

CHAPTER 4

RESULTS AND DISCUSSION

The aim of this pursuit was to synthesize monoester as a potential lubricating oil from coconut oil, which a triglyceride of lauric acid is the main component. By transesterification, triglyceride can be reacted with alcohol to form esters in the presence of concentrated sulphuric acid as catalyst. After that the monoester were treated with hydrogen using platinum as catalyst.

The optimum conditions for transesterification were obtained by varying alcohol, reaction temperature and reaction time. In this research 1-hexanol, 1-octanol, 2-ethyl-1-hexanol, 1-octanol, cyclohexanol were used. The temperature was varied from 70, 80 and 90°C and the reaction time was observed in 1, 2, 3 and 6 hours. After that monoester products were determined by ^{13}C -NMR.

^{13}C -NMR spectrums of coconut oil, 1-hexanol, 1-octanol, 2-ethyl-1-hexanol, 1-octanol were shown in Figure A1, A2, A3, A4, A5, respectively.

Figure A1, ^{13}C -NMR spectrum shown the iminent signal of triglyceride, $-\text{CH}_2\text{-O-}$ and $-\text{CH-O-}$ at 62.3 and 68.8, respectively. In addition to these, Figure A1 also showed signal of unsaturated group at 129.0 ppm.

The ^{13}C -NMR spectrum of 1-hexanol, 1-octanol, 2-ethyl-1-hexanol, cyclohexanol were shown in Figure A2, A3, A4 and A5, respectively.

1. Transesterification of coconut oil with 1-hexanol

The ^{13}C -NMR spectrum of hexyl ester from transesterification was shown in Figure A6. The signal of triglyceride, $-\text{CH}_2\text{-O}$ and $-\text{CH-O-}$ could be seen at 62.3 and 68.8 ppm, respectively. These results indicated that transesterification was incomplete. From Figure A7, when reaction temperature was raised to 80°C , the result showed that the signal at 62.3 and 68.8 ppm was disappeared and the signal of $-\text{CH}_2\text{-O-}$ and C=O of ester product showed at 64.37 and 173.84 ppm. These results indicated that the transesterification reaction was completed.

These experimental results demonstrated that the optimum condition for transesterification of coconut oil with 1-hexanol was the reaction temperature of 80°C and reaction time of 3 hours. In this study, the result product was 87.56 % yield.

The physical and chemical properties of monoester product were shown in Table 4.1. The physical properties were studied as follow :color, pour point, kinetic viscosity at 40 and 100°C , viscosity index and flash point. The oxidation and thermal stability function were analyzed by TGA analyzer. The thermogram of coconut oil and hexyl ester product were shown in Figure A33 and Figure A34.

Table 4.1 The physical and chemical properties of coconut oil and hexyl ester product.

properties	coconut oil	monoester
Color, ASTM	0.5	0.5
Viscosity at 40 °C,cSt	27.72	4.98
Viscosity at 100°C,cSt	5.86	1.86
Viscosity Index (VI)	162.7	192.5
Pour Point (°C)	20	-8
Flash point (°C)	295	195
Oxidation point (°C)	435	350
Oxidation compound,%wt	7.84	2.21

From Table 4.1, this result showed that the pour point of product was entirely different from coconut oil. It was -8°C. The viscosity at 40 and 100°C was 4.98 and 1.86 cSt, respectively and the viscosity index was 192.5. Flash point was 195. The oxidative compounds were 2.21% wt.

2. Transesterification of coconut oil with 1- octanol.

The ¹³C-NMR spectrum of 1-octyl ester from transesterification was shown in Figure A8. The the signal of -CH₂-O and -CH-O- of triglyceride could be seen at 62.3 and 68.8 ppm, respectively. These results indicated that transesterification was incomplete. From Figure A9, when reaction temperature was raised to 90°C, the result showed that the signal at 62.3and 68.8 ppm disappeared and the signal of -CH₂-O- and C=O of ester product

showed at 65.3 and 172.7 ppm. These results indicated that the transesterification reaction was completed.

These experimental results demonstrated that the optimum condition for transesterification of coconut oil with 1-octanol was the reaction temperature of 80°C and reaction time of 3 hours. In this study, the result product was 85.02 % yield.

The physical and chemical properties of monoester product were shown in Table 4.2. The physical properties were studied as follow :color, pour point, kinetic viscosity at 40 and 100°C, viscosity index and flash point. The oxidation and thermal stability function were analyzed by TGA analyzer. The thermogram of coconut oil and 1-octyl ester product were shown in Figure A33 and Figure A36.

Table 4.2 The physical and chemical properties of coconut oil and 1-octyl ester product.

Properties	Coconut oil	Monoester
Color,ASTM	0.5	1.0
Viscosity at 40 °C,cSt	27.72	6.33
Viscosity at 100°C,cSt	5.86	2.20
Viscosity Index (VI)	162.7	183.1
Pour Point (°C)	20	-1
Flash point (°C)	295	198
Oxidation point (°C)	435	365
Oxidation compound,%wt.	7.84	2.99

From Table 4.2, these results showed that the pour point of product was -1°C . The viscosity at 40 and 100°C was 6.33 and 2.20 cSt, respectively and the viscosity index was 183.1. Flash point was 198. The oxidative compounds were 2.99% wt.

3. Transesterification of coconut oil with 2-ethyl -1-hexanol.

The ^{13}C -NMR spectrum of 2-ethyl-hexyl ester from transesterification was shown in Figure A10. The signal of $-\text{CH}_2\text{-O-}$ and $-\text{CH-O-}$ of triglyceride could be seen at 62.3 and 68.8 ppm, respectively. These results indicated that transesterification was incomplete. From Figure A11, when reaction temperature was raised to 80°C , the result showed that the signal at 62.3 and 68.8 ppm disappeared and the signal of $-\text{CH}_2\text{-O-}$ and C=O of ester product showed at 66.3 and 173.7 ppm. These results indicated that the transesterification reaction was completed.

These experimental results demonstrated that the optimum condition for transesterification of coconut oil with 2-ethyl-1-hexanol was the reaction temperature of 80°C and reaction time of 3 hours. In this study, the result product was 85.32 %yield.

The physical and chemical properties of monoester product were shown in Table 4.3. The physical properties were studied as follow :color, pour point, kinetic viscosity at 40 and 100°C , viscosity index and flash point. The oxidation and thermal stability function were analyzed by TGA analyzer. The thermogram of coconut oil and 2-ethylhexyl ester product were shown in Figure A33 and Figure A38.

Table 4.3 The physical and chemical properties of coconut oil and 2-ethyl hexyl ester product.

