

## CHAPTER IV

### RESULT AND DISCUSSION

#### 4.1 Characterization of rice bran oil

Rice bran oil was used as main raw material through out this research. The FTIR,  $^{13}\text{C}$ -NMR and  $^1\text{H}$ -NMR spectra of rice bran oil were shown in Figures A-7, A-8 and A-9, respectively.

Figure A-7, FTIR spectrum showed the C=O group of ester at  $1740\text{ cm}^{-1}$ . The peak at approximately of  $2920\text{ cm}^{-1}$  showed the C-H stretching vibration of an aliphatic hydrogen. The C-O in the ester is overlapped with the functional groups of  $\text{CH}_2$  and  $\text{CH}_3$  at  $1462$  and  $1380\text{ cm}^{-1}$ .

Figure A-8,  $^{13}\text{C}$ -NMR spectrum showed the important signal of triglyceride of rice bran oil at  $62.0$  and  $68.8\text{ ppm}$ . and the signal of C=O appeared at  $174\text{ ppm}$ . In addition, Figure A-8 also showed the signals of unsaturated group at  $127$  and  $129\text{ ppm}$ .

Figure A-9,  $^1\text{H}$ -NMR spectrum showed the important signals of methyl protons ( $\text{CH}_3\text{-C}$ ) and methylene protons ( $\text{-C-CH}_2\text{-C-}$ ) at  $0.9$  and  $1.4\text{ ppm}$ . and the signal of  $\text{-CH}_2\text{-OOC-R-}$  appeared at  $4\text{ ppm}$ .

**Table 4.1 : The physical and chemical properties of mineral oil  
and rice bran oil**

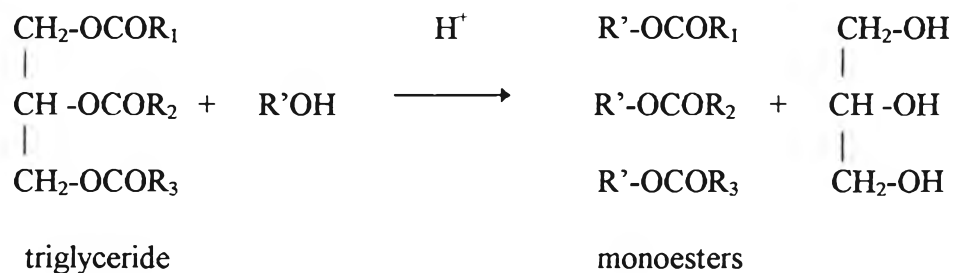
Test Items	60 SN	150 SN	rice bran oil
Color	L 0.5	L 0.5	L 1.0
K.V. at 40°C , cSt.	10.66	29.95	38.68
K.V. at 100°C , cSt.	2.75	5.21	8.43
KVI	96	104	203
Flash point (COC) , °C	176	226	314
Pour point , °C	-9	-12	0
Thermal stability at 0°C	stable	stable	waxy
Thermal stability at RT	stable	stable	stable
Thermal stability at 50°C	stable	stable	stable
Oxidation point , °C	322.456	337.154	340.015 431.551
Oxidative compound , %	4.322	10.317	14.236

The results from Table 4.1 indicated the comparison of physical and chemical properties of rice bran oil and mineral base oils. The color of rice bran oil was darker than mineral base oils. The viscosity at 40° and 100°C , viscosity index and flash point of rice bran oil were higher than mineral base oils but the pour point and thermal stability at 0°C were poorer than mineral base oils. Rice bran oil had two oxidation points when compared with mineral base oils, which had only one oxidation point, due to rice bran oil

had multicomponent system of natural antioxidants and the % oxidative compounds of rice bran oil were also more than mineral base oils.

#### 4.2 Synthesis of monoester

Monoesters were synthesized by transesterification reaction as follows :



R<sub>1</sub> R<sub>2</sub> R<sub>3</sub> were alkyl groups of fatty acids in rice bran oil i.e. palmitic, stearic, myristic, oleic, linoleic, linolenic, palmitoleic etc.<sup>[19]</sup>

R' was an alkyl group of alcohol that was placed to react with rice bran oil i.e. 1-butanol, 1-hexanol, 1-octanol, 2-ethyl-1-hexanol and 4-methyl-2-pentanol.

The optimum condition for transesterification with each alcohol was obtained by varying the reaction time at refluxing temperature. In this study, the reaction time was studied between 2, 3 and 4 hours.

#### 4.2.1 Transesterification of rice bran oil with 1-butanol

The results of butyl ester from transesterification at optimum condition were shown by FTIR,  $^{13}\text{C}$ -NMR and  $^1\text{H}$ -NMR spectra in Figures A-10, A-11 and A-12, respectively.

Figure A-10, FTIR spectrum showed the C=O group of ester at  $1734\text{ cm}^{-1}$ . The peak at approximately of  $2920\text{ cm}^{-1}$  showed the C-H stretching vibration of an aliphatic hydrogen. The C-O in the ester is overlapped with the functional groups of  $\text{CH}_2$  and  $\text{CH}_3$  at  $1462$  and  $1380\text{ cm}^{-1}$ .

