

CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Used polypropylene from battery cases

3.1.2 Industrial hydrogen gas was obtained from TIG Trading Ltd.

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

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

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

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

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

3.1.8 Hydrochloric acid was obtained from Baker Analyzed.

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

3.1.10 Molecular sieve support (4A-DG, type) was obtained from Union Carbide.

3.2 Apparatus and Instruments

3.2.1 Apparatus for measuring pore volume of alumina support CS331-3 consisted 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 adding the deionized water.

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 : 45 °C (5 min) to 65 °C (0 min) at rate 2 °C/min

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

110 °C (2 min) to 260 °C(8min) at rate 5 °C/min

Injection temperature : 260 °C

Detector : MS (EI⁺ 70 ev)

3.2.4 High Pressure Reactor

All experiments for the hydrocracking study of used polypropylene 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

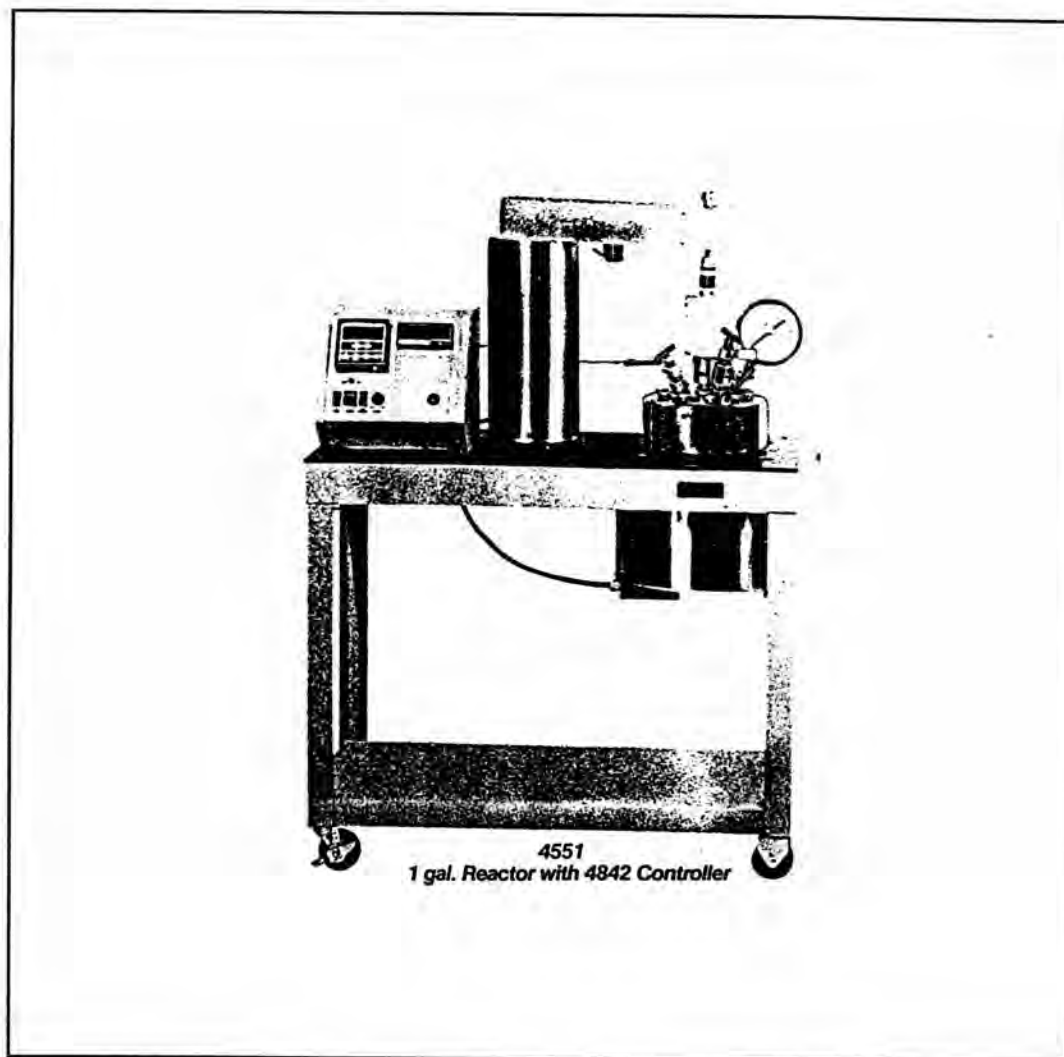
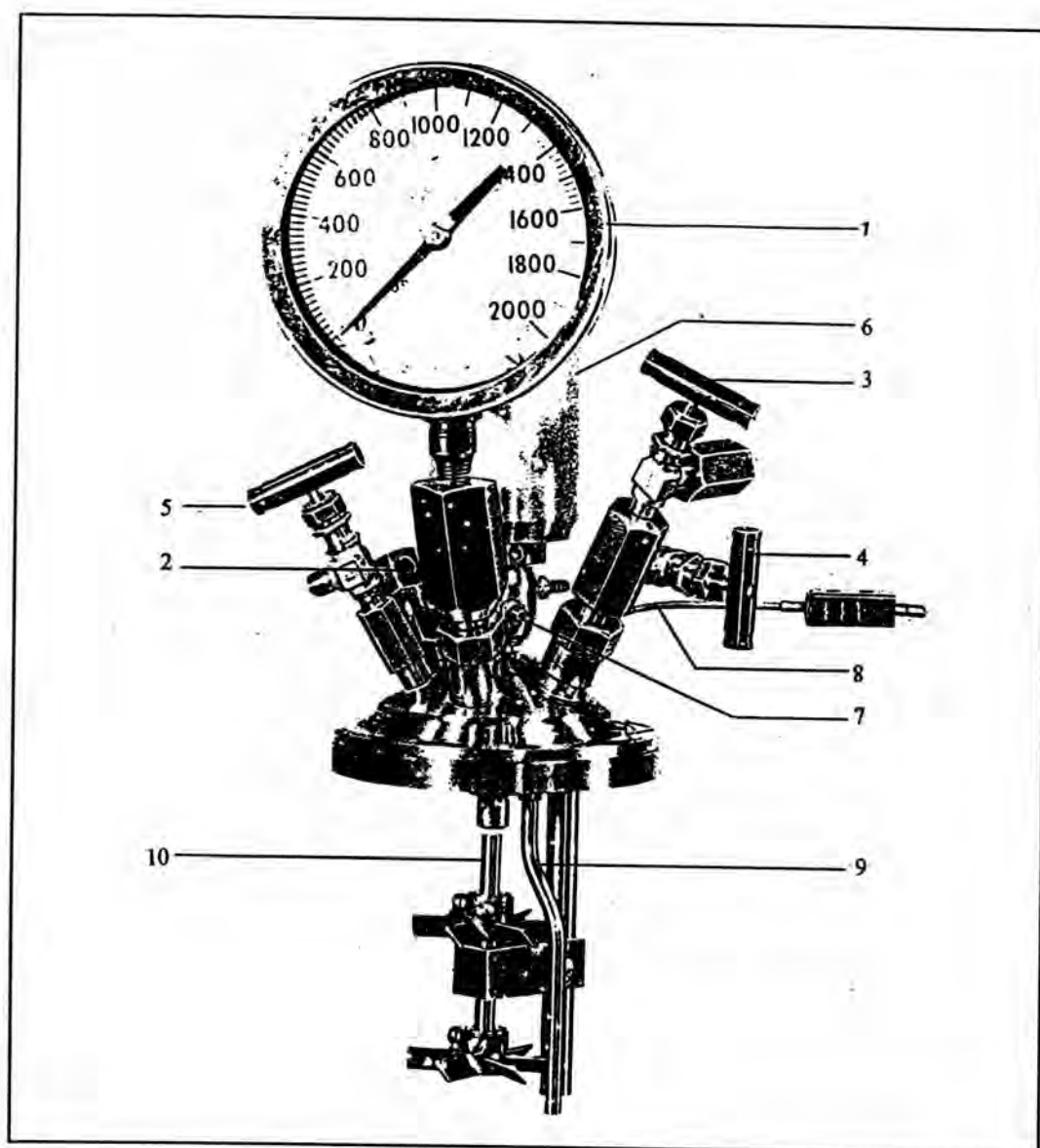


Figure 3.1 Floor Stand Reactor

3.2.4.2 Reactor Fitting (Figure 3.2)

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



- | | |
|------------------------------------|--|
| 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 used model 4842 PID controller from the Parr Instrument Company, was used. 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).

