

CHAPTER 4

RESULTS AND DISCUSSION

The goal of this research was to synthesize monoester as a potential lubricating oil from castor oil; which was mainly a triglyceride of ricinoleic acid, by transesterification reaction with 2-ethylhexanol, in the presence of concentrated sulphuric acid.

The optimum condition for transesterification was obtained by varying reaction temperature and reaction time. In this study, the reaction temperature was varied from 60, 80, 100, 130 and 160°C. While the reaction was performed at various temperature, the reaction time was studied between 3 and 6 hours.

Characteristics of monoester product were determined by ^{13}C -NMR and GC-MS.

The ^{13}C -NMR spectrums of castor oil and 2-ethylhexanol were showed in Figure A1 and A2, respectively.

The results from transesterification of castor oil at various temperatures and times were shown as ^{13}C -NMR spectrums in Figure A3-A12.

From Figure A3 and A4, it could be seen the peak of $-\text{CH}_2\text{-O}-$ and $-\text{CH-O}-$ of triglyceride molecules at 61.9 and 68.7 ppm, respectively. These results showed that if the temperature was as low as 60°C, transesterification was incomplete. From Figure A5, when reaction temperature was 80°C, the result demonstrated that the peak at 61.9 and 68.7 ppm disappeared and the important peak of $-\text{CH}_2\text{-O}-$ and C=O of ester product appeared at 66.4 and 173.6 ppm,

respectively. It indicated that the transesterification reaction was complete in 3 hours.

However, when the temperature was increased to over 100°C, dehydration was occurred. The hydroxyl group was removed with a nearby hydrogen atom to form water and a new double bond. The evidence could be seen by the decrease in the peak of -CH-OH at 71.3 ppm and the increase in the numbers of peak of unsaturation at between 125-135 ppm as shown in Figure A7-A12. The degree of dehydration was increased with the increasing reaction temperature and reaction time.

These experimental results indicated that the optimum condition for transesterification of castor oil was the reaction temperature of 80°C and reaction time of 3 hours. In this study, the result product was 85.66% yield.

The composition of monoester product was determined by GC-MS. The GC-MS was performed in a column packed with DB-1.

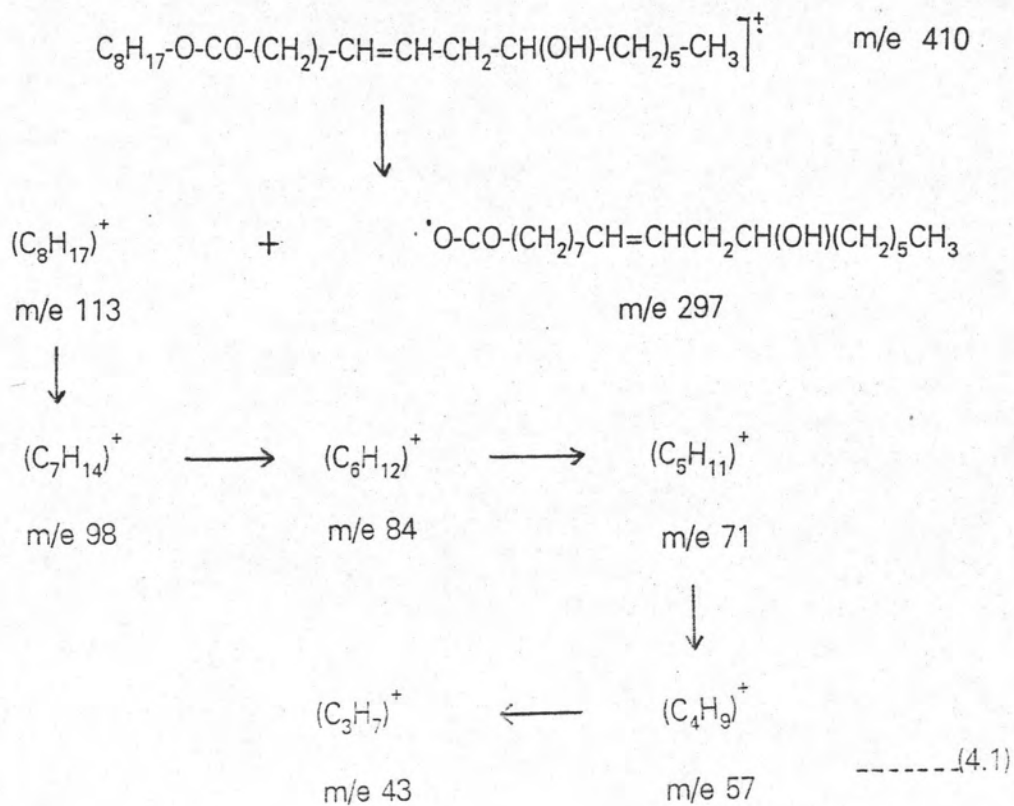
The chromatogram of monoester product was showed in Fig.A22.

