CHAPTER IV

RESULTS AND DISCUSSION

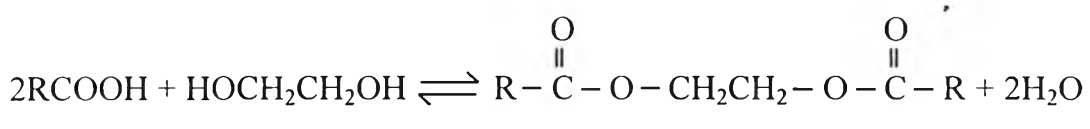
The synthetic diesters were synthesized by esterification reaction from fatty acids (i.e., lauric acid, myristic acid, palmitic acid and stearic acid) with glycols (i.e., 1,2-ethanediol and 1,2-propanediol) in toluene as azeotropic agent and using concentrated sulfuric acid as catalyst. The reaction temperature was carried out at 110°C and the reaction time was 4 hours. The characteristics of the diester products were determined by ^{13}C-NMR and FTIR spectroscopy. The physical and chemical properties were studied such as color, flash point, melting point, total acid number and oxidation and thermal stabilities.

The ^{13}C-NMR spectra of 1,2-ethanediol, 1,2-propanediol, lauric acid, myristic acid, palmitic acid and stearic acid were shown in Figures A1, A2, A3, A4, A5 and A6, respectively. The FTIR spectra were shown in Figures B1, B2, B3, B4, B5 and B6, respectively.

The applications of the diester products as lubricant additives were also studied. The steps of this process were carried out by blending base oils with the small amounts of these diesters. The properties of the base oil and the base oil blended with a diester were demonstrated in Table 4.3, including color, flash point, pour point, kinematic viscosity at 40°C and 100°C, viscosity index and foaming.

4.1 Esterification of lauric acid with 1,2-ethanediol

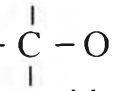
The esterification was carried out by reacting lauric acid with 1,2-ethanediol at 110°C for 4 hours. The product, 1,2-ethanedilaurate was obtained as a waxy solid in 81.72% yield with melting point 53.8°C according to the reaction shown below.



lauric acid 1,2-ethanediol 1,2-ethanedilaurate water

where :

$$R = C_{11}H_{23}$$

The product was characterized by ^{13}C-NMR and FTIR spectroscopy and their spectra were shown in Figures A7 and B7, respectively. From Figure A7, ^{13}C-NMR indicated the important peak of C =O and – CH_2 – O– of diester at 174 and 62 ppm, respectively, while the peak of carboxyl group of fatty acid at 180 ppm disappeared. Figure B7, FTIR spectrum demonstrated that the peak of C= O (carbonyl group) shifted from 1710 (carboxyl group) to 1730 cm^{-1} (ester group) and the peak of  at 1213 cm^{-1} (ester group) appeared. The thermal stability, the oxidation point and the oxidative compounds were analyzed by TGA analyzer and the curve was shown in Figure C1.

The physical and chemical properties of 1,2-ethanedilaurate were tabulated in Table 4.1. The yield of this synthetic diester was shown in Table 4.2.

Table 4.1 The physical and chemical properties of the synthetic diesters

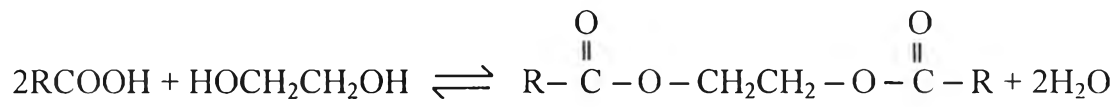
Waxes	Color, ASTM	Flash Point, °C	Melting Point, °C	Total Acid Number, mg of KOH/g	Oxidation Point, °C	Oxidative Compound, %wt	Thermal Stability, °C
1,2-ethanedilaurate	1.5	190	53.8	6.92	316	11.03	251.81
1,2-ethanedimyristate	1.5	194	57.5	3.50	263	26.21	201.51
1,2-ethanedipalmitate	1.5	204	67.2	5.48	350	6.90	269.94
1,2-ethanedistearate	1.5	218	68.7	4.42	353	7.93	258.06
1,2-propanedilaurate	3.5	180	-	2.11	300	8.28	186.86
1,2-propanedimyristate	3.0	212	41.5	3.10	324	12.76	245.20
1,2-propanedipalmitate	2.0	214	52.6	4.34	342	8.62	248.49
1,2-propanedistearate	2.5	220	61.9	3.76	357	6.90	250.39