Figure A-11,  $^{13}\text{C}$ -NMR spectrum showed the peak of triglyceride of rice bran oil at  $62.0$  and  $68.8\text{ ppm}$ . disappeared and the important peaks of  $-\text{CH}_2\text{-O}$  and C=O of monoester products appeared at  $64.0$  and  $174\text{ ppm}$ ., respectively. In addition, Figure A-11 also showed the signals of unsaturated group at  $127$  and  $129\text{ ppm}$ .

Figure A-12,  $^1\text{H}$ -NMR spectrum showed the important signal of methyl protons ( $-\text{CH}_3\text{-C-}$ ) and methylene protons ( $-\text{C-CH}_2\text{-C-}$ ) at  $0.9$  and  $1.4\text{ ppm}$ . and the signal of  $-\text{CH}_2\text{-OOC-R-}$  appeared at  $4\text{ ppm}$ .

These experimental results indicated that the transesterification reaction of rice bran oil with 1-butanol was completed after 2 hours of reaction time. The refluxing temperature was  $84^\circ\text{C}$ . The yield of the resulting product at the reaction time of 2, 3 and 4 hours were  $92.57\%$ ,  $93.00\%$ , and  $92.84\%$ , respectively. These results showed that longer reaction time had no influence on monoester products.

The physical and chemical properties of butyl ester products at reaction time of 2, 3 and 4 hours, as shown in Table 4-2, were studied as follows : color, kinematic viscosity at  $40^\circ$  and  $100^\circ\text{C}$ , viscosity index, pour point, flash point and oxidation stability. The

oxidation stability curve was analyzed by TGA analyzer and the result was shown in Figure A-28.

**Table 4-2 : The physical and chemical properties of rice bran oil and butyl ester products**

Properties	Rice bran oil	butyl ester products		
		2 Hours	3 Hours	4 Hours
Color	L* 1.0	L* 2.0	L* 2.0	L* 2.0
K.V. at 40°C, cSt.	38.68	10.468	10.470	10.472
K.V. at 100°C, cSt.	8.43	3.153	3.160	3.159
KVI	203	182	184	183
Flash point (COC), °C	314	208	207	208
Pour point, °C	0	+6	+6	+6
Thermal stability at 0°C	waxy	waxy	waxy	waxy
Thermal stability at room temp.	stable	stable	stable	stable
Thermal stability at 50°C	stable	stable	stable	stable
Oxidation point, °C	1.) 340.015 2.) 431.551	310.261	-	-
Oxidative compounds, %	14.236	24.070	-	-

\* L means the color of products were lighter than level of standard ASTM color.

The result from Table 4-2 indicated that the color was lower than 2.0 when compared with ASTM standard color and it was darker than rice bran oil. The viscosity at 40° and 100°C were 10.468 and 3.153 cSt., respectively, lighter than rice bran oil due to decreasing of the molecular weight of molecules. The viscosity index was 182 and the flash point was 208°C, less than rice bran oil. The pour point of butyl ester was +6°C, higher than rice bran oil due to decreasing of branching. The oxidation point of butyl ester was 310.261°C and oxidative compounds were 24.070 %.

#### 4.2.2. Transesterification of rice bran oil with 1-hexanol

The results of hexyl ester from transesterification at optimum condition were shown by FTIR,  $^{13}\text{C-NMR}$  and  $^1\text{H-NMR}$  spectra in Figures A-13, A-14 and A-15, respectively.

Figure A-13, FTIR spectrum, showed the  $\text{C=O}$  group of ester at  $1734\text{ cm}^{-1}$ . The peak at approximately of  $2920\text{ cm}^{-1}$  showed the  $\text{C-H}$  stretching vibration of an aliphatic hydrogen. The  $\text{C-O}$  in the ester is overlapped with the functional groups of  $\text{CH}_2$  and  $\text{CH}_3$  at  $1454$  and  $1380\text{ cm}^{-1}$ .

Figure A-14,  $^{13}\text{C-NMR}$  spectrum, showed the peak of triglyceride of rice bran oil at  $62.0$  and  $68.8\text{ ppm}$ . disappeared and the important peaks of  $-\text{CH}_2\text{-O}$  and  $\text{C=O}$  of monoester products appeared at  $64.0$  and  $174\text{ ppm}$ ., respectively. In addition, Figure A-14 also showed the signals of unsaturated group at  $127$  and  $129\text{ ppm}$ .

Figure A-15,  $^1\text{H-NMR}$  spectrum, showed the important signals of methyl protons ( $-\text{CH}_3\text{-C-}$ ) and methylene protons ( $-\text{C-CH}_2\text{-C-}$ ) at  $0.9$  and  $1.4\text{ ppm}$ . and the signal of  $-\text{CH}_2\text{-OOC-R-}$  appeared at  $4\text{ ppm}$ .

