

CHAPTER 4

RESULTS AND DISCUSSION

Firstly, The properties of soybean oil were tested as shown in Table 4-1.

Table 4-1 : The properties of soybean oil

| Properties | Soybean Oil |
|-------------------------|-------------|
| Color,ASTM | L0.5 |
| Viscosity at 40 °C,cSt | 32.252 |
| Viscosity at 100 °C,cSt | 7.738 |
| Viscosity Index (VI) | 223.504 |
| Pour Point (°C) | -12 |
| Flash point (°C) | 327 |
| Oxidation point (°C) | 440 |
| Oxidation compound,%wt. | 19.06 |

From properties of soybean oil in the table 4-1, it indicated that soybean oil properties are not suitable to be use as lubricants because soybean oil contains high oxidation compound which can occur the oxidation reaction easily.

Moreover, soybean oil which contains many fatty acid in the form of triglyceride may be cracked into free fatty acids under the high temperature condition.

The aim of this research is to modify the soybean oil by transforming triglyceride structure of soybeans oil to monoester structures via transesterification and hydrogenation processes.

Transesterification and Hydrogenation

Soybean oil, which contains mainly triglycerides of linoleic acid, oleic acid and lenolenic acid, was reacted with various alcohol, such as isopropanol, 1-butanol, 1-hexanol, 4-methyl-2-pentanol and 2-ethyl-1-hexanol by using concentrated sulfuric acid as a catalyst. The optimum condition of each alcohol was obtained by varying reaction temperature of 70-90°C and reaction time for 1-4 hours.

Next, the monoester products were treated with hydrogenated catalyst in a stirred autoclave batch reactor under hydrogen pressure. The hydrogenated catalyst contained 1% by weight of platinum supported on alumina. The hydrogenation process was optimized by varying the hydrogen partial pressure of 100-200 psi, the catalyst concentration of 15-24 % by weight of oil , the reaction time of 2-3 hours, and the reaction temperature of 100-200 °C. The reaction was monitored by using ^{13}C -NMR.

1. Transesterification and Hydrogenation of Soybean Oil with 2-Ethyl-1-Hexanol

1.1 Transesterification of 2-Ethyl-1-Hexyl ester

After the transesterification of soybean oil and 2-ethyl-1-hexanol at 80 °C for 3 hours, the 2-ethyl-1-hexyl ester was characterized by ^{13}C -NMR as shown in Figure A-3. It was found that the characteristic peaks of soybean oil at the chemical shifts of 62.0 ppm and 68.8 ppm disappeared, but the characteristic peak of $-\text{CH}_2\text{-O-}$ and C=O of monoester product happened at the chemical shifts of 66.4 and 173.3 ppm, respectively. Other peaks of unsaturated group showed the chemical shifts between 127.1 and 131.8 ppm. Therefore, this result indicated that the transesterification of soybean oil with 2-ethyl-1-hexanol was reacted completely. The yield was products 95.80 %.

1.2 Hydrogenation of 2-Ethyl-1-Hexyl Ester

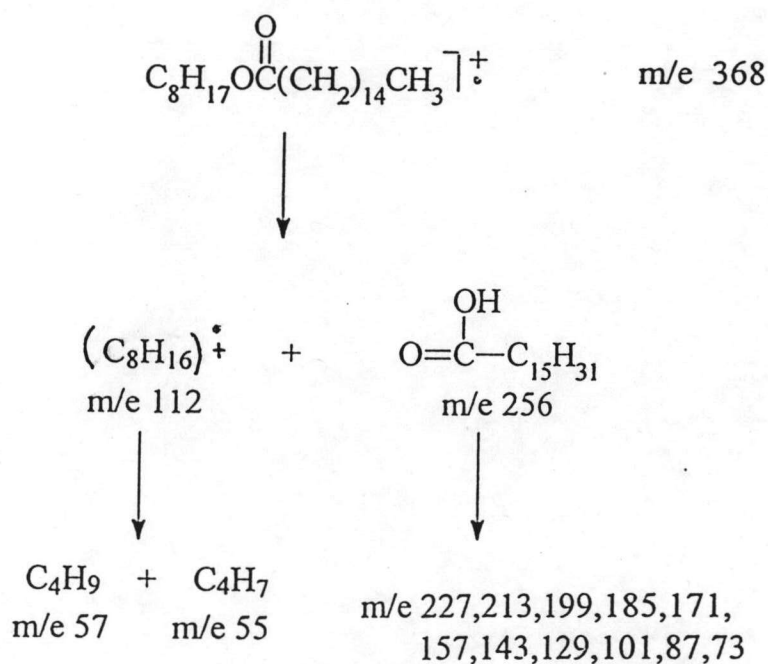
After the hydrogenation of 2-ethyl-1-hexyl ester was carried out under 150 psi of hydrogen partial pressure, 24 % Pt/ Al_2O_3 catalyst by weight of oil and reaction temperature of 150 °C, the hydrogenated ester product gave 92.56 % yield.

The hydrogenated ester characterized by ^{13}C -NMR and GC-MS. The ^{13}C -NMR spectrum of hydrogenated 2-ethyl-1-hexyl ester was shown in Figure A-4. It was found that the peaks of unsaturated group at chemical shift between 127.1 and 131.8 ppm disappeared.