Table 4.2 The yield of the synthetic diesters

	Yield (%)	
	1,2-ethanediol	1,2-propanediol
Lauric acid	81.72	89.64
Myristic acid	78.26	86.98
Palmitic acid	90.62	81.76
Stearic acid	77.39	85.05

4.2 Esterification of myristic acid with 1,2-ethanediol

The esterification was carried out by reacting myristic acid with 1,2-ethanediol at 110°C for 4 hours. The product, 1,2-ethanedimyristate was obtained as a waxy solid in 78.26 % yield with melting point 57.5°C according to the reaction shown below.



myristic acid 1,2-ethanediol 1,2-ethanedimyristate water

where :

$$R = C_{13}H_{27}$$

The product was characterized by ^{13}C-NMR and FTIR spectroscopy and their spectra were shown in Figures A8 and B8, respectively. From Figure A8, ^{13}C-NMR indicated the important peaks of $C=O$ and $-CH_2-O-$ of diester at 174 and 62.5 ppm, respectively, while the peak of carboxyl group of fatty acid at 180 ppm disappeared. Figure B8, FTIR spectrum demonstrated that the peak of $C=O$ (carbonyl group) shifted from 1705 (carboxyl group) to 1710 cm^{-1} (ester group) and the peak of $-\overset{|}{\underset{|}{C}}-O-$ at 1213 cm^{-1} (ester group) appeared. The thermal stability, the oxidation point and the oxidative compounds were analyzed by TGA analyzer and the curve was shown in Figure C2.

The physical and chemical properties of 1,2-ethanedimyristate were tabulated in Table 4.1. The yield of this synthetic diester was shown in Tabel 4.2.

4.3 Esterification of palmitic acid with 1,2-ethanediol

The esterification was carried out by reacting palmitic acid with 1,2-ethanediol at 110°C for 4 hours. The product, 1,2-ethanedipalmitate was obtained as a waxy solid in 90.62% yield with melting point 67.2°C according to the reaction shown below.

$$\underset{\text{palmitic acid}}{2RCOOH} + \underset{\text{1,2-ethanediol}}{HOCH_2CH_2OH} \rightleftharpoons \underset{\text{1,2-ethanedipalmitate}}{R-\overset{O}{\overset{\|}{C}}-O-CH_2CH_2-O-\overset{O}{\overset{\|}{C}}-R} + \underset{\text{water}}{2H_2O}$$

where :

$$R = C_{15}H_{31}$$

The product was characterized by ^{13}C-NMR and FTIR spectroscopy and their spectra were shown in Figures A9 and B9, respectively. From Figure A9, ^{13}C-NMR indicated the important peaks of $C=O$ and $-CH_2-O-$ of diester at 174 and 62.5 ppm, respectively, while the peak of carboxyl group of fatty acid at 180 ppm disappeared. Figure B9, FTIR spectrum demonstrated that the peak of C= O (carbonyl group) shifted from 1705 (carboxyl group) to 1725 cm^{-1} (ester group) and the peak of $-\overset{|}{\underset{|}{C}}-O-$ at 1218 cm^{-1} (ester group) appeared. The thermal stability, the oxidation point and the oxidative compounds were analyzed by TGA analyzer and the curve was shown in Figure C3.

The physical and chemical properties of 1,2-ethanedipalmitate were tabulated in Table 4.1. The yield of this synthetic diester was shown in Table 4.2.

4.4 Esterification of stearic acid with 1,2-ethanediol

The esterification was carried out by reacting stearic acid with 1,2-ethanediol at 110°C for 4 hours. The product, 1,2-ethanedistearate was obtained as a waxy solid in 77.39% yield with melting point 68.7°C according to the reaction shown below.

$$\underset{\text{stearic acid}}{2RCOOH} + \underset{\text{1,2-ethanediol}}{HOCH_2CH_2OH} \rightleftharpoons \underset{\text{1,2-ethanedistearate}}{R-\overset{O}{\overset{\|}{C}}-O-CH_2CH_2-O-\overset{O}{\overset{\|}{C}}-R} + \underset{\text{water}}{2H_2O}$$

where :

