

## CHAPTER IV

### RESULTS AND DISCUSSION

The hydrogenation of methyl ester of castor oil is obviously a complicated reaction. It involves not only several simultaneous and consecutive chemical steps but also physical transfer steps of reaction and products on the catalyst surface. This experiment involved the hydrogenation of methyl ricinoleate which was prepared by transesterification of castor oil with methanol in the presence of concentrated sulfuric acid catalyst. The reaction was performed under the elevated temperature and pressure in the presence of nickel supported on alumina catalyst.

The goal of this research is to investigate the continuous hydrogenation of methyl ricinoleate in the presence of nickel catalysts. The temperature and pressure were optimized in order to achieve the required product.

#### 4.1 Properties of prepared catalysts

The catalysts were prepared by impregnation of nickel on alumina support, which had a pore volume of about 0.64 ml/g. They were characterized by X-ray fluorescence analysis. It showed that the prepared catalyst on alumina support had the amount of metal composition corresponding to the amount of impregnation metal as shown in Figures B1-B3. The amounts of metal composition after metal impregnation are presented in Table 4.1.

**Table 4.1** Analytical results of the prepared nickel catalysts

Concentration of catalyst (% by weight of nickel/weight of alumina)	Amount of nickel (% wt)
10	11.86
15	16.53
20	21.82

#### 4.2 Hydrogenation process

The aim of this study was to choose suitable conditions and the effective catalyst for hydrogenation of methyl ricinoleate. The characterization of original methyl ricinoleate is shown in Table 4.2, Figures C1, D1 and E1.

**Table 4.2** Compositions of methyl ester in original methyl ricinoleate, which obtained from transesterification of castor oil.

Composition	Amount (%)
Methyl stearate	0.90
Methyl oleate	3.10
Methyl linoleate	3.50
Methyl ricinoleate	92.50

### **4.3 Selection of the optimum operating conditions**

The 10 %, 15% and 20% of Ni catalyst were used to determine the optimum operating conditions by varying the reaction temperature and hydrogen/nitrogen pressure.

#### **4.3.1 Effect of the reaction temperature**

The effect of temperature on the hydrogenation has been studied. The observation is made on the nature of the substrate being hydrogenated and the types of catalyst being used.

##### **4.3.1.1 Effect of reaction temperature on hydrogenation process using 10% nickel catalyst**

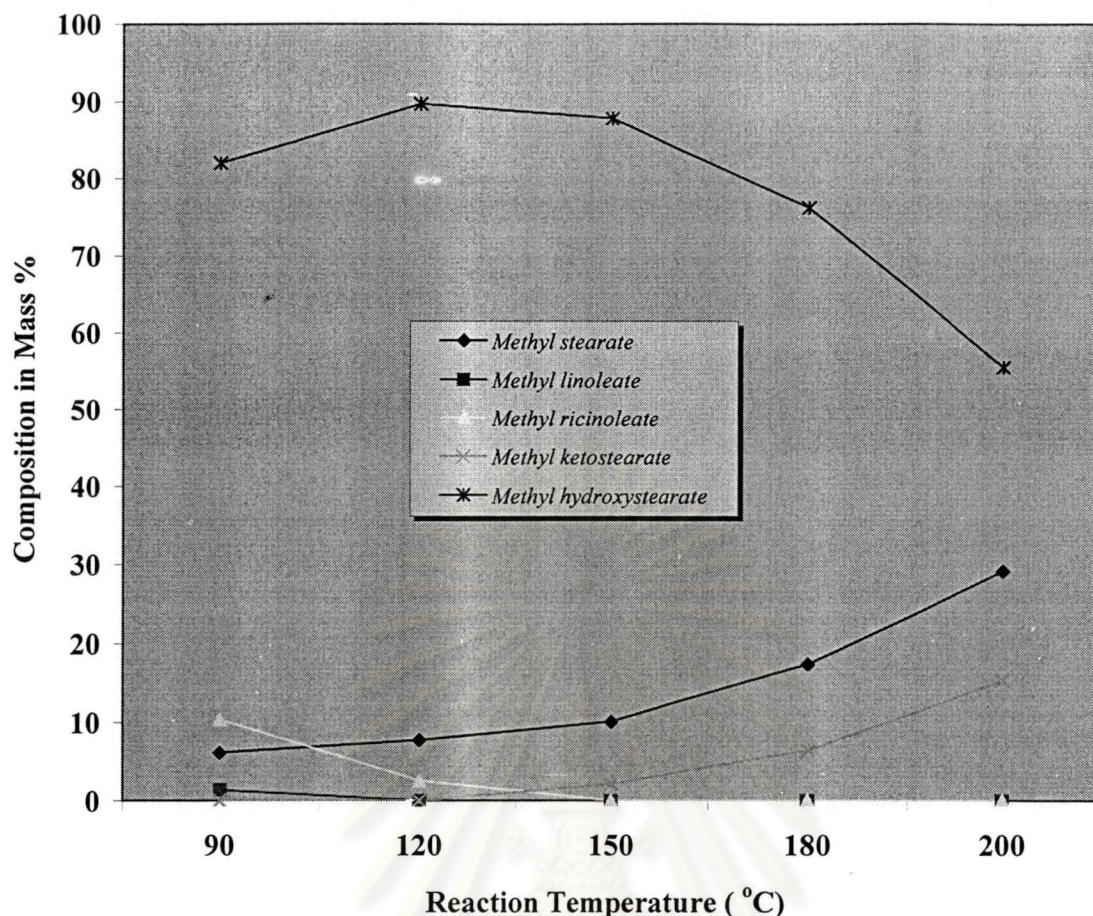
The results of experiment at different temperatures are shown in Table 4.3. The chromatograms in Figures D2-D6 showed that the methyl ester was changed as a function of the time lapse during the hydrogenation reaction. The reaction temperatures were varied at 90, 120, 150, 180, and 200 °C, respectively. The operating condition was carried out by hydrogen/nitrogen pressure at 20 psig.

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**Table 4.3** Analytical results from the hydrogenation of methyl ricinoleate using 10% nickel catalyst at various temperatures and 20 psig hydrogen/nitrogen pressure.

