

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 Limited.

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

3.1.4 Hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) was obtained from Carlo Erba.

3.1.5 Ammonium fluoride (NH_4F) was obtained from BDH Ltd..

3.1.6 Hydrochloric acid was obtained from Baker.

3.1.7 Alumina support (CS331-3 type) was obtained from United Catalyst Inc., USA.

3.2 Apparatus and Instruments

3.2.1 Apparatus for measuring pore volume of alumina support CS331-3 comprised of :

- Buret for charging deionized water.
- Suction flask for charging alumina support.
- Stand and clamp for supporting buret and suction flask.
- Suction pump for removing trapped air for the pores of alumina support before impregnating the solution.

3.2.2 Calcinator

The apparatus model GSM from Carbolite Furnaces was used.

3.2.3 Gas Chromatography-Mass Spectrometer (GC-MS)

The apparatus model GC8000 series and mass detector model MD800 from Fison Instrument were used.

GC conditions

Column : DB-1HT capillary column 30m x 0.25mm ID. x 0.1 μ m film thickness

Carrier : Helium with flow rate of 0.8 ml/min

Oven : 50 °C (2 min) to 150 °C (3 min) at rate 10 °C/min

150 °C (3 min) to 200 °C(3min) at rate 8 °C/min

Injection temperature : 250 °C

Detector : MS (EI⁺ 70 ev)

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, split ring closures and a bomb heater. The reactor could work in a pressure range from 0-2000 psig and a temperature range of 0-450 °C