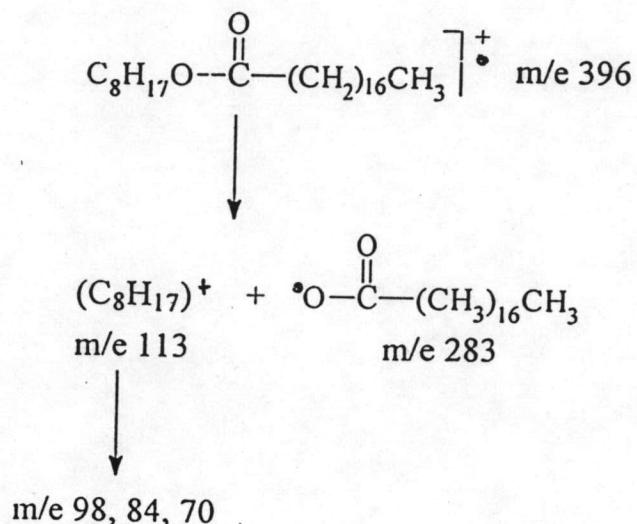
The composition of hydrogenated 2-ethyl-1-hexyl ester product was characterized by GC-MS which was performed in a DB-1 column.

The GC-MS chromatogram was shown in Figure A-17, and Mass spectra of each peak were shown in Figure A-18 to A-19 .

From GC chromatogram in Figure A-17, it indicated that hydrogenated 2-ethyl-1-hexyl ester was composed of the mixture of 2-ethyl-1-hexyl ester of long chain fatty acid. The main components were 2-ethyl-1-hexyl palmitate and 2-ethyl-1-hexyl stearate of retention time 14.526 min. and 16.890 min, respectively. Mass spectrum of 2-ethyl-1-hexyl Palmitate (MW 360), in Figure A-18 showed base peak at 112 due to Mc Lafferty rearrangement as indicated in following equations.



This reaction could occur such as shown in the following equation:



2. Transesterification and Hydrogenation of Soybean Oil with Isopropanol

2.1. Transesterification of Isopropyl Ester

After the transesterification of soybean oil and isopropanol at 80 °C for 3 hours, the isopropyl ester was characterized by ^{13}C -NMR as shown in Figure A-5. It was found that the characteristic peaks of soybean oil at the chemical shifts of 62.0 ppm and 68.8 ppm disappeared, but the characteristic peak of $-\text{CH}_2-\text{O}-$ and $\text{C}=\text{O}$ of monoester product happened at the chemical shifts of 67.2 and 173.1 ppm, respectively. Other peaks of unsaturated group showed the chemical shifts between 127.1-131.2

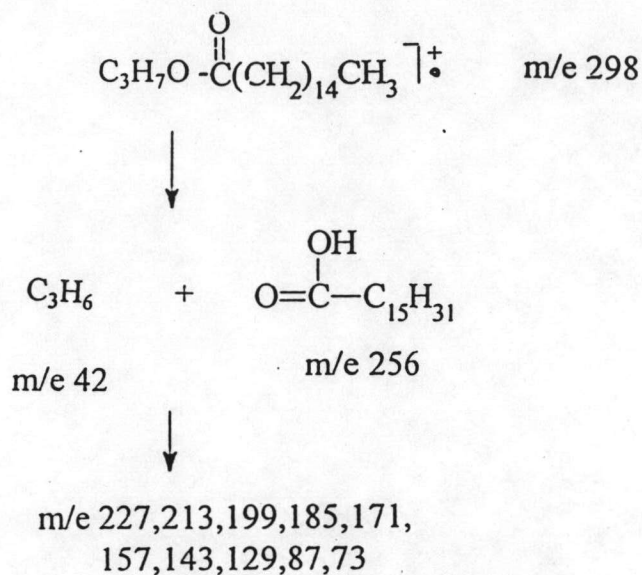
ppm. Therefore, this result indicated that the transesterification of soybean oil with isopropanol was reacted completely. The yield was 90.85%.

2.2 Hydrogenation of Isopropyl Ester

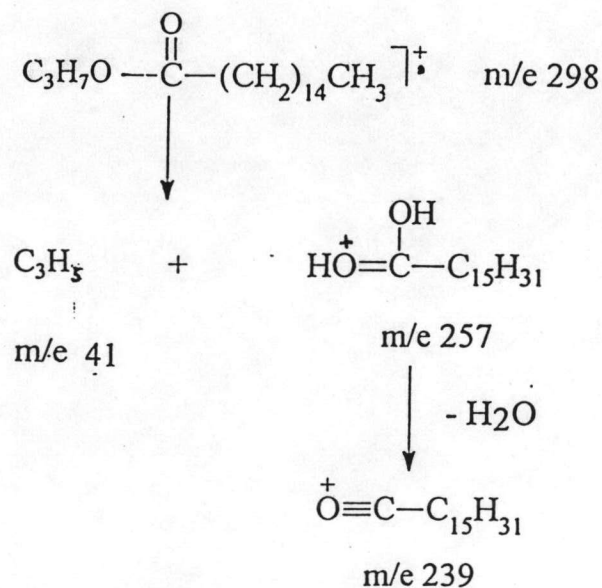
After the hydrogenation of isopropyl ester was carried out under 150 psi of hydrogen partial pressure, 24 % Pt/Al₂O₃ catalyst by weight of oil and reaction temperature of 150 °C, the hydrogenated ester product gave 95.58 % yield.

The hydrogenated ester characterized by ¹³C- NMR and GC-MS. The ¹³C- NMR spectrum of hydrogenated isopropyl ester was shown in Figure A-6. It was found that the peaks of unsaturated group at chemical shift between 127.1 and 131.2 ppm disappeared.