Composition	Reaction temperature (°C)				
	90	120	150	180	200
Methyl stearate	6.14	7.70	10.10	17.38	29.18
Methyl linoleate	1.36	-	-	-	-
Methyl ricinoleate	10.43	2.57	-	-	-
Methyl 12-ketostearate	-	-	2.06	6.43	15.35
Methyl 12-hydroxystearate	82.07	89.73	87.84	76.19	55.47

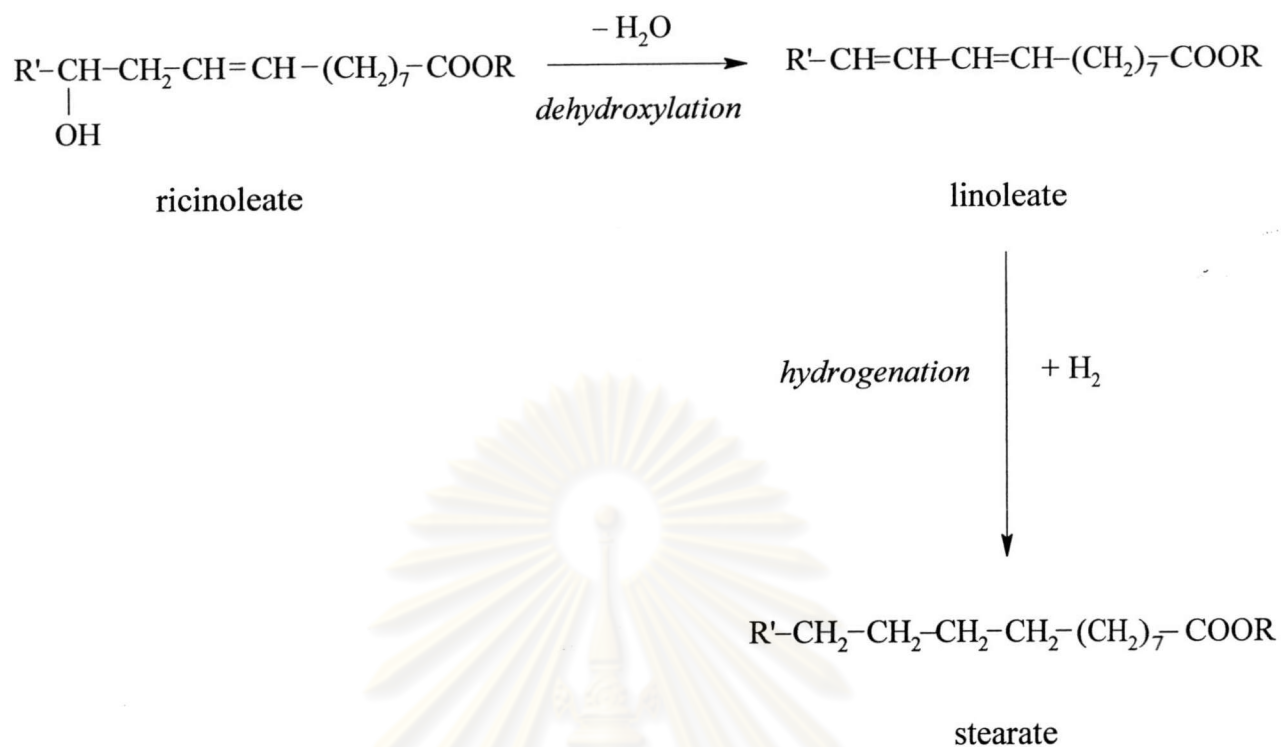
From Table 4.3, it showed that increasing reaction temperature from 90 °C to 120 °C decreased methyl ricinoleate from 10.43% to 2.57% and increased methyl 12-hydroxystearate from 82.07% to 89.73%, respectively. The methyl ricinoleate was completely hydrogenated at 150 °C, which increased methyl stearate from 6.14% to 10.10%. Thus, methyl ricinoleate was partially dehydroxylated with subsequent hydrogenation to methyl stearate. At higher temperature, this reaction was more pronounced and the yield of methyl 12-hydroxystearate was significantly decreased when the temperature was above 180 °C.



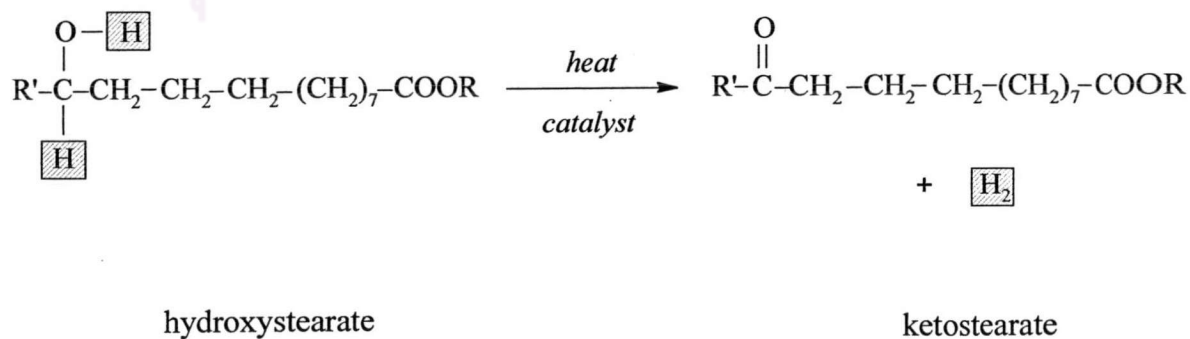
**Figure 4.1** The percentage of methyl ester content from hydrogenation of methyl ricinoleate using 10% nickel catalyst under 20 psig of hydrogen/nitrogen pressure at different temperatures.

From this result, it was observed that methyl linoleate and methyl ricinoleate were completely hydrogenated at 120 °C and 150 °C, respectively. At reaction temperatures higher than 150°C the methyl stearate was increased rapidly due to the dehydroxylation reaction with subsequent hydrogenation reaction.

The dehydroxylation or dehydration reaction of methyl ricinoleate gives dien products. Methyl ricinoleate is dehydrated by eliminating the hydroxyl group with adjacent hydrogen to form water molecule. The products are unsaturated methyl esters with two double bonds of the 9-11 and 9-12 linoleate types. Finally, the dien products are hydrogenated to methyl stearate by the following equation.



The methyl 12-ketostearate was occurred when the reaction was increased to 150 °C and higher by dehydrogenation reaction. There were two steps in the hydrogenation process. The first step is a rapid hydrogenation of methyl ricinoleate to methyl 12-hydroxystearate, the hydrogen coming from the catalyst, followed by the second step that was a slow dehydrogenation to methyl 12-ketostearate by the following reaction.



