

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Materials

- 3.1.1 Used polystyrene (i.e. polystyrene glass etc.)
- 3.1.2 Industrial hydrogen gas was obtained from TIG Trading Ltd..
- 3.1.3 Industrial nitrogen gas was obtained from TIG Trading Ltd.
- 3.1.4 Stannous chloride ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) was obtained from BDH Ltd..
- 3.1.5 Ammonium fluoride ( $\text{NH}_4\text{F}$ ) was obtained from BDH Ltd..
- 3.1.6 Hydrochloric acid was obtained from Baker Analyzed.
- 3.1.7 Iron chloride ( $\text{FeCl}_3 \cdot 2\text{H}_2\text{O}$ ) was obtained from Merck Ltd..
- 3.1.8 Cobalt chloride ( $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ ) was obtained from J.T. Baker.
- 3.1.9 Nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) was obtained from J.T.Baker.
- 3.1.10 Molecular Sieve (4A type) was obtained from Union Carbide Ltd..
- 3.1.11 Alumina support (CS331-3 type) was obtain from United Catalyst Inc., USA.

## 3.2 Apparatus and Instruments

3.2.1 Apparatus for measuring pore volume of alumina support and molecular sieve comprised of:

- Burette for charging deionized water.
- Suction flask for charging alumina support and molecular sieve.
- Stand and clamp for supporting burette 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 (GC)

The apparatus model GC Piona from Hewlett-Packard Company was used. GC conditions followed ASTM D 5443.

Column : Polar, Non-Polar, Tenax<sup>3</sup>, Molsieve<sup>A</sup>, Platinum<sup>A</sup>

Carrier : Helium with flow rates of 16 to 23 mL/min

Injection temperature : 200°C

Detector : Flame Ionization Detector

### 3.2.4 High Pressure Reactor

All experiments in this study were carried out in the apparatus which consisted of three parts as follows

#### 3.2.4.1 Reactor (Figure 3.1)

The bench top reactor was a high pressure batch stirred autoclave model 4562 from Parr Instrument Company with a 600 ml stainless steel cylindrical bomb, split ring closures and a bomb heater. The working pressure must not exceed 3,000 psig and maximum operating temperature was 350°C.

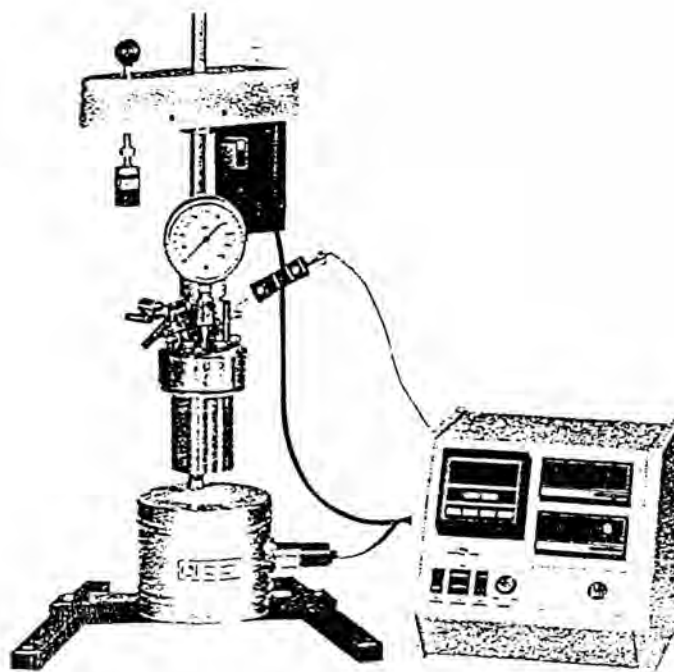


Figure 3.1 Reactor with heater removed.

### 3.2.4.2 Reactor Fitting

The stirring unit of reactor was equipped with convenient valves and fitting for handling the various functions. The parts are indicated below :