The composition of hydrogenated isopropyl ester product was characterized by GC-MS which was performed in a DB-1 column. The GC-MS chromatogram was shown in Figure A-20, and Mass spectra of each peak were shown in Figure A-21 to A-22. From GC chromatogram in Figure A-20, it indicated that hydrogenated isopropyl ester was composed of the mixture of isopropyl ester of long chain fatty acid. The main components were isopropyl palmitate and isopropyl stearate of retention time 8.737 min. and 10.943 min, respectively. Mass spectrum of isopropyl Palmitate (MW 298) in Figure A-21 showed base peak at 42 which due to Mc Lafferty rearrangement as indicated in following equation.



The reaction could occur due to H-shift as shown in the following equation:



3. Transesterification and Hydrogenation of Soybean Oil with 1-Butanol

3.1. Transesterification of Butyl Ester

After the transesterification of soybean oil and 1-butanol at 80 °C for 3 hours, the 1-butyl ester was characterized by ^{13}C -NMR as shown in Figure A-8. It was found that the characteristic peaks of soybean oil at the chemical shifts of 62.0 ppm and 68.8 ppm disappeared, but the characteristic peak of $-\text{CH}_2\text{-O-}$ and C=O of monoester product happened at the chemical shifts of 63.9 and 173.8 ppm, respectively. Other peaks of unsaturated group showed the chemical shifts between 129.0 and 131.8 ppm. Therefore, this result indicated that the transesterification of soybean oil with 1-butanol was reacted completely. The yield was products 92.41 %.

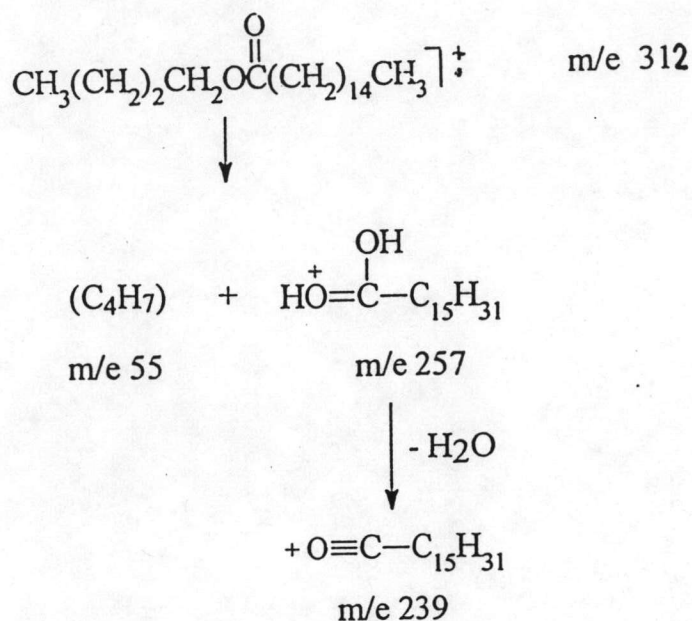
1.2 Hydrogenation of 1-Butyl Ester

After the hydrogenation of 1-butyl ester was carried out under 150 psi of hydrogen partial pressure, 24 % Pt/ Al_2O_3 catalyst by weight of oil and reaction temperature of 150 °C, the hydrogenated ester product gave 95.35 % yield.

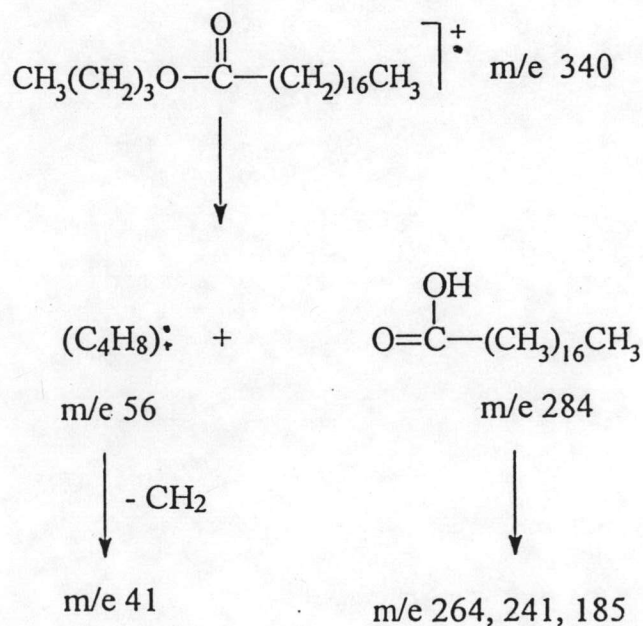
The hydrogenated ester characterized by ^{13}C - NMR and GC-MS. The ^{13}C - NMR spectrum of hydrogenated 1-butyl ester was shown in Figure A-9. It was found that the peaks of unsaturated group at chemical shift between 129.0 and 131.8 ppm disappeared.