Properties	Coconut oil	Monoester
Color,ASTM	0.5	0.5
Viscosity at 40 °C,cSt	27.72	5.31
Viscosity at 100°C,cSt	5.86	1.90
Viscosity Index (VI)	162.7	166.4
Pour Point (°C)	20	min.-15
Flash point (°C)	295	197
Oxidation point (°C)	435	370
Oxidation compound,%wt.	7.84	2.91

From Table 4.3, these results that the pour point of product was min.-15 °C. The viscosity at 40 and 100 ° C was 5.31 and 1.90 cSt, respectively and the viscosity index was 166.4. Flash point was 197. The oxidative compounds were 2.91% wt.

4. Transesterification of coconut oil with cyclohexanol

The ^{13}C -NMR spectrum of cyclohexyl ester from transesterification was shown in Figure A12. The signal of $-\text{CH}_2\text{-O}-$ and $-\text{CH-O}-$ of triglyceride could be seen at 62.3 and 68.8 ppm, respectively. These results indicated that transesterification was incomplete. From Figure A13, when reaction temperature was raised to 80 °C, the result showed that the signal at 62.3 and

68.8 ppm disappeared and the signal of $-\text{CH}_2-\text{O}-$ and $\text{C}=\text{O}$ of ester product showed at 71.9 and 172.7 ppm. These results indicated that the transesterification reaction was completed.

These experimental results demonstrated that the optimum condition for transesterification of coconut oil with cyclohexanol was the reaction temperature of 90°C and reaction time of 6 hours. In this study, the result product was 81.62 % yield.

The physical and chemical properties of monoester product were shown in Table 4.4. The physical properties were studied as follow :color, pour point, kinetic viscosity at 40 and 100°C , viscosity index and flash point. The oxidation and thermal stability function were analyzed by TGA analyzer. The thermogram of coconut oil and cyclohexyl ester product were shown in Figure A33 and Figure A40.

Table 4.4 : The physical and chemical properties of coconut oil and cyclohexyl ester product.

Properties	Coconut oil	Monoester
Color,ASTM	0.5	L1
Viscosity at 40°C ,cSt	27.72	8.81
Viscosity at 100°C ,cSt	5.86	2.73
Viscosity Index (VI)	162.7	152.5
Pour Point ($^\circ\text{C}$)	20	-9
Flash point ($^\circ\text{C}$)	295	180
Oxidation point ($^\circ\text{C}$)	435	370
Oxidation compound,%wt.	7.84	4.72

From Table 4.4, these results showed that the pour point was -9°C . The viscosity at 40 and 100°C was 8.81 and 2.73cSt, respectively and the viscosity index was 152.5. Flash point was 180. The oxidative compounds were 4.72% wt.

To improve the color and oxidation stability, the monoester had to be finally refined through hydrogenation of unsaturated components. In this study, the monoester was treated with hydrogenated catalyst in a stirred batch reactor under hydrogen. The used catalyst contained 3% by weight of platinum supported on alumina.

The hydrogenation process was optimized by varying the following parameters: hydrogen partial pressure, catalyst concentration, reaction time while fixing other parameters, such as reaction temperature, weight of oil and stirring speed. The reaction was monitored by ^{13}C -NMR.

Hydrogenation of hexyl ester

The results of hydrogenated hexyl ester from hydrogenation at optimum condition was analyzed by ^{13}C -NMR and the GC-MS chromatogram was showed in Figure A7 and A14, respectively.

In Figure A7, ^{13}C -NMR spectrum, when hydrogen partial pressure was 100 psi, catalyst concentration was 5% by weight of oil, reaction time was 3 hours, and the reaction temperature was 150°C , it showed that the signal of unsaturated group at between 125.2 and 129.8 ppm was disappeared. These experimental results showed that the optimum conditions for hydrogenation of

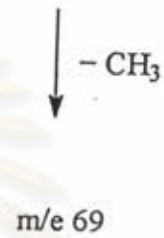
hexyl ester oil using 3% of platinum on alumina as catalyst were 5% of catalyst concentration, and the reaction was performed at 100°C under hydrogen pressure of 100 psi and reaction time 3 hours.

These experimental results indicated that the hydrogenation reaction of hexyl ester was complete at these reaction condition. In this study, the result product was 95.00% yield.

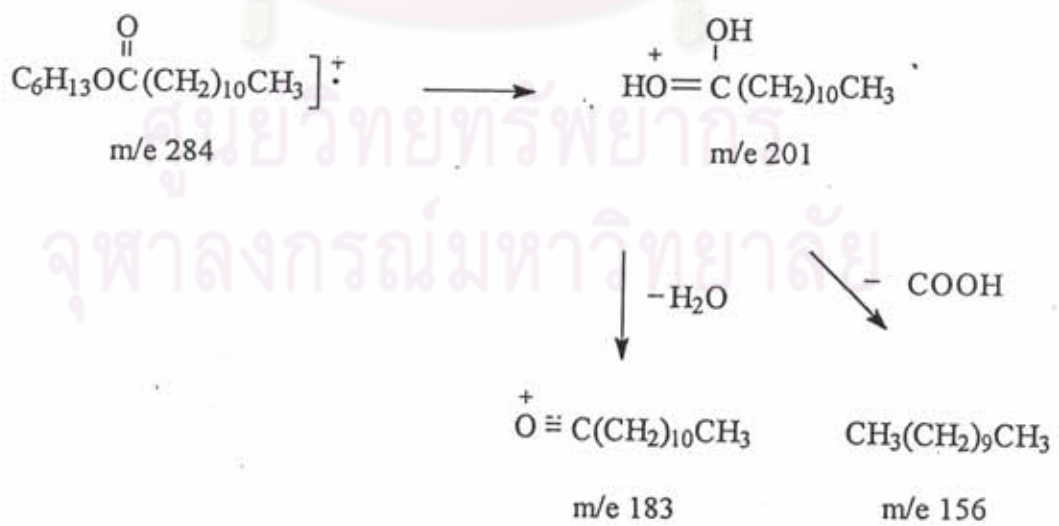
The composition of hydrogenated hexyl ester product at the optimum condition was determined by GC-MS. The GC-MS was performed in a column packed with DB-5. And the GC-MS chromatogram of hydrogenated hexyl ester product was shown in Figure A14. From the chromatogram, it indicated that hydrogenated hexyl ester product was a mixture of hexyl laurate, hexyl myristate, hexyl caprate and hexyl caprilate.

