

CHAPTER III
EXPERIMENTAL



Chemicals

1. Palm oil (commercial grade) was obtained from Pamolar.
2. Lubricating base oil (150SN) was obtained from Nippon Kaiji Kentei Kyokai.
3. 2-Ethyl-1-hexanol (analytical grade) was obtained from Fluka.
4. 1-Hexanol (analytical grade) was obtained from Fluka.
5. Cyclohexanol (analytical grade) was obtained from Fluka.
6. 1-Butanol (analytical grade) was obtained from Fluka.
7. Sulfuric acid (98 % ; analytical grade) was obtained from J.T.Baker.
8. Acetic acid (99.8 % ; Glacial) was obtained from Riedel-de Haen AG.
9. Hydrogen peroxide (30 Gew. %) was obtained from Fluka.
10. Diethyl ether (reagent grade) was obtained from J.T.Baker.
11. Sodium sulfate anhydrous (reagent grade) was obtained from Fluka.
12. Sodium hydrogen carbonate (reagent grade) was obtained from Fluka.
13. 3% Pt on alumina was obtained from United Catalyst Inc.
14. Hydrogen gas (purity 99.5 % minimum ; industrial grade) was obtained from T.I.G. Trading Ltd.

Apparatus and Instruments

1. Fourier-Transform NMR spectrometer : Model AC-F200 (200 MHz), Bruker Spectrospin
2. Fourier-Transform IR spectrometer : Model 1760X, Perkin Elmer
3. Gas Chromatography-Mass Spectrometer : Model MD-800 equipped with a 8000 series GC, Fison Instruments
4. High pressure reactor : Consisting of high pressure batch stirred autoclave model 4561 and a temperature controller model 4841, Parr Instrument Company
5. Colourimeter : The Fisher ASTM (D 1500)
6. Viscometer : Model K-234 A, Hochler Instrument Co., Inc.
7. Pour Point Tester : Model A82, HAKKE
8. Flash Point Tester : Model Cleveland semi-automatic
9. Thermogravimetric Analyzer : Model STA 490 C, Netzsch

Experimental Procedure

1. Transesterification of palm oil

1.1 **General Procedure** In transesterification process, concentrated sulfuric acid (5% by volume of alcohol) and 0.6 mole of an alcohol (The alcohol was varied such as 1-Butanol, 1-Hexanol, Cyclohexanol, and 2-Ethyl-1-hexanol, respectively.) were mixed in 500 ml two necked glass round-bottomed flask, equipped with a magnetic stirrer. Stirred until the mixture was dissolved, 100 g (0.118 mole) of palm oil was added and the flask was

fitted with a condenser and a thermometer. The flask is placed in an oil-bath at various temperatures varying from 70, 80, and 90 °C respectively to select a suitable reaction with continuous stirring for 1-4 hours. The reaction mixture was allowed to cool to room temperature and then the excess acid was neutralized with saturated sodium bicarbonate solution. The mixture was dissolved in diethyl ether and extracted with distilled water (to remove glycerol) in a 500-ml separatory funnel. After removal of the aqueous layer, the organic layer was dried with anhydrous sodium sulfate. Next the diethyl ether was evaporated and the excess alcohol was distilled under reduced pressure. The yield of monoester product was determined by weighing.

1.2. Determination of physical and chemical properties of monoester products

1.2.1 Physical properties

1.2.1.1 Color, ASTM	by ASTM D 1500
1.2.1.2 Kinematic viscosity	by ASTM D 445
1.2.1.3. Viscosity index	by ASTM D 2270
1.2.1.4. Pour point	by ASTM D 97
1.2.1.5. Flash point	by ASTM D 92

1.2.2 Chemical properties

1.2.2.1 The characteristics of monoester products were determined by ¹³C-NMR, and GC-MS.

GC-MS condition

Column : DB-1 Capillary column
30m x 0.25 ID x 0.25 μ m
Carrier gas : Helium, 40 mm/sec
Oven : 80 to 200 $^{\circ}$ C(2 min) rate 25 $^{\circ}$ C/min
200 to 275 $^{\circ}$ C(2 min) rate 5 $^{\circ}$ C/min
Injection temperature : 250 $^{\circ}$ C
Detector : MS (EI⁺ 70) ev

1.2.2.2 The oxidation point and the percentages of oxidative compounds were determined by TGA method under air atmosphere.

TGA condition

Heating rate : 5 $^{\circ}$ C/min
Temperature range : Ambient to 650 $^{\circ}$ C
Atmosphere : Dynamic air 100 ml/min
Reference : Al₂O₃

2. Hydrogenation process

2.1 General Procedure The monoester (300 g), obtained from experimental procedure 1 at optimum operating condition, and the platinum on alumina catalyst (12 g) were charged into the stainless steel reactor. The reactor was then closed and split ring closures were moved into the position from the sides and cap screws were tightened. The gas in the reactor was replaced by purging hydrogen gas and a gas release valve was opened. After

charging for 2 to 3 minutes, a gas release valve was closed and then hydrogen gas was fed until the pressure of the reactor reached working pressure.

The reactor was placed in the heating unit and a thermocouple was inserted into a thermowell. Water was passed into the cooling channel. A power button were switched on. The desired reaction temperature and reaction time were set by the controller. The motor stirring and heater were switched on and then the stirring speed was adjusted to 350 rpm.

After the reaction took place, the heater was switched. When the reaction temperature reached 50 °C, a thermocouple was pulled out and the motor stirring was stopped. Then a gas release valve was opened and the pressure was reduced to atmospheric pressure. Finally, the hydrogenated oil was transferred to a beaker and the catalyst was separated from the mixture by filtering with a Whatman filter No.1. The yield of hydrogenated oil was determined by weighing.

2.2 Determination of physical and chemical properties of hydrotreated oil

2.2.1 Physical properties

2.2.1.1 Color, ASTM by ASTM D 1500

2.2.1.2 Kinematic viscosity by ASTM D 445

2.2.1.3. Viscosity index by ASTM D 2270

2.2.1.4. Pour point by ASTM D 97

2.2.1.5. Flash point by ASTM D 92

2.2.2 Chemical properties

2.2.2.1 The characteristics of hydrogenated oils were determined by ^{13}C -NMR, and GC-MS.

GC-MS condition

Column : DB-1 Capillary column

30m x 0.25 ID x 0.25 μm

Carrier gas : Helium, 40 mm/sec

Oven : 80 to 200 $^{\circ}\text{C}$ (2 min) rate 25 $^{\circ}\text{C}/\text{min}$

200 to 275 $^{\circ}\text{C}$ (2 min) rate 5 $^{\circ}\text{C}/\text{min}$

Injection temperature : 250 $^{\circ}\text{C}$

Detector : MS (EI^+ 70) ev

1.2.2.2 The oxidation point and the percentages of oxidative compounds were determined by TGA method under air atmosphere.

TGA condition

Heating rate : 5 $^{\circ}\text{C}/\text{min}$

Temperature range : Ambient to 650 $^{\circ}\text{C}$

Atmosphere : Dynamic air 100 ml/min

Reference : Al_2O_3

3. Hydroxylation of Alkenes

3.1 General Procedure The process consists of two distinct processes : peroxidation of carbon-carbon double bonds and acid-catalyzed

cleavage of epoxides. Acetic acid (99.8 %, 300 ml; 6 mol) and 70 ml (0.62 mol) of 30 % hydrogen peroxide were placed in a 500-ml three necked glass round bottomed flask, equipped with a magnetic stirrer, a thermometer, and a condenser. The mixture was stirred between 60 and 70°C for 4 hours and then allowed to stand overnight at room temperature. The monoester obtained from experimental procedure 1 at optimum operating condition was slowly introduced from dropping funnel and the temperature of the reaction mixture was maintained between 20 and 25°C by cooling with an ice bath for 4-6 hours. The reaction mixture was then heated up and stirred at 60°C for 1-2 hours. The mixture was dissolved in diethyl ether and extracted with distilled water (to remove most of acetic acid) in a 500-ml separatory. After removal of the aqueous layer, the organic layer was dried with anhydrous sodium sulfate. Next the diethyl ether was distilled under reduced pressure. The yield of the product was determined by weighing.

3.2 Determination of physical and chemical properties from hydroxylation of alkenes

3.2.1 Physical properties

3.2.1.1 Color, ASTM	by ASTM D 1500
3.2.1.2 Kinematic viscosity	by ASTM D 445
3.2.1.3. Viscosity index	by ASTM D 2270
3.2.1.4. Pour point	by ASTM D 97
3.2.1.5. Flash point	by ASTM D 92

3.2.2 Chemical properties

3.2.2.1 The characteristics of monoester products were determined by ^{13}C -NMR, and GC-MS.

GC-MS condition

Column : DB-1 Capillary column

30m x 0.25 ID x 0.25 μm

Carrier gas : Helium, 40 mm/sec

Oven : 80 to 200 $^{\circ}\text{C}$ (2 min) rate 25 $^{\circ}\text{C}/\text{min}$

200 to 275 $^{\circ}\text{C}$ (2 min) rate 5 $^{\circ}\text{C}/\text{min}$

Injection temperature : 250 $^{\circ}\text{C}$

Detector : MS (EI^+ 70) ev

3.2.2.2 The oxidation point and the percentages of oxidative compounds were determined by TGA method under air atmosphere.

TGA condition

Heating rate : 5 $^{\circ}\text{C}/\text{min}$

Temperature range : Ambient to 650 $^{\circ}\text{C}$

Atmosphere : Dynamic air 100 ml/min

Reference : Al_2O_3

4. Blending

4.1 Procedure 15 ml (3% by volume of lubricating base oil) of butyl monoester and 485 ml of lubricating base oil, 150SN, were mixed in a 1 l beaker equipped with a mechanical stirrer. The mixture was stirred until

dissolved. Then the mixture was transferred to the bottle. The quantity of butyl-monoester was varied from 3 to 30 % by volume of lubricating base oil.

4.2 Determination of physical and chemical properties from blending

4.2.1 Physical properties

4.2.1.1 Color, ASTM	by ASTM D 1500
4.2.1.2 Kinematic viscosity	by ASTM D 445
4.2.1.3. Viscosity index	by ASTM D 2270
4.2.1.4. Pour point	by ASTM D 97
4.2.1.5. Flash point	by ASTM D 92

4.2.2 Chemical properties

4.2.2.1 The oxidation point and the percentages of oxidative compounds were determined by TGA method under air atmosphere.

TGA condition

Heating rate	: 5 °C/min
Temperature range	: Ambient to 650 °C
Atmosphere	: Dynamic air 100 ml/min
Reference	: Al ₂ O ₃

Note : Flash point and chemical properties were observed from the sample, with the best physical properties except flash point.