The composition of hydrogenated 1-butyl ester product was characterized by GC-MS which was performed in a DB-1 column. The

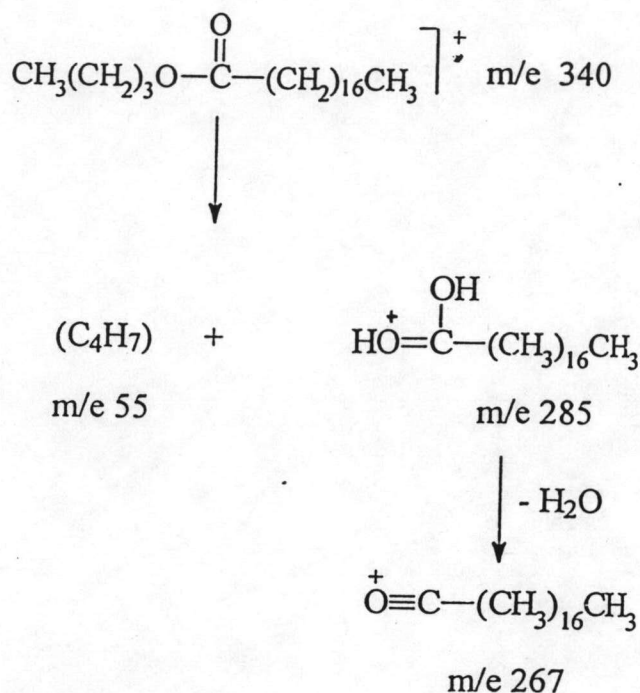
The reaction could occur due to Mc Lafferty as shown in the following equation:



Mass spectrum of butyl stearate (MW 340 in Figure A-25) showed base peak at 56 due to Mc Lafferty rearrangement as shown in the following equation :



This reaction could occur due to H-shift such as shown in the following equation



4. Transesterification and Hydrogenation of Soybean Oil with 1-Hexanol

4.1 Transesterification of Hexyl Ester

After the transesterification of soybean oil and 1-hexanol at 80 °C for 3 hours, the 1-hexyl ester was characterized by ^{13}C -NMR as shown in Figure A-11. It was found that the characteristic peaks of soybean oil at the chemical shifts of 62.0 ppm and 68.8 ppm disappeared, but the characteristic peak of $-\text{CH}_2-\text{O}-$ and $\text{C}=\text{O}$ of monoester product happened at the chemical shifts of 64.2 and 173.3 ppm, respectively. Other peaks of unsaturated group showed the chemical shifts between 127.5 and 131.2 ppm. Therefore, this

result indicated that the transesterification of soybean oil with 1-hexanol was reacted completely . The yield was products 93.60 %.

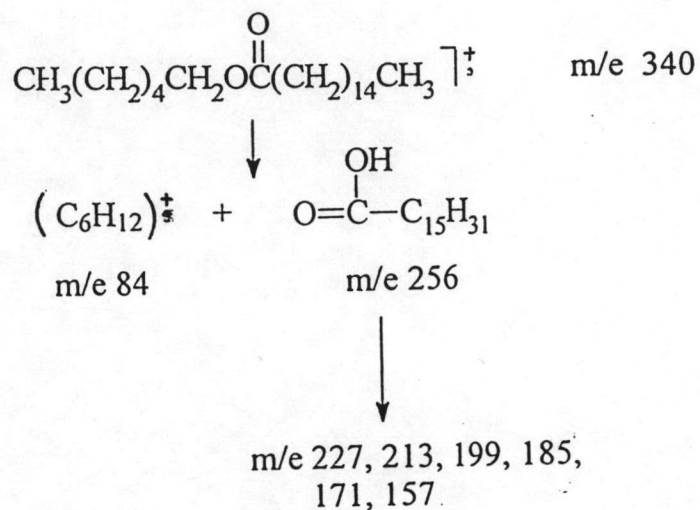
1.2 Hydrogenation of 1-Hexyl Ester

After the hydrogenation of 1-hexyl ester was carried out under 150 psi of hydrogen partial pressure, 24 % Pt/Al₂O₃ catalyst by weight of oil and reaction temperature of 150 °C, the hydrogenated ester product gave 93.75 % yield .

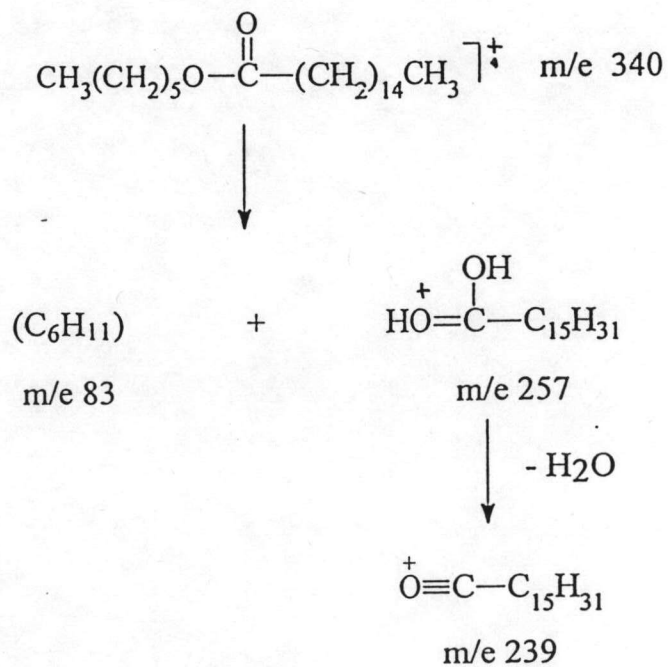
The hydrogenated ester characterized by ¹³C- NMR and GC-MS. The ¹³C- NMR spectrum of hydrogenated 1-hexyl ester was shown in Figure A-13. It was found that the peaks of unsaturated group at chemical shift between 127.5 and 131.1 ppm disappeared.

The composition of hydrogenated 1-hexyl ester product was characterized by GC-MS which was performed in a DB-1 column. The GC-MS chromatogram was shown in Figure A-26, and Mass spectra of each peak were shown in Figure A-27 to A-28 .