Characteristics of their derivatives were confirmed by mass spectrum as shown in Figure A15, A16, A17 and A18, respectively. Mass spectrum of hexyl laurate (MW 284), at retention time 19.56 in Figure A17 showed base peak at 84 due to α -cleavage of ester linkage as the following equation:

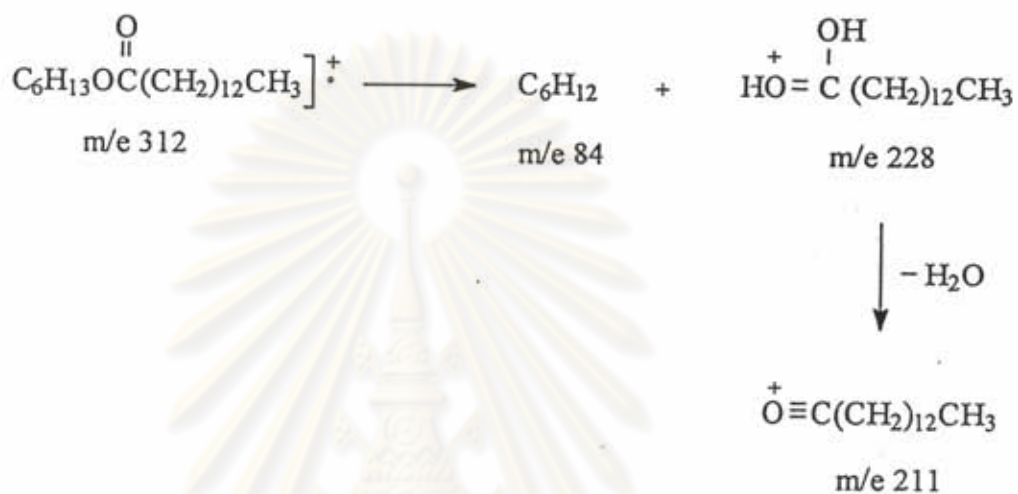
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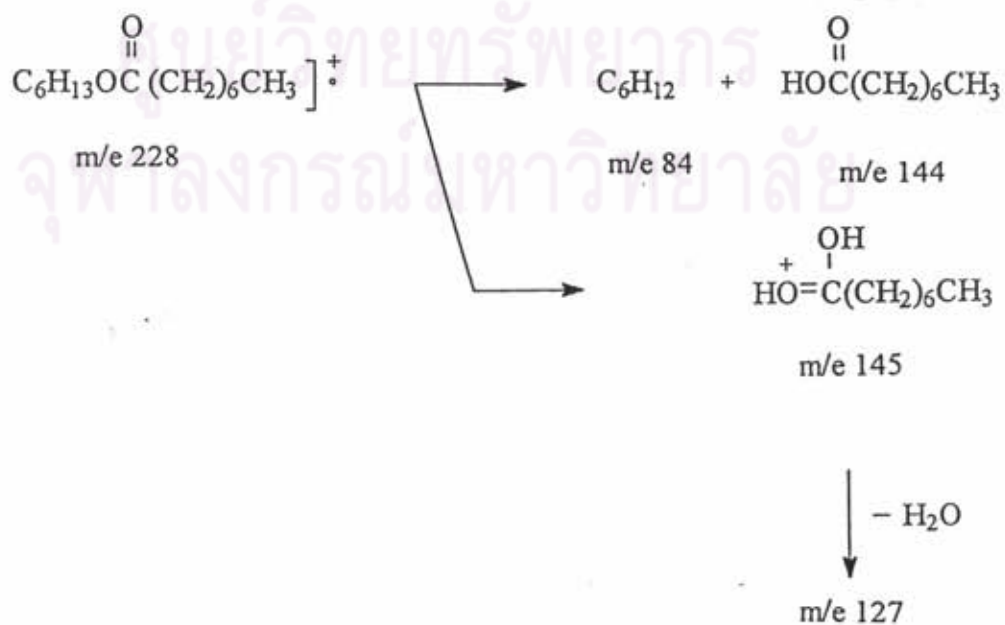
McLafferty rearrangement could be occurred as following:



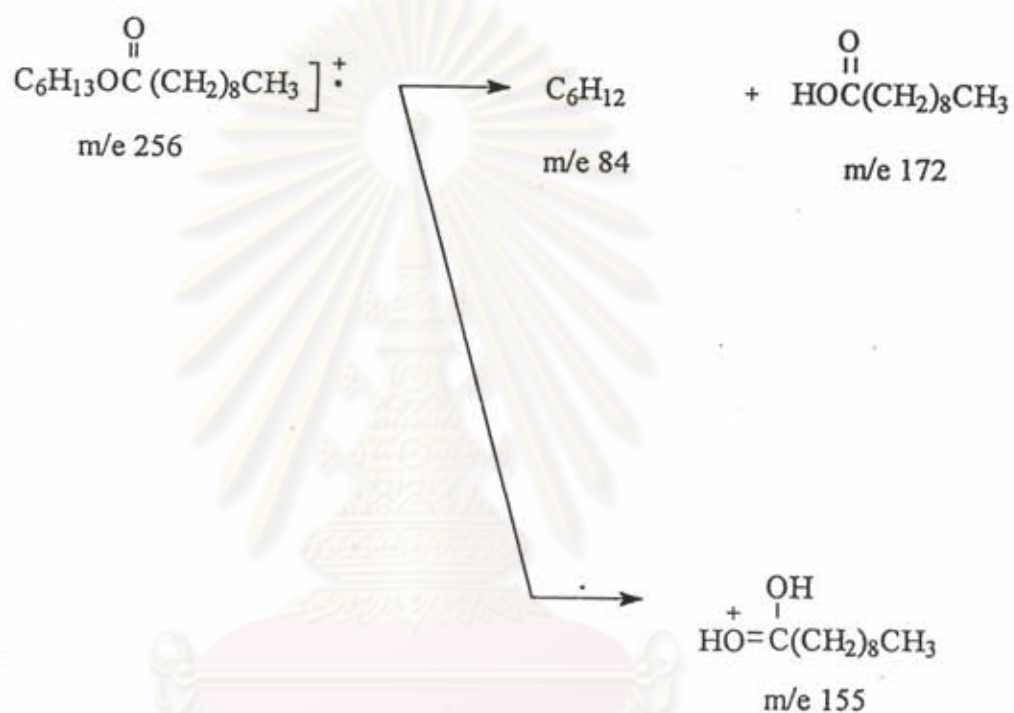
Mass spectrum of hexyl myristate (MW 312) in Figure A18 showed base peak at 84 due to McLafferty rearrangement as the following equation:



Mass spectrum of hexyl caprylate (MW 228) in Figure A15 showed base peak at 84 due to McLafferty rearrangement as the following equation:



Mass spectrum of hexyl caprate (MW 256) in Figure A16 showed base peak at 84 due to McLafferty rearrangement as the following equation:



The physical and chemical properties of hydrogenated hexyl ester product, as showed in Table 4.5, were studied as follow: color, pour point, kinematic viscosity at 40 and 100°C, viscosity index, flash point and oxidation stability. The oxidation and thermal stability curve were analyzed by TGA analyzer and the result were shown in Figure A35.