From chromatogram, it indicated that monoester product was composed of mixture of 2-ethylhexyl ester of long chain fatty acid. The main composition was 2-ethylhexyl ricinoleate.

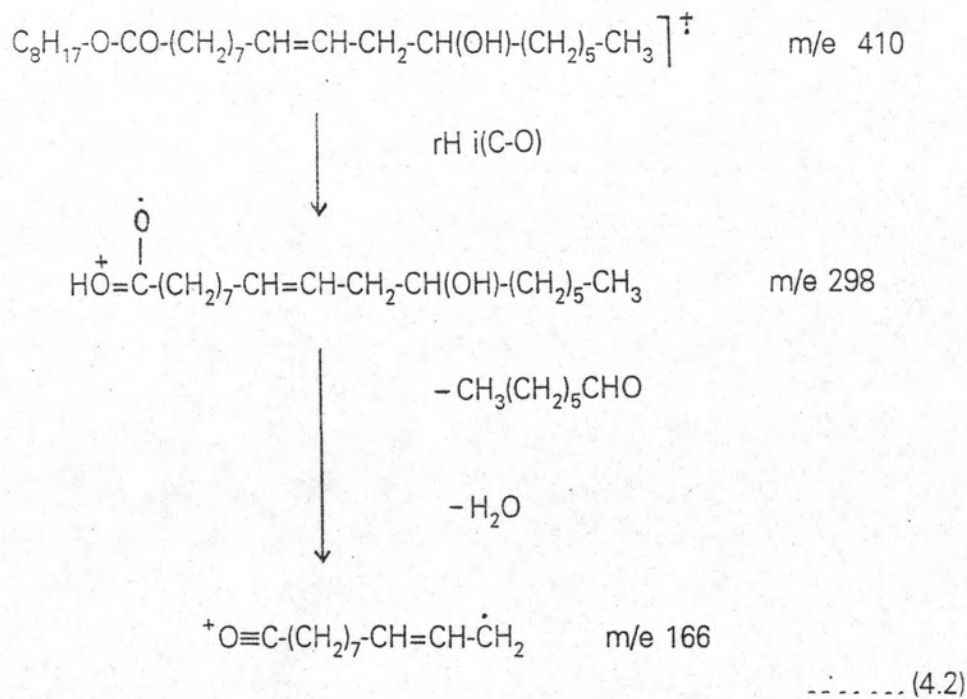
Characteristics of 2-ethylhexyl ricinoleate were confirmed by ^{13}C -NMR and mass spectrum as shown in Fig.A5 and A23, respectively.

^{13}C -NMR showed the peak of -CH₂-O- at 66.4 ppm, C=O at 173.6 ppm, CH-OH at 71.3 ppm and the peak of unsaturated group at between 125-135 ppm.

Mass spectrum showed base peak at 71 and m-297/e at 113 due to α -cleavage of ester linkage as the following equation:



The reaction could be occurred such as the following equation:



The physical and chemical properties of monoester product were demonstrated in table 4.1. The physical properties were studied as follow: color, pour point, kinematic viscosity at 40 and 100°C, viscosity index and flash point. The oxidation and thermal stability functions were analyzed by TGA analyzer.

Table 4.1 The physical and chemical properties of castor oil and monoester product

Properties	Castor oil	Monoester product
Color, ASTM	0.5-1.0	2-2.5
Pour point, °C	-12	<-15
Kinematic viscosity		
@ 40°C, cSt	253.56	29.36
@ 100°C, cSt	19.36	5.57
Viscosity index	86	131
Flash point, °C	-	240
Oxidation point, °C	390	337
Oxidative compounds, %wt	53.61	27.55
Middle point, °C (thermal stability function)	375	335

The results from table 4.1 indicated that the pour point of product was lower than -15°C. Flash point was 240°C. The viscosity at 40 and 100°C was 29.36 and 5.57 cSt, respectively and the viscosity index was 131. The color was increased from 0.5-1 to 2-2.5. The oxidative compounds were 27.55%wt. The

color and oxidative compounds, which resulted from unsaturated components, were still high when comparing with petroleum base oil (table A1).

To improved the color and oxidation stability, the oil had to be finally refined through hydrogenation of unsaturated components.

In this study, the oil was treated with hydrogenated catalyst in a stirred autoclave batch reactor under hydrogen. The used catalyst contained 3% by weight of platinum supported on alumina which available commercially from United Catalyst Inc.,.

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

The first concerned variable parameter was the pressure of the process which was controlled by the hydrogen pressure. . The hydrogenation reaction was carried out at 100°C for 3 hours, using a catalyst concentration of 3% by weight of oil. The hydrogen pressure was varied from 100 and 300 psi.