3.3 Procedure

3.3.1 Measuring Pore Volume of Support

3.3.1.1 Alumina Support CS 331-3 type

The volume measuring apparatus was set up by connecting a suction flask with a vacuum pump and equipping it with a buret containing deionized water. The dry alumina (100 g) was placed in the flask, the vacuum pump was turned on and then deionized water was added to the support until thoroughly. The above procedure was repeated until the water consumption of the support became constant. The pore volume of the alumina support CS 331-3 type was found to be 0.64 ml/g.

3.3.1.2 Molecular Sieve Support 4A type

The procedure in 3.3.1.1 was followed using molecular sieve (100 g) instead of alumina (100 g). This experiment showed that the pore volume of the molecular sieve support 4A type was 0.52 ml/g.

3.3.2 Preparation of Catalysts

3.3.2.1 Ni(5%)-Sn(5%)-F(2%) on alumina

Step 1 :- Tin(II) chloride dihydrate (9.59 g) was dissolved in water (70 ml) and mixed with concentrated hydrochloric acid (10 ml). The solution was poured onto alumina (120 g) which was previously calcined at 520°C for 4 hours. The mixture was left at room temperature for 2 hours,

dried at 120°C for 16 hours, precalcined at 350°C for 2 hours, 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 (23.88 g) in water (70 ml), left at ambient temperature for 2 hours, 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 NH_4F (4.68 g) in water (70 ml), left at room temperature for 2 hours, 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(5%)-Sn(5%)-F(2%) on alumina catalyst. [30-33]

3.3.2.2 Fe(10%)-Sn(5%)-F(2%) on alumina

The procedure in 3.3.2.1 was repeated except in step 2, iron(III) chloride hexahydrate (58.08 g) was used instead of nickel chloride.

3.3.2.3 Co(10%)-Sn(5%)-F(2%) on alumina

The procedure in 3.3.2.1 was repeated except in step 2, cobalt chloride (48.39 g) was used instead of nickel(II) chloride hexahydrate.

3.3.2.4 Ni(5%)-Sn(5%)-F(2%) on Molecular Sieve

The procedure in 3.3.2.1 was repeated except in step 1, molecular sieve (120 g) was used instead of alumina (120 g) and the volume of water of all solutions was 60 ml.

3.3.2.5 Ni(5%)-Sn(5%)-F(1%) on Molecular Sieve

The procedure in 3.3.2.4 was repeated except in step 3, NH_4F (2.34g) was used in 60 ml of water.

3.3.2.6 Ni(5%)-Sn(2.5%)-F(1%) on Molecular Sieve

The procedure in 3.3.2.4 was repeated except in step 1, tin(II) chloride dihydrate (4.80 g) was used in 60 ml of water.

3.3.2.7 Ni(2.5%)-Sn(5%)-F(2%) on Molecular Sieve

The procedure in 3.3.2.4 was repeated except in step 2, nickel(II) chloride hexahydrate (11.94 g) was used in 60 ml of water.

3.3.2.8 Fe(5%)-Sn(5%)-F(2%) on Molecular Sieve

The procedure in 3.3.2.4 was repeated except in step 2, iron(III) chloride hexahydrate (29.04 g) was used in 60 ml of water.

3.3.2.9 Co(5%)-Sn(5%)-F(2%) on Molecular Sieve

The procedure in 3.3.2.4 was repeated except in step 2, cobalt(II) chloride hexahydrate (24.20 g) was used in 60 ml of water.

3.3.2.10 Activation of Catalysts

The catalysts were activated before use by reduction at 400 psig hydrogen pressure in a stainless steel reactor. Then, the high pressure reactor was heated at 400°C for 6 hours to obtain the activated catalyst.

3.3.2.11 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 following the procedure 3.3.2.10 to obtain the reusable catalyst.

3.3.2.12 Characterization of catalysts

The catalysts were characterized by X-ray fluorescence.

3.3.3 Hydrocracking Process

All hydrocracking experiments were done following the procedure described below. Used polypropylene in small pieces (300 g) and the activated catalyst (120 g) were placed in the stainless steel reactor. After the reactor was set to operate at 360°C for 6 hours, the gas in the reactor was replaced by flowing hydrogen gas and hydrogen gas pressure was maintained at 500 psig. When the temperature was raised to 250°C, a stirrer was turned on until the set program was finished at the ambient temperature. The gas was released before transferring the reaction mixture to a 1 liter beaker. The hydrocarbon oil was separated from the catalyst by suction

filtration, dewaxed with methyl ethyl ketone and the yield percentage was calculated. The dewaxed oil was characterized by GC and GC-MS to obtain the molecular weight distribution and the physical properties (color, viscosity index, flash point and etc.) were determined by the procedures listed in 3.3.5.