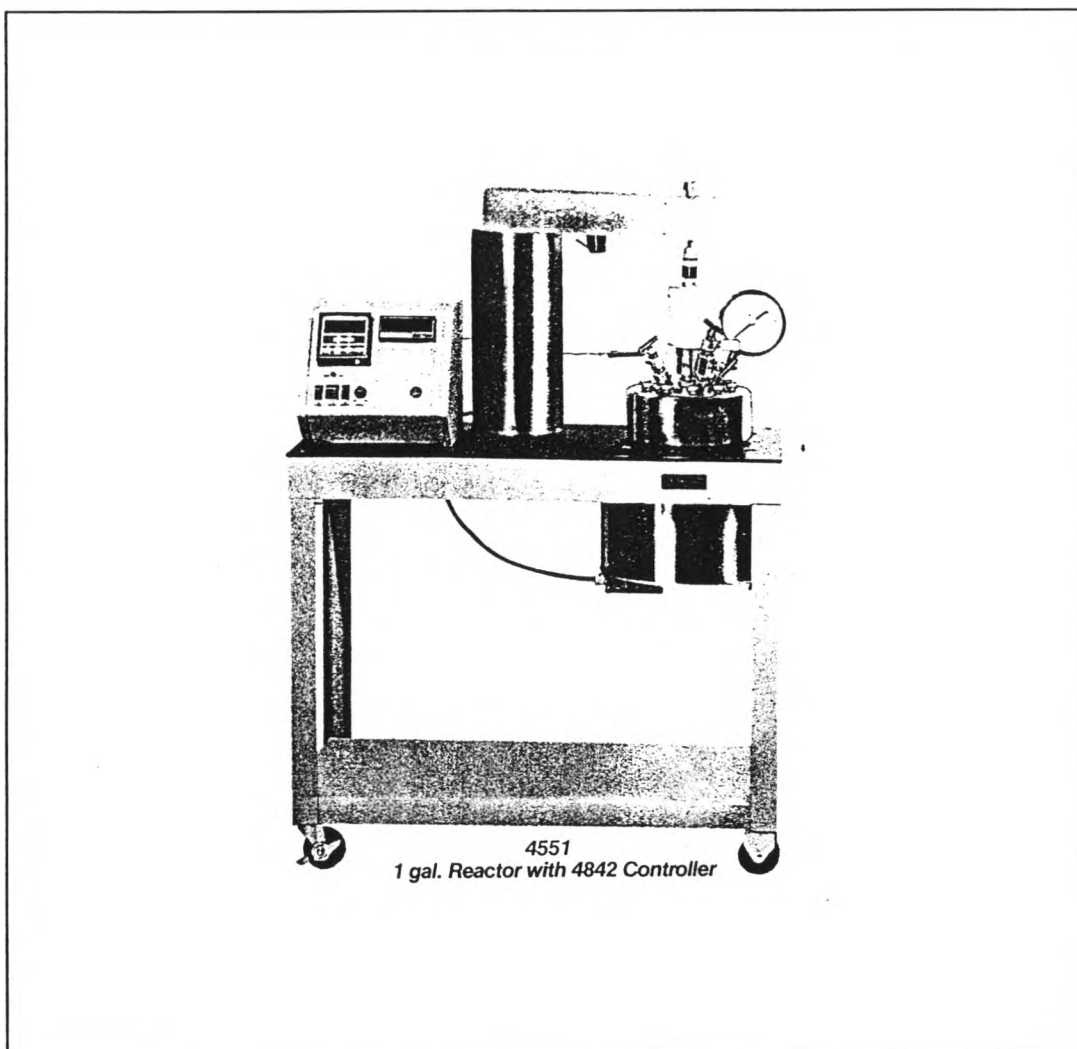
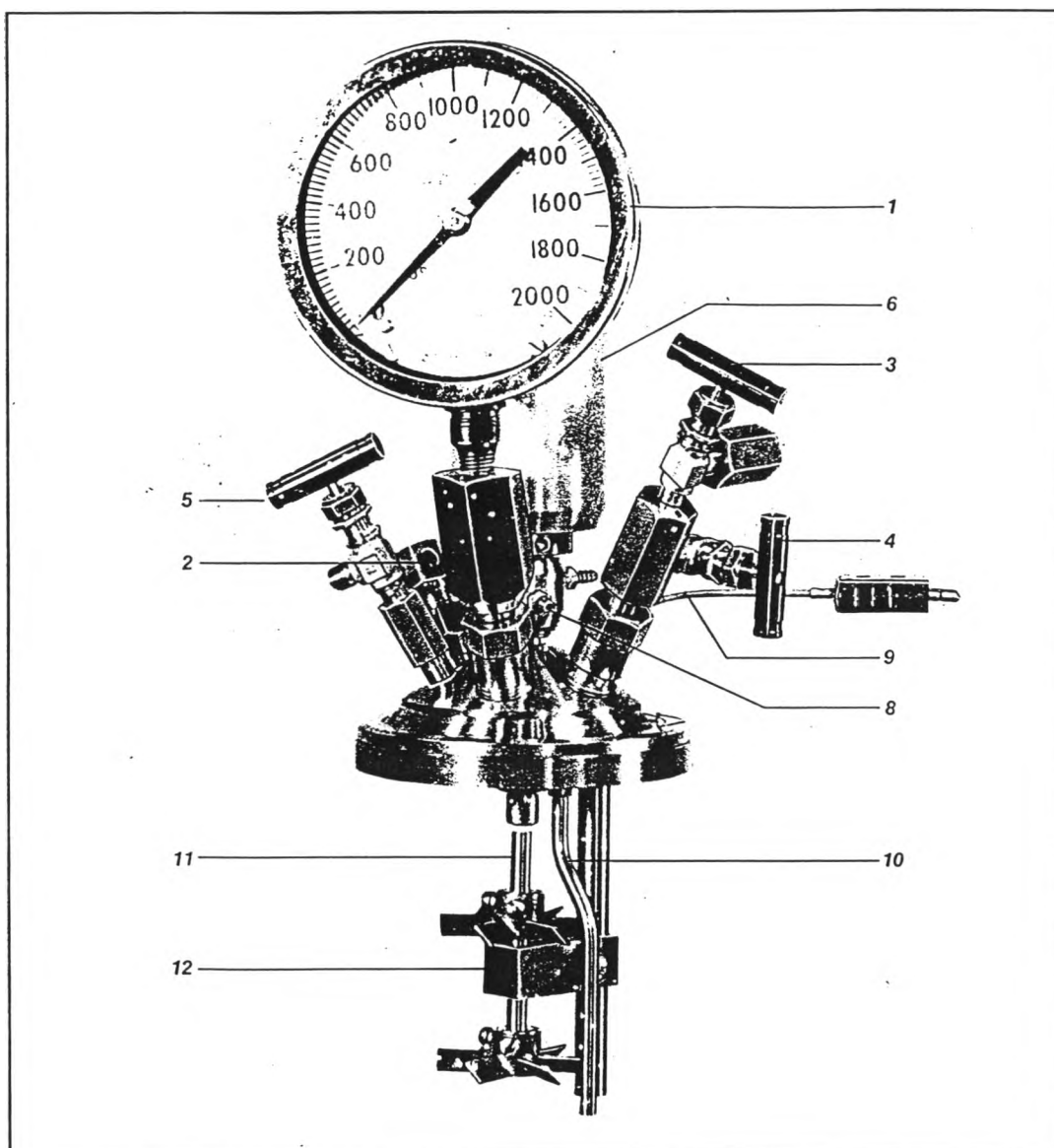