It could be concluded that the optimum reaction temperature for 10% nickel catalyst should be 120 °C because it gave the highest amount of methyl 12-hydroxystearate. Although, the amount of methyl 12-hydroxystearate at 150 °C was higher but it consumed more energy.

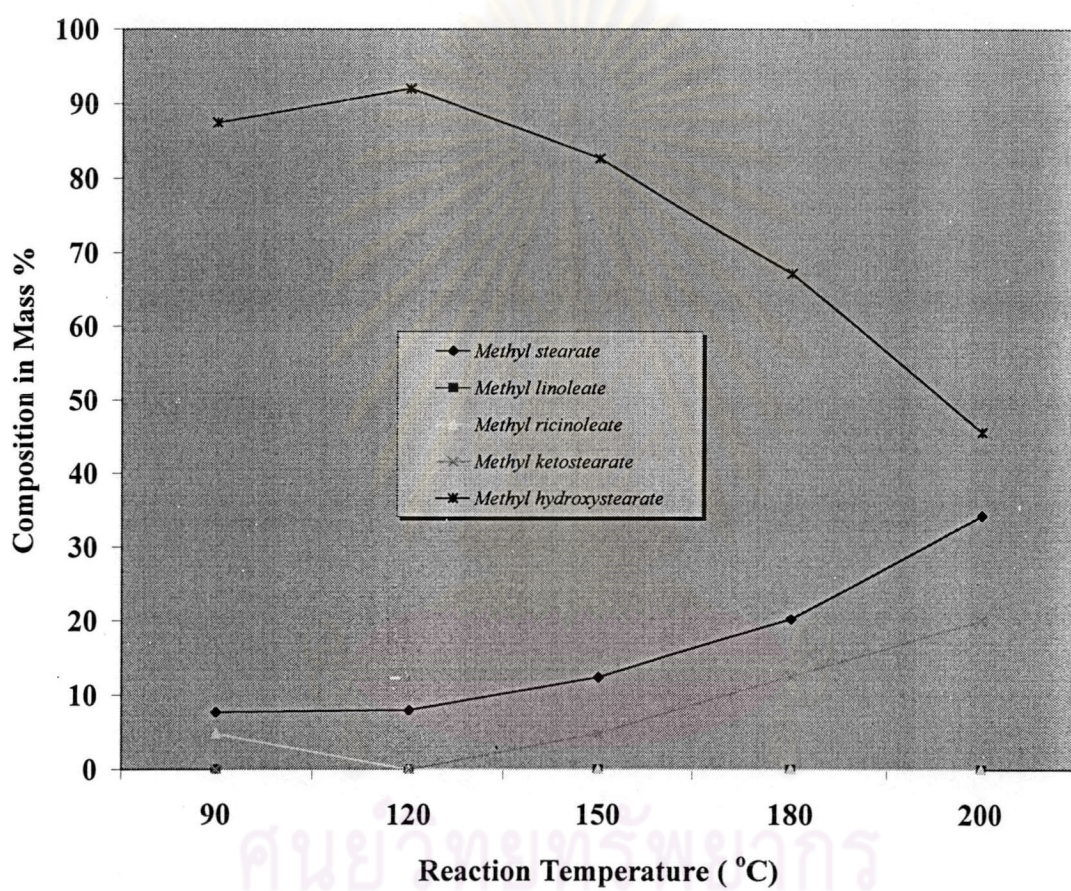
#### 4.3.1.2 Effect of reaction temperature on hydrogenation process using 15% nickel catalyst

This section of experiment was performed under the same condition as that using 10% nickel catalyst but the concentration of catalyst was increased to 15%. The results of experiment at different temperature were shown in Table 4.4. The chromatograms in Figures D7-D1 showed the composition of hydrogenated methyl ricinoleate.

**Table 4.4** Analytical results from the hydrogenation of methyl ricinoleate using 15% nickel catalyst at various temperatures and 20 psig hydrogen/nitrogen pressure.

Composition	Reaction temperature (°C)				
	90	120	150	180	200
Methyl stearate	7.73	7.96	12.43	20.29	34.27
Methyl linoleate	-	-	-	-	-
Methyl ricinoleate	4.82	-	-	-	-
Methyl 12-ketostearate	-	-	4.88	12.56	20.11
Methyl 12-hydroxystearate	87.45	92.04	82.69	67.15	45.62

The result from Table 4.4 indicated that the methyl linoleate and methyl oleate were completely hydrogenated at 90 °C reaction temperature. At 120 °C, methyl 12-hydroxystearate was increased to 92.04%. The amount of methyl stearate and methyl 12-ketostearate was increased rapidly to 34.27% and 20.11%, respectively.



**Figure 4.2** The percentage of methyl ester content from hydrogenation of methyl ricinoleate using 15% nickel catalyst under 20 psig of hydrogen/nitrogen pressure at different temperatures.



The result from Figure 4.2 revealed that the methyl ricinoleate was completely hydrogenated at 120 °C using 15% nickel catalyst, and at 90 °C reaction temperature an amount of methyl ricinoleate was less than those using 10% nickel catalyst. Thus, it indicated that 15% nickel catalyst gave higher rate of hydrogenation than those using 10% nickel catalyst. On the other hand, 15% nickel catalyst gave more amount of methyl 12-ketostearate and methyl stearate when the reaction temperature was above 120 °C.

From Tables 4.3, 4.4 and Figures 4.1, 4.2, it could be concluded that 15% nickel catalyst had better efficiency than 10% nickel catalyst in methyl 12-hydroxystearate production.