3.3.3.1 Hydrocracking Process over Alumina Catalysts

The effect of catalyst type, catalyst concentration and reaction time were studied by following the procedure described in 3.3.3. The reaction mixtures in all experiments were worked up in the same manner to give the desired products.

The effect of catalyst type on alumina support in this research was studied with 3 catalysts, Ni(5%)-Sn(5%)-F(2%)/Al₂O₃, Fe(10%)-Sn(5%)-F(2%)/Al₂O₃, Co(10%)-Sn(5%)-F(2%)/Al₂O₃ and the effect of catalyst concentration and reaction time from each of 3 catalysts was studied by varying the process conditions (25%wt. for 6 hours, 30%wt. for 8 hours, 35%wt. for 10 hours, 40%wt. for 12 hours).

3.3.3.2 Hydrocracking Process over Molecular Sieve Catalysts

The Effect of Catalyst Type on Hydrocracking

The procedure of experiment 3.3.3 was followed except the Fe(5%)-Sn(5%)-F(2%)/MS, Co(5%)-Sn(5%)-F(2%)/MS and Ni(5%)-Sn(5%)-F(2%)/MS were placed in the reactor variously. All of the reaction mixtures were worked up as described in 3.3.3.

The Effect of Element Composition on Hydrocracking

The procedure of experiment in 3.3.3 was followed except that the Ni(5%)-Sn(5%)-F(2%)/MS, Ni(2.5%)-Sn(5%)-F(2%)/MS, Ni(5%)-Sn(2.5%)-F(2%)/MS, Ni(5%)-Sn(5%)-F(1%)/MS were placed in the reactor variously. The reaction mixture was worked up as described in 3.3.3.

The Effect of Catalyst Concentration on Hydrocracking

The procedure of experiment in 3.3.3 was followed except that the best catalyst as determined from studying the effect of catalyst types and the element composition was used at various catalyst concentrations (20, 25, 30, 40% by weight of the used polypropylene). The reaction mixture was worked up as described in 3.3.3.

The Effect of Reaction Time on Hydrocracking

The procedure followed that of experiment 3.3.3 except that 40%wt. of Ni(5%)-Sn(5%)-F(2%)/MS catalyst as determined from studying the effect of catalyst concentrations was used with operation at various reaction times (3, 4, 5, 6 and 12 hours). The reaction mixture was worked up as described in 3.3.3.

The Effect of Temperature on Hydrocracking

The procedure followed that of experiment 3.3.3 except that 40%wt. of Ni(5%)-Sn(5%)-F(2%)/MS catalyst was used with operation at various temperatures (300, 330 and 360°C). The optimum reaction time

(6 hours) obtained from studying the effect of reaction time was used. The reaction mixture was worked up as described in 3.3.3.

The Effect of Hydrogen Pressure on Hydrocracking

The procedure followed that of experiment in 3.3.3 except that 40%wt. of Ni(5%)-Sn(5%)-F(2%)/MS catalyst was used with operation at various hydrogen pressures (300, 400 and 500 psig). The optimum reaction temperature (360°C) obtained from studying the effect of reaction temperature was used and the selected reaction time was 6 hours.

3.3.4 The Physical and Spectroscopic Properties Determination of Product

The physical and chemical properties of the hydrocracking product were determined using the following standard procedures :

Physical properties:

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|------------------------------------|----------------|
| a. API gravity @ 60°F | by ASTM D 1298 |
| b. Calculate Cetane Index | by ASTM D 976 |
| c. Flash Point, °C | by ASTM D 93 |
| d. Distillation | by ASTM D 86 |
| e. Color, Visual | by ASTM D 1500 |
| f. Sulfur content | by ASTM D 129 |
| g. Kinematic Viscosity @ 74°C, cSt | by ASTM D 445 |

Spectroscopic properties:

- a. GC and GC-MS
- b. ¹³C NMR was obtained in CDCl₃.
- c. FTIR