

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Materials

3.1.1 Used polyethylene (i.e. polyethylene bottle etc.).

3.1.2 Industrial hydrogen gas was obtained from TIG Trading Ltd..

3.1.3 Nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) was obtained from Baker Ltd..

3.1.4 Iron chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) was obtained from Merck.

3.1.5 Cobalt chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) was obtained from J.T.Baker.

3.1.6 Stannous chloride ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) was obtained from BDH Ltd..

3.1.7 Ammonium fluoride ( $\text{NH}_4\text{F}$ ) was obtained from BDH Ltd..

3.1.8 Hydrochloric acid was obtained from Baker Analyzed.

3.1.9 Methyl ethyl ketone was obtained from Merck.

3.1.10 Standard  $\text{C}_9$ - $\text{C}_{14}$ - $\text{C}_{16}$  hydrocarbons was obtained from TPI.

3.1.11 Molecular sieve supports (3A-EPG, 4A-DG and 13xPG type) were obtained from Union Carbide.

## **3.2 Apparatus and Instruments**

3.2.1 Micro Pore Sizer for measuring pore volume of molecular sieve support

The Micromeritics model ASAP 2000 was used.

3.2.2 Calcinator

The apparatus model GSM from Carbolite Furnaces was used.

3.2.3 Gas Chromatography (GC)

The apparatus model HP 5890 SERIES II was used.