#### **4.3.1.3 Effect of reaction temperature on hydrogenation process using 20% nickel catalyst**

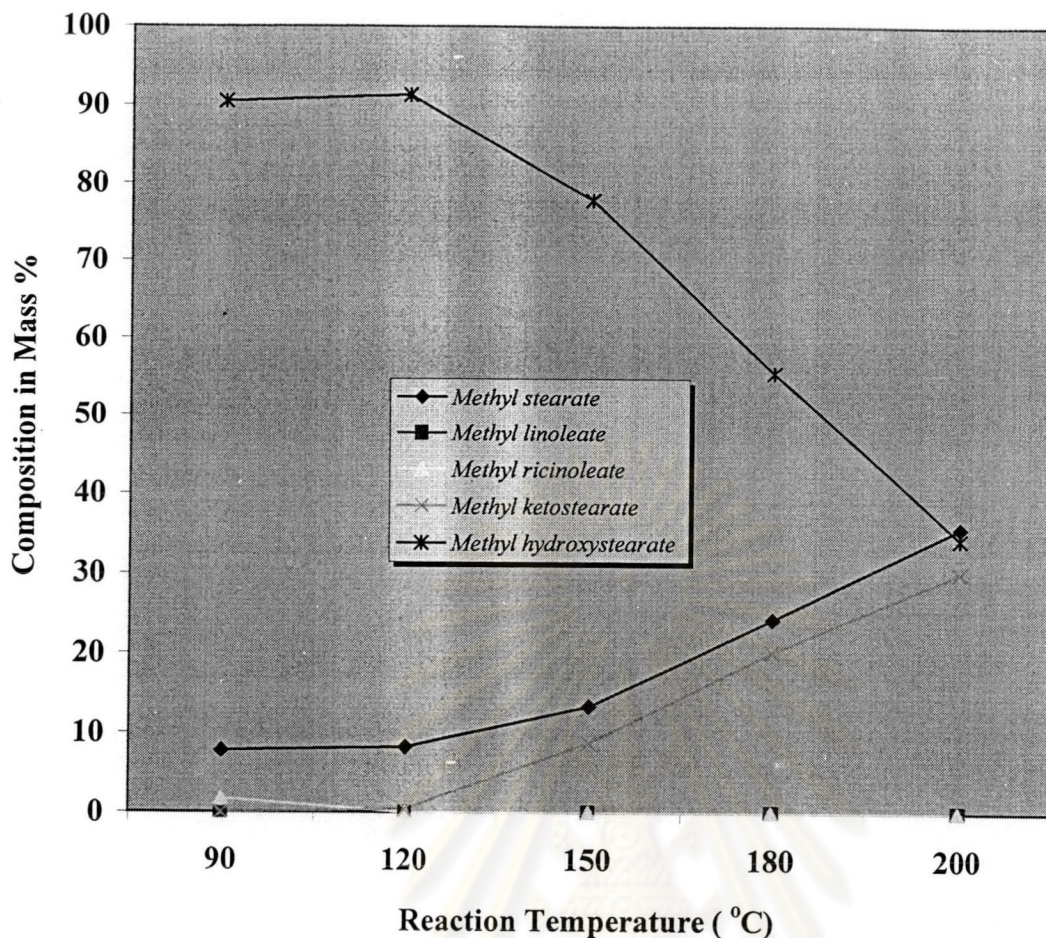
The results in this section of experiment were derived from the performance under the same condition with those using 10% and 15% nickel catalyst. The data was shown in Table 4.5 and Figures D12-D16.

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**Table 4.5** Analytical results from the hydrogenation of methyl ricinoleate using 20% nickel catalyst at various temperatures and 20 psig hydrogen/nitrogen pressure.

Composition	Reaction temperature (°C)				
	90	120	150	180	200
Methyl stearate	7.81	8.24	13.42	24.25	35.68
Methyl linoleate	-	-	-	-	-
Methyl ricinoleate	1.75	-	-	-	-
Methyl 12-ketostearate	-	0.43	8.79	20.23	30.06
Methyl 12-hydroxystearate	90.44	91.33	77.79	55.52	34.26

The result from Table 4.5 indicated that methyl linoleate and methyl oleate were completely hydrogenated at the same reaction temperature as those using 15% nickel catalyst. An amount of methyl ricinoleate was decreased to 1.75% at 90 °C and completely hydrogenated at 120 °C reaction temperature. The yield of methyl 12-hydroxystearate was 91.33% while methyl 12-ketostearate was 0.43%. Similar to that using 15% nickel catalyst, the methyl stearate was increased rapidly to 13.42%, 24.25% and 35.68% at 150, 180 and 200 °C, respectively.



**Figure 4.3** The percentage of methyl ester content from hydrogenation of methyl ricinoleate using 20% nickel catalyst under 20 psig of hydrogen/nitrogen pressure at different temperatures.

The result from Figure 4.3 indicated that at 90 °C reaction temperature the amount of methyl ricinoleate was lower than those using 15% nickel catalyst, so it indicated that the rate of hydrogenation reaction was increased. The methyl ricinoleate was completely hydrogenated at 120 °C, but the methyl 12-ketostearate was occurred and increased rapidly when the reaction temperature was increased.

From Tables 4.3, 4.4, 4.5 and Figures 4.1, 4.2, 4.3, they were shown that 20% nickel catalyst had better efficiency than 10% and 15% nickel catalyst in methyl 12-hydroxystearate production, but it also gave higher amount of methyl 12-ketostearate.

### 4.3.2 Effect of the hydrogen pressure

The second parameter in the hydrogenation process was hydrogen/nitrogen pressure, which was varied at 20, 40 and 60 psig. The catalyst used was 15% nickel catalyst. The conditions were carried out with two different reaction temperatures : 90 and 200 °C.