Table 4.5 : The physical and chemical properties of hexyl ester and hydrogenated hexyl ester product

Properties	hexyl monoester	hydrogenated hexyl monoester
Color,ASTM	0.5	0.5
Viscosity at 40 °C,cSt	4.98	4.52
Viscosity at 100°C,cSt	1.86	1.71
Viscosity Index (VI)	192.5	180.8
Pour Point (°C)	-8	-3
Flash point (°C)	195	186
Oxidation point (°C)	350	360
Oxidation compound,%wt.	2.21	2.29

Hydrogenation of 1-octyl ester

The results of hydrogenated octyl ester from hydrogenation at optimum condition was analyzed by ^{13}C -NMR and the GC-MS chromatogram was showed in Figure A9 and A19, respectively.

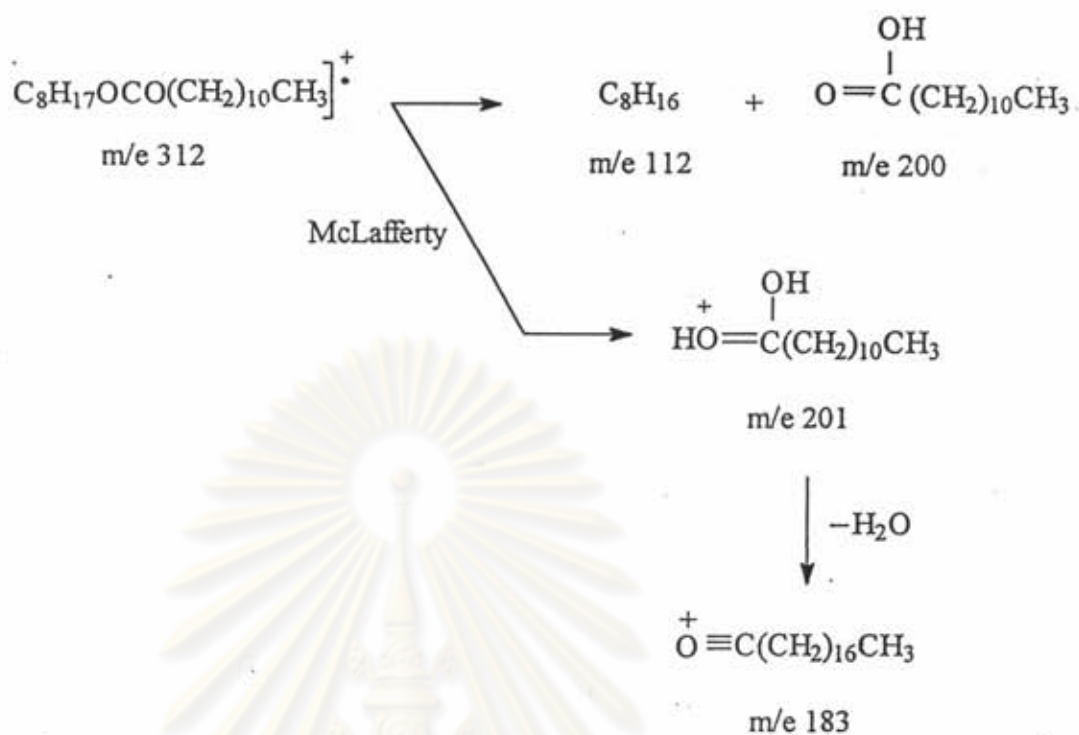
In Figure A9, ^{13}C -NMR spectrum, when hydrogen partial pressure was 100 psi, catalyst concentration was 5% by weight of oil, reaction time was 3 hours, and the reaction temperature was 150°C, it showed that the signal of unsaturated group at between 129.2-130.5 ppm was disappeared. These experimental results showed that the optimum conditions for hydrogenation of

1-octyl ester oil using 3% of platinum on alumina as catalyst were 5% of catalyst concentration, and the reaction was performed at 100°C under hydrogen pressure of 100 psi and reaction time 3 hours.

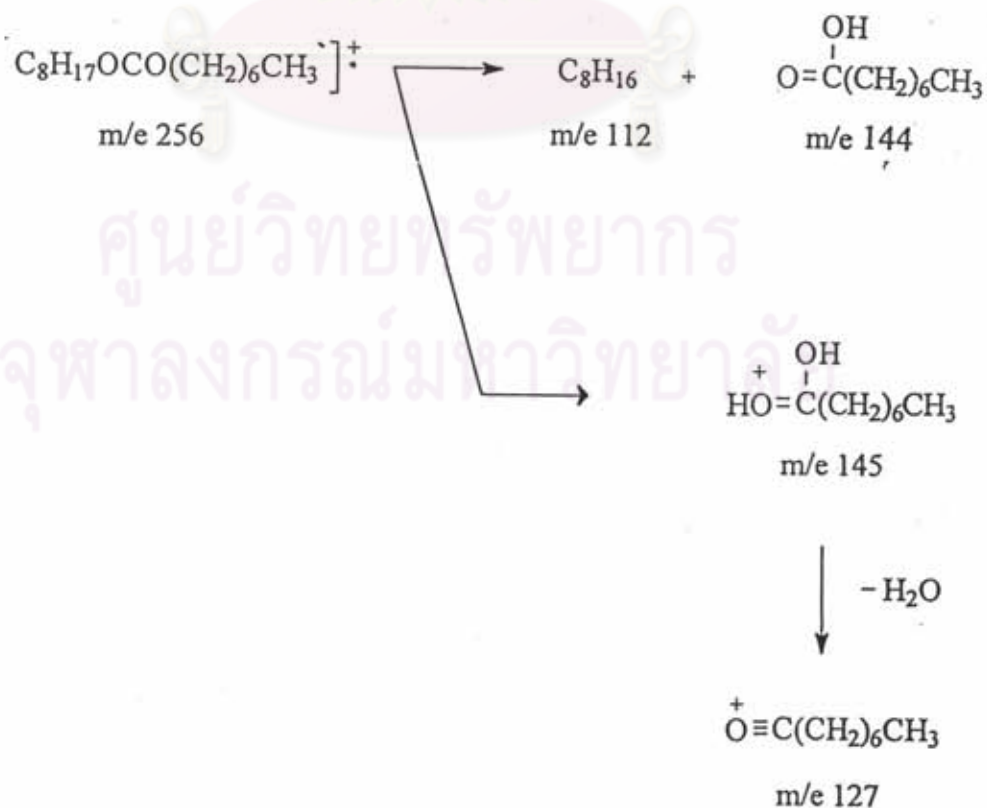
These experimental results indicated that the hydrogenation reaction of hexyl ester was completed at these reaction condition. In this study, the result product was 94.02 % yield.

The composition of hydrogenated hexyl ester product at the optimum condition was determined by GC-MS. The GC-MS was performed in a column packed with DB-5. And the GC-MS chromatogram of hydrogenated 1-octyl ester product was showed in Figure A19. From the chromatogram, it indicated that hydrogenated hexyl ester product was a mixture of 1-octyl laurate, 1-octyl caprate and 1-octyl caprilate.