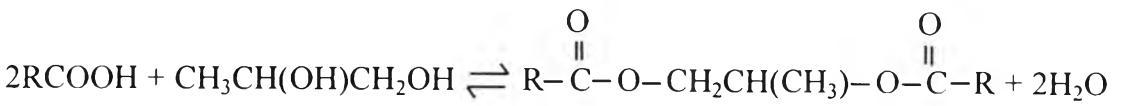
$$R = C_{17}H_{35}$$

The product was characterized by ^{13}C-NMR and FTIR spectroscopy and their spectra were shown in Figures A10 and B10, respectively. From Figure A10, ^{13}C-NMR indicated the important peak of C =O and $-CH_2-O-$ of diester at 173.8 and 62 ppm, respectively, while the peak of carboxyl group of fatty acid at 180 ppm disappeared. Figure B10, FTIR spectrum demonstrated that the peak of C=O (carbonyl group) shifted from 1710 (carboxyl group) to 1725 cm^{-1} (ester group) and the peak of $-\overset{|}{\underset{|}{C}}-O-$ at 1213 cm^{-1} (ester group) appeared. The thermal stability, the oxidation point and the oxidative compounds were analyzed by TGA analyzer and the curve was shown in Figure C4.

The physical and chemical properties of 1,2-ethanedistearate were tabulated in Table 4.1. The yield of this synthetic diester was shown in Table 4.2.

4.5 Esterification of lauric acid with 1,2-propanediol

The esterification was carried out by reacting lauric acid with 1,2-propanediol at 110°C for 4 hours. The product, 1,2-propanedilaurate was obtained as a viscous liquid in 89.64% yield according to the reaction shown below.



lauric acid 1,2-propanediol 1,2-propanedilaurate water

where :

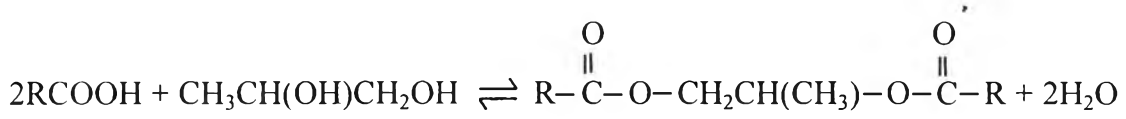
$$R = C_{11}H_{23}$$

The product was characterized by ^{13}C-NMR and FTIR spectroscopy and their spectra were shown in Figures A11 and B11, respectively. From Figure A11, ^{13}C-NMR indicated the important peak of $C=O$, $-CH_2-O-$ and $-\underset{|}{CH}-O-$ of diester group at 173, 66 and 68 ppm, respectively, while the peak of carboxyl group of fatty acid at 180 ppm disappeared. Figure B11, FTIR spectrum demonstrated that the peak of $C=O$ (carbonyl group) shifted from 1710 (carboxyl group) to 1730 cm^{-1} (ester group) and the peak of $-\underset{|}{C}-O-$ at 1213 cm^{-1} (ester group) appeared. The thermal stability, the oxidation point and the oxidative compounds were analyzed by TGA analyzer and the curve was shown in Figure C5.

The physical and chemical properties of 1,2-propanedilaurate were tabulated in Table 4.1. The yield of this the synthetic diester was shown in Table 4.2.

4.6 Esterification of myristic acid with 1,2-propanediol

The esterification was carried out by reacting myristic acid with 1,2-propanediol at 110°C for 4 hours. The product, 1,2-propanedimyristate was obtained as a waxy solid in 86.98% yield with melting point 41.5°C according to the reaction shown below.



$$2RCOOH + CH_3CH(OH)CH_2OH \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-O-CH_2CH(CH_3)-O-\overset{O}{\overset{\|}{C}}-R + 2H_2O$$

myristic acid 1,2-propanediol 1,2-propanedimyristate water

where :

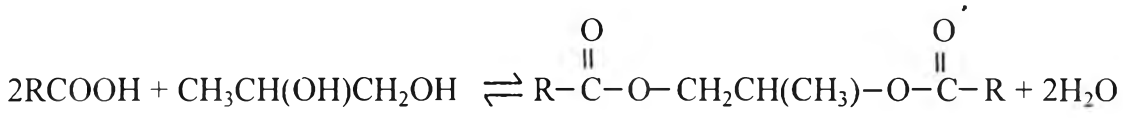
$$R = C_{13}H_{27}$$

The product was characterized by ^{13}C-NMR and FTIR spectroscopy and their spectra were shown in Figures A12 and B12, respectively. From Figure A12, ^{13}C-NMR indicated the important peaks of $C=O$, $-CH_2-O-$ and $-\underset{|}{CH}-O-$ of diester group at 173, 66 and 68 ppm, respectively, while the peak of carboxyl group of fatty acid at 180 ppm disappeared. Figure B12, FTIR spectrum demonstrated that the peak of $C=O$ (carbonyl group) shifted from 1705 (carboxyl group) to 1736 cm^{-1} (ester group) and the peak of $-\underset{|}{C}-O-$ at 1208 cm^{-1} (ester group) appeared. The thermal stability, the oxidation point and the oxidative compounds were analyzed by TGA analyzer and the curve was shown in Figure C6.