GC conditions

Column : DB-1 capillary column 30m x 0.25mm ID. x 0.25  $\mu$ m film thickness

Carrier : Helium with flow rate of 2 ml/min

Oven : 45 °C ( 5 min ) to 65 °C ( 0 min ) at rate 4 °C/min

65 °C ( 0 min ) to 110 °C ( 2 min ) at rate 8 °C/min

110 °C ( 2 min ) to 260 °C ( 10 min ) at rate 5 °C/min

Split ratio : 200 : 1

Injection temperature : 250 °C

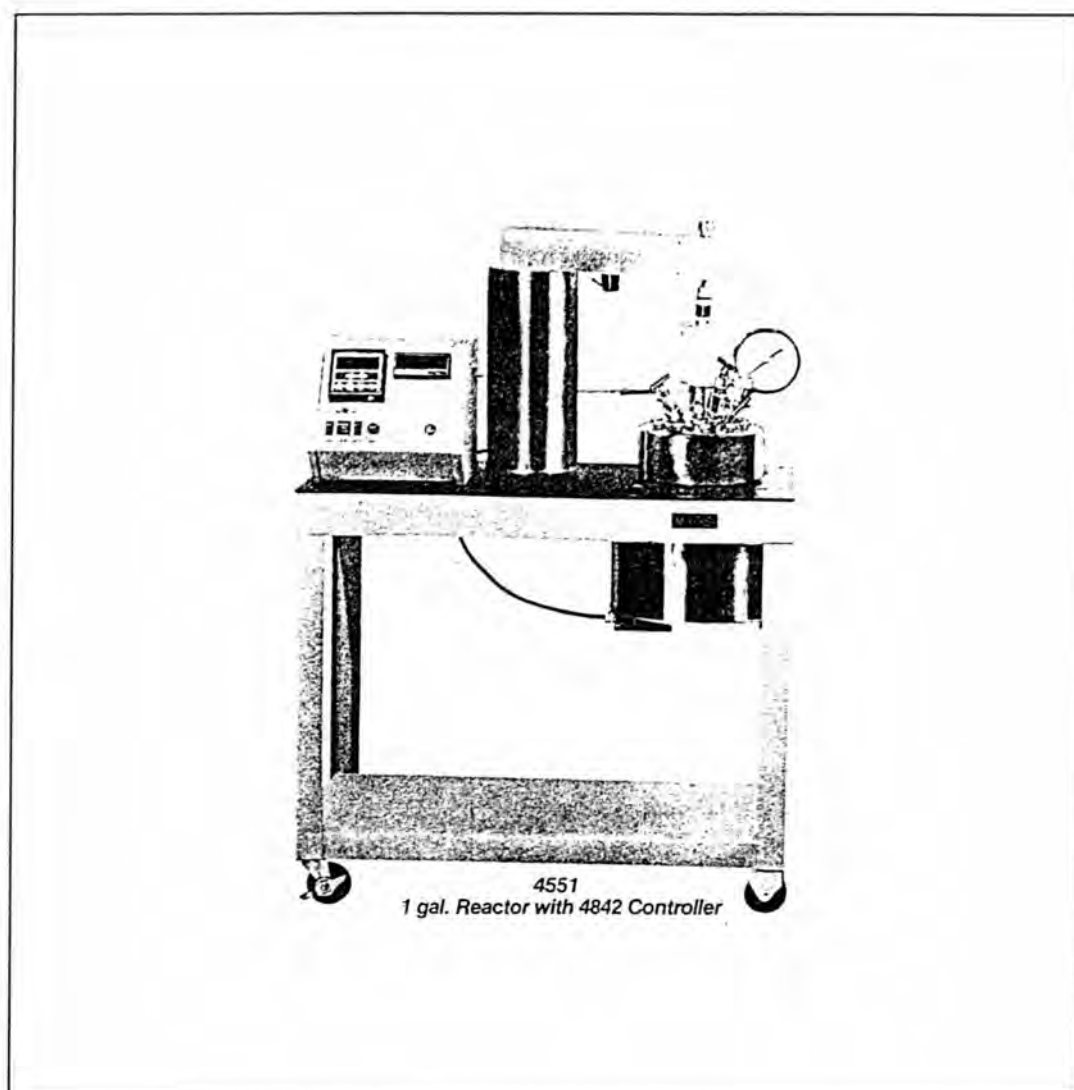
Detector temperature : 260 °C

### 3.2.4 High Pressure Reactor

All experiments for the hydrocracking study of used polyethylene was carried out in the hydrogenation apparatus which consisted of four parts as follows:

#### 3.2.4.1 Reactor (Figure 3.1)

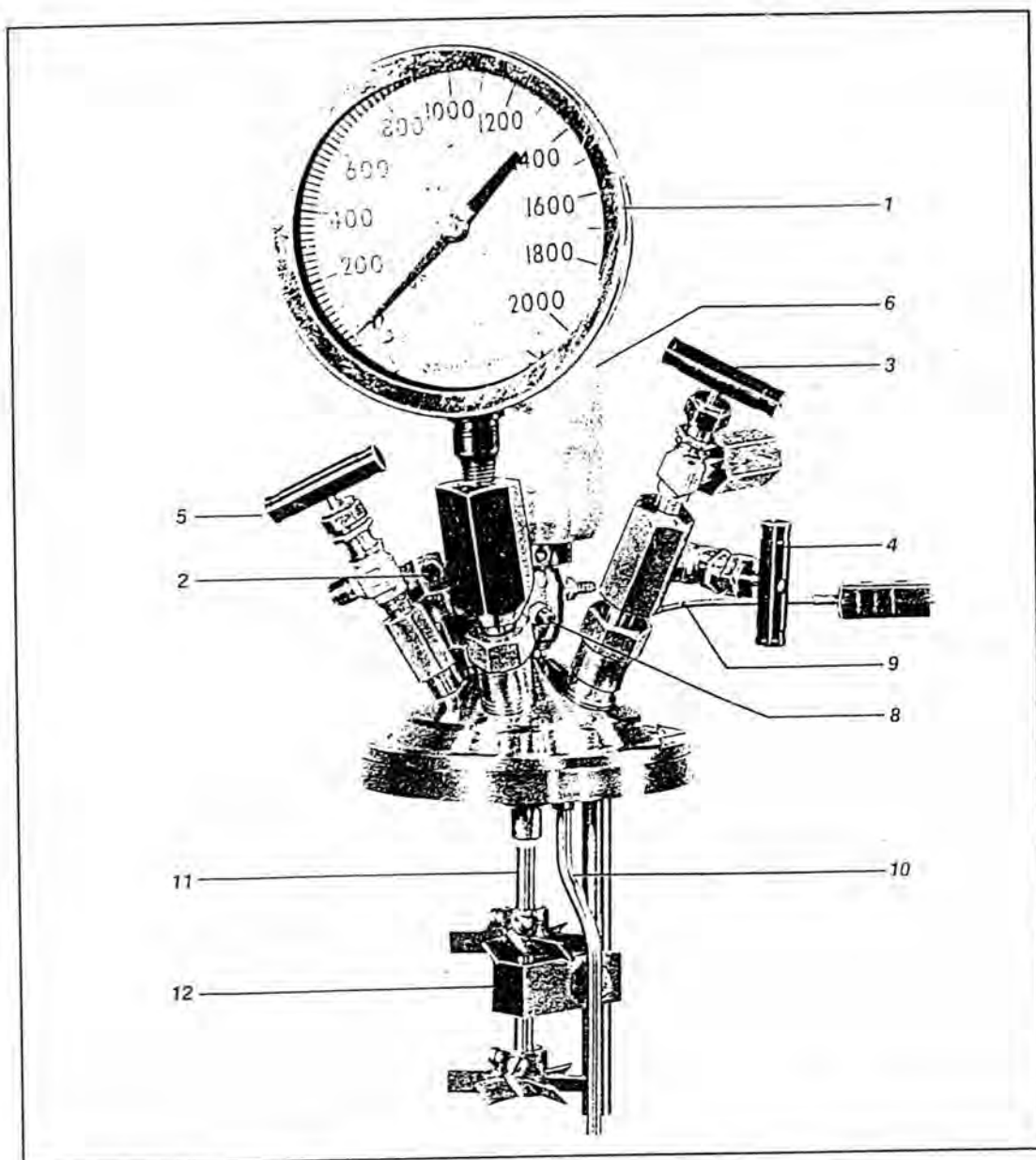
The hydrogenation floor stand reactor was a high pressure batch stirred autoclave model 4551 from Parr Instrument Company with a 3750 cubic centimetres stainless steel 316 cylindrical bomb, spit range from 0 - 2000 psig and a temperature range of 0 - 400 °C