These experimental results indicated that the transesterification reaction of rice bran oil with 1-hexanol was completed after 2 hours of reaction time. The refluxing temperature was  $86^\circ\text{C}$ . The yield of the resulting products at the reaction time of 2, 3 and 4 hours were  $91.54\%$ ,  $91.70\%$ , and  $91.64\%$ , respectively. These results showed that longer reaction time had no influence on monoester products.

The physical and chemical properties of hexyl ester products at reaction time of 2, 3 and 4 hours, as shown in Table 4-3, were studied as follows : color, kinematic viscosity at  $40^\circ$  and  $100^\circ\text{C}$ , viscosity index, pour point, flash point and oxidation

stability. The oxidation stability curve was analyzed by TGA analyzer and the result was shown in Figure A-29.

**Table 4-3 : The physical and chemical properties of rice bran oil and hexyl ester products**

Properties	Rice bran oil	hexyl ester products		
		2 Hours	3 Hours	4 Hours
Color	L* 1.0	L* 2.5	L* 2.5	L* 2.5
K.V. at 40°C, cSt.	38.68	11.530	11.535	11.538
K.V. at 100°C, cSt.	8.43	3.363	3.364	3.363
KVI	203	181	181	181
Flash point (COC), °C	314	230	231	232
Pour point, °C	0	0	0	0
Thermal stability at 0°C	waxy	waxy	waxy	waxy
Thermal stability at room temp.	stable	stable	stable	stable
Thermal stability at 50°C	stable	stable	stable	stable
Oxidation point, °C	1.) 340.015 2.) 431.551	340.749	-	-
Oxidative compounds, %	14.236	20.751	-	-

\* L means the color of products were lighter than level of standard ASTM color.



The result from Table 4-3 indicated that the color was lower than 2.5 when compared with ASTM standard color and it was darker than rice bran oil. The viscosity at 40° and 100°C were 11.530 and 3.363 cSt., respectively, lighter than rice bran oil due to decreasing of the molecular weight of molecules. The viscosity index was 181 and the flash point was 230°C, less than rice bran oil. The pour point of butyl ester was 0°C, higher than rice bran oil due to decreasing of branching. The oxidation point of butyl ester was 340.749°C and oxidative compounds were 20.751 %.

#### 4.2.3. Transesterification of rice bran oil with 1-octanol

The results of octyl ester from transesterification at optimum condition were shown by FTIR,  $^{13}\text{C-NMR}$  and  $^1\text{H-NMR}$  spectra in Figures A-16, A-17 and A-18, respectively.

Figure A-16, FTIR spectrum showed the C=O group of ester at  $1734\text{ cm}^{-1}$ . The peak at approximately of  $2920\text{ cm}^{-1}$  showed the C-H stretching vibration of an aliphatic hydrogen. The C-O in the ester is overlapped with the functional groups of  $\text{CH}_2$  and  $\text{CH}_3$  at  $1462$  and  $1380\text{ cm}^{-1}$ .

Figure A-17,  $^{13}\text{C-NMR}$  spectrum showed the peak of triglyceride of rice bran oil at  $62.0$  and  $68.8\text{ ppm}$ . disappeared and the important peaks of  $-\text{CH}_2\text{-O}$  and C=O of monoester products appeared at  $64.0$  and  $174\text{ ppm}$ ., respectively. In addition, Figure A-17 also showed the signals of unsaturated group at  $127$  and  $129\text{ ppm}$ .

Figure A-18,  $^1\text{H-NMR}$  spectrum showed the important signals of methyl protons ( $-\text{CH}_3\text{-C-}$ ) and methylene protons ( $-\text{C-CH}_2\text{-C-}$ ) at  $0.9$  and  $1.4\text{ ppm}$ . and the signal of  $-\text{CH}_2\text{-OOC-R-}$  appeared at  $4\text{ ppm}$ .

These experimental results indicated that the transesterification reaction of rice bran oil with 1-octanol was completed after 2 hours of reaction time. The refluxing temperature was  $90^\circ\text{C}$ . The yield of the resulting products at the reaction time of 2, 3 and 4 hours were  $90.84\%$ ,  $91.25\%$ , and  $91.47\%$ , respectively. These results showed that longer reaction time had no influence on monoester products.

The physical and chemical properties of octyl ester products at reaction time of 2, 3 and 4 hours, as shown in Table 4-4, were studied as follows : color, kinematic viscosity at  $40^\circ$  and  $100^\circ\text{C}$ , viscosity index, pour point, flash point and oxidation stability. The

oxidation stability curve was analyzed by TGA analyzer and the result was shown in Figure A-30.