The physical and chemical properties of 1,2-propanedimyristate were tabulated in Table 4.1. The yield of this synthetic diester was shown in Table 4.2.

4.7 Esterification of palmitic acid with 1,2-propanediol

The esterification was carried out by reacting palmitic acid with 1,2-propanediol at 110°C for 4 hours. The product, 1,2-propanedipalmitate was obtained as a waxy solid in 81.76% yield with melting point 52.6°C according to the reaction shown below.



palmitic acid 1,2-propanediol 1,2-propanedipalmitate water

where :

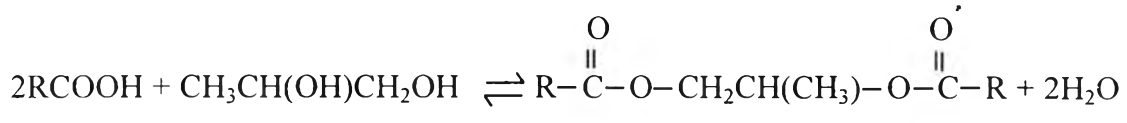
$$R = C_{15}H_{31}$$

The product was characterized by ^{13}C-NMR and FTIR spectroscopy and their spectra were shown in Figures A13 and B13, respectively. From Figure A13, ^{13}C-NMR indicated the important peaks of C = O, $-CH_2-O-$ and $-\underset{|}{CH}-O-$ of diester group at 173, 66 and 68 ppm, respectively, while the peak of carboxyl group of fatty acid at 180 ppm disappeared. Figure B13, FTIR spectrum demonstrated that the peak of C =O (carbonyl group) shifted from 1705 (carboxyl group) to 1725 cm^{-1} (ester group) and the peak of $-\underset{|}{C}-O-$ at 1218 cm^{-1} (ester group) appeared. The thermal stability, the oxidation point and the oxidative compounds were analyzed by TGA analyzer and the curve was shown in Figure C7.

The physical and chemical properties of 1,2-propanedipalmitate were tabulated in Table 4.1. The yield of this synthetic diester was shown in Table 4.2.

4.8 Esterification of stearic acid with 1,2-propanediol

The esterification was carried out by reacting stearic acid with 1,2-propanediol at 110°C for 4 hours. The product, 1,2-propanedistearate was obtained as a waxy solid in 85.05% yield with melting point 61.90°C according to the reaction shown below.



stearic acid 1,2-propanediol 1,2-propanedistearate water

where :

$$R = C_{17}H_{35}$$

The product was characterized by ^{13}C-NMR and FTIR spectroscopy and their spectra were shown in Figures A14 and B14, respectively. From Figure A14, ^{13}C-NMR indicated the important peaks of C = O, $-CH_2-O-$ and $-\underset{|}{CH}-O-$ of diester group at 173, 66 and 68 ppm, respectively, while the peak of carboxyl group of fatty acid at 180 ppm disappeared. Figure B14, FTIR spectrum demonstrated that the peak of C = O (carbonyl group) shifted from 1710 (carboxyl group) to 1730 cm^{-1} (ester group) and the peak of $-\underset{|}{C}-O-$ at 1213 cm^{-1} (ester group) appeared. The thermal stability, the oxidation point and the oxidative compounds were analyzed by TGA analyzer and the curve was shown in Figure C8.

The physical and chemical properties of 1,2-propanedistearate were tabulated in Table 4.1. The yield of this synthetic diester was shown in Table 4.2.

From the results in Table 4.1, it could be seen that the ethylene glycol fatty acid esters with increasing molecular weight due to various fatty acid (C_{12} - C_{18}) used, also increased the flash points and the melting points. Moreover, all of these synthetic diesters had good thermal and oxidation stabilities.

These synthetic diesters were used as lubricant additives by blending with the base oils. The properties of the lubricants in Table 4.3 indicated that the diesters had no effect on the pour point and the flash point of the base oils. However, it increased the viscosity index at the weight ratio of 120:3>120:2>120:1.

