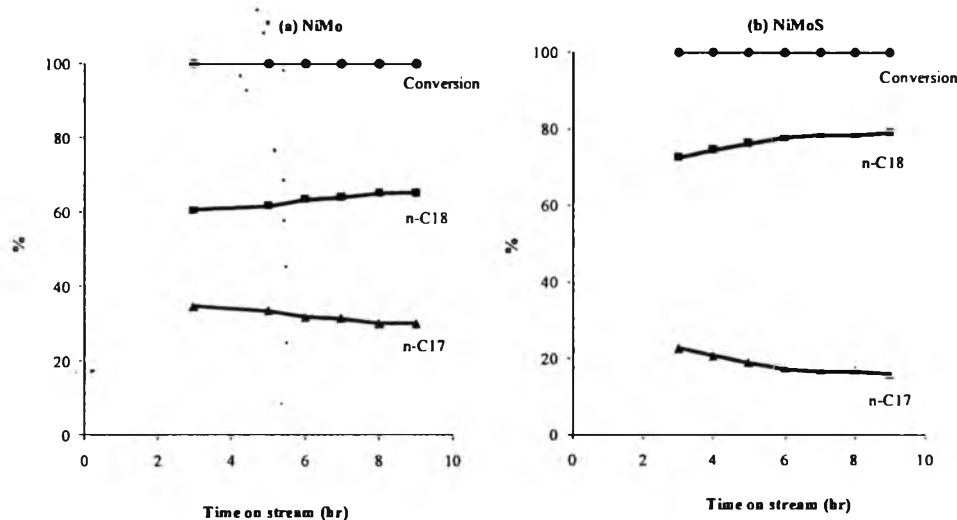


Figure 4.16 (a) Plot of oleic acid conversion and product selectivity versus time on stream, using NiMo/Al₂O₃ as catalyst (temperature: 325°C, Pressure: 500 psig, H₂/oleic acid: 70, WHSV 0.25 hr⁻¹), (b) Plot of oleic acid conversion and product selectivity versus time on stream, using sulphided NiMo/Al₂O₃ as catalyst (temperature: 325°C, Pressure: 500 psig, H₂/oleic acid: 70, WHSV 0.25 hr⁻¹)

4.2.3.3 Deoxygenation of Oleic Acid over Pd/C

The deoxygenation of 5wt% oleic acid in n-dodecane was done over Pd/C catalyst at temperature of 325°C, pressure of 500 psig, H₂/oleic ratio of 70, and weigh hourly space velocity 0.25 hr⁻¹. Figure 4.17 showed that the oleic acid conversion approached 100% as Pd/C was applied as catalyst. In addition, the production of diesel-fuel-like hydrocarbon from the deoxygenation of oleic acid over Pd/C prefers only hydrodecarbonylation pathway, product has one carbon atom less than the reactant, as observed in the major products n-heptadecane (n-C17) and n-pentadecane (n-C15).

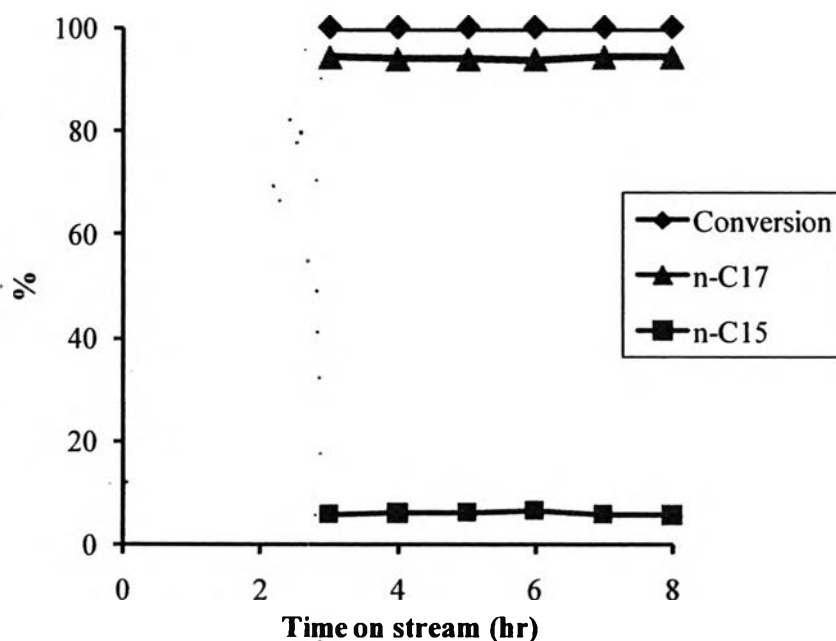


Figure 4.17 Plot of oleic acid conversion and product selectivity versus time on stream, using Pd/C as catalyst (Temperature: 325°C, Pressure: 500 psig, H₂/oleic acid: 70, WHSV 0.25 hr⁻¹)