**Table 4-4 : The physical and chemical properties of rice bran oil and octyl ester products**

Properties	Rice bran oil	octyl ester products		
		2 Hours	3 Hours	4 Hours
Color	L* 1.0	L* 1.5	L* 1.5	L* 1.5
K.V. at 40°C, cSt.	38.68	13.596	13.600	13.615
K.V. at 100°C, cSt.	8.43	3.719	3.720	3.722
KVI	203	174	174	174
Flash point (COC), °C	314	220	220	222
Pour point, °C	0	+6	+6	+6
Thermal stability at 0°C	waxy	waxy	waxy	waxy
Thermal stability at room temp.	stable	stable	stable	stable
Thermal stability at 50°C	stable	stable	stable	stable
Oxidation point, °C	1.) 340.015 2.) 431.551	343.376	-	-
Oxidative compounds, %	14.236	19.212	-	-

\* L means the color of products were lighter than level of standard ASTM color.

The result from Table 4-4 indicated that the color was lower than 1.5 when compared with ASTM standard color and it was darker than rice bran oil. The viscosity at 40° and 100°C were 13.596 and 3.719 cSt., respectively, lighter than rice bran oil due to decreasing of the molecular weight of molecules. The viscosity index was 174 and the flash point was 220°C, less than rice bran oil. The pour point of butyl ester was +6°C, higher than rice bran oil due to decreasing of branching. The oxidation point of butyl ester was 343.376°C and oxidative compounds were 19.212 %.

#### 4.2.4. Transesterification of rice bran oil with 2-ethyl-1-hexanol

The results of 2-ethyl-1-hexyl ester from transesterification at optimum condition were shown by FTIR,  $^{13}\text{C}$ -NMR and  $^1\text{H}$ -NMR spectra in Figures A-19, A-20 and A-21, respectively.

Figure A-19, FTIR spectrum showed the C=O group of ester at  $1734\text{ cm}^{-1}$ . The peak at approximately of  $2920\text{ cm}^{-1}$  showed the C-H stretching vibration of an aliphatic hydrogen. The C-O in the ester is overlapped with the functional groups of  $\text{CH}_2$  and  $\text{CH}_3$  at  $1462$  and  $1380\text{ cm}^{-1}$ .

Figure A-20,  $^{13}\text{C}$ -NMR spectrum showed the peak of triglyceride of rice bran oil at  $62.0$  and  $68.8\text{ ppm}$ . disappeared and the important peaks of  $-\text{CH}_2\text{-O}$  and C=O of monoester products appeared at  $64.0$  and  $174\text{ ppm}$ ., respectively. In addition, Figure A-20 also showed the signals of unsaturated group at  $127$  and  $129\text{ ppm}$ .

Figure A-21,  $^1\text{H}$ -NMR spectrum showed the important signals of methyl protons ( $-\text{CH}_3\text{-C-}$ ) and methylene protons ( $-\text{C-CH}_2\text{-C-}$ ) at  $0.9$  and  $1.4\text{ ppm}$ . and the signal of  $-\text{CH}_2\text{-OOC-R-}$  appeared at  $4\text{ ppm}$ .

These experimental results indicated that the transesterification reaction of rice bran oil with 2-ethyl-1-hexanol was completed after 2 hours of reaction time. The refluxing temperature was  $96^\circ\text{C}$ . The yield of the resulting products at the reaction time of 2, 3 and 4 hours were  $93.78\%$ ,  $93.52\%$ , and  $93.40\%$ , respectively. These results showed that longer reaction time had no influence on monoester products.

The physical and chemical properties of 2-ethyl-1-hexyl ester products at reaction time of 2, 3 and 4 hours, as shown in Table 4-5, were studied as follows : color, kinematic viscosity at  $40^\circ$  and  $100^\circ\text{C}$ , viscosity index, pour point, flash point and

oxidation stability. The oxidation stability curve was analyzed by TGA analyzer and the result was shown in Figure A-31.

**Table 4-5 : The physical and chemical properties of rice bran oil and 2-ethyl-1-hexyl ester products**

Properties	Rice bran oil	2-ethyl-1-hexyl ester products		
		2 Hours	3 Hours	4 Hours
Color	L* 1.0	L* 1.5	L* 1.5	L* 1.5
K.V. at 40°C, cSt.	38.68	14.158	14.162	14.160
K.V. at 100°C, cSt.	8.43	3.744	3.744	3.743
KVI	203	163	163	163
Flash point (COC), °C	314	216	215	216
Pour point, °C	0	-12	-12	-12
Thermal stability at 0°C	waxy	waxy	waxy	waxy
Thermal stability at room temp.	stable	stable	stable	stable
Thermal stability at 50°C	stable	stable	stable	stable
Oxidation point, °C	1.) 340.015 2.) 431.551	327.612	-	-
Oxidative compounds, %	14.236	19.752	-	-

\* L means the color of products were lighter than level of standard ASTM color.

The result from Table 4-5 indicated that the color was lower than 1.5 when compared with ASTM standard color and it was darker than rice bran oil. The viscosity at 40° and 100°C were 14.158 and 3.744 cSt., respectively, lighter than rice bran oil due to decreasing of the molecular weight of molecules. The viscosity index was 163 and the flash point was 216°C, less than rice bran oil. The pour point of butyl ester was -12°C, lower than rice bran oil due to increasing of branching. The oxidation point of butyl ester was 327.612°C and oxidative compounds were 19.752 %.

