

## **CHAPTER III**

### **EXPERIMENTAL**

#### **3.1 Materials**

The materials used in this study were as follow:

- 3.1.1 Used polystyrene (i.e. polystyrene cups, trays etc.)
- 3.1.2 Industrial hydrogen gas was obtained from TIG Public Co., Ltd.
- 3.1.3 Industrial nitrogen gas was obtained from TIG Public Co., Ltd.
- 3.1.4 Hydrochloric acid was obtained from Baker Analyzed.
- 3.1.5 Stannous chloride ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) was obtained from Mallinckrodt.
- 3.1.6 Iron chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) was obtained from Merck Ltd.
- 3.1.7 Nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) was obtained from Carlo Erba.
- 3.1.8 Cobalt chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) was obtained from J.T. Baker.
- 3.1.9 Zinc chloride ( $\text{ZnCl}_2$ ) was obtained from Carlo Erba.
- 3.1.10 Lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ ) was obtained from Fluka.
- 3.1.11 Aluminium nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) was obtained from Merck Ltd.
- 3.1.12 Ammonium fluoride ( $\text{NH}_4\text{F}$ ) was obtained from Merck Ltd.
- 3.1.13 Molecular sieve (4A-DG type) was obtained from Union Carbide Ltd.

## **3.2 Apparatus and Instruments**

### **3.2.1 Pore Sizer**

The Micromeritics Pore Sizer model 9320 was used.

### **3.2.2 Calcinator**

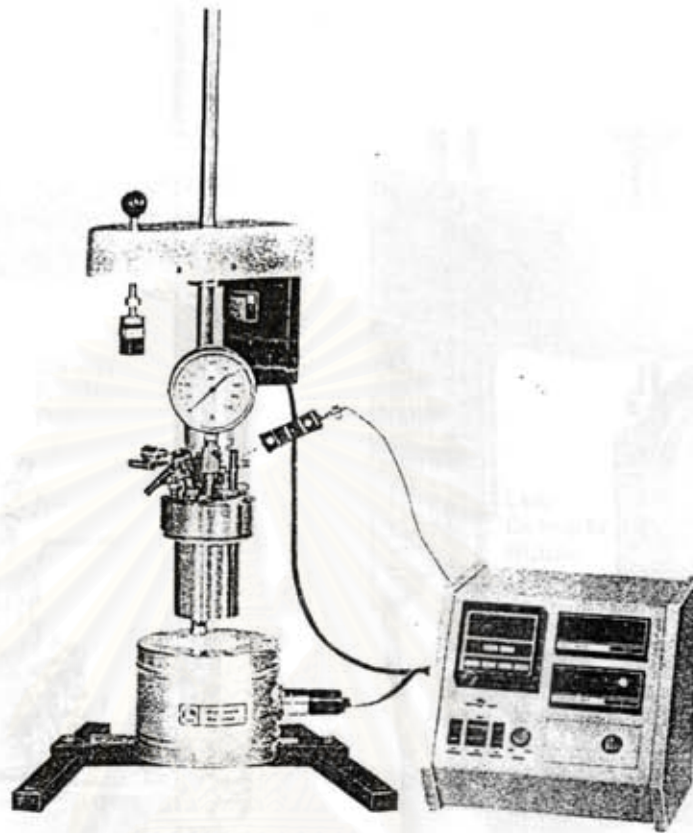
The apparatus model GSM from Carbolite Furnaces was used.

### **3.2.3 High Pressure Reactor**

All experiments for the depolymerization study of used polystyrene was carried out in the apparatus which consisted of three parts as follow :

#### **3.2.3.1 Reactor (Figure 3.1)**

The bench top reactor was a high pressure batch stirred autoclave model 4562 from Parr Instrument Company with 600 ml stainless steel 316 cylindrical bomb, split ring closures and bomb heater. The maximum operating temperature was 350 °C and working pressure must not exceed 3,000 psig.