4.2.3.4 Deoxygenation of Palmitic Acid over NiMo/Al₂O₃

4.2.3.4.1 Effect of Temperature

To study the effect of the reaction temperature, the deoxygenation of 2wt% palmitic acid in dodecane was conducted at 500 psig, WHSV of 0.5 hr⁻¹, and H₂/ palmitic acid ratio of 70. The reaction temperature was changed from 300 to 325°C. The liquid product was collected and analyzed by GC. At 3 hr time on stream, the results showed that the palmitic acid conversions were 67.18% and 86.91% when the reaction was carried out at 300°C and 325°C, respectively. As the reaction temperature increased, it was observed that the selectivity to desired products (n-pentadecane (C15) and n-hexadecane (C16)) increased as shown in Figure 4.21. Simultaneously, the selectivity to intermediate, white solid, decreased with the reaction temperature. These results are similar in case that the feed is oleic acid. To clearly understand the structure of white solid, the unknown intermediate was dissolved in ethanol and analyzed by GC-MS (Agilent 5973 Network Mass Selective Detector equipped with 6890N Network GC system). The chromatogram and mass spectrum of white solid particle was corresponded to that of hexadecanol as depicted in Figure 4.18 and 4.19. Therefore, it is proved that the white solid particle is hexadecanol.

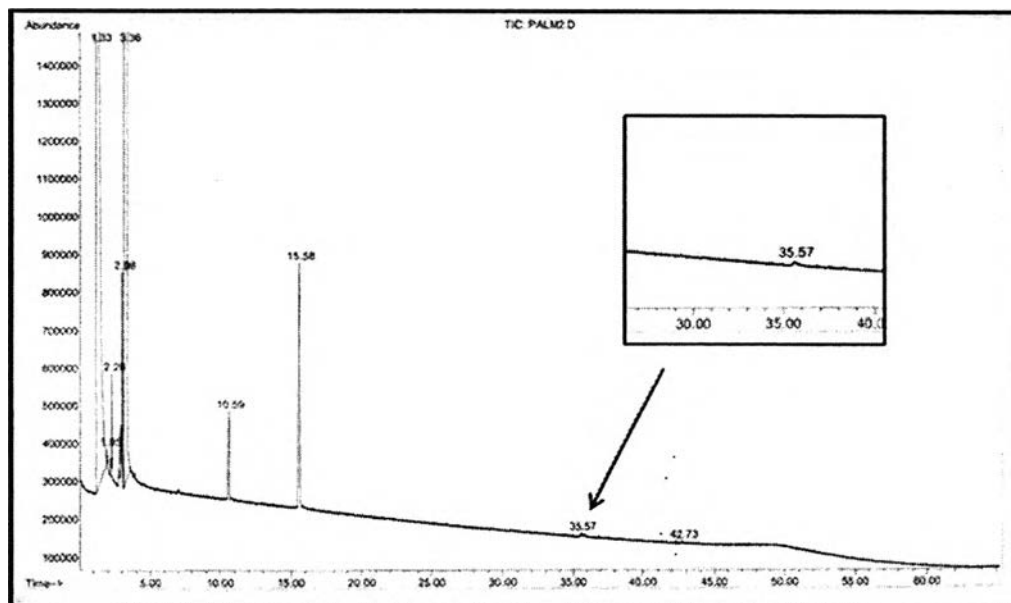
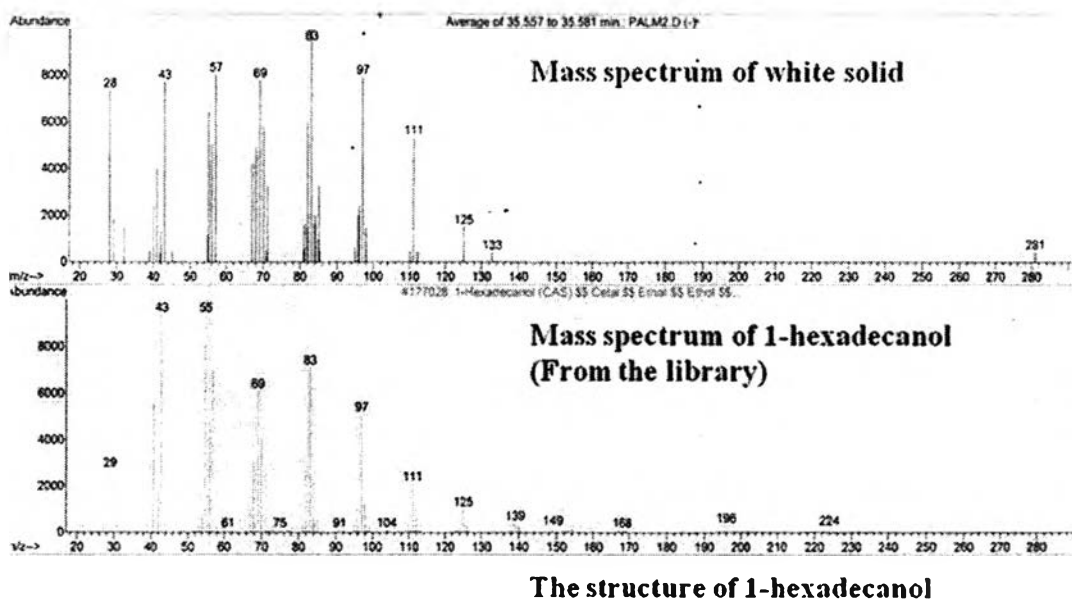