Figure 3.1 Floor Stand Reactor

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 gas inlet valve | 9. a dip tube |
| 4. a liquid sampling valve | 10. a stirring shaft with 6-blade turbine type impellers |
| 5. a gas release valve | |
| 6. a stirrer magnetic drive system | |

Figure 3.2 Reactor Fitting

3.2.4.3 Automatic Temperature Controller

The controller was used a model 4842 PID controller from 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 0-1000 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 Pour Point Tester

The apparatus model A82 from Haake was used

3.2.7 Sulfur Analyzer

The apparatus model SLFA-800 from Horiba was used.

3.2.8 Colorimeter

The Fisher ASTM Colorimeter was used.

3.3 Procedure

3.3.1 Measuring Pore Volume of Alumina Support CS 331-3 type

The alumina support (100 g) was placed in a suction flask which was equipped with a buret containing deionized water. The flask was connected to a vacuum pump. The vacuum pump was applied to evacuate the air from the pores of the support. Deionized water from the buret was added to the support until thoroughly. The volume of deionized water was determined. The procedure described above was repeated until the water consumption by the support became constant. The result of this experiment indicated that the pore volume of the support CS 331-3 type was 0.64 ml/g.

3.3.2 Preparation of Catalysts

3.3.2.1 Pt/F Catalyst : containing Pt(0.3%), F(0.5%) on alumina support

The alumina support was calcined for four hours at 600 °C before use. The alumina support (125.56 g) was impregnated in a solution prepared by dissolving 1 g of hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) in 80 ml of deionized water. The impregnated support was dried at 120 °C and then calcined at 450 °C for 3 hours to obtain the calcined catalyst. The calcined catalyst was reimpregnated with 80 ml of an aqueous solution of NH_4F (1.22 g) (the volume of aqueous solution equivalent to the pore volume of the alumina support) and then was left at room temperature for one hour, dried at 120 °C for 16 hours to obtain the fluoride doped catalyst. This fluoride doped catalyst was calcined in a continuous current of air under the following conditions: hold at 150°C for 1 hour, raise temperature

by 50°C every 15 minutes to 400°C, then hold at 400°C for 1 hour to obtain the Pt/F catalyst.