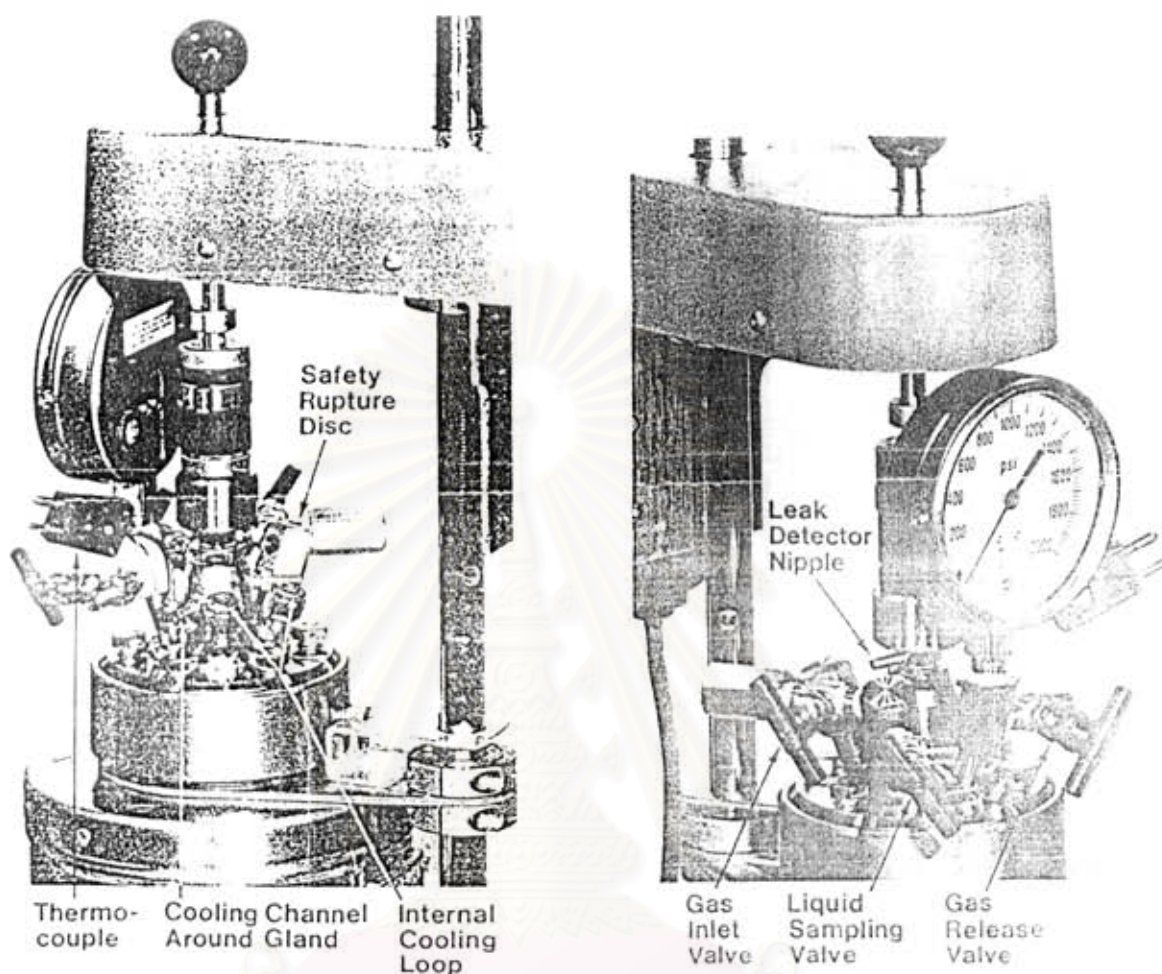


**Figure 3.1** Reactor with heater removed

#### 3.2.3.2 Reactor Fitting (Figure 3.2)

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

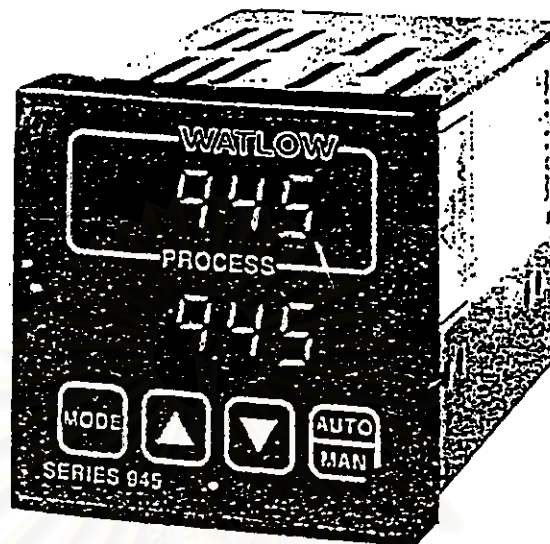
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**Figure 3.2** Reactor Fitting

### 3.2.3.3 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** 1/4 DIN microprocessor-based auto-tuning control

#### 3.2.4 Gas Controllers System

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

#### 3.2.5 X-ray

An X-ray fluorescence apparatus was used.