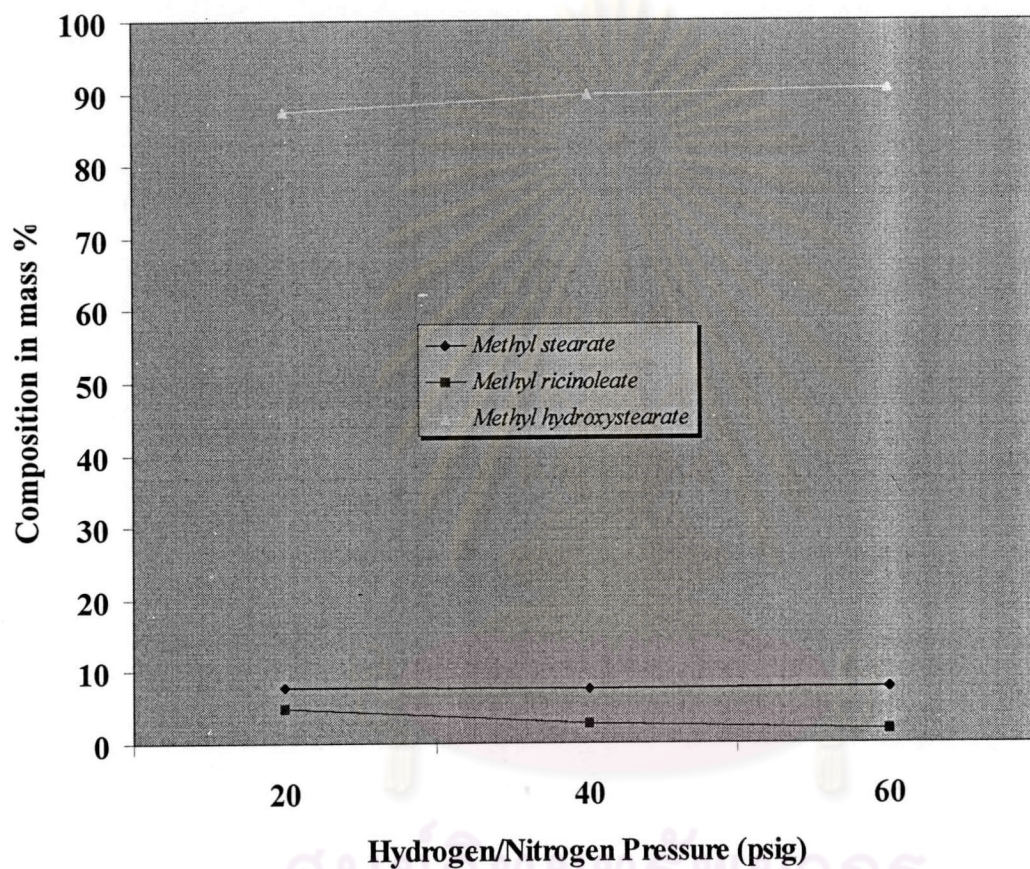
#### 4.3.2.1 Effect of hydrogen pressure at 90 °C reaction temperature

This experiment was performed at 90 °C reaction temperature in order to study the effect of hydrogen pressure with the rate of hydrogenation, which determined the amount of methyl ricinoleate. The results are shown in Table 4.6, Figures 4.4 and D17.

**Table 4.6** Analytical results from the hydrogenation of methyl ricinoleate using 15% nickel catalyst at 90 °C on various hydrogen/nitrogen pressures.

Composition	Hydrogen/nitrogen pressures		
	20	40	60
Methyl stearate	7.73	7.66	7.69
Methyl linoleate	-	-	-
Methyl ricinoleate	4.82	2.65	1.94
Methyl 12-ketostearate	-	-	-
Methyl 12-hydroxystearate	87.45	89.69	90.57

From Table 4.6, it was observed that when hydrogen/nitrogen pressures was increased to 40 and 60 psig the amount of methyl 12-hydroxystearate increased to 86.69% and 90.57% while the methyl ricinoleate decreased to 2.65% and 1.94%, respectively.



**Figure 4.4** The percentage of methyl ester content from hydrogenation of methyl ricinoleate using 15% nickel catalyst at 90 °C reaction temperature on various hydrogen/nitrogen pressures.

In Figure 4.4, it indicated that the methyl 12-hydroxystearate was increased with increasing of hydrogen/nitrogen pressure, so it could be indicated that the rate of hydrogenation also increased when the hydrogen pressure was increased.

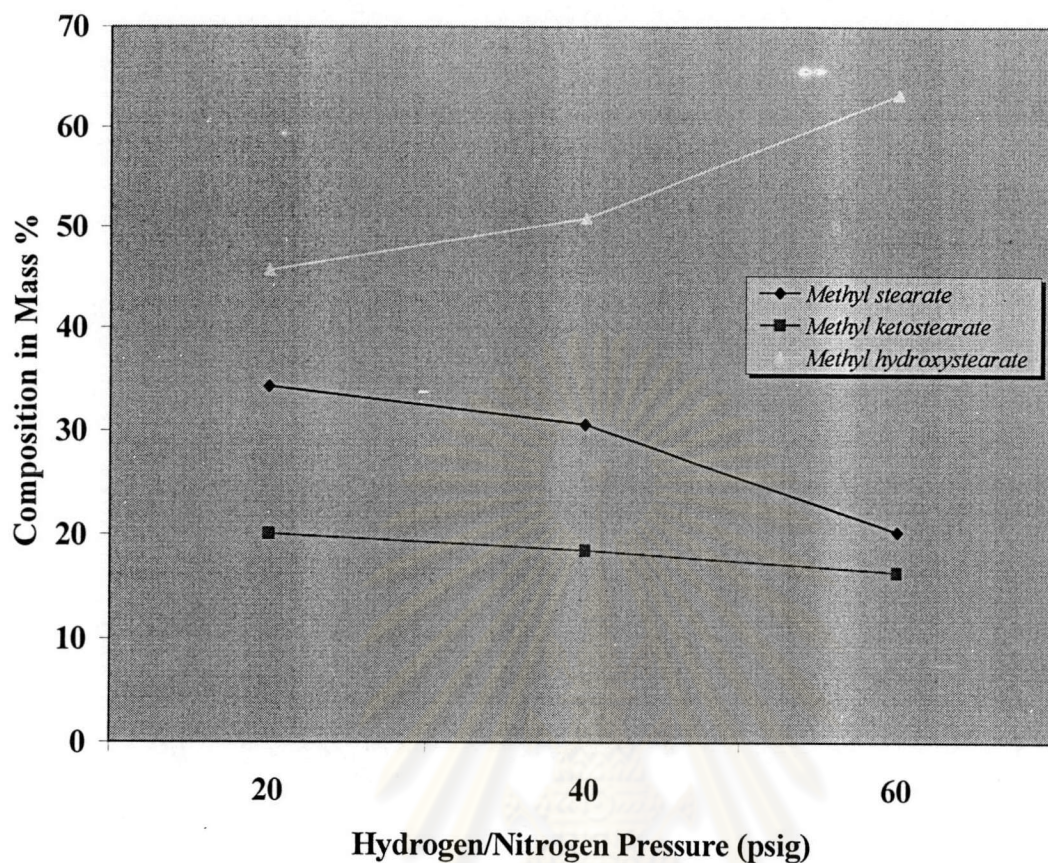
#### 4.3.2.2 Effect of hydrogen pressure at 200 °C reaction temperature

In order to study the effect of hydrogen pressure with the rate of dehydroxylation and dehydrogenation reaction that determined the amount of methyl stearate and methyl 12-ketostearate the reaction was performed at 200 °C. The results are shown in Table 4.7, Figures 4.5 and D18.

**Table 4.7** Analytical results from the hydrogenation of methyl ricinoleate using 15% nickel catalyst at 200 °C on various hydrogen/nitrogen pressures.