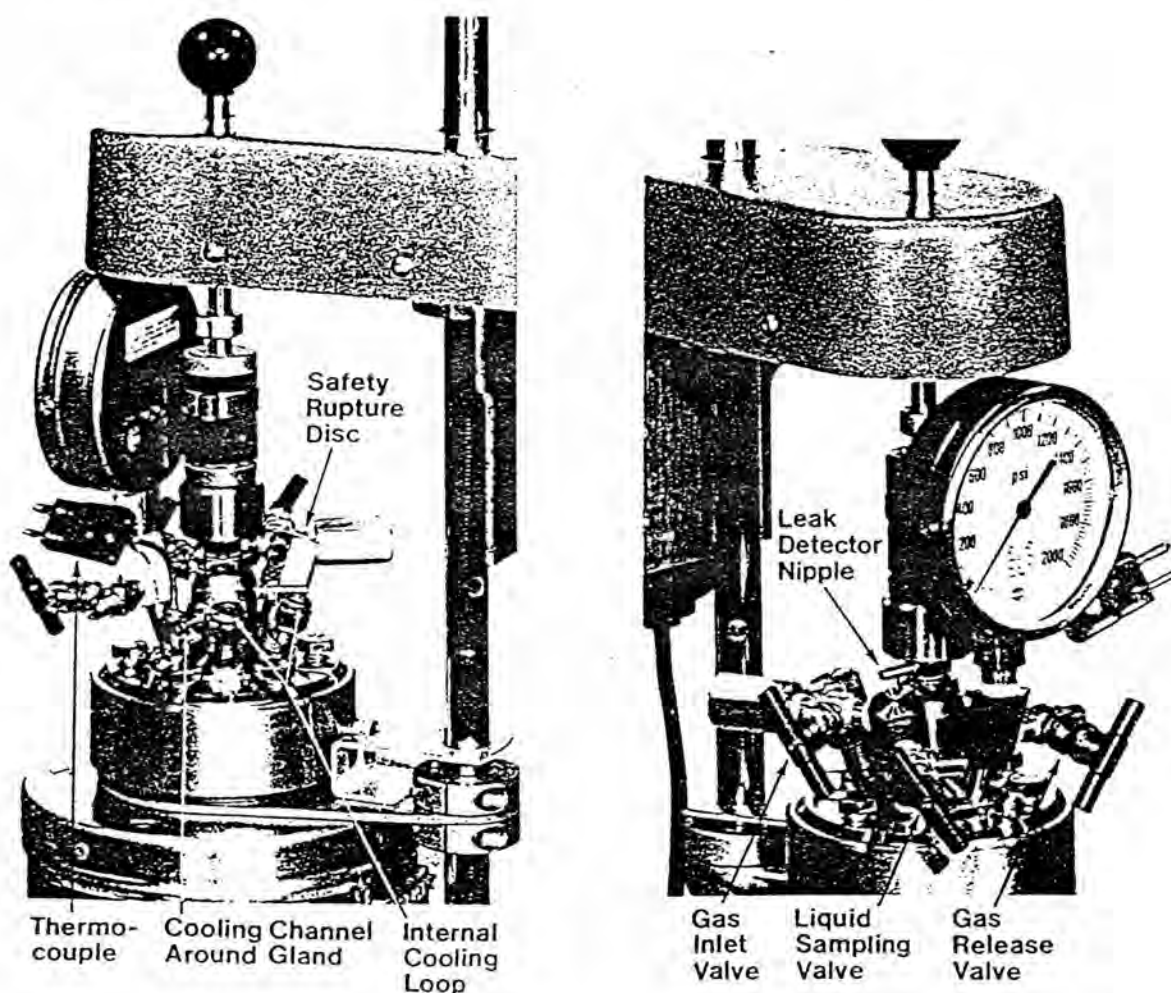


Figure 3.2 Reactor fitting

### 3.2.4.3 Temperature Controller

The controller model 4842 with Watlow Series 945, a microprocessor-based temperature control, from Parr Instrument

Company was used. It was operated in conjunction with a type J thermocouple and included automatic LED indicators to assist monitoring.

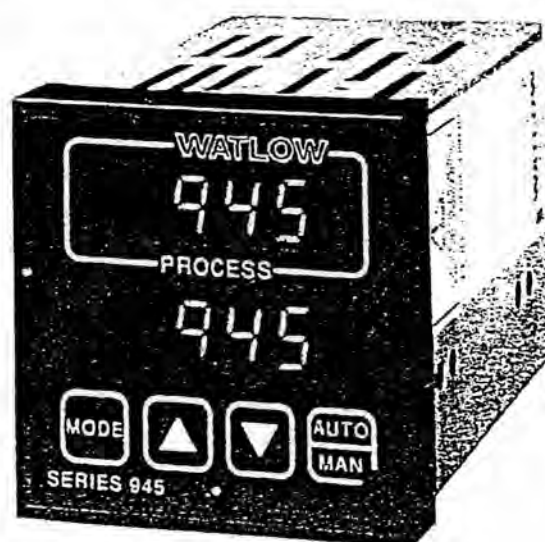


Figure 3.3 ¼ DIN microprocessor-based auto-tuning control

### 3.2.5 Gas Controllers System

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

### 3.2.6 X-ray

The apparatus X-ray fluorescence was used.

