CHAPTER IV

RESULTS AND DISCUSSION

Reaction of monobasic carboxylic acids (e.g. heptanoic acid, octanoic acid, 2-ethyl-hexanoic acid and nonanoic acid) with polyhydric alcohols (e.g. neopentyl glycol, trimethylol propane and pentaerythritol) in toluene (azeotropic agent) using concentrated sulfuric acid as a catalyst, give polyol ester in good yield [Table 4-1, 4-2 and 4-3]. The optimum conditions for esterification of each carboxylic acid and each polyhydric alcohol were obtained at 130 ^{0}C, 3 hours and the percent catalyst was between 0.5 to 1.0 % by weight of acid. Characterization of polyol ester products were determined by ^{13}C-NMR and FTIR analyses [Table 4-4, 4-5 and 4-6].

The optimum conditions for the esterification reaction of monobasic acids with polyhydric alcohols are summarized in Table 4-1, 4-2 and 4-3.

The results from Table 4-1 indicated that the esterification of each carboxylic acid with neopentyl glycol are completed at temperature of 130 ^{0}C, reaction time of 3 hours and 0.5 % catalyst. Under this condition, the yield of neopentyl glycol esters are higher than 90 %.

The results from Table 4-2 indicated that the esterification of each carboxylic acids with trimethylol propane are completed at temperature of 130 ^{0}C, reaction time of 3 hours and 0.5 % catalyst, excepted trimethylol propane tris(2-ethyl-hexanoate) which needed 1.0 % of catalyst. In this study, the yield of each product is about 90 %.

Table 4-1: The optimum condition for synthesis of neopentyl glycol ester products.

Raw material	Reaction temperature (°C)	Reaction time (hr.)	% Catalyst (H_2SO_4)	Yield (%)
heptanoic acid	130	3	0.5	93.76
octanoic acid	130	3	0.5	93.31
nonanoic acid	130	3	0.5	91.51
2-ethyl-hexanoic a	130	3	0.5	90.48

Table 4-2: The optimum condition for synthesis of trimethylol propane ester products.

Raw material	Reaction temperature (°C)	Reaction time (hr.)	% Catalyst (H_2SO_4)	Yield (%)
heptanoic acid	130	3	0.5	91.40
octanoic acid	130	3	0.5	89.76
nonanoic acid	130	3	0.5	90.88
2-ethyl-hexanoic	130	3	1.0	89.79

Table 4-3: The optimum condition for synthesis of pentaerythritol ester products.

Raw material	Reaction temperature(°C)	Reaction time (hr.)	% Catalyst (H_2SO_4)	Yield (%)
heptanoic acid	130	3	1.0	93.65
octanoic acid	130	3	1.0	91.32
nonanoic acid	130	3	1.0	91.41
2-ethyl-hexanoic a	130	4.5	1.0	90.34

The results from Table 4-3 indicated that the optimum condition for synthesis of pentaerythritol ester products are completed at temperature of 130 ^{0}C, reaction time of 3 hours, excepted pentaerythritol tetrakis(2-ethyl-hexanoate) which required 4.5 hours. The percent catalyst is 1.0 %. In this study, the yield of each product is about 90 %.

The reaction of 2-ethyl-hexanoic acid with polyhydric alcohols (trimethylol propane and pentaerythritol) used more reaction time and more catalyst than other polyol ester, perhaps because of steric hindrance of branched acid.

As an example, neopentyl glycol was reacted with heptanoic acid under condition [Table 4-1] described in general procedure to obtain neopentyl glycol bis(heptanoate). The IR spectrum (Figure B8) indicated a C=O group at 1737 cm^{-1}. The OH stretching of neopentyl glycol disappeared which indicated completion of the reaction. ^{13}C-NMR spectrum (Figure A8) indicated a C=O ester group at 174 ppm. together with C-O group at 69 ppm.

Other polyol esters gave similar spectroscopic properties and those properties were tabulated in Table 4-4, 4-5 and 4-6.

The physical and chemical properties of the polyol esters are summarized in Table 4-7.

The results from Table 4-7, indicated that polyol esters made from the linear acids have higher viscosity indices, flash points, oxidation points and pour points than corresponding esters made from branched chain acid. Increasing chain length of straight chain acids gave polyol esters with increasing viscosity, viscosity index, flash point and oxidation point.

The number of hydroxyl groups of the polyol available for esterification also has effect on viscosity of the ester. In general, the more the hydroxyl groups the polyols have the higher the viscosity, flash point and oxidation point of polyol esters. It could be summarized as the following :

Pentaerythritol ester > Trimethylolpropane ester > Neopenthyl glycol ester

Table 4-4: Spectroscopic properties of neopentyl glycol esters

Neopentyl glycol ester of	FTIR (Wave number)		^{13}C-NMR (Chemical shift, ppm.)
	C=O str. cm^{-1}.	C-O str. cm^{-1}.	
heptanoic acid	1737	1175	174, 69, 34.5, 34, 31, 29, 25, 22, 21, 13.5
octanoic acid	1729	1168	174, 69, 34.5, 34, 31, 29, 24, 22, 21, 14
nonanoic acid	1745	1106	173, 69, 35, 32, 29, 25, 23, 22, 13
2-ethyl-hexanoic a.	1740	1176	176, 69, 48, 35, 32, 30, 26,23, 22, 14, 12