The results from hydrogenation of monoester oil which conducted at various hydrogen pressure of 100 and 300 psi were shown in table 4.2

Table 4.2 Physical Properties of hydrogenated oil obtained at different hydrogen pressure while fixing reaction temperature 100°C, catalyst concentration 3%, reaction time 3 hrs.

Properties	Oil before hydrogenation	Hydrogenated oil at hydrogen pressure (psi)	
		100	300
color, ASTM	2-2.5	0.5-1	0.5-1
pour point, °C	<-15	-9	-2
kinematic viscosity			
@ 40°C, cSt	29.36	35.44	30.58
@ 100°C, cSt	5.57	6.46	5.88
viscosity index	131	138	140

From table 4.2, the results showed that after hydrogenation, the pour point of oil was increased rapidly from lower than -15°C to -9 and -2°C when hydrogen pressure was 100 and 300 psi, respectively. The viscosity index of hydrogenated oil at pressure of 100 psi was increased from 131 to 138. The viscosity index of hydrogenated oil was scarcely changed when hydrogen pressure was increasing to 300 psi. The color of hydrogenated oil was 0.5-1.0.

From these results, the optimum hydrogen pressure was 100 psi.

However, in the determination of optimum operating condition, other parameters were considered. Thus the further study looked for the suitable concentration of catalyst. The used catalyst concentration was varied from 1 to 4% by weight of oil.

The hydrogenation process was studied at 100°C, under hydrogen pressure of 100 psi and a reaction time of 3 hours. The concentration of catalyst was varied from 1, 2, 3 and 4% by weight of oil.

From this experiment, when the catalyst concentrations were 1 and 2%, unsaturated components were still remained (see Fig. A15-A16). So the properties of hydrogenated oil which was obtained when using 1 and 2% of catalyst concentration were not reported in this study.

The results from hydrogenation of oil using catalyst concentration of 3 and 4% by weight were shown in table 4.3.

Table 4.3 Physical Properties of hydrogenated oil obtained using various concentration of catalyst while fixing reaction temperature 100°C, reaction time 3 hrs, under hydrogen pressure 100 psi.

Properties	Oil before hydrogenation	Hydrogenated oil at catalyst concentration (%wt)	
		3	4
color, ASTM	2-2.5	0.5-1	0.5-1
pour point, °C	<-15	-9	-10
kinematic viscosity @ 40°C, cSt	29.36	35.44	31.96
@ 100°C, cSt	5.57	6.46	6.24
viscosity index	131	138	149

From table 4.3, the color of hydrogenated oil was remained constant at 0.5-1.0. The pour point of hydrogenated oil was increased from lower than -15°C to -9 and -10°C when the catalyst concentration were 3 and 4%, respectively. The viscosity index was rapidly increased from 131 to 149 if the catalyst concentration was 4%

From this study, it could be seen that the increase in catalyst concentration did not effect the color and the pour point of hydrogenated oil but increased higher viscosity index. It was a result from the increasing catalyst concentration would increase the active site of the catalyst and also increase the rate of reaction. However, the quantity of catalyst to be used must appropriate depend on the properties of feedstock and economic aspect.

From these results, the optimum catalyst concentration which was selected was 4% by weight of oil.

The next parameter was the reaction time. The reaction time was varied from 2, 3, 4 and 5 hours while fixing other parameters. The hydrogenation was studied at 100°C , under hydrogen pressure 100psi and 4% of catalyst concentration.

From this experiment, when the reaction time was 2 hours, unsaturated components were still remained (see Fig. A18). Its properties were not reported in this work.

The results from hydrogenation of oil when performed at various reaction time of 3, 4 and 5 hours were shown in table 4.4.

Table 4.4 Physical Properties of hydrogenated oil obtained at various reaction time while fixing reaction temperature 100°C, catalyst concentration 4%, under hydrogen pressure 100 psi.

Properties	Oil before hydrogenation	Hydrogenated oil at reaction time (hrs.)		
		3	4	5
color, ASTM	2-2.5	0.5-1	0.5-1	0.5-1
pour point, °C	<-15	-10	-4	+1
kinematic viscosity				
@ 40°C, cSt	29.36	31.96	25.12	16.17
@ 100°C, cSt	5.57	6.24	5.35	4.27
viscosity index	131	149	154	185

From table 4.4, while the longer the reaction time was spent, the higher the viscosity index were resulted. The viscosity index was increased from 131 to 149, 154 and 185 when the reaction time was 3, 4 and 5 hours, respectively. The pour points were rapidly increased when the reaction time was passed. When the reaction time was 4 and 5 hours, the pour point was -4 and +1°C, respectively. It was too high to use in automotive lubrication. It indicated that the lengthen of time would increase the degree of hydrogenation reaction. The evidence could be seen by the decrease in the peak of -CH-OH at 71.3 ppm as shown in Figure A17, A19 and A20.

These results demonstrated that the optimum reaction time was apparently at 3 hours because the pour point of oil was suitable for use as a lubricating oil.

