

CHAPTER 3

EXPERIMENTAL

3.1 Apparatus and Chemicals

1.1 Chemicals

1. Light distillate was obtained from Fang Oil Refinery.
2. Chlorinated paraffins was a gift from Thai Plastic and Chemical Co., Ltd.
3. 3 % Platinum on alumina was obtained from United Catalysts Inc., U.S.A.
4. Chlorine gas, nitrogen gas and hydrogen gas were obtained from TIG Trading Ltd.
6. Aluminum chloride was obtained from anhydrous Fluka.
7. Silver nitrate was obtained from BDH.
8. Sodium metal was obtained from Ajak Chemical Ltd.
9. Ammonium ferric sulphate was obtained from Fluka.
10. Benzoyl peroxide was obtained from Fluka.
11. Potassium thiocyanate was obtained from Fluka.
12. Nitrobenzene was obtained from Fluka.
13. Fullers earth was obtained from Fluka.
14. Miscellaneous solvents were distilled before use.

3.1.2 Apparatus

1. Fourier-Transform NMR Spectrometer
model AC-F 200 (200 MHz), Bruker Spectrospin
2. Gas Chromatograph-Mass Spectrometer
MD 800, Fison Instruments
3. Thermogravimetric Analyzer
model TA30, Shimadzu
4. Hydrogenator
Consisting of a high pressure batch stirred autoclave model 4561 and a temperature controller model 4841 from the Parr Instrument Company.
5. Viscometer
model K-234 A, Hochler Instrument Co., Inc.
6. Pour point Tester
model A82, HAAKE
7. Sulfur Analyzer
model SLFA-800; HOBIRA
8. Colorimeter
The Fisher ASTM
9. Apparatus for chlorination
A round-bottomed flask was equipped with a mechanical stirrer, a thermometer, a gas inlet and a gas trap. Chlorine gas was premixed with nitrogen gas by three way which was connected with chlorinator. Flow rate of chlorine was adjusted at chlorinator.

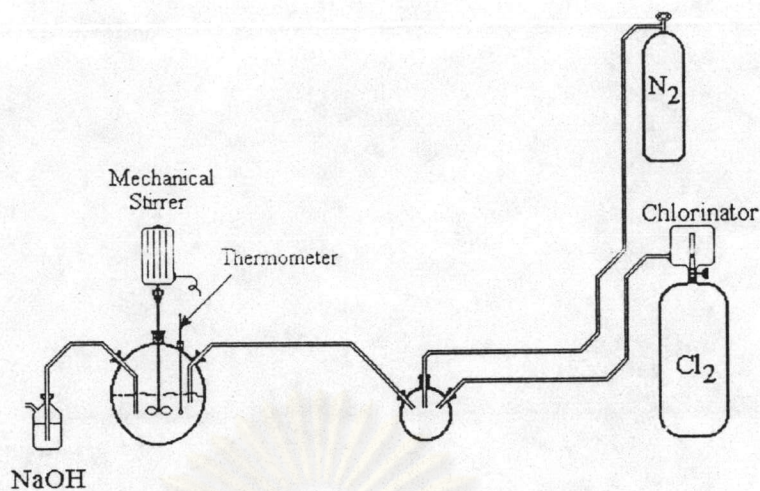


Figure 3.1 Apparatus for chlorination

9. Apparatus for alkylation

A round-bottomed flask was equipped with a Claisen connecting tube, a water-cooled condenser, a gas trap and an addition funnel.