### 3.2.6 Gas Chromatography (GC)

The apparatus model GC PIONA from Hewlett-Packard Company was used. GC conditions following the ASTM D5443-93 (their compositions and percentage were calculated by this instrument with the library search program).

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

Inject temperature : 200 °C

Detector : Flame Ionization Detector

## 3.3 Procedure

### 3.3.1 Measuring Pore Volume of Molecular Sieve 4A-DG Type

The pore volume of molecular sieve 4A-DG type was measured by mercury and gas penetration method, using Micromeritics Pore Sizer. The pore volume was 0.52 ml/g.

### 3.3.2 Preparation of Catalysts

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

The molecular sieve was calcined at 600 °C for 4 hours before use. One hundred grams of molecular sieve was impregnated to the point of incipient wetness with a solution containing 9.50 g of SnCl<sub>2</sub>.2H<sub>2</sub>O, dissolved in 40 ml of water and 10 ml of hydrochloric acid. The mixture was stirred for 2



hours at room temperature and dried at 120 °C for 16 hours, thereafter precalcined for 2 hours at about 350 °C, calcined at 600 °C for 2 hours. The solid obtained was immersed in a solution containing 24.00 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , dissolved in 50 ml of water. The mixture was stirred for 2 hours at room temperature. After drying at 120 °C for 16 hours and calcining at 350 °C for 2 hours, the catalyst was reimpregnated with a solution of 3.90 g  $\text{NH}_4\text{F}$  in 50 ml of water and stirred for 2 hours at room temperature. The mixture was dried at 120 °C for 16 hours and calcined under the following condition : held at 150 °C for an hour, raised the temperature 50 °C every 15 minutes to 400 °C, then held at 400 °C for an hour. The Fe(5%)-Sn(5%)-F(2%) catalyst was obtained.

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

The procedure as in 3.3.2.1 was followed by using 20.20 g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  instead of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . The Ni(5%)-Sn(5%)-F(2%) catalyst was obtained.

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

The procedure as in 3.3.2.1 was followed by using 20.10 g of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  instead of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . The Co(5%)-Sn(5%)-F(2%) catalyst was obtained.

#### 3.3.2.4 Fe(5%)-Zn(5%)-F(2%) on Molecular Sieve

The procedure as in 3.3.2.1 was followed by using 10.42 g of  $\text{ZnCl}_2$  instead of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ . The Fe(5%)-Zn(5%)-F(2%) catalyst was obtained.

#### 3.3.2.5 Fe(5%)-Pb(5%)-F(2%) on Molecular Sieve

The procedure as in 3.3.2.1 was followed by using 7.99 g of  $\text{Pb}(\text{NO}_3)_2$  instead of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ . The Fe(5%)-Pb(5%)-F(2%) catalyst was obtained.

#### 3.3.2.6 Fe(5%)-Al(2%)-F(2%) on Molecular Sieve

The procedure as in 3.3.2.1 was followed by using 27.79 g of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  instead of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ . The Fe(5%)-Al(2%)-F(2%) catalyst was obtained.

#### 3.3.2.7 Fe(5%)-Al(3%)-F(2%) on Molecular Sieve

The procedure as in 3.3.2.1 was followed by using 41.69 g of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  instead of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ . The Fe(5%)-Al(3%)-F(2%) catalyst was obtained.



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

The procedure as in 3.3.2.1 was followed by using 69.48 g of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  instead of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ . The Fe(5%)-Al(5%)-F(2%) catalyst was obtained.