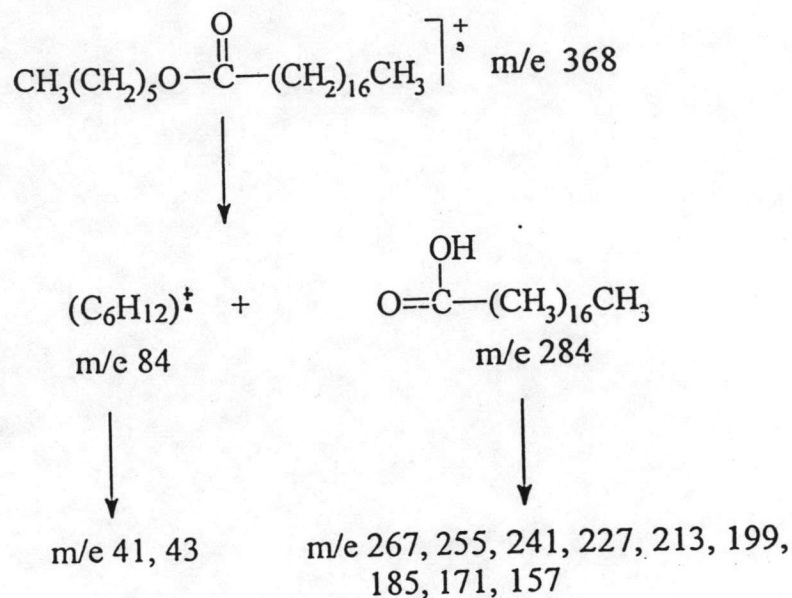
From GC-MS chromatogram in Figure A-26, it indicated that hydrogenated 1-hexyl ester was composed of the mixture of 1-hexyl ester of long chain fatty acid. The main components were 1-hexyl palmitate and 1-hexyl stearate of retention time 13.069 min. and 15.360 min, respectively. Mass spectrum of 1-hexyl palmitate (MW340) in Figure A-27 showed base peak at 84 which due to Mc Lafferty rearrangement as indicated in the following equation .



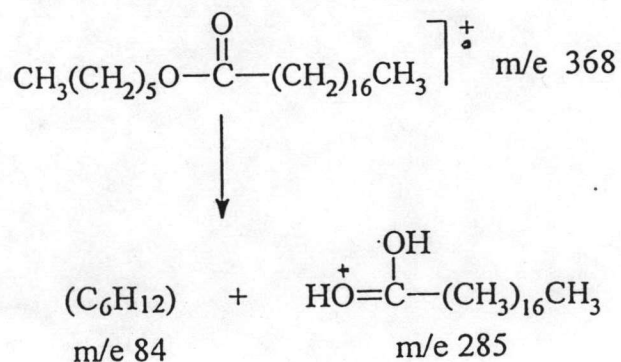
The reaction could occur due to Mc Lafferty as shown in the following equation:



Mass spectrum of hexyl stearate (MW 368) in Figure A-28 showed the base peak at 84 due to McLafferty rearrangement as shown in the following equation :



This reaction could occur due to H-shift such as the following equation :



5. Transesterification and Hydrogenation of Soybean Oil with 4-Methyl-2-Pentanol

5.1 Transesterification of 4-Methyl-2-Pentyl Ester

After the transesterification of soybean oil and 4-methyl-2-pentanol at 80 °C for 3 hours, the 4-methyl-2-pentyl ester was characterized by ^{13}C -NMR as shown in Figure A-15. It was found that the characteristic peaks of soybean oil at the chemical shifts of 62.0 ppm and 68.8 ppm disappeared, but the characteristic peak of $-\text{CH}_2\text{-O-}$ and C=O of monoester product happened at the chemical shifts of 68.9 and 173.3 ppm, respectively. Other peaks of unsaturated group showed the chemical shifts between 127.8 and 131.7 ppm. Therefore, this result indicated that the transesterification of soybean oil with 4-methyl-2-pentanol was reacted completely. The yield was products 90.55 %.

1.2 Hydrogenation of 4-methyl-2-pentyl ester

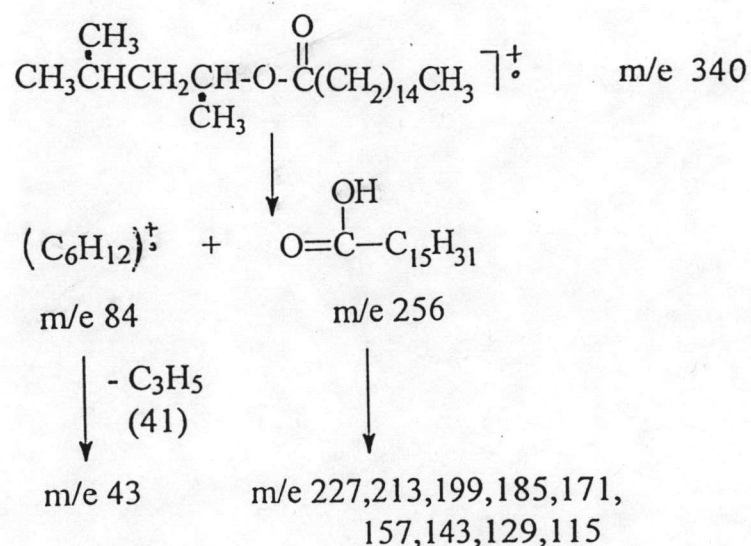
After the hydrogenation of 4-methyl-2-pentyl ester was carried out under 150 psi of hydrogen partial pressure, 24 % Pt/ Al_2O_3 catalyst by weight of oil and reaction temperature of 150 °C, the hydrogenated ester product gave 93.33 % yield.