**Figure 3.1** Floor Stand Reactor

#### 3.2.4.2 Reactor Fitting (Figure 3.2)

The stirring unit of reactor was equipped with convenient valves and fittings for handling the various functions. The parts were indicated with the following number.



- |                                    |                                                          |
|------------------------------------|----------------------------------------------------------|
| 1. a pressure gauge                | 7. a water cooling channel                               |
| 2. a safety rupture disc           | 8. a thermocouple                                        |
| 3. a safety rupture disc           | 9. a dip tube                                            |
| 4. a gas inlet valve               | 10. a stirring shaft with 6-blade turbine type impellers |
| 5. a liquid sampling valve         |                                                          |
| 6. a gas release valve             |                                                          |
| 7. a stirrer magnetic drive system |                                                          |

**Figure 3.2** Reactor Fitting

#### 3.2.4.3 Automatic Temperature Controller

The controller was a model 4842 PID controller of the Parr Instrument Company. It was operated in conjunction with a dual thermocouple. There were various enhancement modules to assist in monitoring and controlling the temperature, pressure and stirring speed. Stirring speed could be adjusted in the range of 1-1000 rpm.

#### 3.2.4.4 Gas Controllers System

The system consisted of a hydrogen tank with a pressure regulator (0-2000 psig).

#### 3.2.6 Viscometer

The apparatus Cannon Automatic Viscometer model CAV-3 was used.

#### 3.2.7 Pour Point Tester

The automatic cloud and pour point tester model CPP 97 was used.

#### 3.2.8 Sulfur Analyzer

X-ray fluorescence was used.

### 3.2.9 Colorimeter

The Fisher ASTM D 1500 was used.

### 3.2.10 Distillation

The automatic distillation was used.

### 3.2.11 Flash Point Tester

The automatic flash point was used.

## 3.3 Procedure

### 3.3.1 Measuring Pore Volume of Support

The pore volumes of molecular sieve support 4A-DG, 3A-EPG and 13xPG types were determined by the Micro Pore Sizer according to Brunauer Emmett Teller (BET) method.

### 3.3.2 Preparation of Catalysts [19-22]

#### 3.3.2.1 Ni/Sn/F Catalyst : containing Ni(10%),Sn(5%),F(2%) on molecular sieve (4A-DG type) support

Step 1 :- The molecular sieve was dried at 120 °C for 16 hours before use. The molecular sieve (120 g) was impregnated with

a solution of tin(II) chloride dihydrate (11.41 g) in water (60 ml) and mixed with concentrated hydrochloric acid (10 ml). The impregnated support was dried at 120 °C for 16 hours, precalcined for 2 hours at about 350 °C and then calcined at 500 °C for 2 hours to obtain the calcined solid.

Step 2 :- The calcined solid was reimpregnated with a solution of nickel (II) chloride hexahydrate (48.60 g) in water (70 ml), dried at 120 °C for 16 hours and then calcined at 500 °C for 2.5 hours.

Step 3 :- The calcined solid from step 2 was reimpregnated with a solution of  $\text{NH}_4\text{F}$  (4.68 g) in water (70 ml), dried at 120 °C for 16 hours and then calcined under the following conditions : held at 150 °C for 1 hour, the temperature was raised by 50 °C every 15 minutes to 400 °C, then held at 400 °C for 1 hour, to obtain the Ni(10%)-Sn(5%)-F(2%) on molecular sieve (4A-DG type) catalyst.