3.3.2.2 Pt/Sn/Cl/F Catalyst: containing Pt(0.3%), Sn(0.15%), Cl(1.21%), F(0.5%) on alumina support [43]

The alumina support (125.56 g) was calcined for four hours at 600°C. This alumina support was added into solution containing 0.36 g of stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) dissolved in 70 ml of water and 10 ml of hydrochloric acid. The impregnated support was dried at 120°C, precalcined for 2 hours at about 350°C and then calcined at 500°C for 2 hours. The calcined solid was immersed in 80 ml of a solution 1 g hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$). After drying at 120°C, followed by calcination at 530°C for 2 hours the calcined catalyst was obtained. That calcined catalyst was reimpregnated with 80 ml of an aqueous solution containing NH_4F (1.22 g) and then was left at room temperature for one hour before drying at 120°C for 16 hours to obtain the fluoride doped catalyst. This fluoride doped catalyst was calcined in a continuous current of air under the previous conditions (3.3.2.1).

3.3.2.3 Pt/Sn/Cl/F catalyst : containing Pt(0.3%), Sn(0.15%), Cl(1.21%), F(2%) on alumina support

The preparation procedure, except the amount of NH_4F (4.89 g), was similar to the procedure of 3.3.2.2.

3.3.2.4 Pt/Sn/Cl/F Catalyst: containing Pt(0.3%), Sn(0.3%), Cl(1.21%), F(0.5%) on alumina support

The preparation procedure was similar to the procedure of 3.3.2.2, except that the amount of stannous chloride was 0.71g.

3.3.2.5 Pt/Sn/Cl/F Catalyst : containing Pt(0.6%), Sn(0.15%), Cl(1.21%), F(0.5%) on alumina support

The preparation procedure was similar to the procedure of 3.3.2.2, except that the amount of hexachloroplatinic acid was 2 g.

3.3.2.6 Ni/Sn/Cl/F catalyst : containing Ni (5%), Sn (0.15%), Cl(1.21%), F(0.5 %) on alumina support[44]

The alumina support 125.56 g was added to 80 ml of an aqueous solution of nickel chloride (25.42 g). The mixture was dried at 120°C and calcined at 500°C for 2 hours to obtain the calcined catalyst. That calcined catalyst was reimpregnated with 80 ml of aqueous stannous chloride (0.357 g). It was dried at 120°C and was calcined at 400°C for 5 hours. The solid was reimpregnated with 80 ml of an aqueous solution containing NH₄F (1.22 g), left at room temperature for 1 hours and then dried at 120°C for 16 hours to obtain the fluoride catalyst. This fluoride catalyst was calcined under the previous conditions (3.3.2.1).

3.3.2.7 Ni/Sn/Cl/F Catalyst : containing Ni(5%), Sn(5%), Cl(1.21%) and F(2%) on alumina support

The preparation procedure was similar to the procedure of 3.3.2.6 except 11.93 g of stannous chloride and 4.89 g of NH_4F were used.

3.3.2.8 Ni/Sn/Cl/F Catalyst: containing Ni(10%), Sn(5%), Cl(1.21%), F(2%) on alumina support

The preparation procedure was similar to the procedure of 3.3.2.7 except that 50.84 g of nickel chloride was used.

3.3.2.9 Co/Sn/Cl/F Catalyst : containing Co(5%), Sn(5%), Cl(1.21%) and F(2%) on alumina support

The preparation procedure was similar to the procedure of 3.3.2.8 except that 50.84 g of nickel chloride was used instead of 31.00 g of cobalt chloride.

3.3.2.10 Activation and characterization of Catalysts

The prepared catalysts were activated before use by reduction with hydrogen in a stainless steel reactor. The reactor was closed and air in the reactor was replaced by hydrogen gas at 400 psig. The high pressure reactor was heated at 400°C for 6 hours to obtain the activated catalyst. The obtained catalysts were characterized by X-ray fluorescence.

3.3.3 Hydrocracking Process

3.3.3.1 The Effect of Catalyst Type on hydrocracking

Used polyethylene in small pieces (300 g) and the activated Pt/Sn/Cl/F catalyst (120 g) were placed in the stainless steel reactor. The gas in the reactor was replaced by hydrogen gas by successive dilution and then the hydrogen gas at the required pressure was maintained. The reactor was operated at the preset temperature (400°C) and for the reaction time (12 hours). After the reaction took place, heating was stopped and the reaction mixture was stirred until the mixture was cooled to room temperature. The pressure was released and the reaction mixture was transferred to a 1 liter beaker and the catalyst was separated by suction filtration to give hydrocarbon oil. The molecular weight distribution of this oil was determined by GC-MS.