Table 4-5: Spectroscopic properties of trimethylol propane esters

Trimethylol propane ester of	FTIR (Wave number)		^{13}C-NMR (Chemical shift, ppm.)
	C=O str. cm^{-1}.	C-O str. cm^{-1}.	
heptanoic acid	1746	1156	173, 63.5, 41, 34, 31.5, 29, 25, 23, 22, 14, 7
octanoic acid	1745	1175	174, 64, 40.5, 34, 32, 29, 25, 23, 22, 14, 7
nonanoic acid	1752	1159	173.5, 63.5, 41, 35, 32, 29, 26, 23, 14, 7
2-ethyl-hexanoic a.	1740	1175	176, 63, 58, 41, 31, 29, 25, 23, 14, 12, 7

Table 4-6: Spectroscopic properties of pentaerythritol esters

Pentaerythritol ester of	FTIR (Wave number)		^{13}C-NMR (Chemical shift, ppm.)
	C=O str. cm^{-1}.	C-O str. cm^{-1}.	
heptanoic acid	1746	1175	173, 62, 42, 35, 31, 29, 25, 23, 14
octanoic acid	1737	1168	174, 62, 42, 34, 32, 28, 25, 23, 14
nonanoic acid	1737	1106	173, 63.5, 41, 34, 32, 29, 25, 23, 14
2-ethyl-hexanoic a.	1745	1176	175, 61, 47, 42, 32, 29, 25, 23, 14, 12

Table 4-7:The physical and chemical properties of polyolesters

properties	Polyol ester 1	Polyol ester 2	Polyol ester 3	Polyol ester 4	Polyol ester 5	Polyol ester 6	Polyol ester 7	Polyol ester 8	Polyol ester 9	Polyol ester 10	Polyol ester 11	Polyol ester 12
Color, ASTM	1	1	1	1.5	1	1.5	1.5	2	1.5	2	2	2.5
Pour Point,°C	-50>	-20	-26	-50>	-50>	-50>	-50>	-50>	-8	-4	-1	-11
Kinematic Viscosity												
@ 40 °C	6.29	6.94	9.43	7.35	13.45	17.75	20.60	14.70	19.96	26.80	35.10	44.80
@ 100 °C	2.03	2.19	2.70	2.01	3.40	4.11	4.62	3.33	4.24	5.21	6.34	6.39
Viscoity Index	119	126	130	44	130	136	146	93	122	128	133	88
Flash Point, °C	203	212	218	198	242	260	268	233	261	280	293	245
Oxidation Point, °C	307	350	360	325	375	382	420	360	410	460	480	390
OxidativeCompounds,%wt	0.42	3.74	7.50	0.73	2.61	6.28	9.43	1.02	9.00	5.23	3.52	13.09

Polyol Ester 1 : Neopentyl glycol bis(heptanoate)
Polyol Ester 2 : Neopentyl glycol bis(octanoate)
Polyol Ester 3 : Neopentyl glycol bis(nonanoate)
Polyol Ester 4 : Neopentyl glycol bis(2-ethyl hexanoate)
Polyol Ester 5 : Trimethylol propane tris(heptanoate)
Polyol Ester 6 : Trimethylol propane tris(octanoate)
Polyol Ester 7 :Trimethylol propane tris(nonanoate)
Polyol Ester 8 :Trimethylol propane tris(2-ethyl- hexanoate)
Polyol Ester 9 : Pentaerythritol tetrakis(heptanoate)
Polyol Ester 10 :Pentaerythritol tetrakis(octanoate)
Polyol Ester 11 :Pentaerythritol tetrakis(nonanoate)
Polyol Ester 12 :Pentaerythritol tetrakis(2-ethyl-hexanoate)

Therefore, from this study it would be able to select appropriate polyol esters for the specific application. For example, polyol ester base on trimethylol propane may be good candidate for refrigeration oils as their properties are comparable to those of commercial refrigeration oils shown in Table 4 -8 and 4 -9.

Table 4-8 :The physical and chemical properties of commercial refrigeration oils (Castrol Icematic Series).

GRADE	Density @ 15 °C	Viscosity @ 40 °C cSt.	Viscosity @ 100 °C cSt.	VI	Flash point °C	Pour point °C
ICEMATIC 44	0.875	12.5	2.80	44	156	-45
ICEMATIC 66	0.880	31.7	4.69	41	165	-36
ICEMATIC 99	0.895	68.0	7.40	55	192	-30
ICEMATIC 266	0.910	29.5	4.10	-	165	-54
ICEMATIC 299	0.920	55.5	5.94	7	183	-54
ICEMATIC 2284	0.860	63.6	6.50	15	186	-70

Table 4-9 : The physical and chemical properties of commercial refrigeration oils (Castrol Icematic SW Series).

GRADE	Density @ 15 °C	Viscosity @ 40 °C cSt.	Viscosity @ 100 °C cSt.	VI	Flash point °C	Pour point °C
ICEMATIC SW 22	0.995	22.0	4.70	132	230	-60
ICEMATIC SW 32	0.995	32.0	5.70	118	245	-54
ICEMATIC SW 46	0.979	44.9	6.90	110	254	-42
ICEMATIC SW 68	0.965	68.0	8.80	101	250	-39
ICEMATIC SW 100	0.965	100.0	11.4	98	255	-30
ICEMATIC SW 150	0.975	150.0	15.1	99	260	-29
ICEMATIC SW 220	0.980	220.0	19.3	99	290	-26

It can be seen from Table 4-8 and 4-9 that the physical and chemical properties of commercial refrigeration oils vary to a large extent. Viscosity index can vary from 7 to 132 while pour point varies from -26 to -70 ^{0}C. Therefore, it is likely to find suitable applications for polyol esters obtained from this study. For example, neopentyl glycol bis(2-ethyl-hexanoate) may find applications applied to those of Icematic 44 and Icematic 66. Similarly, trimethylolpropane tris(2-ethyl-hexanoate) may find applications in the area of Icematic SW series. However, some properties may have to be adjusted using suitable additives before they can be used in industry.