The last concerned variable parameter was the reaction temperature. The hydrogenation process was carried out under hydrogen pressure 100 psi, reaction time 3 hours, and using catalyst concentration 4% by weight of oil. The reaction temperature was varied from 80 and 100°C.

The results from hydrogenation of oil which performed at 80°C showed that the unsaturated components were still remained (see Figure A21). Its properties were not reported in this work. At 100°C, the physical properties of hydrogenated oil were as follow: the color was 0.5-1, the viscosity index was 149 and the pour point was -10°C.

From these results, the optimum reaction temperature was 100°C.

In conclusion, the best condition for hydrogenation of monoester oil using 3% of platinum on alumina as catalyst were 4% of catalyst concentration, at 100°C, under hydrogen pressure 100 psi and reaction time 3 hours. In this work, the result product was 92.73% yield.

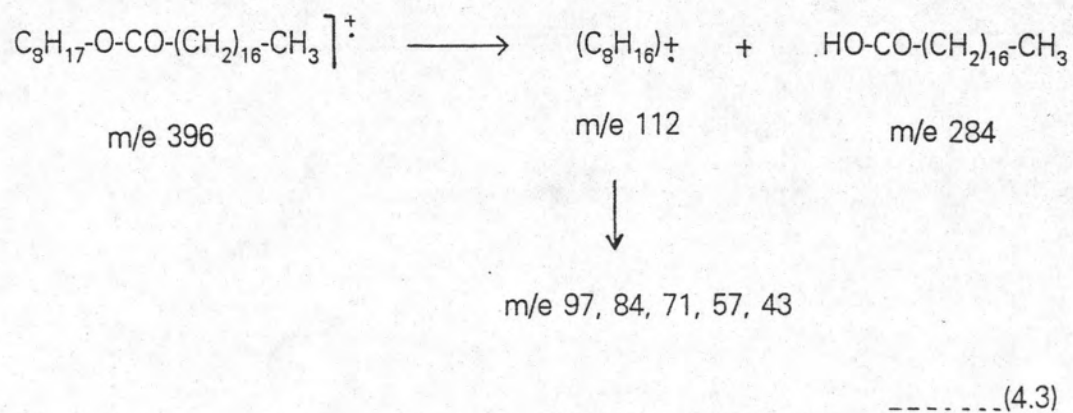
The composition of hydrogenated oil obtained at the best condition was determined by GC-MS. The GC-MS was performed in a column packed with DB-1.

The chromatogram of hydrogenated oil was showed in Fig.A24.

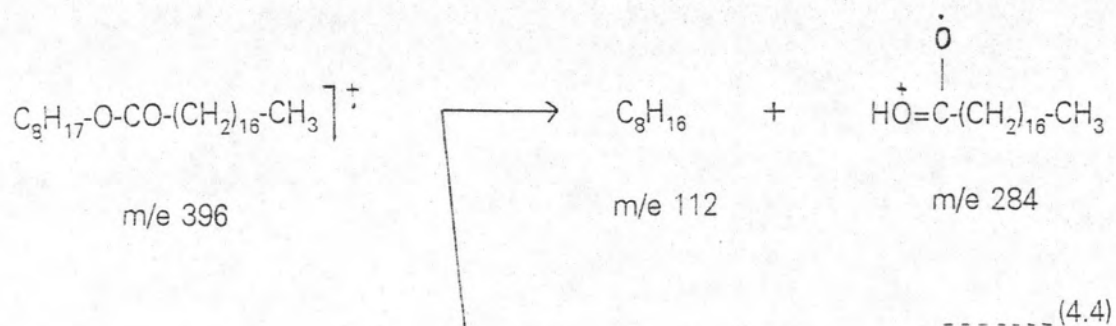
From the chromatogram, it indicated that the hydrogenated oil was mixtures of 2-ethylhexyl stearate, 2-ethylhexyl-12-hydroxy stearate and 2-ethylhexyl ricinoleate derivative.

Characteristics of 2-ethylhexyl stearate, 2-ethylhexyl-12-hydroxy stearate and 2-ethylhexyl ricinoleate derivative were confirmed by mass spectrum as shown in Fig.A25, A26 and A27, respectively.