The results also indicated that they could be used to reduce foam formation in the base oils. Particularly, at the weight ratio of 120:3, it was the weight ratio that suitable to be used as an antifoaming agent in lubricants. The results were within specification of the Thai Industrial Standards which were demonstrated below:

Sequence (cm^3/cm^3)	I	II	III
Foaming (ASTM 892) (Foaming tendency/foaming stability)	≤25/0	≤150/0	≤25/0

These synthetic diesters could be used as lubricating agent with antifoaming property. They had the ester functionality which was biodegradable and low toxicity. Therefore, it could be used to replace commercial silicone antifoaming agent such as polydimethylsiloxane.

Table 4.3 The properties of the lubricants

	Color, ASTM	Flash Point, °C	Pour Point, °C	Kinematic Viscosity at 40°C, cSt	Kinematic Viscosity at 100°C, cSt	Viscosity Index	Foaming		
							Sequence I	Sequence II	Sequence III
1. base oil	0.5	252	-9	78.796	9.514	97.075	140/0	30/0	100/0
2. base oil : diester 1*									
- 120 : 3	0.5	256	-6	72.396	9.175	101.459	25/0	15/0	25/0
- 120 : 2	0.5	256	-9	73.231	9.198	100.350	35/0	20/0	25/0
- 120 : 1	0.5	260	-9	76.416	9.419	99.219	35/0	30/0	45/0
3. base oil : diester 2*									
- 120 : 3	0.5	254	-6	72.369	9.266	103.621	30/0	25/0	5/0
- 120 : 2	0.5	254	-6	74.710	9.362	101.138	30/0	40/0	5/0
- 120 : 1	0.5	254	-9	77.023	9.436	98.513	40/0	40/0	10/0
4. base oil : diester 3*									
- 120 : 3	0.5	256	-6	75.232	9.362	100.131	15/0	15/0	10/0
- 120 : 2	0.5	254	-9	76.652	9.453	99.506	50/0	15/0	15/0
- 120 : 1	0.5	256	-9	79.263	9.520	96.403	60/0	20/0	20/0
5. base oil : diester 4*									
- 120 : 3	0.5	252	-6	74.301	9.314	100.852	25/0	25/0	15/0
- 120 : 2	0.5	252	-9	75.228	9.387	100.697	35/0	25/0	25/0
- 120 : 1	0.5	262	-9	77.232	9.475	98.955	60/0	25/0	25/0

* diester 1 = 1,2-ethanedilaurate diester 3 = 1,2-ethanedipalmitate
diester 2 = 1,2-ethanedimyristate diester 4 = 1,2-ethanedistearate

Table 4.3 (Continued)

	Color, ASTM	Flash Point, °C	Pour Point, °C	Kinematic Viscosity at 40°C, cSt	Kinematic Viscosity at 100°C, cSt	Viscosity Index	Foaming		
							Sequence I	Sequence II	Sequence III
6. base oil : diester 5*									
- 120 : 3	0.5	252	-9	72.354	9.228	102.773	30/0	15/0	15/0
- 120 : 2	0.5	254	-9	74.008	9.262	100.245	50/0	20/0	20/0
- 120 : 1	0.5	252	-9	76.144	9.403	99.364	30/0	25/0	50/0
7. base oil : diester 6*									
- 120 : 3	0.5	252	-9	73.023	9.223	101.304	25/0	15/0	10/0
- 120 : 2	0.5	254	-9	74.741	9.338	100.538	25/0	20/0	15/0
- 120 : 1	0.5	252	-9	76.521	9.445	99.570	90/0	25/0	75/0
8. base oil : diester 7*									
- 120 : 3	0.5	256	-6	74.615	9.345	100.940	15/0	20/0	10/0
- 120 : 2	0.5	256	-9	75.683	9.423	100.629	50/0	25/0	15/0
- 120 : 1	0.5	256	-9	76.918	9.452	99.025	60/0	20/0	40/0
9. base oil : diester 8*									
- 120 : 3	0.5	256	-6	74.574	9.284	99.669	25/0	25/0	15/0
- 120 : 2	0.5	256	-9	75.809	9.377	99.414	35/0	25/0	25/0
- 120 : 1	0.5	252	-9	76.918	9.451	99.005	60/0	15/0	70/0

* diester 1 = 1,2-propanedilaurate diester 3 = 1,2-propanedipalmitate
diester 2 = 1,2-propanedimyrista diester 4 = 1,2-propanedistearate