#### 4.2.5. Transesterification of rice bran oil with 4-methyl-2-pentanol

The results of 4-methyl-2-pentyl ester from transesterification at optimum condition were shown by FTIR,  $^{13}\text{C-NMR}$  and  $^1\text{H-NMR}$  spectra in Figures A-22, A-23 and A-24, respectively.

Figure A-22, FTIR spectrum showed the  $\text{C=O}$  group of ester at  $1740\text{ cm}^{-1}$ . The peak at approximately of  $2920\text{ cm}^{-1}$  showed the C-H stretching vibration of an aliphatic hydrogen. The C-O in the ester is overlapped with the functional groups of  $\text{CH}_2$  and  $\text{CH}_3$  at  $1475$  and  $1380\text{ cm}^{-1}$ .

Figure A-23,  $^{13}\text{C-NMR}$  spectrum showed the peak of triglyceride of rice bran oil at  $62.0$  and  $68.8\text{ ppm}$ . disappeared and the important peaks of  $-\text{CH}_2-\text{O}$  and  $\text{C=O}$  of monoester products appeared at  $64.0$  and  $174\text{ ppm}$ ., respectively. In addition, Figure A-23 also showed the signals of unsaturated group at  $127$  and  $129\text{ ppm}$ .

Figure A-24,  $^1\text{H-NMR}$  spectrum, showed the important signals of methyl protons ( $-\text{CH}_3-\text{C}-$ ) and methylene protons ( $-\text{C}-\text{CH}_2-\text{C}-$ ) at  $0.9$  and  $1.4\text{ ppm}$ . and the signal of  $-\text{CH}_2-\text{OOC}-\text{R}-$  appeared at  $4\text{ ppm}$ .

These experimental results indicated that the transesterification reaction of rice bran oil with 4-methyl-2-pentanol was completed after 2 hours of reaction time. The yield of the resulting products at the reaction time of 2, 3 and 4 hours were  $92.38\%$ ,  $93.05\%$ , and  $92.78\%$ , respectively. These results showed that longer reaction time had no influence on monoester products.

The physical and chemical properties of 4-methyl-2-pentyl ester products at reaction time of 2, 3 and 4 hours, as shown in Table 4-6, were studied as follows : color, kinematic viscosity at  $40^\circ$  and  $100^\circ\text{C}$ , viscosity index, pour point, flash point and



oxidation stability. The oxidation stability curve was analyzed by TGA analyzer and the result was shown in Figure A-32.

**Table 4-6 : The physical and chemical properties of rice bran oil and 4-methyl-2-pentyl ester products**

Properties	Rice bran oil	4-methyl-2-pentyl ester products		
		2 Hours	3 Hours	4 Hours
Color	L 1.0	L 4.0	L 4.0	L 4.0
K.V. at 40°C, cSt.	38.68	22.029	22.032	22.101
K.V. at 100°C, cSt.	8.43	5.229	5.230	5.240
KVI	203	182	182	182
Flash point (COC), °C	314	224	224	225
Pour point, °C	0	-6	-6	-6
Thermal stability at 0°C	waxy	waxy	waxy	waxy
Thermal stability at room temp.	stable	stable	stable	stable
Thermal stability at 50°C	stable	stable	stable	stable
Oxidation point, °C	1.) 340.015 2.) 431.551	1.) 313.649 2.) 387.329	-	-
Oxidative compounds, %	14.236	26.304	-	-

\* L means the color of products were lighter than level of standard ASTM color.

The result from Table 4-6 indicated that the color was lower than 4.0 when compared with ASTM standard color and it was darker than rice bran oil. The viscosity at 40° and 100°C were 22.029 and 5.229 cSt., respectively, lighter than rice bran oil due to decreasing of the molecular weight of molecules. The viscosity index was 182 and the flash point was 224°C, less than rice bran oil. The pour point of butyl ester was -6°C, lower than rice bran oil due to increasing of branching. The oxidation point of butyl ester was 13.649°C and oxidative compounds were 26.304 %.

From the test results, the refluxing temperature of each monoester was different due to less of toluene, which functioned as azeotroping agent in reaction and purity of each alcohol which reacted. This may be incompletely reaction occurred.

### 4.3 Comparison of the properties of monoesters

The physical and chemical properties of monoesters after 2 hours of reaction time were compared as follows :

**Table 4-7 : The physical and chemical properties of monoesters**

Test Items	butyl ester	hexyl ester	octyl ester	2-ethyl-1-hexyl ester	4-methyl-2-pentyl ester
Color	L 2.0	L 2.5	L 1.5	L 1.5	L 4.0
K.V. at 40°C , cSt.	10.468	11.530	13.596	14.158	22.029
K.V. at 100°C , cSt.	3.153	3.363	3.719	3.744	5.229
KVI	182	181	174	163	182
Flash point (COC) , °C	208	230	220	216	224
Pour point , °C	+6	0	+6	-12	-6
Thermal stability at 0°C	waxy	waxy	waxy	waxy	waxy
Thermal stability at room temp.	stable	stable	stable	stable	stable
Thermal stability at 50°C	stable	stable	stable	stable	stable
Oxidation point , °C	310.261	340.749	343.376	327.612	313.649 387.329
Oxidative compound , %	24.070	20.751	19.212	19.752	26.304

From Tables 4-1 and 4-7, comparison each property of monoesters, rice bran oil and mineral oil were indicated as follows :

**Color** : Eventhough the color of monoesters were darker when comparing with mineral base oil, this can be rectified if the products, which be blended, had the color additive in the formulation.