Figure 4.18 The picture of product with white solid chromatogram analyzed by GC-MS.



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Figure 4.19 The mass spectrum of white solid obtained from GC/MS compared to that of 1-hexadecanol from NIST Library.

From the deoxygenation of oleic acid, it was proposed that the intermediate product is octadecanol and stearic acid. Based on the proposed pathway of deoxygenation of oleic acid over NiMo/Al₂O₃ as depicted in Figure 4.12, the reaction pathway of deoxygenation of palmitic acid over NiMo/Al₂O₃ is proposed in Figure 4.20, that is palmitic acid is hydrogenated to hexadecanol. After that, hexadecanol is dehydrated to hexadecene and followed by hydrogenation of hexadecene to hexadecane. However, hexadecanol can be cracked to pentadecene and further hydrogenated to pentadecane having CO as by-product. This path is called hydrodecarbonylation.

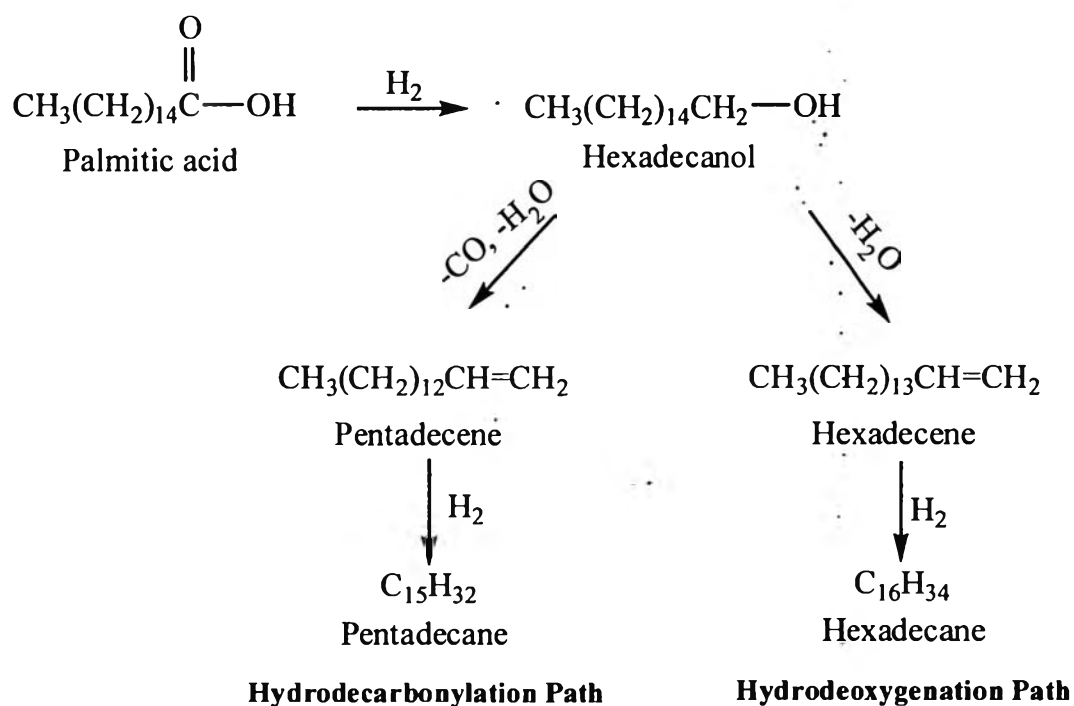


Figure 4.20 Reaction pathway of deoxygenation of palmitic acid.

In the consideration of hydrocarbon products, Figure 4.21 shows that the selectivity to hexadecane (C16) is higher than n-pentadecane (C15) at all reaction temperature. Therefore, it clearly indicates that deoxygenation of palmitic acid over NiMo/Al₂O₃ is preferably occurred via hydrodeoxygenation compared to hydrodecarbonylation, like deoxygenation of oleic acid over Ni-Mo/Al₂O₃.

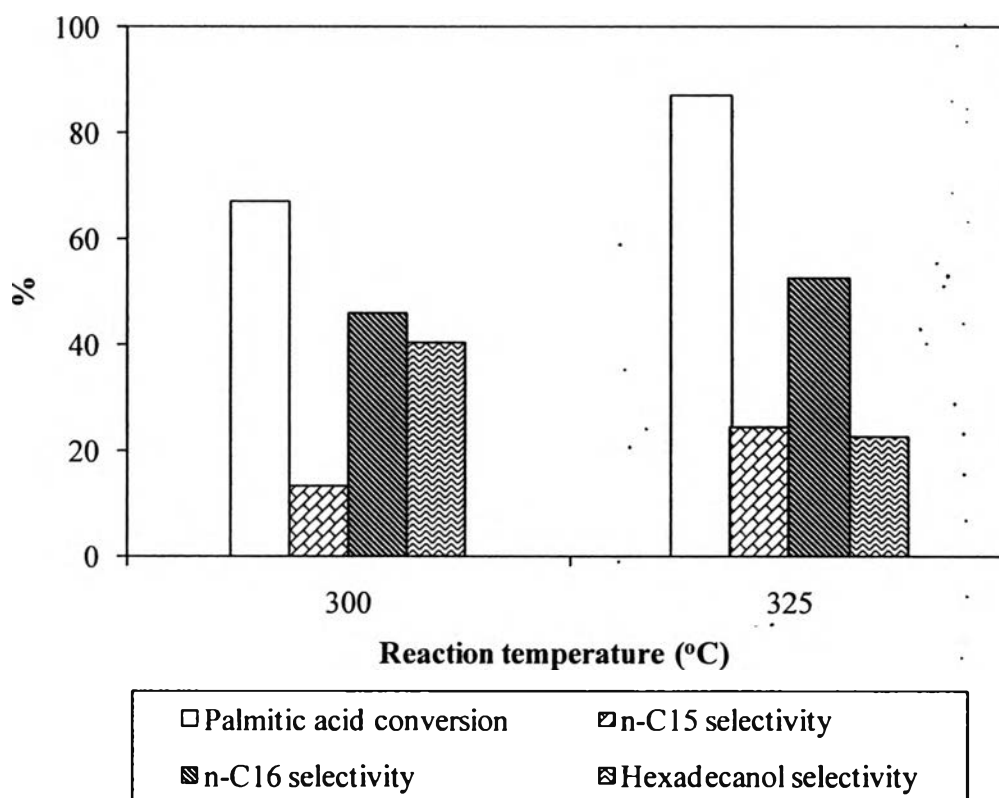


Figure 4.21 Plot of palmitic acid conversion and product selectivity versus reaction temperature using NiMo/Al₂O₃ as catalyst (pressure: 500 psig, WHSV: 0.5 hr⁻¹, H₂/palmitic acid: 70, and feed flow rate: 0.277 ml/min).