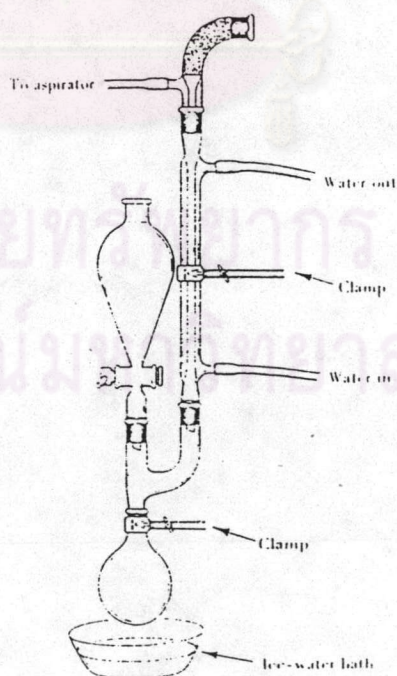


Figure 3.2 Apparatus for alkylation

3.2 Procedure

3.2.1 Dewaxing of Light Distillate by Methyl Ethyl Ketone

This process consists of three main segments: precipitation, filtration and solvent recovery. Precipitation began with slowly heating of light distillate (749 g) to temperature of 45 °C to completely melt wax before adding cooled methyl ethyl ketone (2700 ml). The ratio by volume between solvent and oil was 3:1. The solvent oil mixture was chilled to the dewaxing temperature of 0 °C by refrigeration. The wax crystals were then filtered through a buchner funnel under reduced pressure. The mixture was quickly filtered before the temperature had a chance to rise above 5 °C and allowed suction to continue for several minutes to completely remove oil from the wax. The filtrate was collected and the oil was recovered from the filtrate by simple distillation.

3.2.2 Determination of the Physical and Chemical Properties of Dewaxed Oil as follow :

Physical properties:

- | | |
|------------------------|----------------|
| 1. Color, Visual | by ASTM D 1500 |
| 2. Kinematic viscosity | by ASTM D 445 |
| 3. Viscosity index | by ASTM D 2270 |
| 4. Pour point | by ASTM D 97 |

Chemical properties:

1. The structure was characterized by ^{13}C -NMR (CDCl_3) and GC-MS.

Condition for GC:

Column : DB-1 Capillary column 30m x 0.25 ID x 0.25 μm

Carrier gas : Helium, 40 cm/sec

Oven : 80 °C (2min) to 300 °C (15 min) at rate 4 °C/min

Injection temperature : 290 °C

Condition for MS:

Positive electron impact 70 eV

2. The composition (%Cp, %Cn and %Ca) was determined by ^{13}C -NMR (CDCl_3)
3. The percentages of oxidative compounds were determined by Thermogravimetric Analyzer

Condition for TGA:

Sample weight : 9.5 mg

Sensitivity range : ± 5 mg

Heating rate : 5 °C/min

Temperature range : Ambient to 600 °C

Atmosphere : Air 100 ml/min

Chart speed : 1.25 mm/min

TD range : 10 mv/min

4. Sulfur content by ASTM D 129

3.2.3 Chlorination of Paraffin Oil and Dewaxed Oil

3.2.3.1 Effect of temperature on properties of chlorinated products from paraffin oil

A 500 mL rounded-bottom glass reactor was equipped with a mechanical stirrer, a thermometer, a gas inlet and a gas trap. Paraffin oil (250 g) and benzoyl peroxide (0.25 g) were charged into a reactor. They were pre-heated to 50 °C and then chlorine gas, mixed with nitrogen gas, was introduced, using flow rate of chlorine at 2.5 lb/24hrs. The silicone oil bath was used to maintain the temperature. The reaction was allowed for 6 hrs. The effect of reaction temperature on properties of products was studied by varying temperature at 60, 80, 100 and 120 °C, respectively.

3.2.3.2 Determination of the physical and chemical properties of chlorinated products from paraffin oil.

The viscosity of products was measured by viscometer. The structure were characterized by ^{13}C -NMR and GC-MS. The chlorine content was determined by two steps procedure. First, chlorinated products (0.5 g) were digested by sodium in methanol method. Chlorinated products were refluxed with methanol (30 ml), small pieces of sodium (10 g) were gradually added. After the sodium has dissolved, the reaction was allowed to continue for 30 mins. Then, water (20-40 mL) was added and methanol was distilled off. After that the volume of solution was made up to 100 ml. The amount of chlorine was determined by Volhard's back titration. Silver nitrate solution (0.1 M) was used as primary standard to standardize potassium thiocyanate solution (0.1 M). The chloride solution (10 ml) was transferred quantitatively to erlenmeyer flask, then silver nitrate solution (20 ml), nitric acid (3F, 5ml), and

erlenmeyer flask, then silver nitrate solution (20 ml), nitric acid (3F, 5ml), and ferric alum indicator (1 ml) were added. After shaking thoroughly, titrated with potassium thiocyanate solution with constant agitation, until a reddish-brown color appeared at the end point and the color must be permanent after strong shaking.