Composition	Hydrogen/nitrogen pressures		
	20	40	60
Methyl stearate	34.27	30.62	20.29
Methyl linoleate	-	-	-
Methyl ricinoleate	-	-	-
Methyl 12-ketostearate	20.11	18.53	16.44
Methyl 12-hydroxystearate	45.62	50.85	63.27

From this result, it was observed that when hydrogen/nitrogen pressure was increased from 20 to 40 and 60 psig, the amount of methyl 12-hydroxystearate increased from 45.62% to 50.85% and 63.27% while the methyl stearate and methyl 12-ketostearate decreased from 34.27% to 30.62% and 20.29%, and from 20.11% to 18.53% and 16.44%, respectively.



**Figure 4.5** The percentage of methyl ester content from hydrogenation of methyl ricinoleate using 15% nickel catalyst at 200 °C reaction temperature on various hydrogen/nitrogen pressures.

From Figure 4.4, the result showed that the methyl 12-hydroxystearate was increased with increasing hydrogen/nitrogen pressure while the methyl stearate and methyl 12-ketostearate were decreased, due to the rate of dehydroxylation and dehydrogenation reaction decreased with increasing the hydrogen pressure.

### 4.3.3 Effect of catalyst concentration

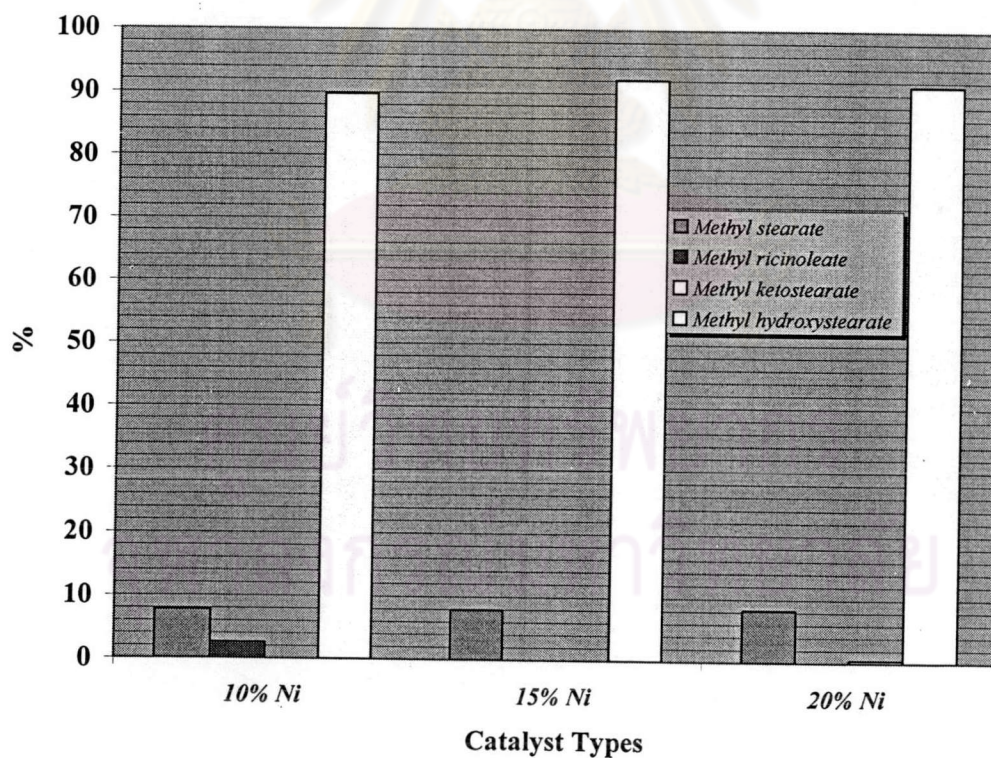
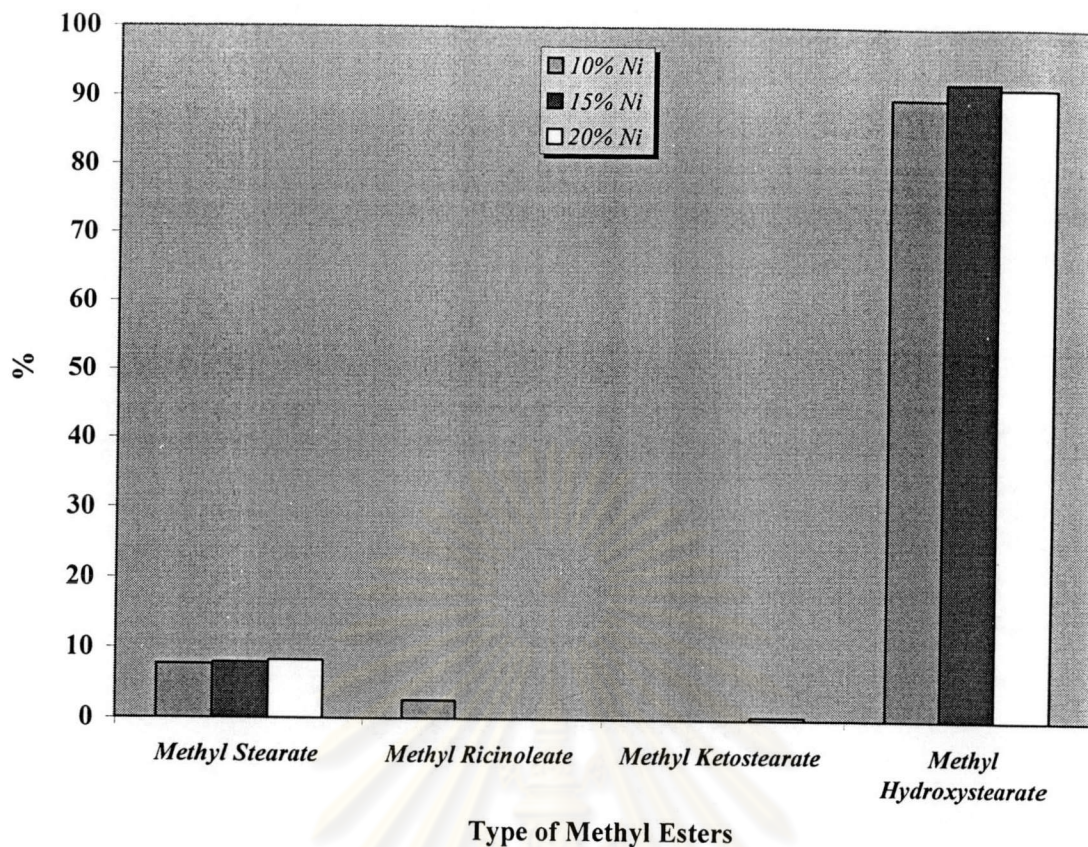
The effect of catalyst concentrations on hydrogenation of methyl ricinoleate was studied using three concentrations of catalysts under the same preparation condition. The impregnated nickel catalysts contained 10% Ni, 15% Ni and 20% Ni on alumina support were used.