4.2.3.4.2 Effect of Reaction Pressure

The deoxygenation of 2wt% palmitic acid in n-dodecane was performed over NiMo/Al₂O₃ catalyst at temperature of 325°C, WHSV of 0.5 hr⁻¹, and H₂/palmitic acid ratio of 70. The reaction pressure was varied from 350 to 500 psig. It was found that palmitic acid conversion was 81.66 and 85.68 when the reaction was operated at 350 psig and 500 psig, respectively. In term of product selectivity, it was found that the selectivity to n-pentadecane and n-hexadecane increased with reaction pressure as shown in Figure 4.22. As a result, the selectivity to hexadecanol decreased at higher reaction pressure. The C16/C15 ratio is used instead of C18/C17 ratio to indicate what reaction pathway of deoxygenation of palmitic acid is likely to occur. The C16/C15 ratio is higher than one at all reaction pressure, therefore, the deoxygenation of palmitic acid over NiMo/Al₂O₃ catalyst is likely to occur via hydrodeoxygenation compared to hydrodecarbonylation.

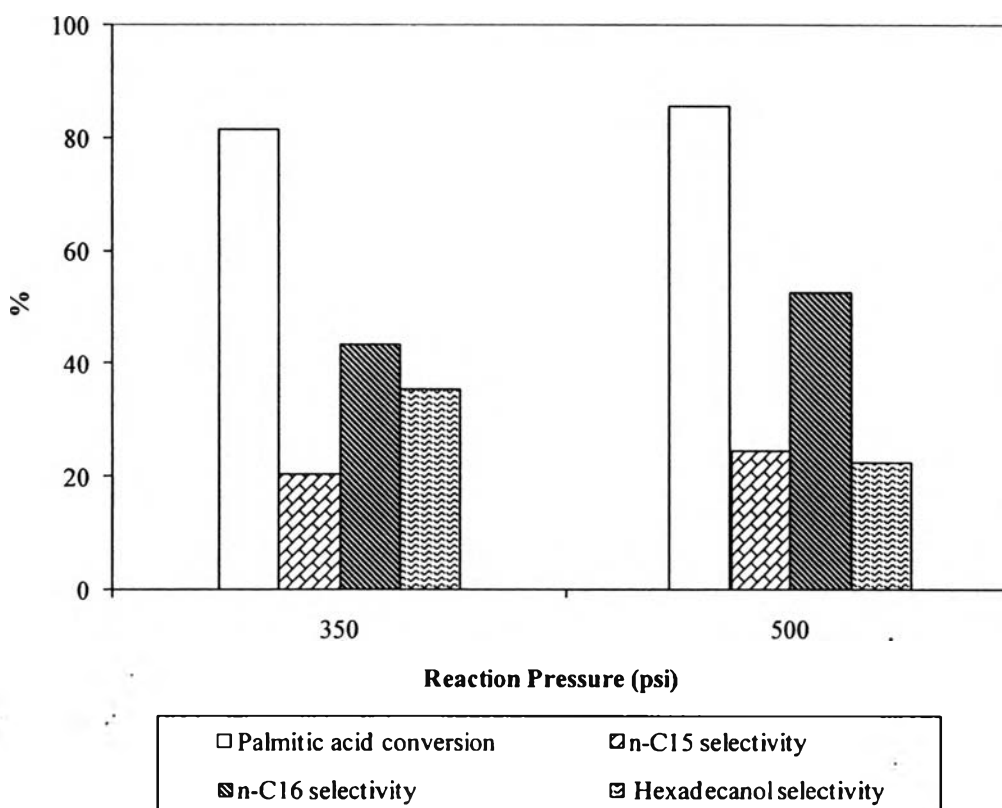


Figure 4.22 Plot of palmitic acid conversion and product selectivity versus reaction pressure using NiMo/Al₂O₃ as catalyst (temperature: 325°C, WHSV: 0.5 hr⁻¹, H₂/oleic acid: 70, and feed flow rate: 0.277 ml/min).