**Kinematic viscosity at 40° and 100°C** : From Table 4-7, considering the results of the viscosity at 40°C and 100°C, it was found that increasing the number of carbon chain length caused higher viscosity. From the results mentioned above, viscosity at 40°C and 100°C of octyl ester was higher than hexyl ester and butyl ester respectively. When comparing the hexyl ester and 4-methyl-2-pentyl ester, which have six carbons of alcohol chain with different structure, it was found that 4-methyl-2-pentyl ester has a higher viscosity at 40°C and 100°C than hexyl ester. This is because 4-methyl-2-pentyl ester has a branching structure which is caused of high viscosity. With the same reason, 2-ethyl-1-hexyl ester also has a higher viscosity at 40°C and 100°C than octyl ester, which has different structure of eight carbons of alcohol chain.

**Viscosity index** : The viscosity index of monoesters were higher than mineral base oil but lower than rice bran oil. This indicated that the viscosity of rice bran oil was a little bit changed when the temperature was changed while the viscosity of mineral oil changed mostly when the temperature was changed.

**Flash point** : The flash point of monoesters were nearly the same as mineral base oil but lower than rice bran oil due to the triglyceride structure of rice bran oil caused of high molecular weight than monoesters and mineral oil, so the flash point of rice bran oil was higher than monoesters and mineral oil.

**Pour point** : The pour point of monoesters, which have the same number of carbons of alcohol with different structure, was considered. It is found that the monoester, which has branching, will give a lower pour point than the monoester which has a straight chain molecule. So, 4-methyl-2-pentyl ester has a lower pour point than hexyl ester and 2-ethyl-1-hexyl ester has a lower pour point than octyl ester.

**Thermal stability** : The thermal stability of monoesters, rice bran oil and mineral base oil at room temperature and 50°C were stable but at 0°C, the monoesters and rice bran oil were waxy.

**Oxidation stability** : The oxidation points of monoesters, rice bran oil and mineral base oil were nearly the same but the % oxidative compounds of monoesters were higher than mineral base oil. Rice bran oil had 2 oxidation points due to its multicomponent system of natural antioxidants.

When overall properties were considered, it is found that the monoesters, which had properties nearly approaching the mineral base oil, were 4-methyl-2-pentyl ester and 2-ethyl-1-hexyl ester. Other monoesters such as butyl ester, hexyl ester and octyl ester had pour point that were too high, so they were poorer than mineral base oil. However, all the monoesters had higher viscosity indices than mineral base oil.

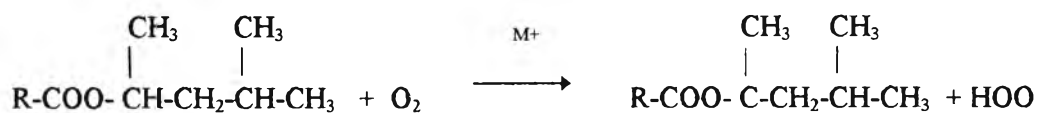
When 4-methyl-2-pentyl ester was compared with 2-ethyl-1-hexyl ester, it was found that the oxidation stability of 4-methyl-2-pentyl ester was poorer than 2-ethyl-1-hexyl ester due to the fact that the prior had two oxidation points. This indicated that 4-

methyl-2-pentyl ester was more easily oxidized than 2-ethyl-1-hexyl ester and there were more oxidative compounds of 4-methyl-2-pentyl ester than 2-ethyl-1-hexyl ester.

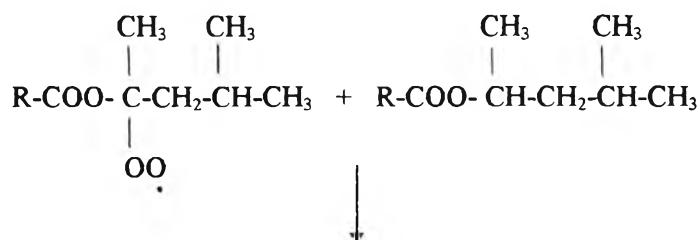
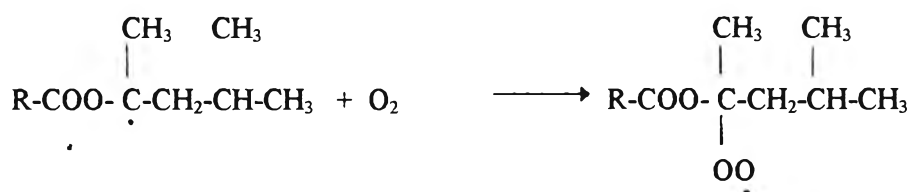
The oxidation can be described by the well-established free radical mechanism. An alkyl radical that is formed reacts irreversibly with oxygen to form an alkyl peroxy radical in the propagation stage. Termination may be affected by the combination of the radical species to yield unreactive species.

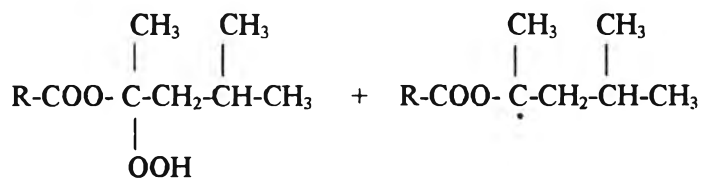
Considering the TGA thermogram of 4-methyl-2-pentyl ester, it was found that the ester had two oxidation points which indicated that it can be oxidized easily. The oxidation mechanism of 4-methyl-2-pentyl ester is shown as follows :

I) Initiation of the radical chain reaction : The initiation stage of 4-methyl-2-pentyl ester (only one part) is :

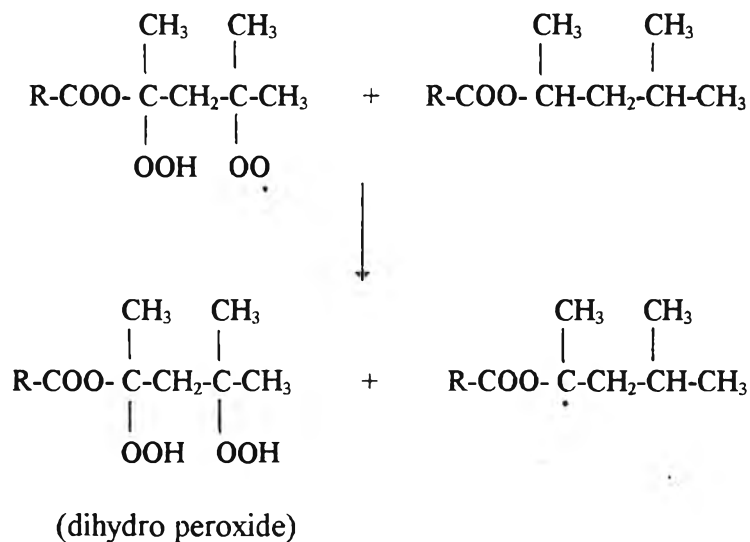
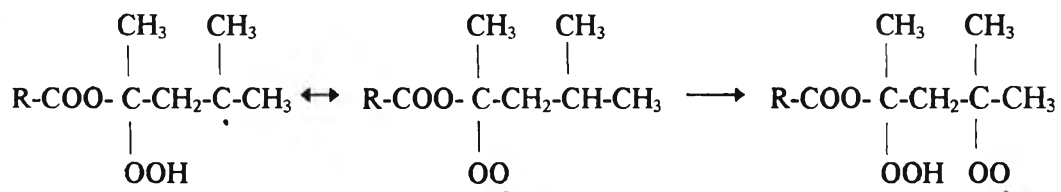


II) Propagation of the radical chain reaction :

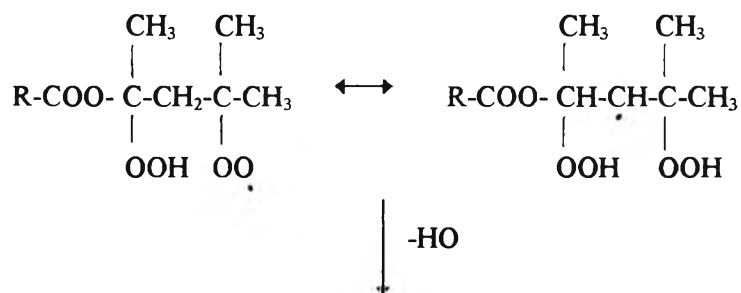


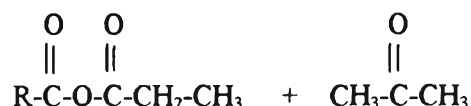


A more favourable route of hydrogen abstraction by a peroxy radical occurs via an intramolecular propagation.



### III) Termination of the radical chain reaction :





#### 4.4 Lubricating base oil (150 SN) blended with 2-ethyl-1-hexyl ester

Due to the high viscosity index of 2-ethyl-1-hexyl ester, this process had been studied about ability of 2-ethyl-1-hexyl ester as viscosity index improvers in lubricating industries and can also be confirmed by blending a small amount of 2-ethyl-1-hexyl ester with mineral base oil, which was shown in Table 4.8.

**Table 4-8 : The physical and chemical properties of lubricating base oil blended with 2-ethyl-1-hexyl ester.**

Properties	2-ethyl-1-hexyl ester blended in composition (%)							
	3 %	5 %	8 %	10 %	13 %	15 %	20 %	25 %
Color	L 0.5	L 0.5	L 0.5	L 0.5	L 0.5	L 0.5	L 0.5	L 0.5
K.V. at 40°C , cSt.	28.53	27.78	26.86	26.52	25.58	25.10	24.07	23.23
K.V. at 100°C , cSt.	5.10	5.06	4.97	4.94	4.87	4.83	4.73	4.66
Viscosity Index (VI)	107	109	110	111	113	115	116	119
Pour point , °C	-9	-9	-9	-9	-9	-6	-6	-6
Flash point , °C	216	220	226	228	228	234	230	216

From Table 4.8, the 2-ethyl-1-hexyl ester obtained from transesterification reaction was blended with lubricating base oil (150 SN). The kinematic viscosity at 40°



and 100°C of the blended oils decreased but the viscosity index of the blended oil increased from 104 to 119 when it contains the 2-ethyl-1-hexyl ester 25 % wt. Although the pour point of the blended oil is increased, when the lubricants is blended by using 2-ethyl-1-hexyl ester, the pour point depressant should be added to decrease the pour point. The flash point of the blended oils was nearly the same when more contents of 2-ethyl-1-hexyl ester were used.

**Table 4-9 : The physical properties of different types of standard lubricant**

Type of Lubricant	Physical Properties				
	K.V. at 40°C	K.V. at 100°C	KVI	Flash Point (°C)	Pour Point (°C)
Engine Oil	-	4.1-6.6	> 90	> 190	< -5
2 Stroke Oil	-	5.6-7.8	> 95	> 70	< -5
Automotive Gear Oil	-	13.5-15.5	> 85	> 200	< -5
Industrial Gear	28.8-35.2	-	> 90	> 200	< -10
Hydraulic Oil	9.0-11.0	2.5 Typical	> 75	> 125	< 12
Turbine Oil	28.8-35.2	5.0 Typical	> 90	> 160	< -6
Refrigerator Compressor Oil	28.8-35.2	5.7 Typical	> 90	> 200	< -20
Air Compressor Oil	28.8-35.2	5.6 Typical	> 90	> 200	< -10
Heat Transfer Oil	28.8-35.2	5.4 Typical	> 90	> 200	-

Consideration about the physical and chemical properties of each monoester, the monoester can be blended with all types of lubricant which shown in Table 4.9, but some of them had to be added some additives, for example; if butyl ester was blended to engine oil, the pour point depressant should be added in the formulation to improve the quality of product. However, it depended on the formulation of the lubricant. If the monoester was blended with mineral base oil as semi-synthetic lubricant, some additives to improve its quality should be required but if the monoester was with other synthetic base oils, the additives to improve some qualities may not be necessary.

According to the above discussion, the research studied only physical and chemical properties and the esters which synthesized were synthetic base oil, so more informations concerning its performance of product in practice were required if the product would be actually blended.

#### 4.5 Comparison of the properties of 2-ethyl-1-hexyl ester from palm oil and rice bran oil

**Table 4.10 : The physical and chemical properties of 2-ethyl-1-hexyl ester product from palm oil and rice bran oil**

Properties	Palm oil	2-ethyl-1-hexyl ester	Rice bran oil	2-ethyl-1-hexyl ester
Color	L 1.0	L 2.0	L 1.0	L 1.5
K.V. at 40°C , cSt.	40.26	7.85	38.68	14.16
K.V. at 100°C , cSt.	8.37	2.46	8.43	3.74
KVI	190	152	203	163
Flash point, °C	314	240	314	216
Pour point, °C	+12	-12	0	-12
Oxidation point, °C	361	307	340	328
Oxidative compounds, %	37.37	9.36	14.24	19.75

The result from Table 4-10 indicated that 2-ethyl-1-hexyl ester from palm oil had color lower than 2.0, kinematic viscosity at 40° and 100°C were 7.85 and 2.46 cSt., respectively, viscosity index was 152. Flash point and pour point were 240° and -12°C, respectively. The oxidation point was 340°C and the oxidative compounds was 9.36 %.

2-Ethyl-1-hexyl ester from rice bran oil had color lower than 1.5, kinematic viscosity at 40° and 100°C were 14.16 and 3.74 cSt., respectively, viscosity index was

163. Flash point and pour point were 216° and -12°C, respectively. The oxidation point was 328°C and the oxidative compounds was 19.75 %.

From Table 4-10, the viscosity at 40° and 100°C of 2-ethyl-1-hexyl ester from rice bran oil was higher than from palm oil due to the components of fatty acids in rice bran oil had high molecular weight than palm oil. The viscosity index, flash point and pour point were nearly the same but the oxidation point and % oxidative compounds of 2-ethyl-1-hexyl ester from rice bran oil were higher than from palm oil due to % unsaturated fatty acids in rice bran oil were more than palm oil.