### 3.2.7 Nuclear Magnetic Resonance Spectrometer (NMR Spectrometer)

The NMR model AC-F 200 from Bruker at 50 MHz for  $^{13}\text{C}$  spectra and 200 HMz for  $^1\text{H}$  spectra was used.

### 3.3 Procedure

#### 3.3.1 Measuring Pore Volume

##### 3.3.1.1 Alumina Support CS 331-3 Type

The alumina support (100 g) was placed in a suction flask which was equipped with a burette 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 burette 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.

##### 3.3.1.2 Molecular Sieve 4A Type

Following the procedure as in experiment 3.3.1, the pore volume of the molecular sieve 4A was 0.52 ml/g.

#### 3.3.2 Preparation of Catalysts

3.3.2.1 Fe/Sn/F Catalyst : Containing Fe(5%), Sn(5%), F(2%) on Molecular Sieve

The molecular sieve was calcined for four hours at 600°C before use. The molecular sieve (120.00 g) was added into solution tin (II) chloride dihydrate (9.59 g, 0.04 mol) in water (60 ml) and hydrochloric acid (10 ml). 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 a solution of Iron (III) chloride dihydrate (29.04 g, 0.15 mol) in water (60 ml). 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 a solution of ammoniumfluoride (4.68 g, 0.13 mol) in water (60 ml) and then 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 following conditions : 150°C for 1 hour, then the temperature was raise by 50°C every 15 minutes to 400°C, then held at 400°C for 1 hour to obtain the Fe/Sn/F catalyst.

#### 3.3.2.2 Fe/Sn/F Catalyst : Containing Fe(5%), Sn(5%), F(2%) on Alumina Support

The procedure of 3.3.2.1 was employed except the alumina in water (70 ml) was used in place of molecular sieve in water (60 ml).

#### 3.3.2.3 Fe/Sn/F Catalyst : Containing Fe(2.5%), Sn(5%), F(2%) on Molecular Sieve

The procedure of 3.3.2.1 was employed except that a different quantity of Iron (III) chloride trihydrate (14.52 g, 0.07 mol) was used.

3.3.2.4 Fe/Sn/F Catalyst : Containing Fe(5%), Sn(2.5%), F(2%) on Molecular Sieve

The procedure of 3.3.2.1 was employed except that a different quantity of Tin (II) chloride dihydrate (4.80 g, 0.02 mol) was used.

3.3.2.5 Fe/Sn/F Catalyst : Containing Fe(5%), Sn(5%), F(1%) on Molecular Sieve

The procedure of 3.3.2.1 was employed except that a different quantity of Ammoniumfluoride (2.34 g, 0.06 g) was used.

3.3.2.6 Ni/Sn/F Catalyst : Containing Ni(5%), Sn(5%), F(2%) on Molecular Sieve

The procedure of 3.3.2.1 was employed except that nickel (II) chloride hexahydrate (23.88 g, 0.10 mol) was used in placed of that Iron (III) chloride trihydrate (29.04 g, 0.15 mol).

3.3.2.7 Co/Sn/F Catalyst:Containing Co(5%), Sn(5%), F(2%) on Molecular Sieve



The procedure of 3.3.2.1 was employed except that cobalt (II) chloride dihydrate (24.20 g, 0.15 mol) was used in place of that Iron (III) chloride trihydrate (29.04 g, 0.15 mol).

### 3.3.3 Hydrocracking Process

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

Used Polystyrene which was cut into small pieces (50 g) and the activated Fe(5%)/Sn(5%)/F(2%) on molecular sieve catalyst (20 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 (325°C), the pressure (500 psig) and for the reaction time (3 hours). After the reaction had been proceeding to the specified period of time, the 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 compounds. The compounds were distilled to purify, then they were determined the components by GC.

The experiment was repeated according to the procedure described above for the Ni(5%)/Sn(5%)/F(2%) on molecular sieve, Co(5%)/Sn(5%)/F(2%) on molecular sieve 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. They were also determined by GC and the % yield were calculated.

### 3.3.3.2 The Effect of % component of Fe/Sn/F on Molecular Sieve on Hydrocracking

The procedure as in experiment 3.3.3.1 was followed except that the reaction was operate at various % component of Fe/Sn/F on molecular sieve catalyst, (containing Fe(5%)/Sn(5%)/F(2%), Fe(2.5%)/Sn(5%)/F(2%), Fe(5%)/Sn(2.5%)/F(2%) and Fe(5%)/Sn(5%)/F(1%) ). The reaction mixture was worked up in the same manner as above.