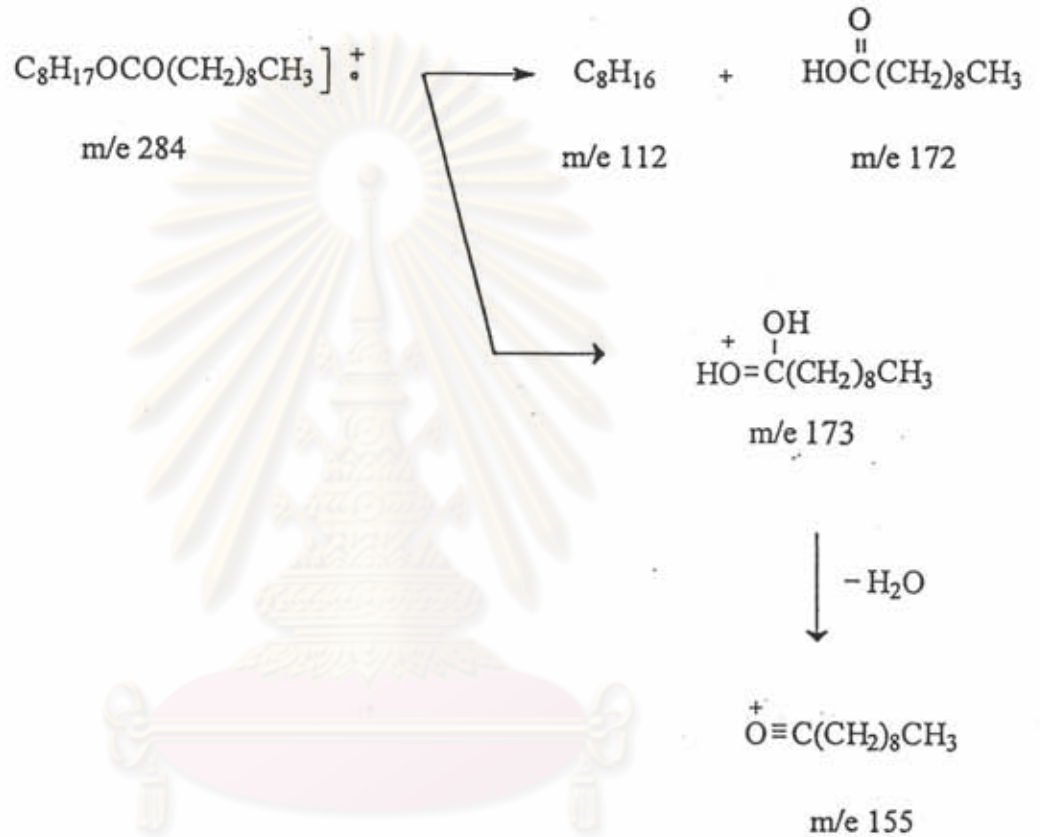
Characteristics of their derivatives were confirmed by mass spectrum as shown in Figure A20, A21 and A22, respectively. Mass spectrum of 1-octyl laurate (MW 312), at retention time 23.19 in Figure A22 showed base peak at 112 due to α -cleavage of ester linkage which can be explained as in the following equation:



Mass spectrum of 1-octyl caprylate (MW 256), at retention time 16.277 in Figure A20 showed base peak at 112 due to α -cleavage of ester linkage as the following equation:



Mass spectrum of 1-octyl carbate (MW 284), at retention time 19.284 in Figure A21 showed base peak at 112 due to α -cleavage of ester linkage as the following equation:



The physical and chemical properties of hydrogenated 1-octyl ester product, as showed in Table 4.6, were studied as follow: color, pour point, kinematic viscosity at 40 and 100°C, viscosity index, flash point and oxidation stability. The oxidation and thermal stability curve were analyzed by TGA analyzer and the result were shown in Figure A37.

Table 4.6 : The physical and chemical properties of 1-octyl ester and hydrogenated 1-octyl ester product

Properties	1-octyl monoester	hydrogenated 1-octyl monoester
Color,ASTM	1.0	0.5
Viscosity at 40 °C,cSt	6.33	6.08
Viscosity at 100°C,cSt	2.20	2.13
Viscosity Index (VI)	183.1	180.8
Pour Point (°C)	-1	5
Flash point (°C)	198	190
Oxidation point (°C)	365	365
Oxidation compound,%wt.	2.99	1.46

Hydrogenation of 2-ethylhexyl ester

The results of hydrogenated 2-ethylhexyl ester from hydrogenation at optimum condition was analyzed by ^{13}C -NMR and the GC-MS chromatogram was showed in Figure A11 and A23, respectively.

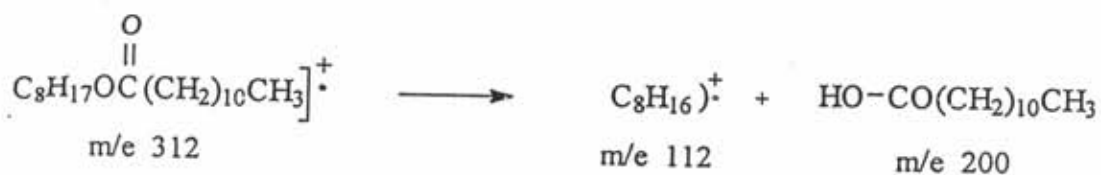
In Figure A11, ^{13}C -NMR spectrum, when hydrogen partial pressure was 100 psi, catalyst concentration was 5% by weight of oil, reaction time was 3 hours, and the reaction temperature was 150°C, it showed that the signal of unsaturated group at between 129.4-129.7 ppm. was disappeared. These

experimental results showed that the optimum conditions for hydrogenation of 2-ethyl-hexyl ester oil using 3% of platinum on alumina as catalyst were 5% of catalyst concentration, and the reaction was performed at 150°C under hydrogen pressure of 100 psi and reaction time 3 hours indicated that the hydrogenation reaction of 2-ethylhexyl ester was completed at these reaction condition. In this study, the result product was 92.25 % yield.

The composition of hydrogenated 2-ethyl-hexyl ester product at the optimum condition was determined by GC-MS. The GC-MS was performed in a column packed with DB-5. And the GC-MS chromatogram of hydrogenated 2-ethylhexyl ester product was showed in Figure A23. From GC-MS chromatogram, it indicated that hydrogenated 2-ethyl-hexyl ester product was a mixture of 2-ethylhexyl laurate, 2-ethylhexyl myristate, 2-ethylhexyl caprate and 2-ethylhexyl caprilate.