4.2.3.4.3 Effect of H₂/Palmitic Acid Molar Ratio

The deoxygenation of 2wt% palmitic acid in dodecane was carried out over NiMo/Al₂O₃ catalyst at 325°C, 500 psig, and WHSV of 0.5 hr⁻¹. The palmitic acid ratios were investigated at 70, 140, and 210. The results show that the palmitic conversion was reached 100% when the reaction was done at 140 and 210 compared to the reaction operated at ratio of 70 as shown in Figure 4.23. Consequently, hexadecanol was completely converted to hydrocarbon product as the H₂/palmitic acid ratio increased. When the H₂/palmitic acid ratio was increased from 70 to 140 the selectivity of pentadecane (C15) increased. However, the ratio was increased from 140 to 210, the selectivity to C15 and C16 did not significantly change. Moreover, the C16/C15 ratio is higher than one in all H₂/palmitic acid ratios. Then,

the deoxygenation of palmitic acid over NiMo/Al₂O₃ is likely to occur via hydrodeoxygenation compared with hydrodecarbonylation.

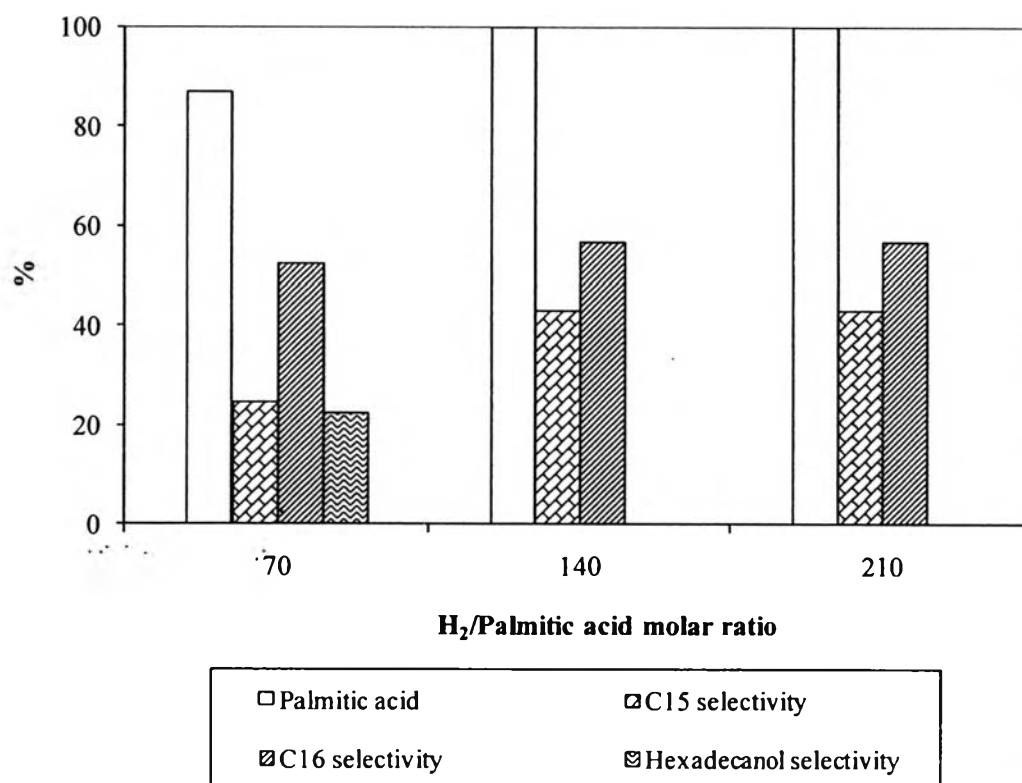


Figure 4.23 Plot of palmitic acid conversion and product selectivity versus H₂/palmitic acid ratio using NiMo/Al₂O₃ as catalyst (temperature: 325°C, pressure: 500 psig, WHSV: 0.5 hr⁻¹, and feed flow rate: 0.235 ml/min).

4.2.3.4.4 Effect of Weigh Hourly Space Velocity (WHSV)

The deoxygenation of 2wt% palmitic acid in dodecane was done over NiMo/Al₂O₃ catalyst at 325°C, 500 psig, and H₂/palmitic ratio of 70. Weigh Hourly Space Velocity, WHSV, is varied from 0.1 to 0.5 hr⁻¹. Figure 4.23 showed that the palmitic acid conversion approached 100% as the contact time increased from 2 hr to 10 hr. In addition, the total selectivity to C15 and C16 increased with contact time and no hexadecanol was observed.