Three concentrations of catalysts were employed in this section of experiment under the same condition, including the reaction temperature at 120 °C and 20 psig hydrogen/nitrogen pressure. The results are shown in Table 4.8, Figure 4.6.

**Table 4.8** Analytical results from the hydrogenation of methyl ricinoleate using various catalyst concentrations, at 120 °C reaction temperature and under 20 psig hydrogen/nitrogen pressure.

Composition	Catalyst concentrations (% weight of nickel per weight of alumina)		
	10%	15%	20%
Methyl stearate	7.70	7.96	8.24
Methyl linoleate	-	-	-
Methyl ricinoleate	2.57	-	-
Methyl 12-ketostearate	-	-	0.43
Methyl 12-hydroxystearate	89.73	92.04	91.33





**Figure 4.6** The percentage of methyl ester content using different concentrations of catalyst at 120 °C reaction temperature under 20 psig hydrogen/nitrogen pressure.

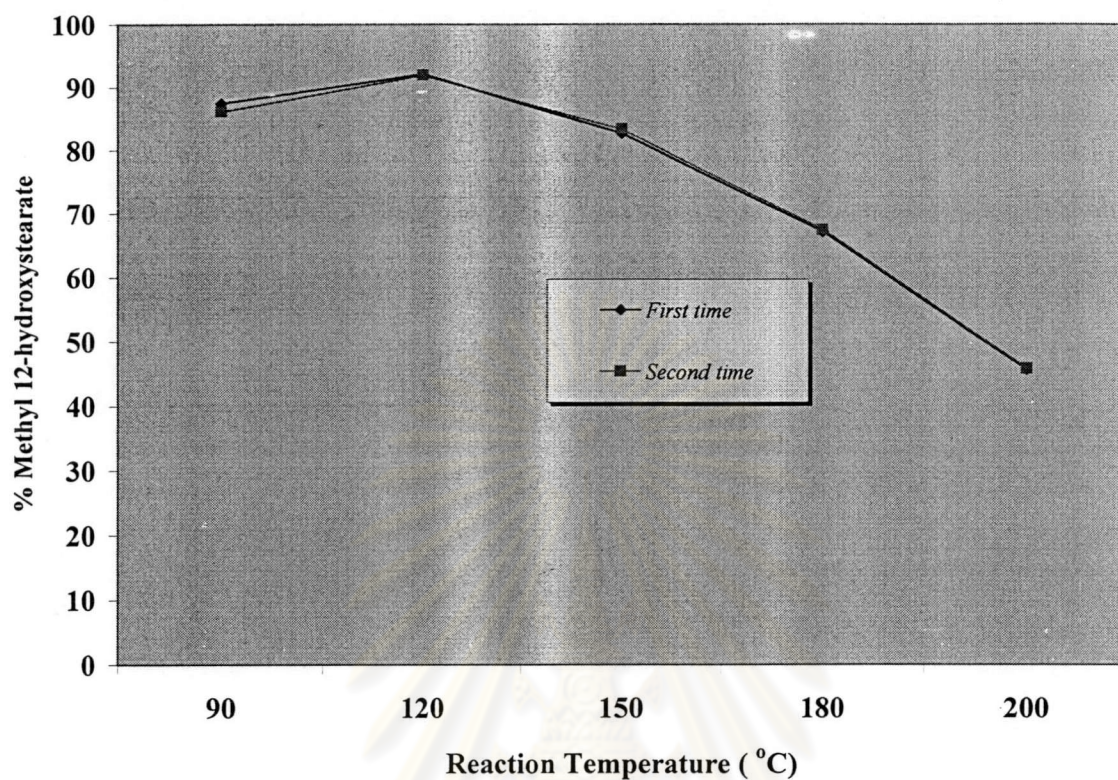
From the comparative results for the hydrogenation of methyl ricinoleate using different concentrations of nickel catalysts, it indicated that the 15% nickel catalyst gave better performance than the 10% nickel catalyst in the production of methyl 12-hydroxystearate. Although, 20 % nickel catalyst provided higher rate of hydrogenation but the amount of methyl 12-hydroxystearate was lower than that of 15% nickel catalyst, due to the formation of the methyl 12-ketostearate in the dehydrogenation reaction.

#### 4.3.4 Reproducibility of used catalyst

The reproducibility of the hydrogenation reaction of methyl ricinoleate using 15% nickel catalyst at various reaction temperatures under 20 psig hydrogen/nitrogen pressure was studied. The result is shown in Table 4.9 and Figure 4.7.

**Table 4.9** Analytical results from the hydrogenation of methyl ricinoleate in the reproducibility test of 15% nickel catalyst, at various reaction temperatures under 20 psig hydrogen/nitrogen pressure.

No. of used	Amount(%) of 12-hydroxystearate at various temperature (°C)				
	90	120	150	180	200
1 <sup>st</sup>	87.45	92.04	82.69	67.15	45.62
2 <sup>nd</sup>	86.08	91.89	83.29	67.54	45.89



**Figure 4.7** The percentage of methyl 12-hydroxystearate from hydrogenation of methyl ricinoleate by reproducibility test of 15% nickel catalyst at various reaction temperature under 20 psig hydrogen/nitrogen pressure.