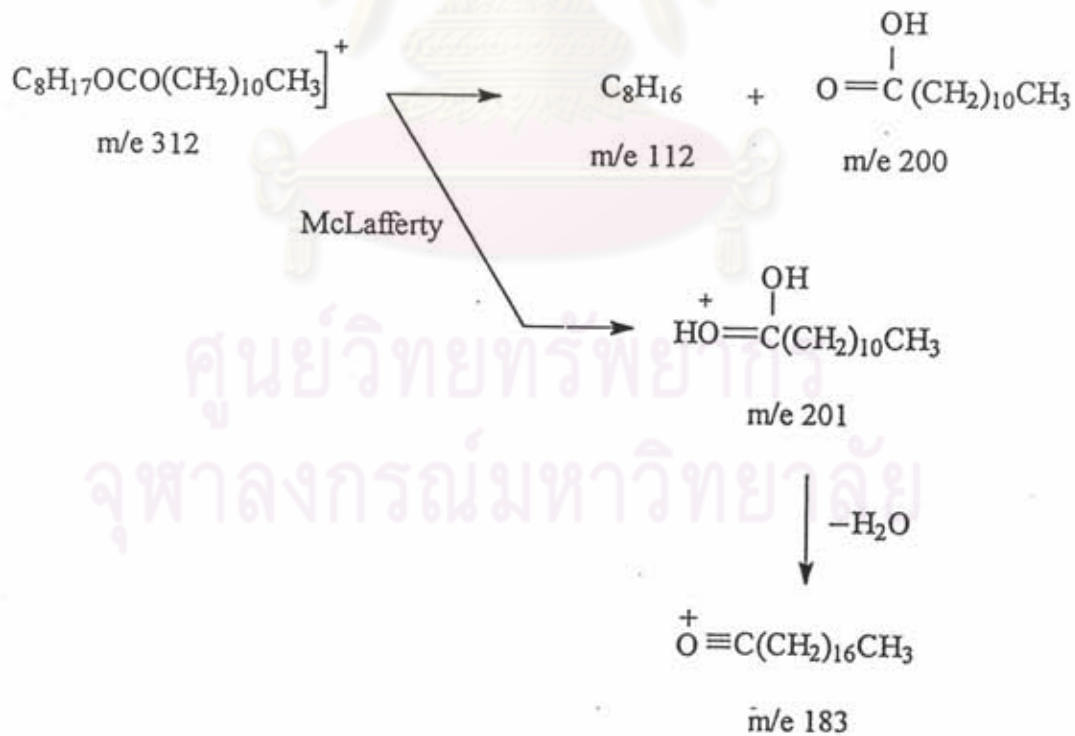
Characteristics of their derivatives were confirmed by mass spectrum as shown in Figure A24, A25, A26 and A27, respectively. Mass spectrum of 2-ethyl-hexyl laurate (MW 312), at retention time 21.812 in Figure A24 showed base peak at 112 due to α -cleavage of ester linkage which can be explained as in the following equation:

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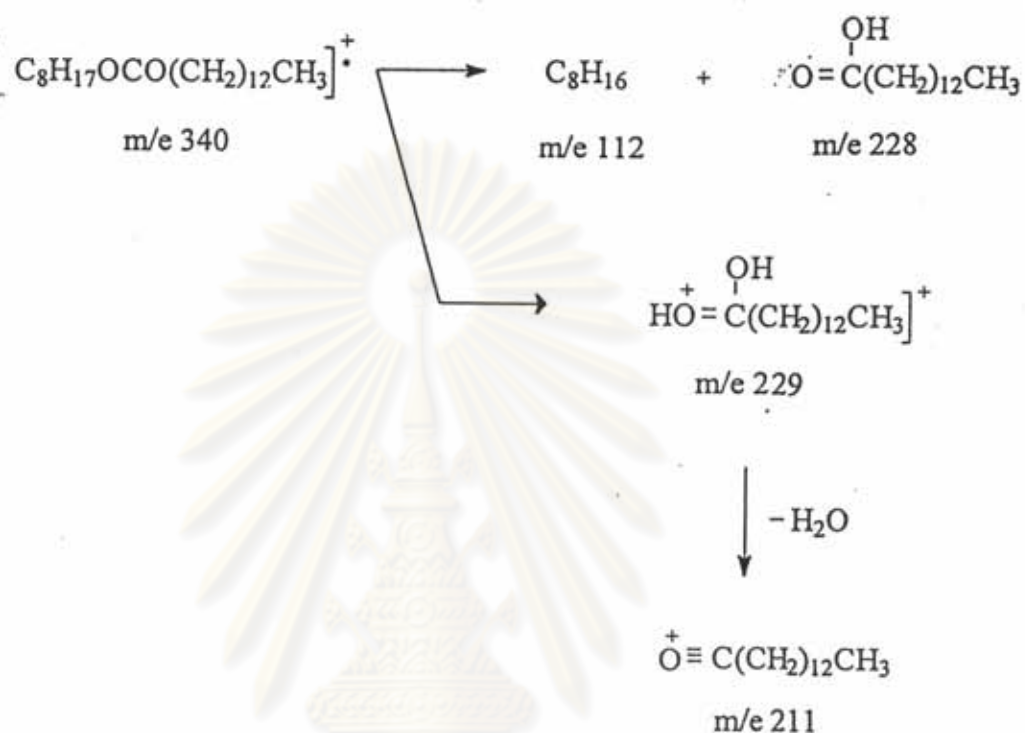


m/e 97, 84, 71, 57

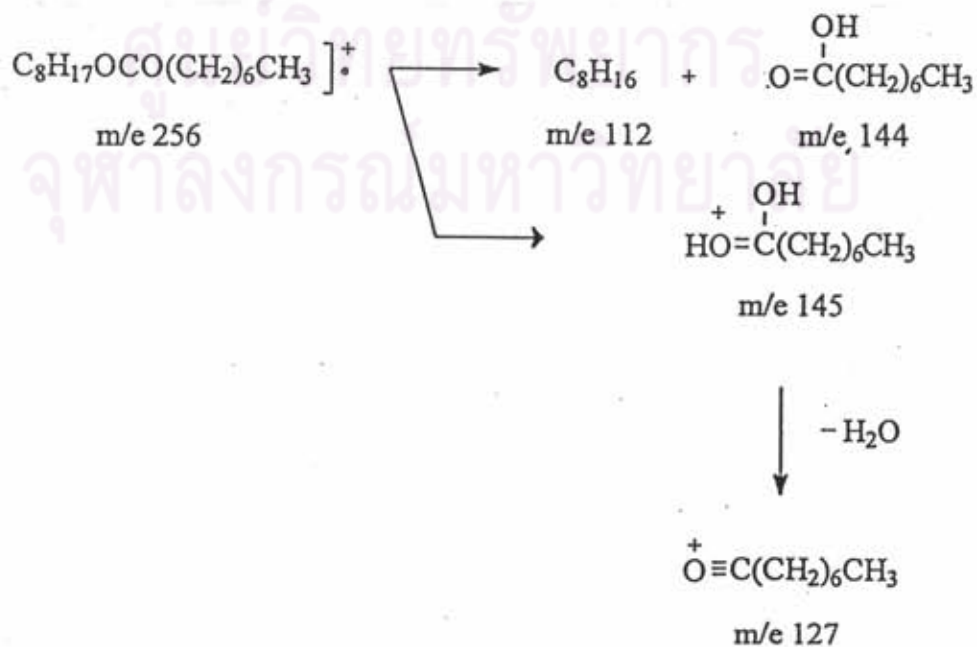
McLafferty rearrangement could be occurred as following:



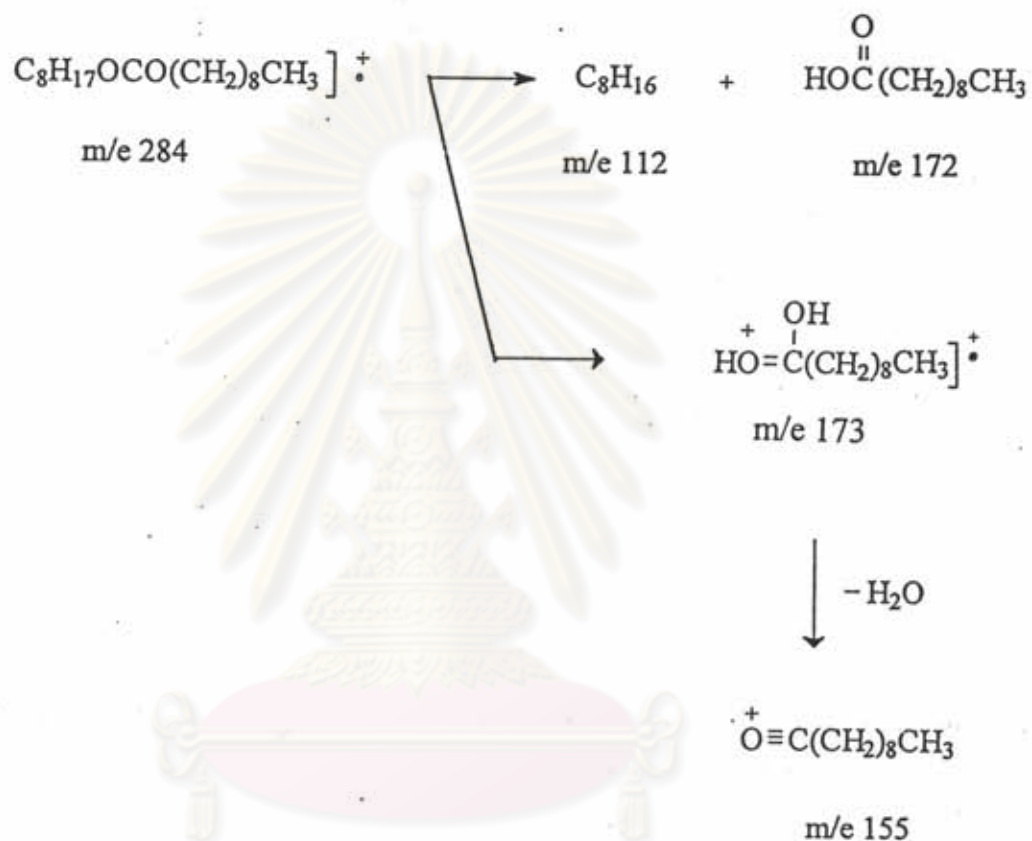
Mass spectrum of 2-ethylhexyl myristate (MW 340) in Figure A25 show base peak at 112 due to McLafferty rearrangement as the following equation:



Mass spectrum of 2-ethyl-hexyl carpryrate (MW 256) in Figure A27 show base peak at 112 due to McLafferty rearrangement as the following equation:



Mass spectrum of 2-ethyl-hexyl carprate(MW 284) in Figure A26 show base peak at 112 due to McLafferty rearrangement as the following equation:



The physical and chemical properties of hydrogenated 2-ethylhexyl ester product, as showed in Table 4.7, were studied as follow: color, pour point, kinematic viscosity at 40 and 100°C, viscosity index, flash point and oxidation stability. The oxidation and thermal stability curve were analyzed by TGA analyzer and the result were shown in Figure A39.

Table 4.7 : The physical and chemical properties of 2-ethylhexyl ester and hydrogenated 2-ethylhexyl ester product

Properties	2-ethylhexyl monoester	hydrogenated 2-ethylhexyl monoester
Color,ASTM	0.5	0.5
Viscosity at 40 °C,cSt	5.31	5.53
Viscosity at 100°C,cSt	1.90	1.93
Viscosity Index (VI)	166.4	155.1
Pour Point (°C)	min.-15	min.-15
Flash point (°C)	197	188
Oxidation point (°C)	370	390
Oxidation compound,%wt.	2.91	1.50

Hydrogenation of cyclohexyl ester

The results of hydrogenated cyclohexyl ester from hydrogenation at optimum condition was analyzed by ^{13}C -NMR and the GC-MS spectrum was showed in Figure A13 and A28, respectively.

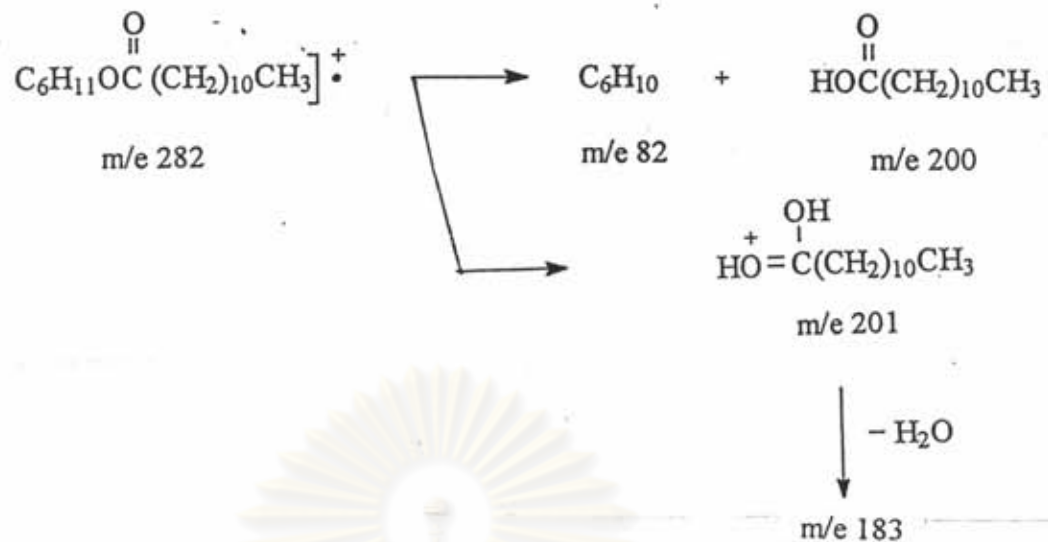
In Figure A13, ^{13}C -NMR spectrum, when hydrogen partial pressure was 100 psi, catalyst concentration was 5% by weight of oil, reaction time was 3 hours, and the reaction temperature was 150°C, it showed that the signal of unsaturated group at between 129.5-129.7 ppm. was disappeared. These

experimental results indicated that the optimum conditions for hydrogenation of cyclohexyl ester oil using 3% of platinum on alumina as catalyst were 5% of catalyst concentration, at 100°C under hydrogen pressure 100 psi and reaction time 3 hours.