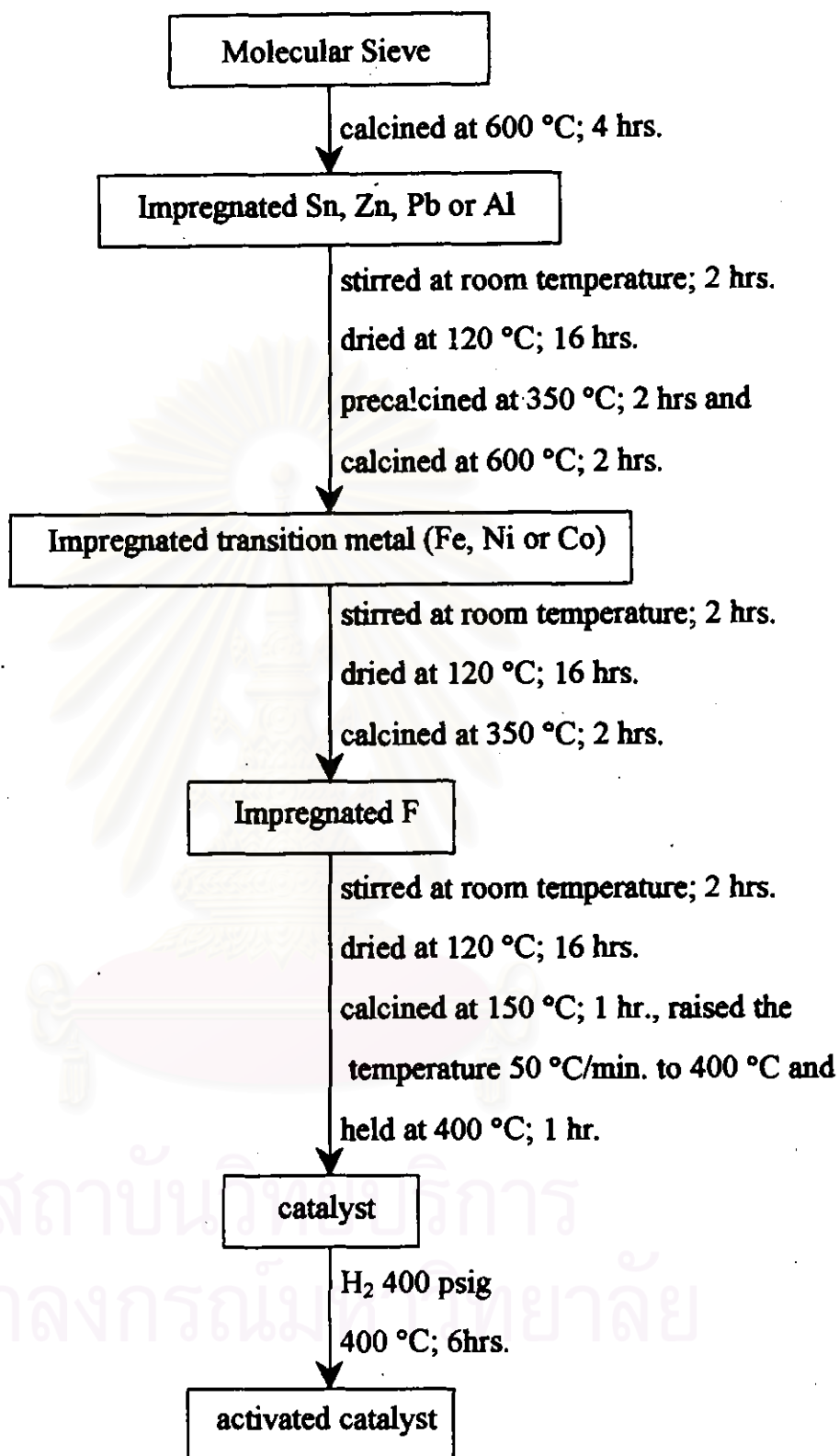
### 3.3.2.9 Activation of Catalysts

The catalyst was activated by reduction with 400 psig hydrogen pressure in a stainless steel reactor. The high pressure reactor was heated at 400 °C for 6 hours. The activated catalyst was obtained.

### 3.3.2.10 Regeneration of Catalysts

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

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**Figure 3.4** Flow chart of catalyst preparation

### 3.3.3 Hydrocracking Process

Used polystyrene about 50 g from cups, reduced beforehand into particles about 0.5 to 1 cm in size, was mixed with a measured amount (15% by weight) of activated catalyst and the mixture was added into the autoclave reactor. The latter was closed, purged sequentially with nitrogen and hydrogen and then pressurized with hydrogen to an initial pressure of 400 psig. The reactor was heated to a temperature of 350 °C. When the temperature raise to about 270 °C, a stirrer was turned on at 150 rpm. At the end of the reaction run (90 min.) the reactor was cooled down to room temperature for an hour and depressurized. The reaction mixture was transferred to a 250 ml beaker. The used catalyst was separated by suction filtration to give hydrocarbon compounds. The compounds were purified by distillation and identified by GC.