#### 3.3.2.2 Fe/Sn/F Catalyst: containing Fe(10%),Sn(5%),F(2%) on molecular sieve (4A-DG type) support

The procedure of experiment 3.3.2.1 was employed except that the amount of iron (III) chloride trihydrate (58.13 g) was used instead of nickel (II) chloride hexahydrate (48.60 g).



**3.3.2.3 Co/Sn/F Catalyst: containing Co(10%),Sn(5%),F(2%)  
on molecular sieve (4A-DG type) support**

The procedure of experiment 3.3.2.1 was employed except that the amount of cobalt (II) chloride hexahydrate (48.47 g) was used instead of nickel (II) chloride hexahydrate (48.60 g).

**3.3.2.4 Ni/Sn/F Catalyst: containing Ni(10%),Sn(5%),F(1%)  
on molecular sieve (4A-DG type) support**

The procedure of experiment 3.3.2.1 was employed except that a different quantity of ammonium fluoride (2.34 g) was used.

**3.3.2.5 Ni/Sn/F Catalyst: containing Ni(10%),Sn(2.5%),F(2%)  
on molecular sieve (4A-DG type) support**

The procedure of experiment 3.3.2.1 was employed except that a different quantity of tin (II) chloride dihydrate (5.70 g) was used.

**3.3.2.6 Ni/Sn/F Catalyst: containing Ni(5%),Sn(5%),F(2%)  
on molecular sieve (4A-DG type) support**

The procedure of experiment 3.3.2.1 was employed except that a different quantity of nickel (II) chloride hexahydrate (24.30 g) was used.

**3.3.2.7 Ni/Sn/F Catalyst: containing Ni(10%),Sn(5%),F(2%)  
on molecular sieve (3A-EPG type) support**

The procedure of experiment 3.3.2.1 was employed except that a different type of molecular sieve (3A-EPG type) support.

**3.3.2.8 Ni/Sn/F Catalyst: containing Ni(10%),Sn(5%),F(2%)  
on molecular sieve (13xPG type) support**

The procedure of experiment 3.3.2.1 was employed except that a different type of molecular sieve (13xPG type) support.

**3.3.2.9 Activation and Characterization of Catalysts**

The prepared catalyst was introduced into the stainless steel reactor. The latter was closed and air in the reactor was replaced by flowing hydrogen gas (about 10-20 psig) for 2 times. The reactor

was operated under hydrogen pressure of 400 psig, reaction time of 400 °C for 6 hours to obtain the activated catalyst. The catalyst was characterized by X-ray fluorescence.

#### **3.3.2.10 Regeneration of Catalysts**

The used catalyst was washed four times with hexane in a ratio of catalyst to hexane 1 : 2 by volume. The washed catalyst was dried at 120 °C for 16 hours, calcined at 500 °C for 4 hours and then activated by following the procedure 3.3.2.9 to obtain the reusable catalyst.

#### **3.3.2.11 Characterization of Catalysts**

The catalysts were characterized by X-ray fluorescence.

#### **3.3.3 Hydrocracking Process**

Used polyethylene in small pieces (300 g) and the activated catalyst (120 g) were introduced into the stainless steel reactor. The gas in the reactor was removed by purging the system with some partial pressure of hydrogen gas (about 10-20 psig) for 2 times. The reaction was operated at various conditions in procedure

3.3.3.1-3.3.3.7 with stirring speed set at 500 rpm. After the reaction took place, heating was stopped and the reaction mixture was stirred until the mixture was cooled down to room temperature and depressurized. Products were transferred to a 1 liter beaker. The hydrocarbon oil was dewaxed with methyl ethyl ketone (MEK). MEK was added to the beaker with stirring. The ratio by volume between solvent and oil was 3 : 1. The solvent and oil mixture was chilled to the dewaxing temperature of 0 °C by refrigeration. The mixture was then quickly filtered through a Buchner funnel under reduced pressure to separate the crystallized wax. The temperature of the solution remained below 5 °C. Suction was continued for several minutes until the oil was removed completely from the wax. The filtrate was collected and the oil was removed from the filtrate by simple distillation to obtain dewaxed oil and the yield was calculated. The dewaxed oil was characterized by GC compared with the retention times of the standard C<sub>9</sub>-C<sub>14</sub>-C<sub>16</sub> hydrocarbons and the physical properties ( color, viscosity index, flash point and etc.) were determined by the procedure listed in 3.2.6-3.2.11. The used catalyst and wax mixture was dewaxed with hexane to obtain the used catalyst before regeneration by following the procedure 3.3.2.10.