The hydrogenated ester characterized by ^{13}C - NMR and GC-MS. The ^{13}C - NMR spectrum of hydrogenated 4-methyl-2-pentyl ester was shown in Figure A-16. It was found that the peaks of unsaturated group at chemical shift between 127.8 and 131.7 ppm disappeared.

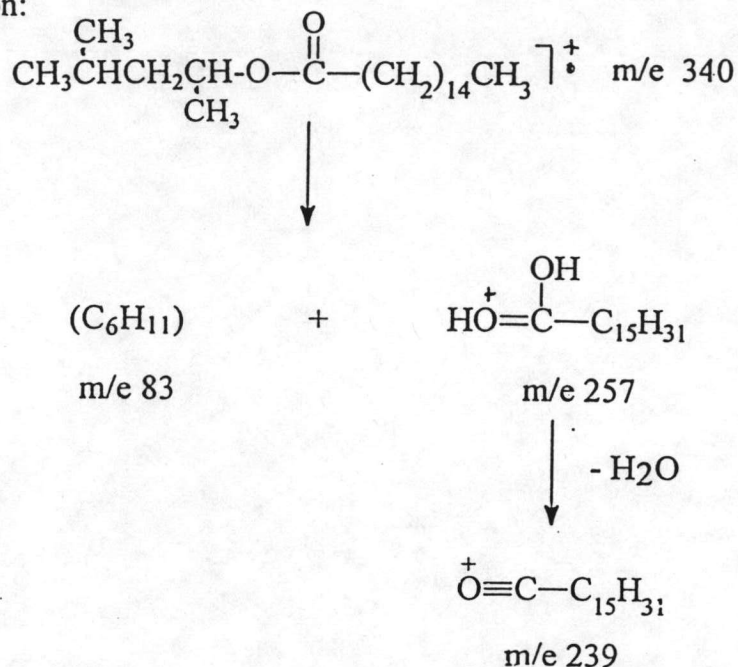
The composition of hydrogenated 4-methyl-2-pentyl ester product was characterized by GC-MS which was performed in a DB-1 column.

The GC-MS chromatogram was shown in Figure A-29, and Mass spectra of each peak were shown in Figure A-30 to A-31 .

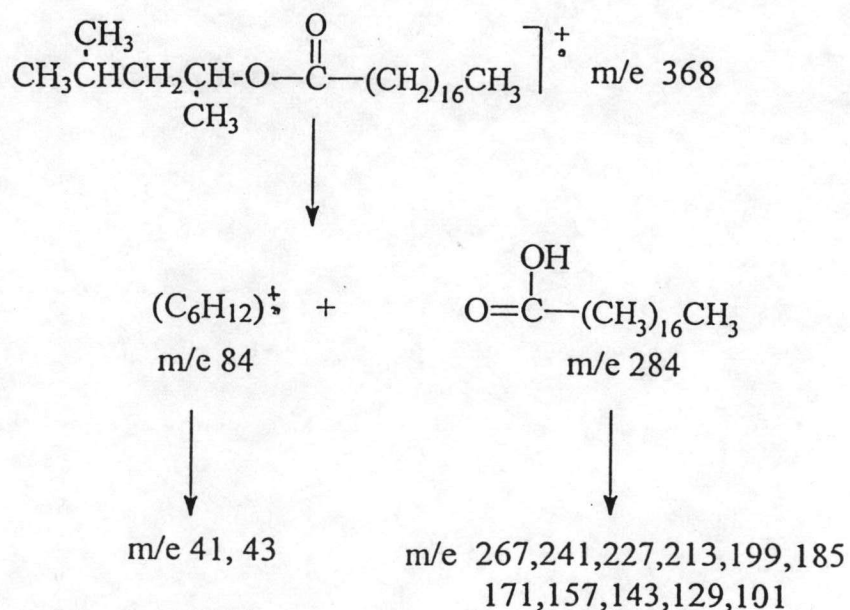
From GC-MS chromatogram in Figure A-29, it indicated that hydrogenated 4-methyl-2-pentyl ester was composed of the mixture of 4-methyl-2-pentyl ester of long chain fatty acid. The main components were 4-methyl-2-pentyl palmitate and 4-methyl-2-pentyl stearate of retention time 12.991 min. and 15.301 min, respectively. Mass spectrum of 2-ethyl-1-hexyl Palmitate (MW 360), in Figure A-18 showed base peak at 112 due to Mc Lafferty rearrangement as indicated in following equations. Mass spectrum of 4-methyl-2-pentyl palmitate (MW340) in Figure A-30 showed base peak at 84 which due to Mc Lafferty rearrange as indicated in the following equation:



The reaction could occur due to H-shift as shown in the following equation:



Mass spectrum of 4-methyl-2-pentyl stearate (MW 368) in Figure A-31 showed base peak at 84 due to Mc Lafferty rearrangement as shown in the following equation :



This reaction could occur due to H-shift as shown in the following equation :

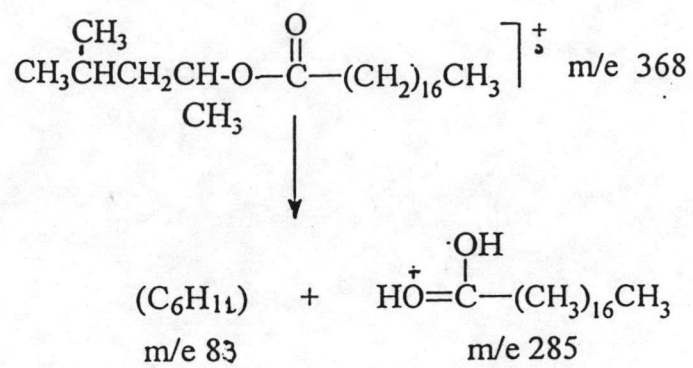


Table 4-2 : The Physical and Chemical Properties of monoester

| Properties | 2-Ethyl- 1-hexyl ester | Isopropyl ester | 1-Butyl ester | 1-Hexyl ester | 4-Methyl- 2-pentyl ester |
|------------------------------|------------------------------|--------------------|------------------|------------------|--------------------------------|
| Color | L1.0 | L1.0 | 1.0 | 1.0 | L3.5 |
| Viscosity at 40 °C , cSt | 6.96 | 6.66 | 5.29 | 5.95 | 6.81 |
| Viscosity at 100 °C, cSt | 2.35 | 2.29 | 2.04 | 2.15 | 2.37 |
| Viscosity Index (VI) | 180.632 | 184.173 | 245.039 | 204.915 | 200.872 |
| Pour Point (°C) | -12 | -12 | -11 | -12 | -13 |
| Flash Point (°C) | 235 | 205 | 214 | 214 | 264 |
| Oxidation Point (°C) | 360 | - | - | - | - |
| Oxidation compound, % wt. | 7.26 | - | - | - | - |

Table 4-3 : The Physical and Chemical Properties of Hydrogenated ester

| Properties | Hydrogenated 2-ethyl - 1-Hexyl ester | Hydrogenated isopropyl ester | Hydrogenated Butyl ester | Hydrogenated Hexyl ester | Hydrogenated 4-methyl-2- pentyl ester |
|---|--|------------------------------------|-----------------------------|-----------------------------|---|
| Color,ASTM | L1.5 | L0.5 | L1.5 | L1.0 | L1.0 |
| Viscosity at 40 °C,cSt | 10.17 | 5.73 | 7.24 | 7.96 | 9.12 |
| Viscosity at 100°C,cSt | 3.05 | 2.09 | 2.46 | 2.56 | 2.89 |
| Viscosity Index (VI) | 173.034 | 203.623 | 193.666 | 172.173 | 179.028 |
| Pour Point (°C) | 4 | 3 | 8 | 11 | 7 |
| Flash point (°C) | 234 | 198 | 212 | 215 | 220 |
| Oxidation point (°C) | 390 | 360 | 360 | 370 | 350 |
| Oxidation compound, %wt. | 1.08 | 10.94 | 6.21 | 1.51 | 9.84 |
| Total Acid Number(TAN) ,mg KOH/g | 0.72 | 0.81 | 0.72 | 0.74 | 0.68 |
| Copper Stripe Corrosion at 3 hours,100 °C | 1b | 1b | 1b | 1b | 1b |

From Table 4-3, All properties of each hydrogenated monoesters demonstrated that the pour point value is still higher than zero Celsius degree which is not suitable to use in many countries that have the temperature below zero Celsius degree, but they can be accepted as lubricants in the tropical country such as Thailand.

Each hydrogenated monoester has the physical and chemical properties that are not much different one another. However, they can be noticed that the more long chain of alcohol using, the more viscosity taking place. But, the shorter chain of alcohol using, the more viscosity index occurring such as the isopropyl ester gives the highest viscosity index. About the oxidation stability, the oxidation points and oxidation compounds of all hydrogenated esters are accepted at the oxidation point more than 300 °C, and the oxidation compounds not more than 10 wt%.

Again, other properties of flash point, and copper stripe corrosion of all hydrogenated ester are also accepted at flash point above 200 °C, and copper stripe corrosion in a range of the copper stripe number 1. About total acid number (TAN) in these hydrogenated esters, they are in the limit value of hydraulic lubricants at 0.7 mg KOH/g.

Furthermore, these hydrogenated esters have high value of viscosity index. Therefore, if these hydrogenated esters are blended with petroleum base oil numbered 150 SN to be the viscosity index improver additive, it will be useful.

Lubricating Base Oil (150 SN) Blended With Hydrogenated Ester

For study about VI improver, the based oil number 150 SN was chosen to blend with the products obtained from hydrogenation process for study of the ability of viscosity index (VI) improver.

1. Lubricating Base Oil (150 SN) Blended with Hydrogenated Isopropyl Ester

In the table 4-4 , it indicated that the viscosity index of the blended lube base oil and hydrogenated isopropyl ester increased from 103 to 120. The pour point also increased from -9 to -3.

Table 4-4: The results of lubricating base oil (150 SN) blended with hydrogenated isopropyl ester.

| Properties | Lube base oil (150 SN) | Hydrogenated isopropyl ester in composition (%) | | | | | |
|------------------------|---------------------------|---|---------|---------|---------|---------|---------|
| | | 3% | 5% | 8% | 13% | 18% | 20% |
| Color, ASTM | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Viscosity at 40 °C,cSt | 30.54 | 25.98 | 25.57 | 24.87 | 22.53 | 20.07 | 19.81 |
| Viscosity at 100°C,cSt | 5.25 | 4.84 | 4.81 | 4.75 | 4.53 | 4.25 | 4.24 |
| Viscosity Index (VI) | 103.85 | 107.349 | 109.208 | 110.308 | 115.036 | 117.906 | 120.003 |
| Pour Point (°C) | -9 | -9 | -9 | -8 | -6 | -5 | -3 |

2. Lubricating Base Oil (150 SN) Blended with Hydrogenated 1-Butyl Ester

In the table 4-5, it indicated that the viscosity index of the blended lube base oil and hydrogenated butyl ester increased from 103 to 122. The pour point also increased from -9 to -1.