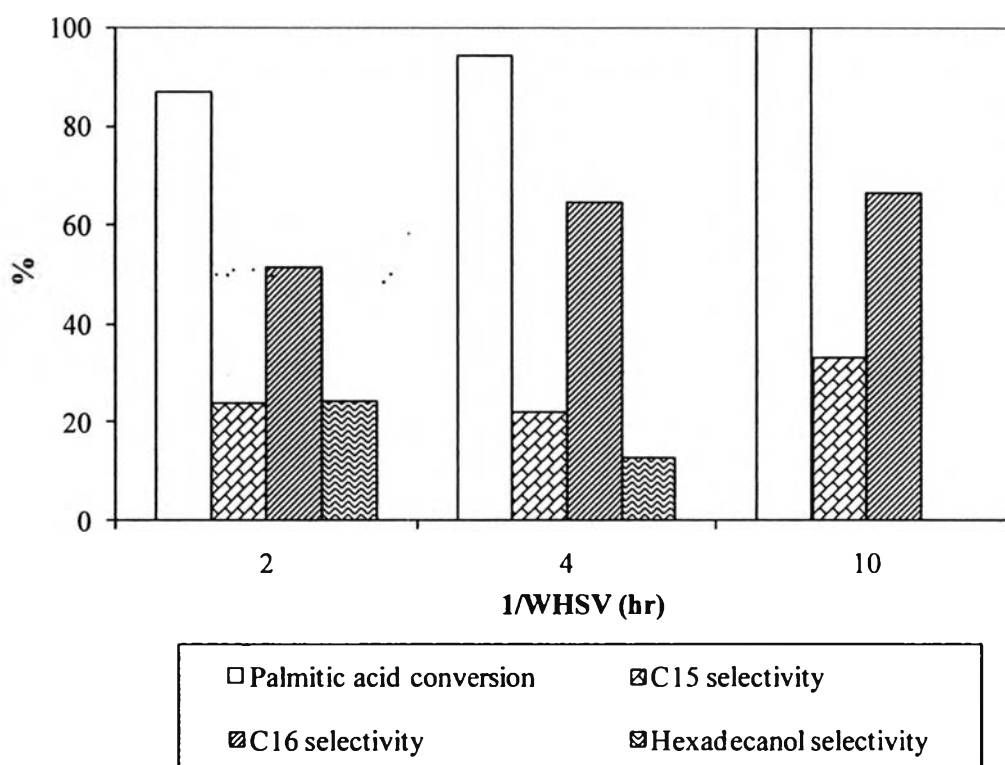


Figure 4.24 Plot of palmitic acid conversion and product selectivity versus WHSV using NiMo/Al₂O₃ as catalyst (temperature: 325°C, pressure: 500 psig, H₂/palmitic acid: 70, and feed flow rate: 0.277 ml/min).

4.2.3.5 Deoxygenation of Palmitic Acid over Sulphided NiMo/Al₂O₃

To study the effect of sulphided NiMo/Al₂O₃ catalyst, the deoxygenation of 2wt% palmitic acid in n-dodecane was conducted at temperature of 325°C, pressure of 500 psig, WHSV of 0.1 hr⁻¹, and H₂/palmitic acid ratio of 70. The liquid product was collected and analyzed by GC. The result showed that the palmitic acid was completely converted to hydrocarbon products (C15 and C16) when the reaction was carried out at this condition. As shown in Figure 4.25, the pre-sulphided catalyst increased the catalytic activity of the hydrogenation catalyst. Furthermore, the reaction pathway of the sulphided NiMo/Al₂O₃ (NiMoS) under hydrogen atmosphere still prefers hydrodeoxygenation to hydrodecarbonylation pathway.

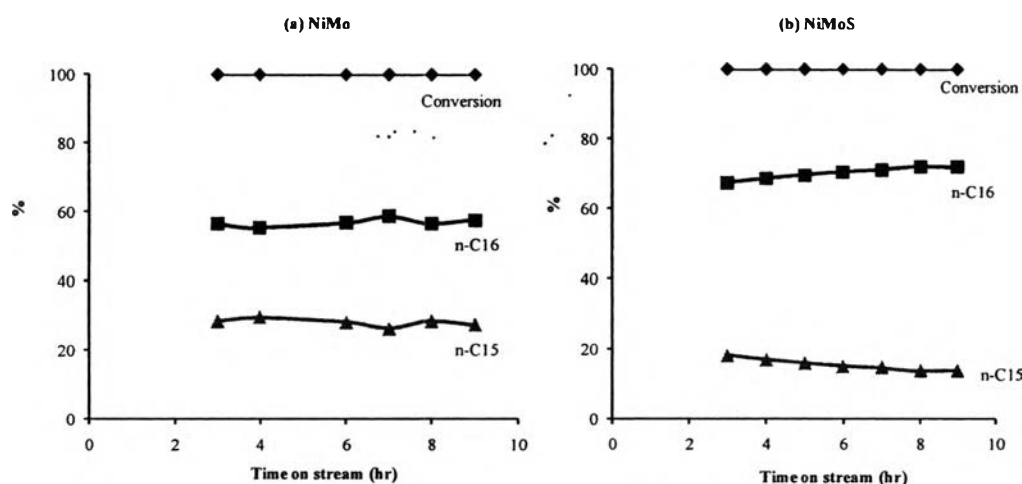


Figure 4.25 Plot of hydrocarbon products selectivity (wt%) versus time on stream (TOS) compared between unsulphided NiMo/Al₂O₃ and sulphided NiMo/Al₂O₃ catalyst (temperature: 325°C, pressure: 500 psig, WHSV: 0.1 hr⁻¹, and H₂/palmitic acid ratio: 70).

4.2.3.6 Deoxygenation of Palmitic Acid over Pd/C

The deoxygenation of 2wt% oleic acid in n-dodecane was done over Pd/C catalyst at temperature of 325°C, pressure of 500 psig, H₂/oleic ratio of 70, and weigh hourly space velocity 0.1 hr⁻¹. Figure 4.26 showed that the palmitic acid conversion approached 100% as Pd/C was applied as catalyst. In addition, the production of diesel-fuel-like hydrocarbon from the deoxygenation of palmitic acid over Pd/C prefers only hydrodecarbonylation pathway, product has one carbon atom less than the reactant, as observed in the major products n-hexadecane (n-C16) and n-pentadecane (n-C15).

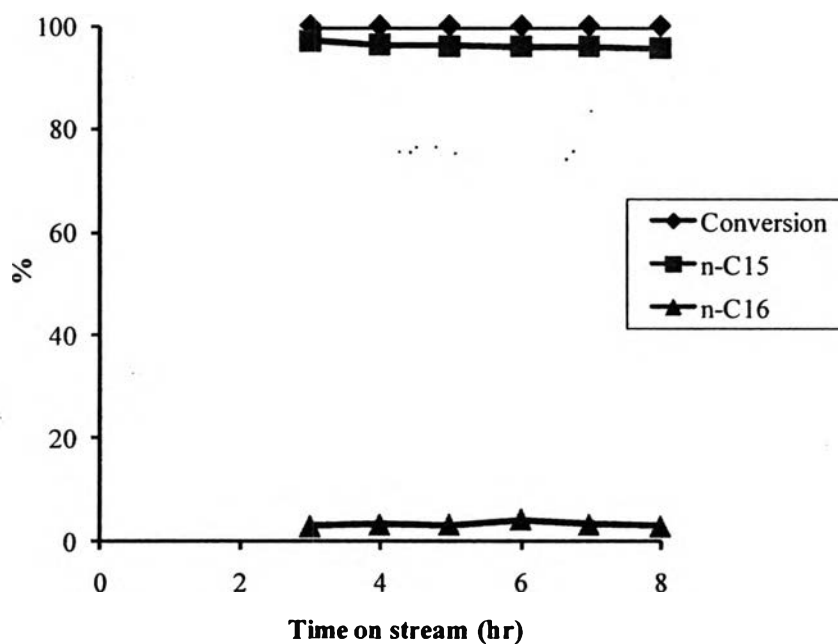


Figure 4.26 Plot of palmitic acid conversion and product selectivity versus time on stream, using Pd/C as catalyst (Temperature: 325°C, Pressure: 500 psig, H₂/oleic acid: 70, WHSV 0.1 hr⁻¹)