#### 3.3.3,1 The Effect of Catalyst Type on Hydrocracking

The effect of catalyst type was studied by following the procedure as mentioned in 3.3.3, with various catalyst types, i.e. Fe(5%)-Sn(5%)-F(2%), Ni(5%)-Sn(5%)-F(2%), Co(5%)-Sn(5%)-F(2%), Fe(5%)-Zn(5%)-F(2%), Fe(5%)-Pb(5%)-F(2%), Fe(5%)-Al(2%)-F(2%), Fe(5%)-Al(3%)-F(2%) and Fe(5%)-Al(5%)-F(2%).

### 3.3.3.2 The Effect of Temperature on Hydrocracking

The effect of temperature was studied by following the procedure as mentioned in 3.3.3, using the optimum catalyst (Fe(5%)-Sn(5%)-F(2%)) obtained from 3.3.3.1 with reaction temperatures of 300 and 350 °C.

### 3.3.3.3 The Effect of Pressure on Hydrocracking

The effect of pressure was studied by following the procedure as mentioned in 3.3.3, using the optimum reaction temperature (350 °C) obtained from 3.3.3.2 and Fe(5%)-Sn(5%)-F(2%) catalyst with initial hydrogen pressures of 300 and 400 psig.

### 3.3.3.4 Further Study of the Catalyst Activity on Hydrocracking

The catalyst activity was studied by following the procedure as mentioned in 3.3.3, using the optimum initial hydrogen pressure (400 psig) obtained from 3.3.3.3, reaction temperature (350 °C) and Fe(5%)-Sn(5%)-F(2%) catalyst.

The experiment was repeated by following the procedure as described above. At first, the regenerated Fe(5%)-Sn(5%)-F(2%) catalyst was used and after that it was regenerated and used for the second time.

### **3.3.4 Cracking Process under Nitrogen Pressure**

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

The effect of reaction time was studied by following the procedure as mentioned in 3.3.3, but purged with nitrogen, pressurized with initial nitrogen pressure of 500 psig and used Fe(5%)-Sn(5%)-F(2%) catalyst for 180 and 90 minutes.

#### **3.3.4.2 The Effect of Pressure on Cracking under Nitrogen Pressure**

The effect of pressure was studied by following the procedure as mentioned in 3.3.3, using the optimum reaction time (90 min.) obtained from 3.3.4.1 and Fe(5%)-Sn(5%)-F(2%) catalyst with various initial nitrogen pressures (200, 300, 400 and 500 psig).

#### **3.3.4.3 The Effect of Temperature on Cracking under Nitrogen Pressure**

The effect of temperature was studied by following the procedure as mentioned in 3.3.3, using the optimum initial nitrogen pressure (300 psig) obtained from 3.3.4.2, reaction time (90 min.) and Fe(5%)-Sn(5%)-F(2%) catalyst at reaction temperatures of 300 and 350 °C.

#### **3.3.4.4 The Effect of Catalyst Type on Cracking under Nitrogen Pressure**

The effect of catalyst type was studied by following the procedure as mentioned in 3.3.3, using the optimum reaction temperature

(350 °C) obtained from 3.3.4.3, initial nitrogen pressure (300 psig) and reaction time (90 min.) with various catalyst types (Fe(5%)-Sn(5%)-F(2%), Ni(5%)-Sn(5%)-F(2%), Co(5%)-Sn(5%)-F(2%), Fe(5%)-Zn(5%)-F(2%), Fe(5%)-Pb(5%)-F(2%) and Fe(5%)-Al(2%)-F(2%)).

#### **3.3.4.5 The Effect of Catalyst Concentration on Cracking under Nitrogen Pressure**

The effect of catalyst concentration was studied by following the procedure as mentioned in 3.3.3, using initial nitrogen pressure of 300 psig, reaction temperature (350 °C), reaction time (90 min.) and the optimum catalyst (Fe(5%)-Sn(5%)-F(2%)) obtained from 3.3.4.4 with catalyst concentrations of 10 and 15% by weight.

#### **3.3.4.6 Further Study of the Catalyst Activity on Cracking under Nitrogen Pressure**

The catalyst activity was studied by working in the same manner as 3.3.3.4, but using Fe(5%)-Sn(5%)-F(2%) catalyst with the optimum concentration (15% by weight) obtained from 3.3.4.5 and pressurized with initial nitrogen pressure of 300 psig at 350 °C for 90 minutes.

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

The hydrocarbon products were identified by GC.