The experiment was repeated according to the procedure described above for the Pt/F catalyst and commercial catalyst obtained from a refinery. For each experiment the reaction mixture was worked up in the same manner as above to give the desired products. The molecular weight distribution of these products were determined by GC-MS. The physical properties (color, viscosity index and pour point) of these products were determined by the procedures listed in 3.3.4 and the % yield was calculated.

3.3.3.2 The Effect of % component of Pt/Sn/Cl/F on Hydrocracking

Following the procedure as in experiment 3.3.3.1 excepting the Pt(0.15%)/Sn(0.15%)/Cl(1.21%)/F(0.5%) catalyst (105 g) were placed

in the stainless steel reactor. The reaction mixture was worked up in the same manner as above.

The experiment was repeated according to the procedure described above for Pt(0.3%)/Sn(0.15%)/Cl(1.21%)/F(2%) catalyst, Pt(0.3%)/Sn(0.3%)/Cl(1.21%)/F(0.5%) catalyst and Pt(0.6%)/Sn(0.15%)/Cl(1.21%)/F(0.5%) catalyst. For each experiment the reaction mixture was worked up in the same manner as above to give the desired products. Liquid products were analyzed by GC/MS.

3.3.3.3 The Effect of Catalyst Concentration on Hydrocracking

Following the procedure as in experiment 3.3.3.1 except that the reaction was operated at various catalyst concentrations (30, 35 and 40 % by wt of used polyethylene) using the optimum catalyst, (containing Pt(0.6%), Sn(0.15%), Cl(1.21%) and F(0.5%) on alumina), as determined from 3.3.3.2. The reaction mixture was worked up in the same manner as described in 3.3.3.1.

3.3.3.4 The Effect of Reaction Time on Hydrocracking

Following the procedure as in experiment 3.3.3.3 except that the reaction was operated at various reaction times (4, 8, 10 and 12 hours) using 40 %wt of Pt(0.6%)/Sn(0.15%)/Cl(1.21%)/F(0.5%) catalyst obtained from 3.3.3.3. The reaction mixture was worked up in the same manner as described in 3.3.3.1.

3.3.3.5 The Effect of Temperature on Hydrocracking

Following the procedure as in experiment 3.3.3.1 except that the reaction was operated at various temperatures (300, 350 and 400°C) for the optimum reaction time (12 hrs) obtained from 3.3.3.4 and used 40 %wt of Pt(0.6%)/Sn(0.15%)/Cl(1.21%)/F(0.5%) catalyst.

3.3.3.6 The Effect of Hydrogen Pressure on Hydrocracking

Following the procedure as in experiment 3.3.3.1 except that the reaction was operated at various hydrogen pressures (400, 500 and 600 psig) and the optimum reaction temperature (400°C) obtained from 3.3.3.5. The selected reaction time was 12 hours and 40 %wt of Pt(0.6%)/Sn(0.15%)/Cl(1.21%)/F(0.5%) catalyst was used.

3.3.4 The Physical and Chemical Properties Determination of Product

The physical and chemical properties of the hydrocracked product were determined using following standard procedure as follow:

Physical properties:

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|-------------------------------|----------------|
| a. API gravity @ 60°F | by ASTM D 1298 |
| b. Specific Gravity @ 60/60°F | by ASTM D 1298 |
| c. Color, Visual | by ASTM D 1500 |
| d. Pour point | by ASTM D 97 |
| e. Distillation | by ASTM D 86 |
| f. Lead content | by ASTM D 3116 |

g. Sulfur content

by ASTM D 129

Chemical properties:

- a. The molecular weight distribution was determined by GC-MS
- b. ^{13}C NMR spectra were obtained in CDCl_3 .