Table 4-5: The results of lubricating base oil (150 SN) blended with hydrogenated butyl ester.

| Properties | Lube base oil (150 SN) | Hydrogenated butyl ester in composition (%) | | | | | |
|-------------------------|---------------------------|---|---------|---------|---------|---------|---------|
| | | 3% | 5% | 8% | 13% | 18% | 20% |
| Color, ASTM | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Viscosity at 40 °C, cSt | 30.54 | 25.99 | 25.29 | 23.13 | 22.92 | 20.80 | 20.49 |
| Viscosity at 100°C, cSt | 5.25 | 4.87 | 4.81 | 4.59 | 4.59 | 4.38 | 4.35 |
| Viscosity Index (VI) | 103.85 | 110.045 | 111.243 | 113.951 | 115.983 | 120.433 | 122.011 |
| Pour Point (°C) | -9 | -9 | -8 | -6 | -3 | -2 | -1 |

3. Lubricating Base Oil (150 SN) Blended with Hydrogenated Hexyl Ester

In the table 4-6, it indicated that the viscosity index of the blended lube base oil and hydrogenated hexyl ester increased from 103 to 122. The pour point also increased from -9 to -1.

Table 4-6: The results of lubricating base oil (150 SN) blended with hydrogenated hexyl ester.

| Properties | Lube base oil (150 SN) | Hydrogenated hexyl ester in composition (%) | | | | | |
|------------------------|---------------------------|---|---------|---------|---------|---------|---------|
| | | 3% | 5% | 8% | 13% | 18% | 20% |
| Color, ASTM | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Viscosity at 40 °C,cSt | 30.54 | 26.93 | 26.50 | 25.76 | 23.27 | 21.34 | 20.86 |
| Viscosity at 100°C,cSt | 5.25 | 4.98 | 4.91 | 4.87 | 4.42 | 4.42 | 4.41 |
| Viscosity Index (VI) | 103.85 | 106.921 | 108.440 | 112.101 | 116.626 | 118.385 | 122.689 |
| Pour Point (°C) | -9 | -9 | -8 | -5 | -2 | -1 | -1 |

4. Lubricating Base Oil (150 SN) Blended with Hydrogenated 4-Methyl-2-Pentyl Ester

In the table 4-7, it indicated that the viscosity index of the blended lube base oil and hydrogenated 4-methyl-2-pentyl ester increased from 103 to 128. The pour point also increased from -9 to -3.

Table 4-7: The results of lubricating base oil (150 SN) blended with hydrogenated 4-methyl-2-pentyl ester.

| Properties | Lube base oil (150 SN) | Hydrogenated 4-methyl-2-pentyl ester in composition (%) | | | | | |
|------------------------|---------------------------|---|---------|---------|---------|---------|---------|
| | | 3% | 5% | 8% | 13% | 18% | 20% |
| Color, ASTM | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Viscosity at 40 °C,cSt | 30.54 | 25.96 | 25.36 | 24.39 | 21.27 | 20.76 | 20.38 |
| Viscosity at 100°C,cSt | 5.25 | 4.85 | 4.81 | 4.72 | 4.43 | 4.44 | 4.40 |
| Viscosity Index (VI) | 103.85 | 108.349 | 110.533 | 112.067 | 119.991 | 126.845 | 128.251 |
| Pour Point (°C) | -9 | -9 | -7 | -5 | -5 | -5 | -3 |

5. Lubricating Base Oil (150 SN) Blended with Hydrogenated 2-Ethyl-1-Hexyl Ester

In the table 4-8, it indicated that the viscosity index of the blended lube base oil and hydrogenated 2-ethyl-1-hexyl ester increased from 103 to 126. The pour point also increased from -9 to -2.

Table 4-8: The results of lubricating base oil (150 SN) blended with hydrogenated 2-ethyl-1-hexyl ester.

| Properties | Lube base oil (150 SN) | Hydrogenated 2-ethyl-1-hexyl ester in composition (%) | | | | | |
|-------------------------|---------------------------|---|---------|---------|---------|---------|---------|
| | | 3% | 5% | 8% | 13% | 18% | 20% |
| Color, ASTM | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Viscosity at 40 °C, cSt | 30.54 | 24.32 | 23.58 | 21.63 | 19.77 | 19.15 | 18.78 |
| Viscosity at 100°C, cSt | 5.25 | 4.68 | 4.62 | 4.43 | 4.24 | 4.19 | 4.17 |
| Viscosity Index (VI) | 103.85 | 109.432 | 112.098 | 116.184 | 120.390 | 123.503 | 126.886 |
| Pour Point (°C) | -9 | -9 | -9 | -7 | -5 | -5 | -2 |

All of the blending results demonstrated that these hydrogenated esters are able to increase the viscosity index .By adding these hydrogenated esters 20 % by weight, the viscosity index of petroleum base oil increased from 100 to 120, and the pour point also got below zero Celsius degree .

Moreover, the viscosity index of the hydrogenated esters containing branch chain structure of alcohol such as 2-ethyl-1-hexyl ester and 4-methyl-2-pentyl ester, was higher than that of the hydrogenated esters containing straight chain structure of alcohol such as 1-hexyl ester.