### **3.3.3.1 The Effect of Catalyst Type on Hydrocracking**

The procedure was repeated according to experiment 3.3.3 for Ni(10%)-Sn(5%)-F(2%) / MS(4A-DG), Fe(10%)-Sn(5%)-F(2%) / MS(4A-DG) and Co(10%)-Sn(5%)-F(2%) / MS(4A-DG) with 40%wt of used polyethylene. The reactor was operated at the preset temperature (390 °C), pressure (600 psig) and for the reaction time (4 hours). The reaction mixture was worked up in the same manner as described in 3.3.3.

### **3.3.3.2 The Effect of Element Composition on Hydrocracking**

The procedure of experiment in 3.3.3 was employed except that the Ni(10%)-Sn(5%)-F(2%) / MS(4A-DG), Ni(10%)-Sn(5%)-F(1%) / MS(4A-DG), Ni(10%)-Sn(2.5%)-F(2%) / MS(4A-DG) or Ni(5%)-Sn(5%)-F(2%) / MS(4A-DG) was placed in the reactor. The reaction was operated under the same conditions as 3.3.3.1. The reaction mixture was worked up in the same manner as described in 3.3.3.

### **3.3.3.3 The Effect of Reaction Time on Hydrocracking**

The procedure of experiment in 3.3.3 was employed except that the reactor was operated at the preset temperature (390 °C), pressure (600 psig), various times (30 minutes, 2 and 4 hours) and using 40%wt of optimum catalyst, Ni(10%)-Sn(5%)-F(2%) / MS (4A-DG), as determined from 3.3.3.2. The reaction mixture was worked up in the same manner as described in 3.3.3.

### **3.3.3.4 The Effect of Reaction Temperature on Hydrocracking**

The procedure of experiment in 3.3.3 was employed except that the reactor was operated at the preset pressure (600 psig), various temperatures (350, 370 and 390 °C), the optimum reaction time (4 hours) obtained from 3.3.3.3 and using 40%wt of Ni(10%)-Sn(5%)-F(2%) / MS(4A-DG) catalyst. The reaction mixture was worked up in the same manner as described in 3.3.3.

### **3.3.3.5 The Effect of Hydrogen Pressure on Hydrocracking**

The procedure of experiment in 3.3.3 was employed except that the reactor was operated at various pressure (400, 500 and 600

psig), the optimum temperature (390 °C) obtained from 3.3.3.4, the reaction time (4 hours) and using 40%wt of Ni(10%)-Sn(5%)-F(2%) / MS(4A-DG) catalyst. The reaction mixture was worked up in the same manner as described in 3.3.3.

### **3.3.3.6 The Effect of Catalyst Concentration on Hydrocracking**

The procedure of experiment in 3.3.3 was employed except that the reactor was operated at the optimum pressure (500 psig) obtained from 3.3.3.5, temperature (390 °C), the reaction time (4 hours) and various concentrations (20, 30 and 40%wt) of Ni(10%)-Sn(5%)-F(2%) / MS(4A-DG) catalyst. The reaction mixture was worked up in the same manner as described in 3.3.3.

### **3.3.3.7 The Effect of Molecular Sieve Support Type on Hydrocracking**

The procedure of experiment in 3.3.3 was employed except that the various types (4A-DG, 3A-EPG and 13xPG type) of molecular sieve, the optimum 40%wt of Ni(10%)-Sn(5%)-F(2%) / MS catalyst obtained from 3.3.3.6, the temperature (390 °C), the pressure (500 psig) and using the reaction time (4 hours). The reaction mixture was worked up in the same manner as described in 3.3.3.

### 3.3.3.8 The Physical Properties and Characterization of

#### Product

The physical properties and characterization of the hydrocracking product were determined using the following standard procedure :

Physical properties :

- |                                     |                |
|-------------------------------------|----------------|
| a. API gravity @ 60 °F              | by ASTM D 1298 |
| b. Flash Point, °C                  | by ASTM D 93   |
| c. Distillation, °C                 | by ASTM D 86   |
| d. Color, Visual                    | by ASTM D 1500 |
| e. Sulfur content                   | by ASTM D 129  |
| f. Kinematic Viscosity @ 40 °C, cSt | by ASTM D 445  |
| g. Pour Point, °C                   | by ASTM D 97   |

Characterization : Gas chromatography (GC)