3.2.3.3 Effect of reaction time on properties of chlorinated products from paraffin oil and dewaxed oil

The paraffin oil and dewaxed oil were chlorinated by the same procedure as 3.2.3.1. The selected temperature was obtained from 3.2.3.1. The effect of reaction time on properties of products was studied by varying time from 3, 6, 9, 12 and 15 hrs, respectively.

3.2.3.4 Determination of the physical and chemical properties of chlorinated products from paraffin oil and dewaxed oil.

The procedures were the same as 3.2.3.2.

3.2.4. Alkylation of Chlorinated Paraffins with Toluene

Chlorinated paraffins from TPC were alkylated with toluene, using the ingredients listed in table 3.1, in the following manner. Anhydrous powdered aluminum chloride was placed in the flask and immediately covered with toluene. Chlorinated paraffins were dissolved in toluene and they were placed in the dropping funnel. An ice-water bath was prepared so that it would be ready to cool the reaction mixture. The water was turned on to the reflux condenser and then the solution of chlorinated paraffins was begun adding dropwise to the aluminum chloride. The reaction mixture was stirred by a

magnetic stirrer. After all chlorinated paraffins has been added, refluxed at 60 °C for 4 hrs. After that, the reaction was stopped by adding water slowly until all the aluminum chloride had been totally destroyed. The toluene layer was separated and evaporated at diminished pressure to yield the crude product which was distilled under reduced pressure.

Table 3.1 Amount of ingredients used in alkylating chlorinated paraffins

Mole ratio ^a	Chlorinated paraffins (g)	Toluene (g)	Aluminum chloride (g)
1:1	200	232	30
1:2	200	464	30
excess	200	excess	30

^a Mole ratio between chlorine content and toluene

3.2.5 Determination of the physical and chemical properties of alkylated products as follow:

Physical properties:

1. Color, Visual by ASTM D 1500
2. Kinematic viscosity by ASTM D 445
3. Viscosity index by ASTM D 2270
4. Pour point by ASTM D 97

Chemical properties:

1. The structure was characterized by ¹³C-NMR (CDCl₃)

3.2.6 Self-condensation of Chlorinated Paraffins with Anhydrous Aluminum Chloride.

The procedure of self-condensation of chlorinated paraffins from TPC and dewaxed light distillate oil was the same as 3.2.5 but toluene was substituted by hexane as solvent. The amount of anhydrous aluminum chloride was used only 5 % by weight of chlorinated paraffins.

3.2.7 Determination of the Physical and Chemical Properties of Self-condensed Products as follow:

Physical properties:

- | | |
|------------------------|----------------|
| 1. Color, Visual | by ASTM D 1500 |
| 2. Kinematic viscosity | by ASTM D 445 |
| 3. Viscosity index | by ASTM D 2270 |
| 4. Pour point | by ASTM D 97 |

Chemical properties:

1. The structure was characterized by ^{13}C -NMR (CDCl_3)

3.2.8 Hydrogenation

The dewaxed base oil (100 g) was charged into the reactor and platinum on alumina (6 g) was added. The reactor was then closed and split ring closurer were moved into the position from the sides and cap screws were tightened. Oxygen gas was removed from the reactor by feeding hydrogen gas and a gas release value was opened. After charging for 5 mins, a gas release value was closed. After that hydrogen gas was fed until the pressurs 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 and the desired temperature was setted at the temperature controller. The motor stirring and heater were switched on.

The reaction was allowed to continue for the specified time. After that the heater were switched off to stop the reaction. 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 to reduce the pressure. The hydrogenated oil was poured into a beaker. Finally, the catalyst was separated from the mixture by filtering with a Whatman filter No.1.

3.2.9 Determination of the Physical and Chemical Properties of the Hydrogenated Products

Physical properties:

1. Color, Visual by ASTM D 1500
2. Kinematic viscosity by ASTM D 445
3. Viscosity index by ASTM D 2270
4. Pour point by ASTM D 97

Chemical properties:

1. The structure was characterized by ^{13}C -NMR (CDCl_3) and GC-MS.

Condition for GC:

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Condition for TGA:

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Sensitivity range : ± 5 mg

Heating rate : 5 °C/min

Temperature range : Ambient to 600 °C

Atmosphere : Air 100 ml/min

Chart speed : 1.25 mm/min

TD range : 10 mv/min

4. Sulfur content by ASTM D 129

ศูนย์วิจัยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย