

CHAPTER IV

EXPERIMENT

In the present study of the effect of electron donor on the isotacticity of propylene polymerization by Ziegler - Natta catalyst, the experiments were divided into three parts : (i) catalyst preparation (ii) polymerization and (iii) characterization of polymer products. The details of the experiments were discussed below.

4.1 CHEMICALS

Chemicals used were of Analytical Grade except where specified.

Propylene gas (C_3H_6 , 98.5%vol.) was supplied from Union Carbide Thailand Limited (Thailand). It was purified by passing through a column packed with molecular sieve 3A supplied by Union Carbide Thailand Limited to remove traces of moisture before entering reactor.

Ultra high purity hydrogen gas (H_2 , 99.999%vol.) and ultra high purity nitrogen gas (N_2 , 99.999%vol.) were supplied from T.I.G. Trading Limited

(Thailand). Each gas was purified by passing through the column packed with molecular sieve 3A to remove traces of moisture.

Hexane (C_6H_{14}) polymerization grade used as the polymerization solvent was received from Shell Co., Ltd. (Netherland).

Heptane (C_7H_{16}) was received from JT Baker Co., Ltd (USA) and used without further purification as solvent for extracting atactic polypropylene.

Titanium tetrachloride ($TiCl_4$) was used as received from Wako Pure Chemical Industries Limited (Japan) without further purification.

Triethylaluminum ($Al(C_2H_5)_3$, ca. 300 mmol/l in hexane) was used as received from Bangkok Polyethylene Co. Ltd. (Thailand) without further purification.

Anhydrous Magnesium Chloride ($MgCl_2$ from Aldrich (Germany) was used as received without further purification.

Tetraethoxysilane ($Si(OC_2H_5)_4$), Methyltriethoxysilane ($CH_3Si(OC_2H_5)_3$), Dimethyldiethoxysilane ($((CH_3)_2Si(OC_2H_5)_2)$), Trimethylethoxysilane ($((CH_3)_3SiOC_2H_5)$), and Phenyltriethoxysilane ($C_6H_5Si(OC_2H_5)_3$) were used as

external electron donor as received from Fluka Chemical Industries Limited (Germany) without further purification.

4.2 EQUIPMENT

Equipment of this research were divided into 2 parts : catalyst preparation equipment and polymerization equipment.

4.2.1 Catalyst Preparation Equipment

All of catalyst preparations were carried out in ultrahigh purity nitrogen atmosphere and glove bags were used for all transferring processes as shown in Figure 4.1.

4.2.1.1 Glass Mill Pot

As shown in Figure 4.2, 250 cm³ glass mill pot containing 120 ceramic balls with 1 cm. in diameter was equipped with 220 volt AC motor for grinding of catalyst support.

4.2.1.2 Catalyst Preparation Bottle

A 100 cm³ glass bottle with 2 septums and magnetic bar was used as catalyst preparation bottle as shown in Figure 4.3.

4.2.2 Polymerization Equipment

Polymerization equipment consisted of six parts as shown in Figure 4.4 and the characterization instruments as follows:

4.2.2.1 Polymerization Reactor

As shown in Figure 4.5, the polymerization reactor which was a batch stirred autoclave model 4521 from Parr Instrument Company (USA) consisted of 2000 cm³ stainless steel 316 cylindrical bomb, bomb head, a bomb heater, a stirrer and a cooling coil. The reactor was operable in the pressure range of 0-1900 psig and the temperature range of 0 - 350 °C.

4.2.2.2 Adjustable Speed Motor Controller

The controller used as shown in Figure 4.6 was model 64 EEn from Parr Instrument Company (USA). The stirring speed was adjustable in the range of 0 - 1000 rpm.

4.2.2.3 Automatic Temperature Controller

The controller set as shown in Figure 4.7 consisted of a magnetic contactor connected to a variac and RKC model PF-8B1C-M temperature controller and Eurotherm digital temperature indicator model type 141 from Eurotherm Worthing Co. (England). It was operated in conjunction with a thermocouple installed in a thermowell attached to the bomb head of the

polymerization reactor to provide temperature read-out. A dial setting was used to establish a set point at any temperature within the range of 0 - 400 °C.

4.2.2.4 Cooling System

The system as shown in Figure 4.8 was divided into 2 parts, one for cooling the reaction and another for cooling the system. Due to the rapid rate of polymerization at the beginning of the exothermic reaction, the reaction temperature immediately increased and was very high, even the automatic temperature controller could not suffice for keeping the reaction at the desired temperature. The immersion cooling coil was added. The other cooling system contributed by the Eyela cooling bath model CA101 from Tokyo Rikakikai (Japan) was used to remove the frictional heat from the mechanical stirring system.

4.2.2.5 Gas Distribution System

As shown in Figure 4.9, the system consisted of a hydrogen and an ultra high purity nitrogen, and propylene feeding lines made of copper pipe with diameter of 1/8 inch. and ball valves.

4.2.2.6 Catalyst Feeding Unit

A glass cylinder with two stop-cocks at both ends, a septum cap for injection through at the middle, and 500 cm³ capacity connecting to 250 cm³ co-

catalyst storage bottle were used as the catalyst feeding unit as shown in Figure 4.10. By means of the closed system to prevent air and moisture, this unit was attached to the polymerization reactor and the hexane storage. A prepared suspension of catalyst components was introduced into the reactor by passing oxygen-free nitrogen stream through the glass cylinder.

4.2.2.7 Characterization Instruments

The instruments used to characterize catalysts and polypropylene products were specified in the following.

B.E.T surface area model ASAP2000 from Micromeritics (USA) as shown in figure in Figure 4.11 was used to determine the surface area of catalyst support. The surface area of $MgCl_2$ were measured by nitrogen adsorption with continuous flow method at the liquid nitrogen temperature. The amount of gas needed to form a mononuclear layer on the surface of sample could be determined from measurement of the volume of gas adsorbed. The B.E.T. equation was used for surface area calculation.

Soxhlet-type extractor with a boiling heptane shown in Figure 4.12 was used for determining the isotactic content. Polypropylene product weighed about 2.0-2.2 g was placed in cellulose thimble and then was extracted in Soxhlet-type extractor for 6 hr. in nitrogen atmosphere. The fraction of the whole polymer

unextracted x 100 was taken as a percent index of isotacticity (%II) according to the equation:

$$\% \text{ II} = \frac{\text{insoluble weight of polypropylene} \times 100}{\text{total weight of polypropylene}}$$

Scanning electron microscope (SEM) model JSM-5400 from JEOL (Japan) as shown in Figure 4.13 was employed to investigate the polymer morphology. The polymer samples were coated with gold particles by ion sputtering device to provide electrical contact to the specimen.

4.3 CATALYST PREPARATION PROCEDURE

In catalyst preparation procedure, there were many patents and papers about this topic. Supported Ziegler-Natta could be prepared by 3 ways : ball-milling of support, dissolving support in solvent and Grignard compound [15,16]. First method was applied in this work because it was less complicated and easier to control the condition.

15 g of Anhydrous MgCl_2 was ground in glass mill pot in N_2 atmosphere for 60 hours [26] . Ground MgCl_2 obtained from this process have $16 \text{ m}^2/\text{g}$ surface area by B.E.T. analysis. 1 g of ground support was transferred to catalyst preparation bottle containing 25 cm^3 polymerization grade refluxed hexane by glove bag method then stirred by magnetic stirrer then impregnated with 0.05 cm^3 TiCl_4 before used.

4.4 POLYMERIZATION PROCEDURE

Propylene polymerization was carried out in the 2000 cm³ reactor, which was equipped with all parts described above and several valves for gas feeding, catalyst dosing, and gas releasing, as shown in Figure 4.4.

Before starting up the reaction, the system was checked for leaks by pressurizing with high-pressure ultra high purity nitrogen gas for an hour and looked whether pressure dropped or not. The reactor was dried at 120 °C for an hour, ultra high purity nitrogen gas purged with and alternately vacuumed for 3 times. After cooling to 25 °C, the 500 cm³ suspension of catalyst was prepared in such a way to obtain the required of catalyst compositions by the reaction of triethylaluminum from storage bottle and titanium tetrachloride-magnesium chloride suspended in hexane that was injected to the glass cylinder by glass syringes under nitrogen atmosphere and introduced into the reactor.

The reaction temperature was gradually increased at a rate 2 °C per minute to 85 °C and propylene gas was consequently introduced and kept at a required total pressure. During 90 minutes for polymerization, propylene was continuously supplied at a constant partial pressure, the temperature was kept at 90 °C and agitator speed was kept at 750 revolution per minute.

By stopping admission of the propylene gas, depressurizing and cooling the reaction, the polymerization reaction was quenched by water and then the polymer was immediately separated and dried overnight. Further characterization of polymer was done.

The study of propylene polymerization was divided into two parts. First, the suitable polymerization conditions and their effects on propylene polymerization were studied on the catalyst and co-catalyst system. Second, after the best condition had been determined, the study of effects of external electron donor addition were done. The experimental investigation of conditions and effects on the polymerization were conducted as follows:

4.4.1 Effect of Al/Ti Ratio

Varying triethylaluminum concentration : titanium tetrachloride 8.936 mmol liter⁻¹ in hexane solution was used and the triethylaluminum concentration was varied with the Al/Ti mole ratios. The reaction conditions were 90 °C, 100 psi of total pressure, C₃H₆/H₂ ratio of 3, and 90 minutes of polymerization time.

4.4.2 Effect of Hydrogen Ratio

The polymerization was carried out to investigate the effect of hydrogen ratio on the catalytic activity by the total pressure was constant. The Al/Ti mole

was kept constant as the best selected from part 4.4.1. The following is the experimental conditions for the polymerization.

TiCl₄ concentration = 8.936 mmol liter⁻¹

Temperature = 90 °C

Polymerization time = 90 minutes

n-hexane = 500 cm³

4.4.3 Effect of Total Pressure

During the study, the total pressure was varied without hydrogen because the pressure gauge had no scale for hydrogen pressure at such low ratio and others parameters were kept constant.

4.4.4 Effect of Reaction Temperature

The propylene polymerization was carried out to investigate the effect of reaction temperature on the catalytic and activity. The reaction temperature was varied from 60 to 90 °C whereas other parameters were kept constant.

4.4.5 Effect of External Electron Donors

The propylene polymerization was further investigated by external electron donors modified conventional Ziegler-Natta catalyst at the suitable condition obtained from the previous section. The amount of external electron donors were fixed at 0.05 mole electron donor/Al .

4.4.6 Effect of External Electron Donor Concentrations

The best external electron donor was chosen from the previous section . The external electron donor/Al molar ratios were varied from 0.025, 0.05, 0.10 and 0.20.

4.5 CHARACTERIZATION OF THE POLYPROPYLENE PRODUCT

This polypropylene product has remarkable chemical inertness, particularly at ordinary temperatures to most chemicals, including acids and alkalies. For the reason, chemical analysis procedure available for characterization of polypropylene was few. As a consequence of this, a quantitative measurements of physical properties and determinations of the involved chemicals and physical structure have become increasingly important. In this work the polypropylene products were characterized by the following methods.

4.5.1 Isotactic Content

The isotactic content of a polypropylene can be determined in a number of ways. The most widely used method involved extracting the polymer in a Kumagawa or a Soxhlet-type extractor with a boiling solvent [40]. For isotactic polypropylene, boiling heptane was commonly used. The fraction of the whole polypropylene unextracted x 100 was taken as a percent index of isotacticity. Figure 4.12 showed a extraction apparatus.

This method was very valuable for it allowed a facile determination of an index related to isotacticity; it, however, possessed certain deficiencies. For polymers that had similar molecular weights (and molecular weight distributions), the relative comparison was valid. But polymers that had very low or very high molecular weights the method gave false comparisons. A polymer that had very low molecular weights, such as $[\eta] = 0.1-0.8$ dl/g, would be considerably more soluble in hot solvent than one that had $[\eta] = 2-4$ dl/g, even though both had identical isotacticity. High molecular weight polymers might show lower solubility due to higher solution viscosity [40].

4.5.2 Morphology

The term of morphology was referred to the shape, texture, or form of such a polypropylene. Scanning Electron Microscope (SEM) technique was the effective method to investigate these morphologies.

4.4.3 Activity

The term of "catalyst activity" in this work is expressed in gram of polypropylene produced by 1 gram-atom of titanium during 1 hour 30 minutes of polymerization time (gPP/gTi-hr).

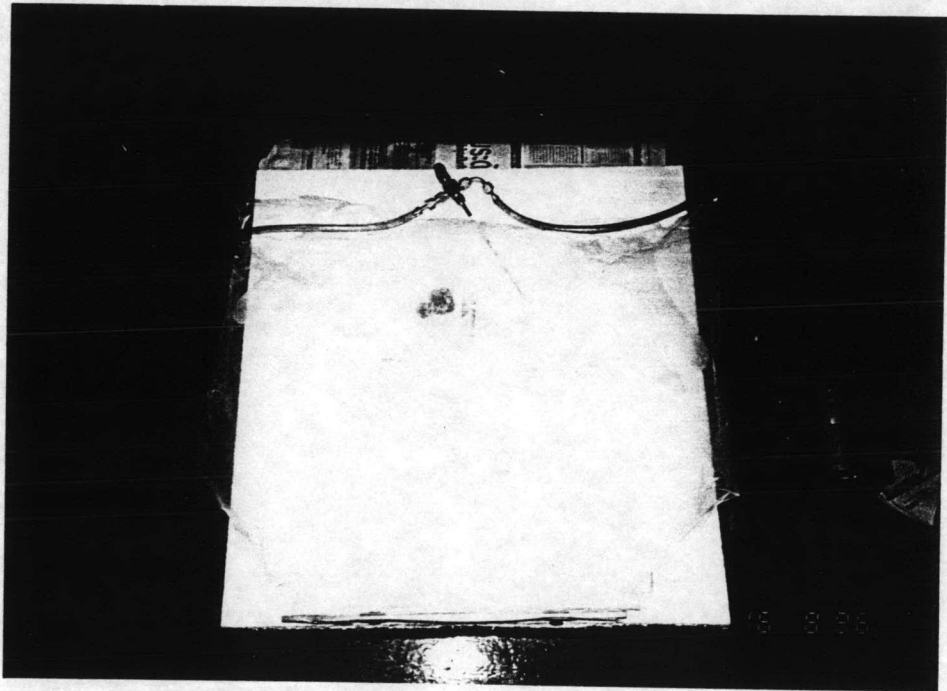


Figure 4.1 Glove Bag Set

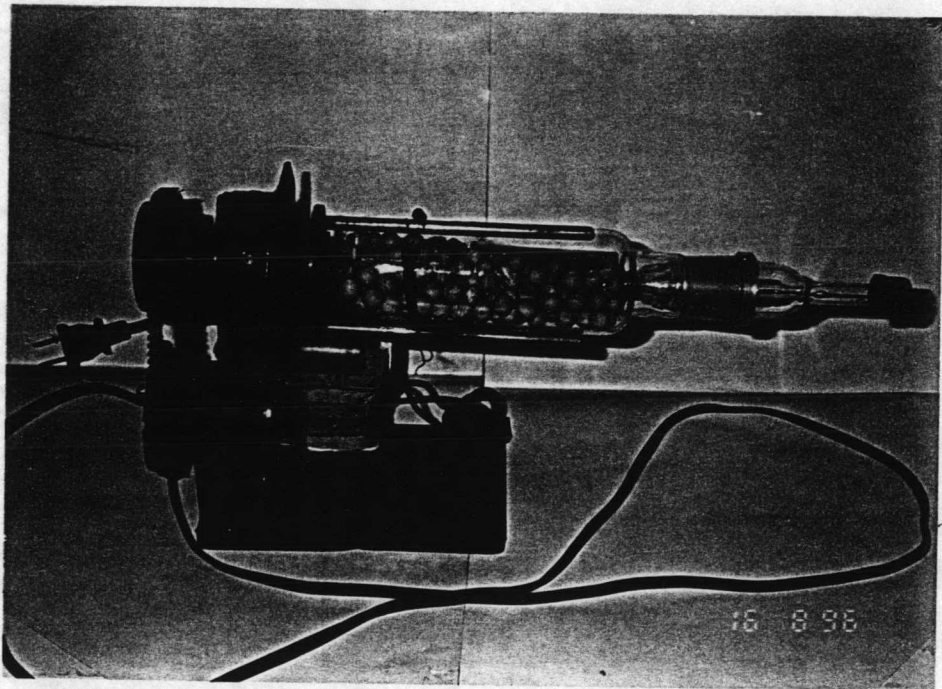
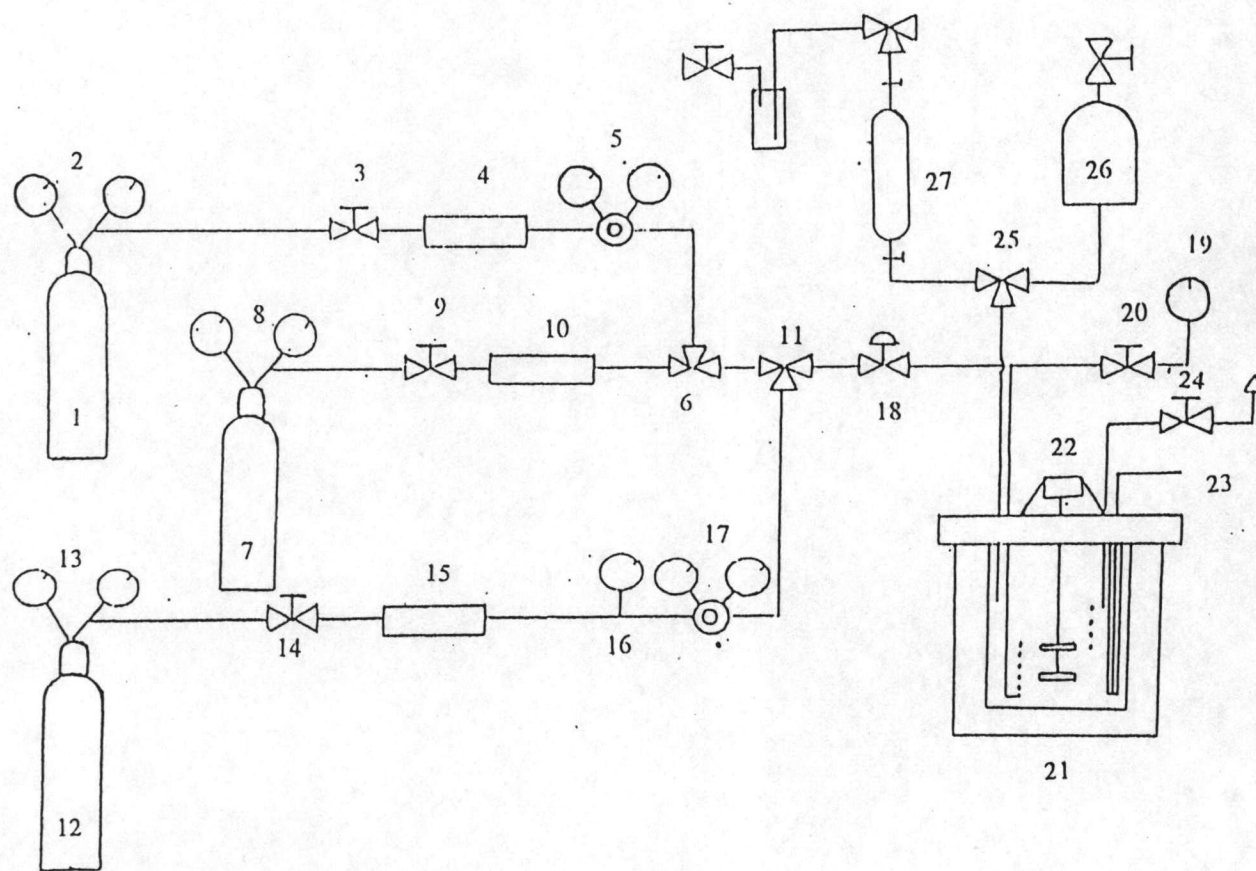


Figure 4.2 Glas Mill Pot



Figure 4.3 Catalyst preparation Bottle



1. H₂ cylinder
2. Pressure regulator
3. On-off valve
4. Moisture removal unit
5. Pressure regulator
6. Three-way valve
7. N₂ cylinder
8. Pressure regulator
9. On-off valve
10. Moisture removal unit
11. Three-way valve
12. C₃H₆ cylinder
13. Pressure regulator
14. On-off valve
15. Moisture removal unit
16. Pressure gauge
17. Pressure regulator
18. On-off valve
19. Pressure gauge
20. On-off valve
21. Reactor
22. Adjustable speed motor
23. Thermocouple
24. On-off valve
25. Three-way valve
26. Hexane storage
27. Catalyst preparation unit

Figure 4.4 Polymerization Equipment

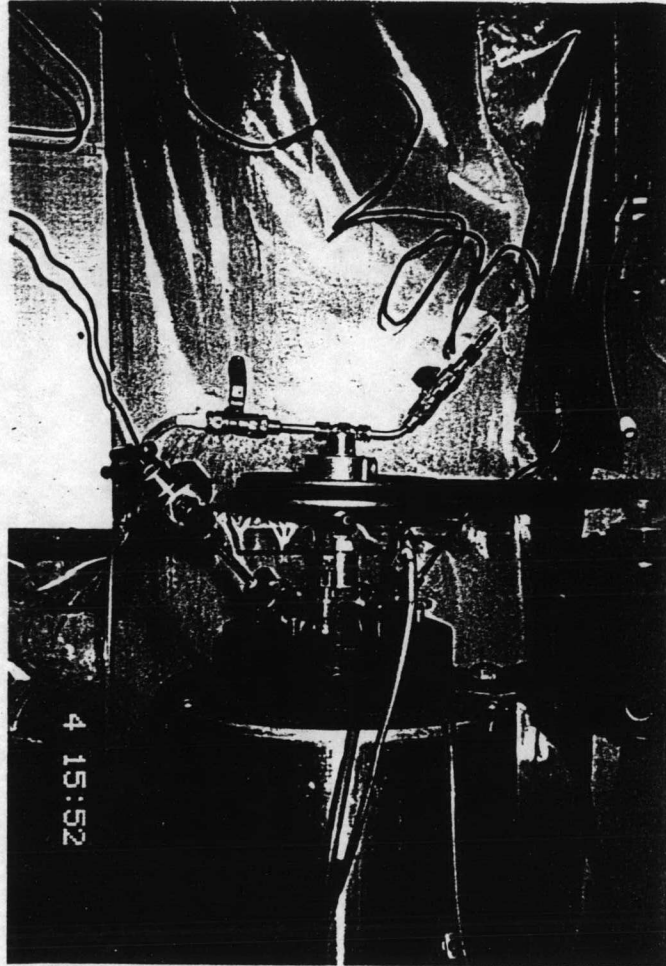


Figure 4.5 Polymerization Reactor

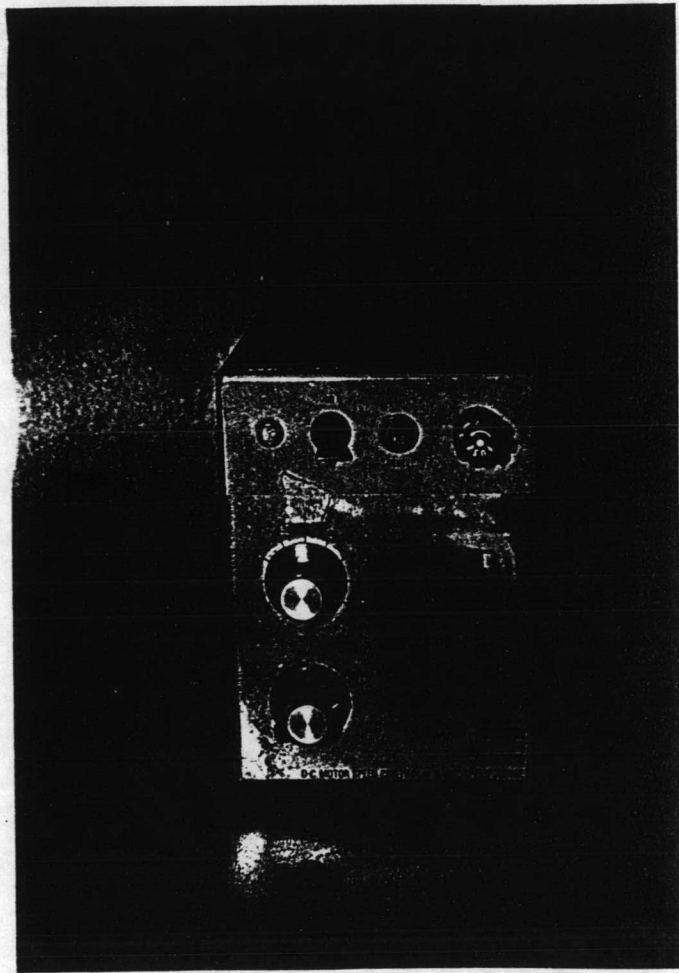


Figure 4.6 Adjustable Speed Motor Controller

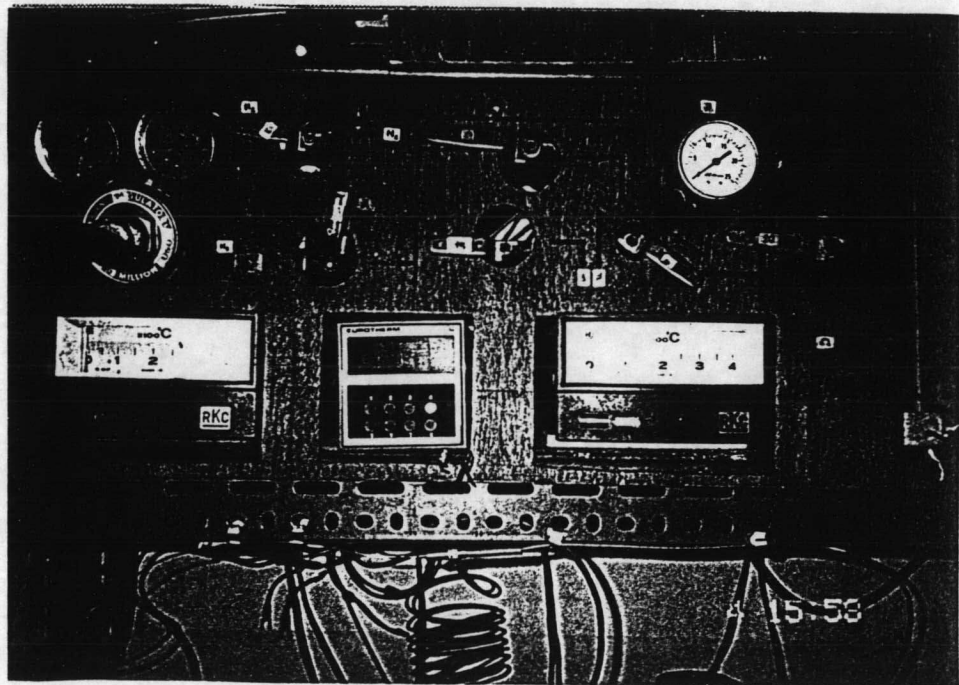


Figure 4.7 Automatic Temperature Controller

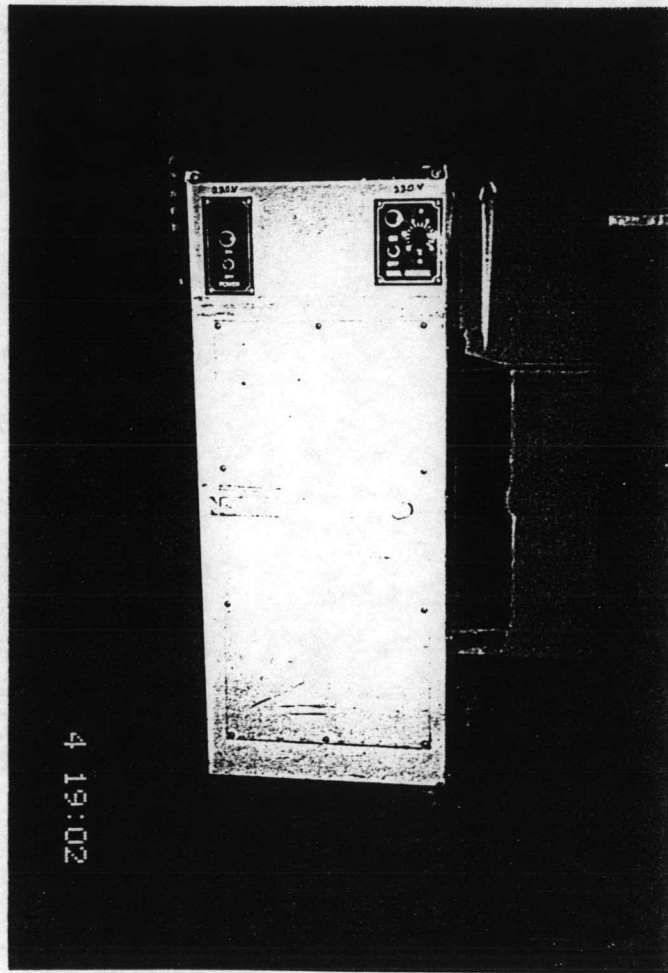


Figure 4.8 Cooling System

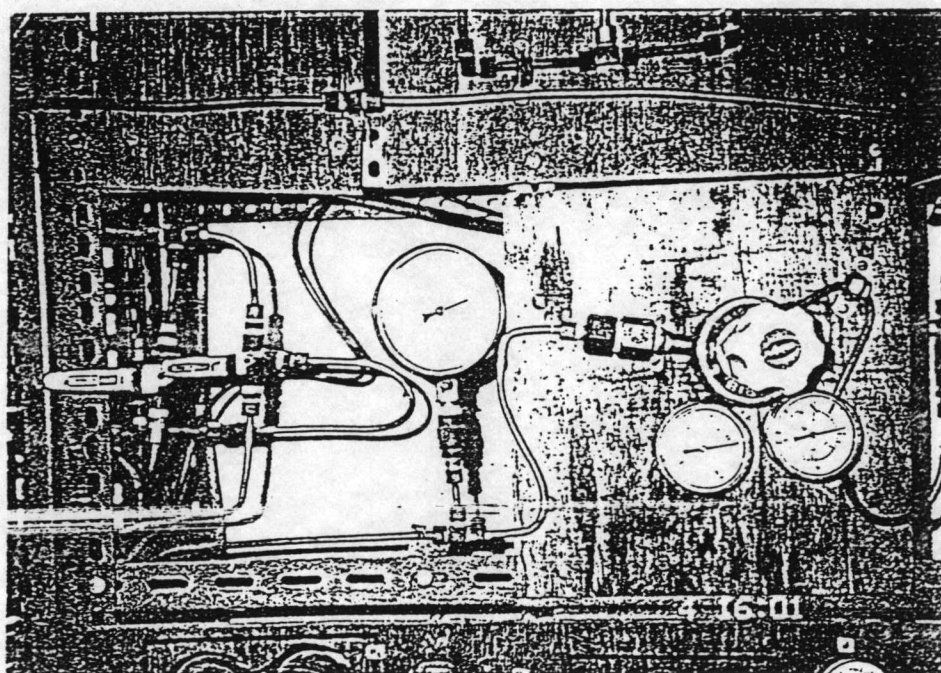


Figure 4.9 Gas Distribution System

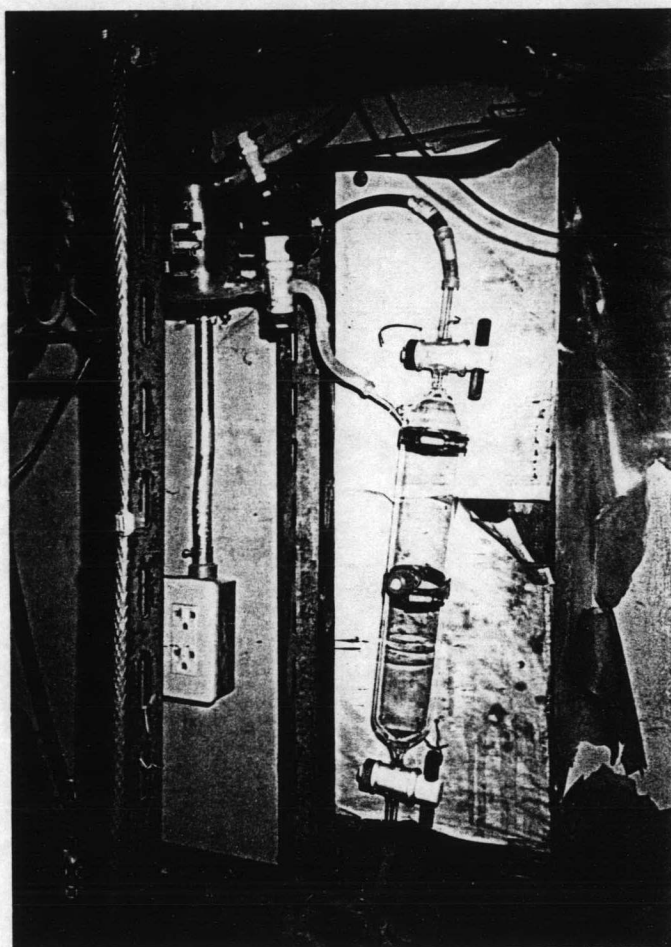


Figure 4.10 Catalyst Feeding Unit

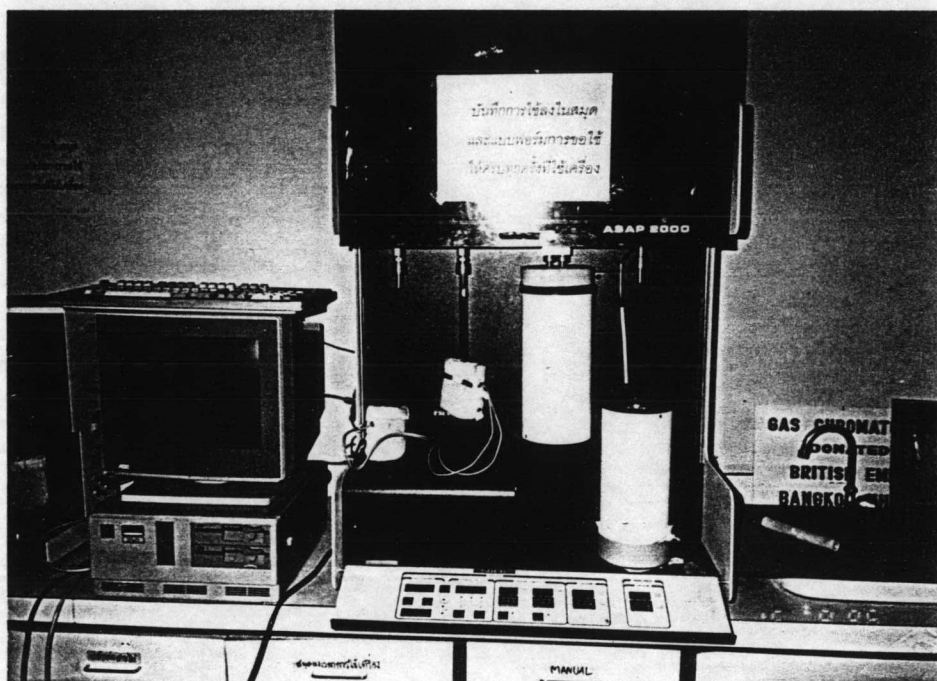


Figure 4.11 B.E.T. surface area

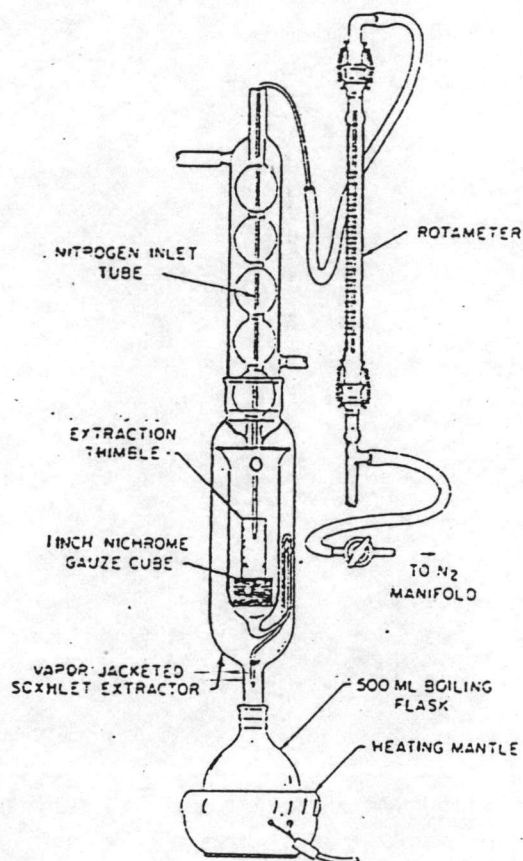


Figure 4.12 Soxhlet-type Extractor

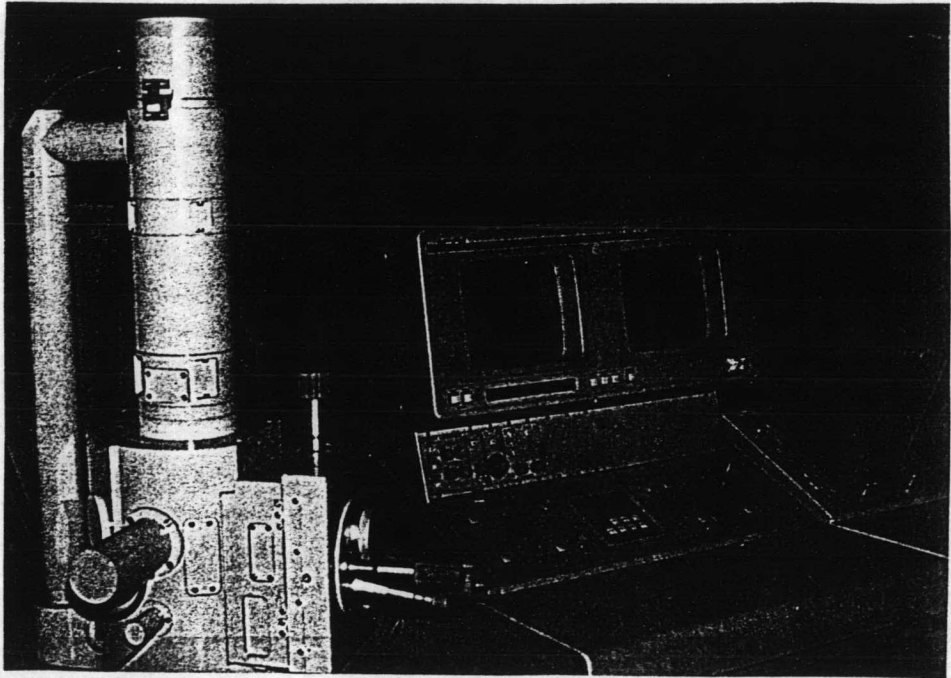


Figure 4.13 Scanning Electron Microscope