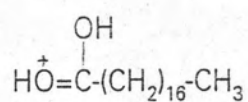
Mass spectrum of 2-ethylhexyl stearate (MW 396) in Fig.A25 showed base peak at 112 due to α -cleavage of ester linkage as the following equation:



The reaction could be occurred such as the following equation:

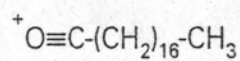


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m/e 285

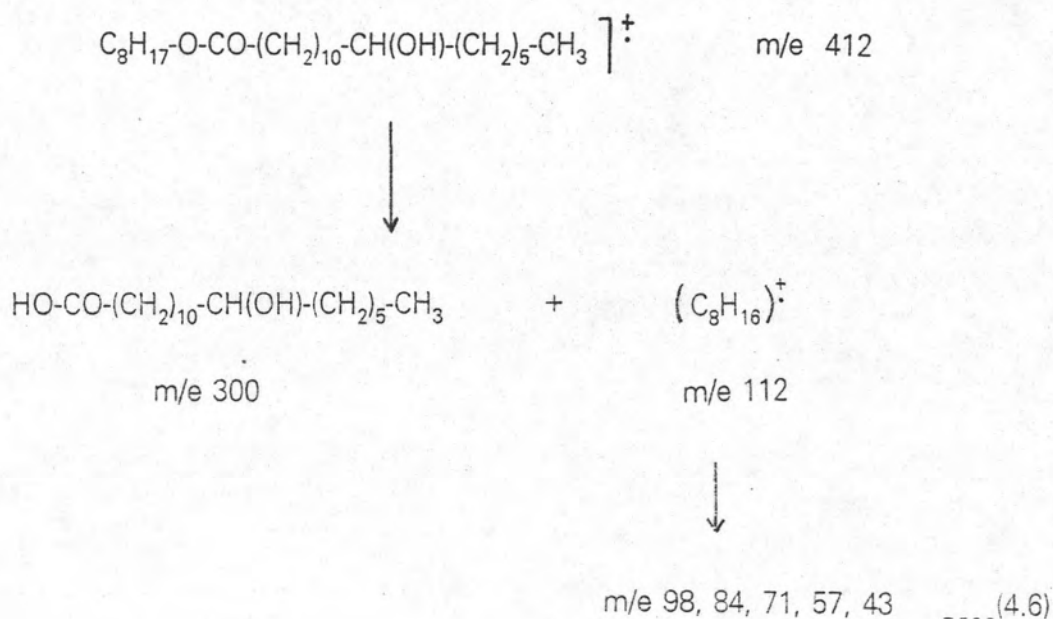
-H₂O



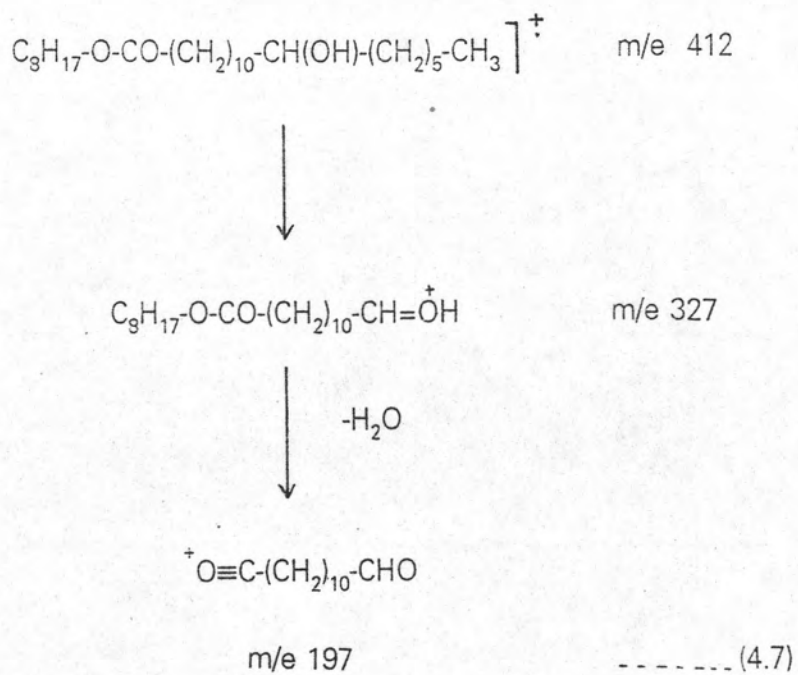
m/e 267

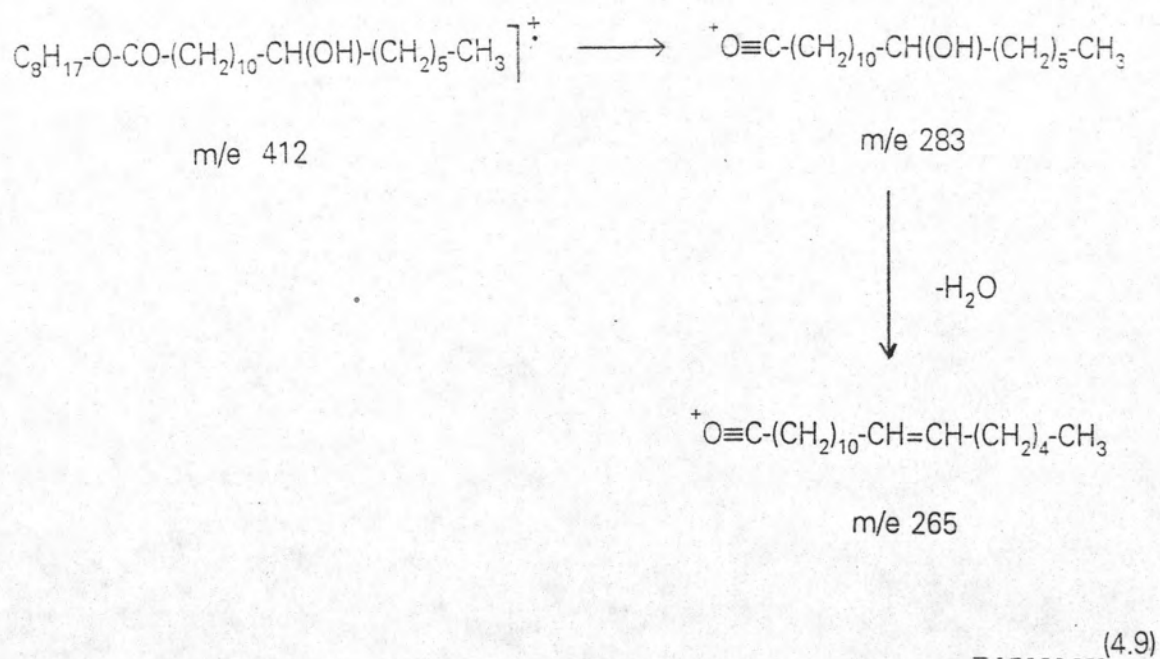
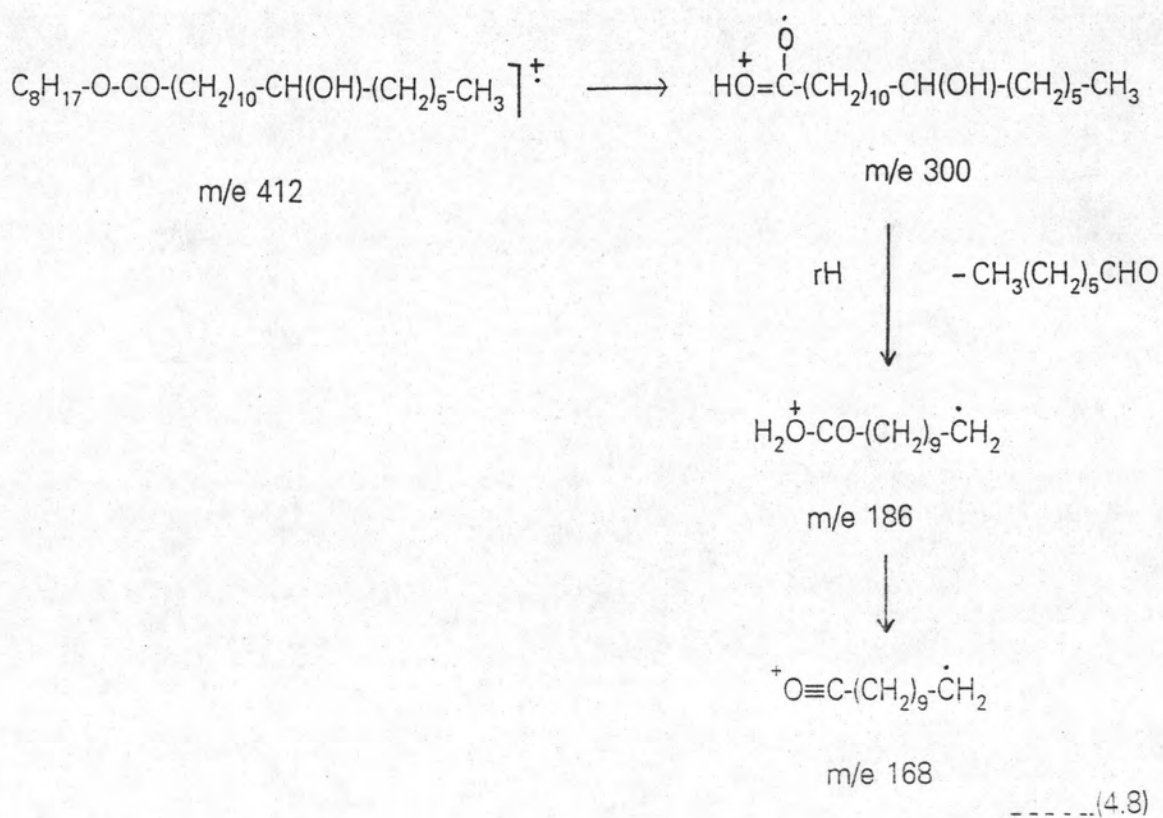
----- (4.5)

Mass spectrum of 2-ethylhexyl-12-hydroxy stearate (MW 412) in Fig.A26 showed base peak at 57 and m-300/e at 112 due to α -cleavage of ester linkage as the following equation:



The reaction could be occurred such as the following equation:





2-Ethylhexyl ricinoleate derivative was obtained from side reaction of hydrogenation process. Depending on reaction condition, dehydrogenation reaction could be occurred to yield the keto ester. A mechanism of dehydrogenation reaction had been proposed as shown in Fig.4.1.

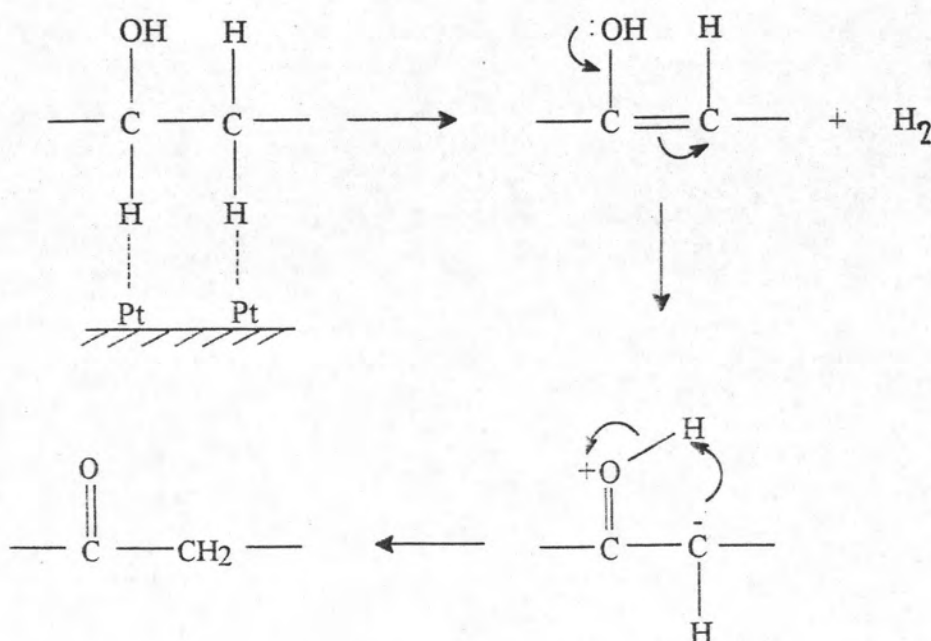
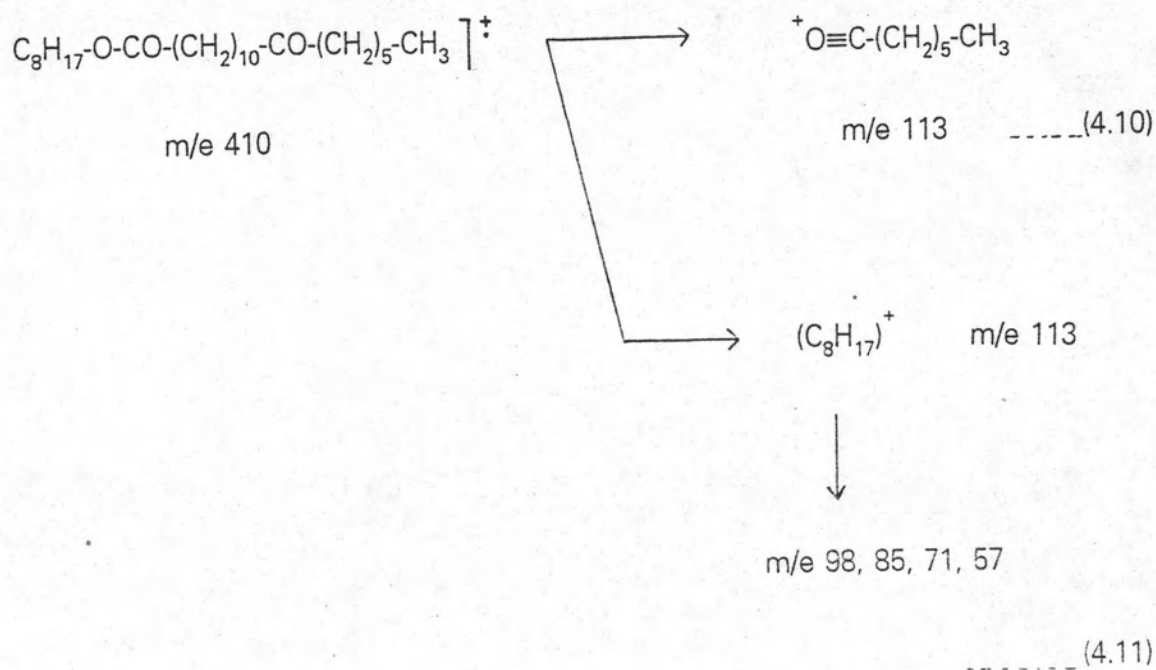


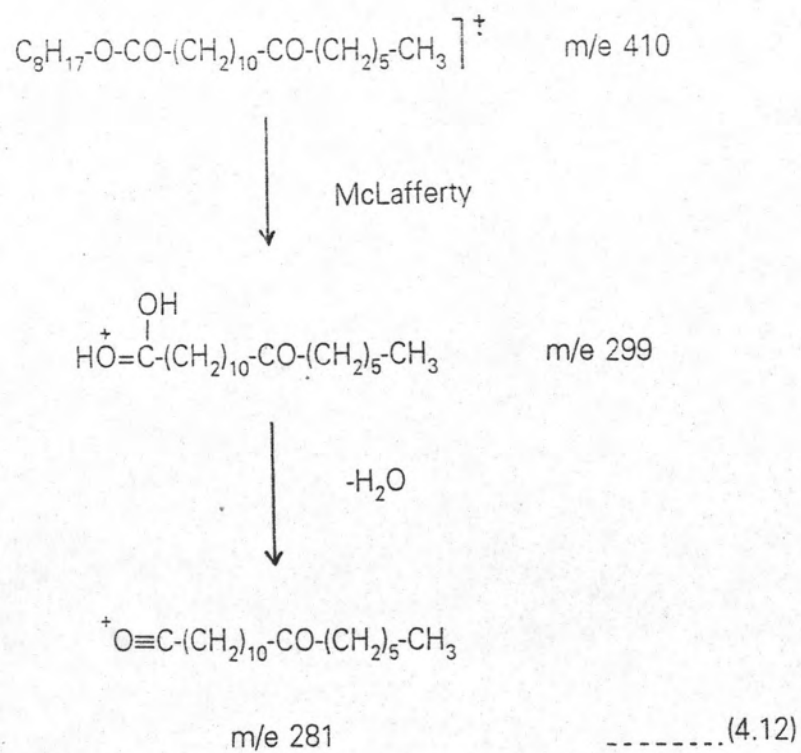
Figure 4.1 Mechanism of dehydrogenation reaction on platinum supported on alumina catalyst

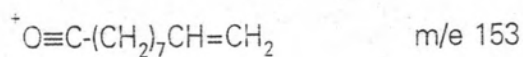
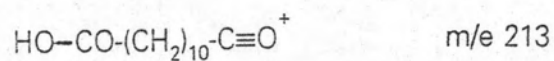
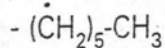
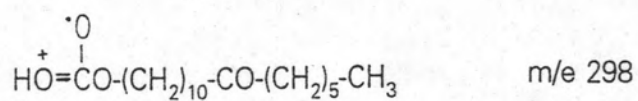
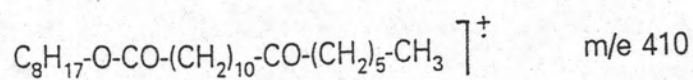
Characteristic of the keto ester product (MW 410) was confirmed by mass spectrum as shown in Fig.A27.

From the mass spectrum in Fig.A27, it showed base peak at 113 due to α -cleavage of ester linkage and α -cleavage of carbonyl group as the following equation:

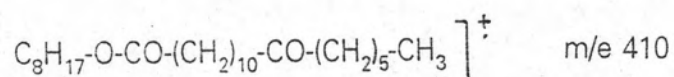


The reaction could be occurred such as the following equation:

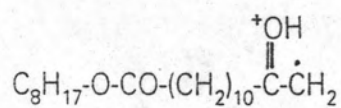




----- (4.13)



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m/e 340

----- (4.14)

From this study, it could be concluded that the main compositions of hydrogenated oil were:

- (1) 2-ethylhexyl stearate ($C_{26}H_{52}O_2$)
- (2) 2-ethylhexyl-12-hydroxy stearate ($C_{26}H_{52}O_3$)
- (3) 2-ethylhexyl-12-keto stearate ($C_{26}H_{50}O_3$)

The properties of hydrogenated oil obtained at the best condition were shown in table 4.5.

Table 4.5 The physical and chemical properties of castor oil, oil before hydrogenation and hydrogenated oil

Properties	Castor oil	Oil before hydrogenation	Hydrogenated oil
Color, ASTM	0.5-1.0	2-2.5	0.5-1.0
Pour point, °C	-12	<-15	-10
Kinematic viscosity			
@ 40°C, cSt	253.56	29.36	31.96
@ 100°C, cSt	19.36	5.57	6.24
Viscosity index	86	131	149
Flash point, °C	–	240	238
Oxidation point, °C	390	337	330
Oxidative compounds, %wt	53.61	27.55	15.96
Middle point, °C	375	335	330
(thermal stability function)			

Table A1 showed the physical properties of imported lubricating base oils from various sources. The comparison between these properties and the properties of hydrogenated oil found that hydrogenated oil is suitable in the automotive uses because of its low pour point, high viscosity index and good thermal and oxidation stability.