### 3.3.3.3 The Effect of Reaction Time on Hydrocracking

The procedure as in experiment 3.3.3.1 was followed except that the reactor was operated at the preset temperature (350°C), the pressure (500 psig) and various time (1,1.5 and 2 hours) using optimum catalyst, (containing Fe(5%)/Sn(5%)/F(2%) on molecular sieve), 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 Catalyst Concentration on Hydrocracking

The procedure as in experiment 3.3.3.1 was followed except that the reactor was operated at the preset temperature (350°C), the pressure (500 psig) and various catalyst concentrations (10, 15, 20 and 40% by wt of used polystyrene) using the optimum reaction time (1.5 hours) obtained from 3.3.3.3 and Fe(5%)/Sn(5%)/F(2%) on molecular sieve.

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

The procedure as in experiment 3.3.3.1 was followed except that the reactor was operated at the pressure (500 psig) and various temperature (325, 350°C) for the optimum catalyst concentration 15% wt of Fe(5%)/Sn(5%)/F(2%) on molecular sieve catalyst obtained from 3.3.3.4 and using the reaction time (1.5 hours). The reaction mixture was worked up in the same manner as described in 3.3.3.1.

#### 3.3.3.6 The Effect of Pressure on Hydrocracking

The procedure as in experiment 3.3.3.1 was followed except that the reactor was operated at various pressures (300, 350, 400 and 500 psig), the optimum reaction temperature (350°C) obtained from 3.3.3.5, the reaction time (1.5 hours) and using 15% wt of Fe(5%)/Sn(5%)/F(2%) on molecular sieve catalyst. The reaction mixture was worked up in the same manner as described in 3.3.3.1.

#### 3.3.3.7 The Effect of Support of Catalyst on Hydrocracking

The procedure as in experiment 3.3.3.1 was followed except that the reactor was operated at two support of catalyst (molecular sieve and alumina support), the optimum reaction pressure (350 psig) obtained from 3.3.3.6, the reaction time (1.5 hours), the reaction temperature

(3.5°C) and using 15% wt of Fe(5%)/Sn(5%)/F(2%) on molecular sieve catalyst. The reaction mixture was worked up in the same manner as described in 3.3.3.1.

### 3.3.4 Cracking Process under Nitrogen Pressure

#### 3.3.4.1 The Effect of Reaction Time on Cracking under Nitrogen Pressure

The procedure as in experiment 3.3.3.1 was followed except that the preset nitrogen pressure (150 psig) and the reaction time (6 hours). The reaction mixture was worked up in the same manner as above.

The experiment was repeated according to the procedure described above for the reaction time (5 and 5.5 hours). The hydrocarbon compounds were analyzed by GC.

#### 3.3.4.2 The Effect of Catalyst Concentration of Pt/Sn/F on Molecular Sieve on Cracking under Nitrogen Pressure

The procedure as in experiment 3.3.3.1 was followed except that the reactor was operated at the preset temperature (350°C), the pressure (150 psig) and various catalyst concentrations (5, 10, 20 and 40% wt of Fe(5%)/Sn(5%)/F(2%)) using the optimum reaction time (6 hours) obtained from 3.3.4.1. The reaction mixture was worked up in the same manner as described in 3.3.3.1.

#### 3.3.4.3 The Effect of Temperature on Hydrocracking under Nitrogen Pressure

The procedure as in experiment 3.3.3.1 was followed except that the reactor was operated at various temperature (325, 350°C) for the optimum catalyst concentration 10% wt of Fe(5%)/Sn(5%)/F(2%) on molecular sieve catalyst obtained from 3.3.4.2 and using the reaction time (6 hours). The reaction mixture was worked up in the same manner as described in 3.3.3.1.

#### 3.3.4.4 The Effect of Pressure on Hydrocracking under Nitrogen Pressure

The procedure as in experiment 3.3.3.1 was followed except that the reactor was operated at various nitrogen pressure (0 and 100) for the optimum temperature (350°C) obtained from 3.3.4.3, using catalyst concentration 10% wt of Fe(5%)/Sn(5%)/F(2%) on molecular sieve catalyst and the reaction time (6 hours). The reaction mixture was worked up in the same manner as described in 3.3.3.1.

#### 3.3.5 The Determination of the Component of the Product

The hydrocracked product was analyzed by GC, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR were recorded.