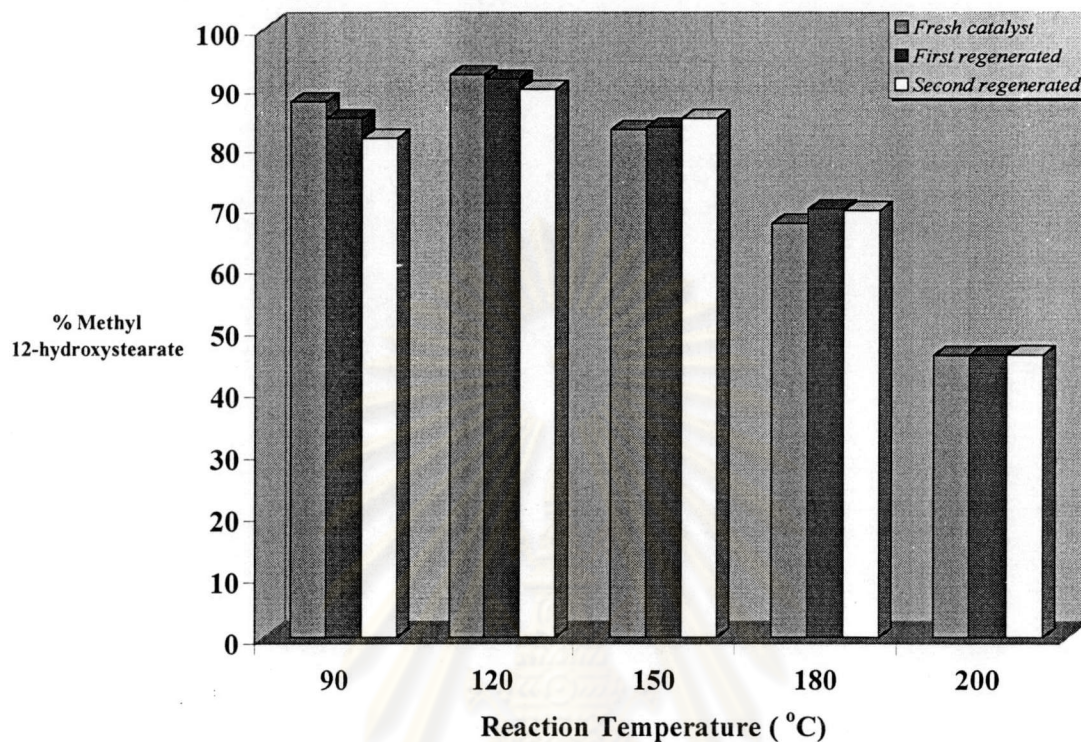
The results from Table 4.9 and Figure 4.7 indicated that the reaction was reproducible as observed from insignificant variation of the percentage amount of methyl 12-hydroxystearate.

#### 4.3.5 Activity of regenerated catalyst

In order to study the activity of regenerated catalyst, this section of experiment was carried out twice with 15% nickel catalyst under the same condition at 120 °C reaction temperature and under 20 psig hydrogen/nitrogen pressure. The results are shown in Table 4.10 and Figure 4.8.

**Table 4.10** Analytical results from the hydrogenation of methyl ricinoleate using regenerated catalyst at 120 °C reaction temperature and 20 psig hydrogen/nitrogen pressure.

No. of regeneration	Amount(%) of 12-hydroxystearate at various temperature (°C)				
	90	120	150	180	200
1 <sup>st</sup>	87.45	92.04	82.69	67.15	45.62
2 <sup>nd</sup>	84.59	91.36	83.12	69.54	45.69
3 <sup>rd</sup>	81.24	89.59	84.56	69.22	45.47



**Figure 4.8** The percentage of methyl 12-hydroxystearate from hydrogenation of methyl ricinoleate using regenerated 15% nickel catalyst at various reaction temperatures under 20 psig hydrogen/nitrogen pressure.

#### 4.4 Analysis of hydrogenated product

The hydrogenated methyl ricinoleate that obtained from optimum condition, which various reaction temperatures under 20 psig hydrogen/nitrogen pressure and using 15% nickel catalyst, was analyzed for iodine value and melting point. The result is shown in Table 4.11.

**Table 4.11** Comparative analysis results for the properties of methyl ricinoleate and hydrogenated product.

Materials	Properties	
	Iodine value	Melting point ( °C)
Methyl ricinoleate	81.77	-
Hydrogenated product at		
- 90 °C	3.21	42.0
- 120 °C	1.18	49.0
- 150 °C	1.21	49.5
- 180 °C	1.19	50.5
- 200 °C	1.23	52.5

## 4.5 Determination of spectroscopic properties

The  $^{13}\text{C}$ -NMR, GC and GC-MS were used to identify the products obtained from hydrogenation reaction of methyl ricinoleate.

### 4.5.1 $^{13}\text{C}$ -NMR spectrum

Bruker ACF 200 nuclear magnetic resonance spectrometer was used to characterize the castor oil, methyl ricinoleate and hydrogenated methyl ester, which obtained from the reaction. The  $^{13}\text{C}$ -NMR spectrums are shown in Figures E1-E7 in Appendix E.

The  $^{13}\text{C}$ -NMR spectrum of castor oil is shown in Figure E1, which indicated the signal of triglycerides ( $-\text{CH}_2\text{-O}-$ ) of castor oil at 61.97 and 68.80 ppm, the signal of parafinic carbons ( $\text{CH}_2$ ,  $\text{CH}_3$ ) at 13.98 to 36.69 ppm, the signal of olefinic carbons ( $\text{C}=\text{C}$ ) at 125.45 to 132.42 ppm. The carbonyl carbons ( $\text{C}=\text{O}$ ) appeared at 172.65 to 173.05 ppm, and the signal of hydroxyl ( $-\text{OH}$ ) at 71.26 ppm.

The  $^{13}\text{C}$ -NMR spectrum of methyl ester shown in Figure E2 demonstrated that the important signals of methyl ester ( $\text{O}-\text{CH}_3$ ) and carbonyl ( $\text{C}=\text{O}$ ) of methyl ester appeared at 51.24 and 174.13 ppm, respectively.

The  $^{13}\text{C}$ -NMR spectra of hydrogenated methyl esters are shown in Figures E3-E7 which indicated the decreasing of the olefinic carbons ( $\text{C}=\text{C}$ ) when the rate of hydrogenation was increased.

#### 4.5.2 GC-MS technique

The composition and amount of methyl ester at various conditions were determined by GC-MS, which performed by using DBwax capillary column and the GC-MS chromatograms are shown in Figures C1-C20 and mass spectra are shown in Figures C1-C6. The retention times of each methyl ester are shown in Table 4.12.

**Table 4.12** The retention time of each methyl ester.

Methyl ester	Retention time (min)
Methyl stearate	11.45
Methyl oleate	11.77
Methyl linoleate	12.31
Methyl ricinoleate	13.06
Methyl 12-ketostearate	13.11
Methyl 12-hydroxystearate	13.28

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