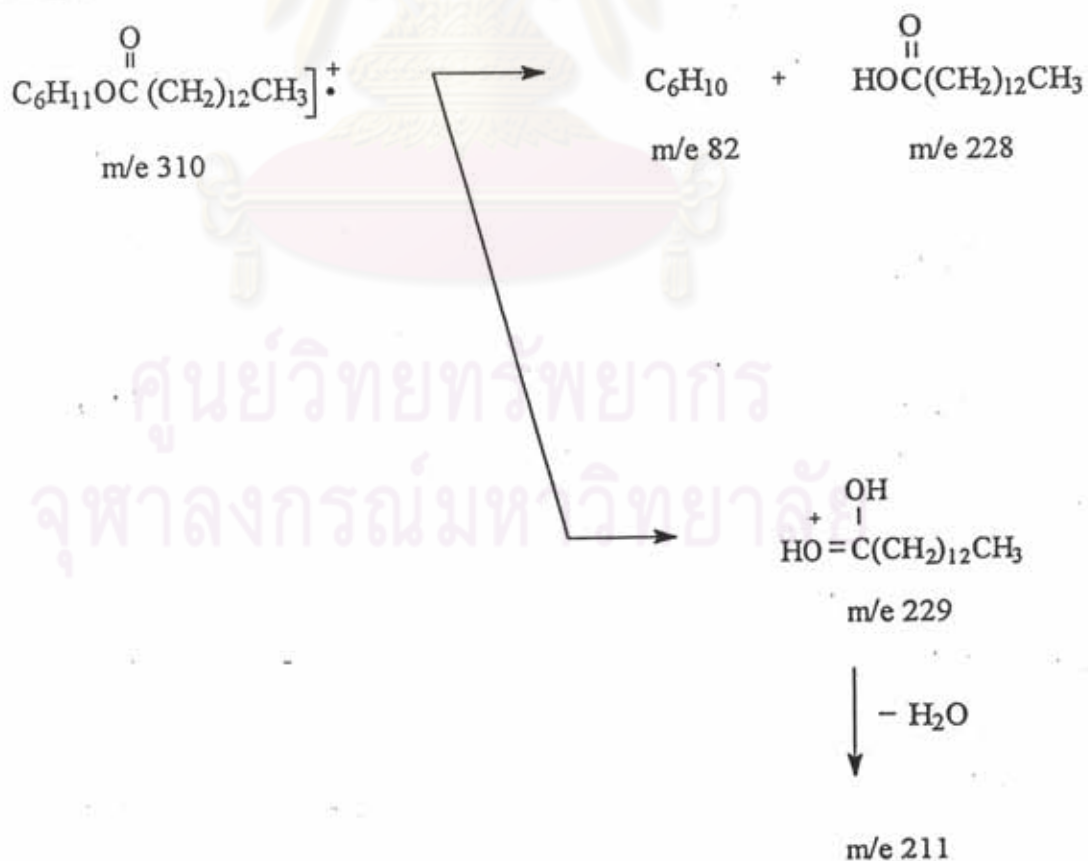
These experimental results indicated that the hydrogenation reaction of cyclohexyl ester was completed at these reaction condition. In this study, the result product was 90.15 % yield. The composition of hydrogenated cyclohexyl ester product at the optimum condition was determined by GC-MS. The GC-MS was performed in a column packed with DB-5. The GC-MS chromatogram of hydrogenated cyclohexyl ester product was showed in Figure A28.

From the chromatogram, it indicated that hydrogenated cyclohexyl ester product was a mixture of cyclohexyl laurate, cyclohexyl myristate, cyclohexyl caprate and cyclohexyl caprilate. Characteristics of their derivatives were confirmed by mass spectrum as shown in Figure A29, A30, A31, A32, respectively.

Mass spectrum of cyclohexyl laurate (MW 282), at retention time 20.564 in Figure A29 showed base peak at 82 due to α -cleavage of ester linkage which can be indicated as in the following equation:



Mass spectrum of cyclohexyl myristate (MW 310) in Figure A30 show base peak at 82 due to McLafferty rearrangement as the following equation:



The physical and chemical properties of hydrogenated cyclohexyl ester product, as showed in Table 4.8, were studied as follow: color, pour point, kinematic viscosity at 40 and 100°C, viscosity index, flash point and oxidation stability. The oxidation and thermal stability curve were analyzed by TGA analyzer and the result were shown in Figure A41.

Table 4.8 : The physical and chemical properties of cyclohexyl ester and hydrogenated cyclohexyl ester product

Properties	cyclohexyl monoester	hydrogenated cyclohexyl monoester
Color,ASTM	L1	0.5
Viscosity at 40 °C,cSt	8.81	8.74
Viscosity at 100°C,cSt	2.73	2.69
Viscosity Index (VI)	152.5	154.4
Pour Point (°C)	-9	-6
Flash point (°C)	180	176
Oxidation point (°C)	370	380
Oxidation compound,%wt.	4.72	3.23

From the results, alcohols varied in this research were 1-hexanol, 1-octanol, 2-ethyl-1-hexanol and cyclohexanol to be obtained the desirable

properties. When 1-hexanol was used, viscosity was too low then 1-octanol could be altered for the reason that increasing the molecular weight also increased viscosity. Although increasing viscosity, the pour point was also increasing too. This was one disadvantage of long chain molecule backbone. 2-Ethyl-1-hexanol could be altered in straight chain structure. It has been found that high viscosity index were obtained and also had low pour point but the viscosity was relatively low. Then cyclic group in molecule backbone such as cyclohexanol was used.

It could be found that hydrogenated cyclohexyl ester product had suitable properties for use in lubricating works, when compared with the specification of lubricating oil, especially as the lubricant for two-stroke engine.

Table 4.9 Specification of two-cycle lubricant

Properties	Limit
Flash point, °c	min. 70
Viscosity, Kinematic, @100°C	9.0-12.0
Viscosity index	min 98
Color	green
Pour point, °c	max -5
Sulphated ash, %wt	max 0.5

:TIS 1040-1991 of Thai Industrial Standard Institute, Ministry of industry

From Table 4.9 when compared the kinematic viscosity at 100°C to hydrogenated cyclohexyl ester it could be noticed that the viscosity of ester was

too low, but it wasn't seriously, due to polyisobutylene (PIBs) was the major component in two-stroke engine oils which used as VI improvers have predominantly a molecule mass of 10,000 to 15,000, possess a good viscosity increasing effect and was oxidatively and thermally stable.



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