CHAPTER IV

EXPERIMENT

In the present study of the propylene polymerization with Ziegler - Natta catalyst, the experiments were divided into two parts : (i) polymerization and (ii) characterization of polymer products. The details of the experimeent were discussed in the following.

4.1 CHEMICALS

Chemicals used were of Analytical grade except where specified.

Propylene gas (98.5% pure) was supplied from Union Carbide Thailand Limited. It was purified by passing through a column packed wiht molecular sieve 3A supplied from Union Carbide Thailand Limited to remove traces of moisture.

Pure hydrogen gas and ultra high purity nitrogen gas were supplied from T.I.G. Trading Limited. They were purified by passing through the column packed with molecular sieve 3A to remove traces of moisture.

Hexane (polymerization grade) used as the polymerization solvent was received from Shell Co., Ltd. and stored over molecular sieve 5A.

Heptane used as solvent for extracting atactic polypropylene was received from JT Baker Co., Ltd. without further purification.

Titanium tetrachloride was used as received from Waco Pure Chemical Industries Limited without further purification.

Triethylaluminum (Ca 15% in hexane) was used as received from Tokyo Kasei without further purification.

Tetraethoxysilane, Methyltriethoxysilane, Dimethyldiethoxysilane, Trimethylethoxysilane, and Phenyltriethoxysilane were used as external electron donor as received from Fluka Chemical Industries Limited without further purification.

4.2 EQUIPMENT

All experiments were carried out in the polymerization apparatus which consisted of six parts (Figure 4.1 show Flow Diagram of the Polymerization System) and the characterization instruments as follows:

4.2.1 Polymerization Reactor

As shown in Figure 4.2, the polymerization reactor which was a pressure stirred autoclave model 4521 from Parr Instrument Company consisted of 2000 cm^3 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 Adjustable Speed Motor Controller

The controller used as shown in Figure 4.3 was model 64 EEn from Parr Instrument Company. The stirring speed was adjustable in the range of 0 - 1000 rpm.

4.2.3 Automatic Temperature Controller

The controller set as shown in Figure 4.4 consisted of a magnetic contactor connected to a variac, an RKC model PF-8B1C-M temperature controller and a Eurotherm digital temperature indicator model type 141. It was operated in conjunction with a thermocouple installed in a thermowell attached to the bomb head 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.

4.2.4 Cooling System

The system as shown in Figure 4.5 was provided into 2 parts, one for cooling reaction and another for cooling 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 was used to remove the frictional heat from the mechanical stirring system.

4.2.5 Gas Distribution System

As shown in Figure 4.6, the system consisted of a hydrogen and an ultra high purity nitrogen, and propylene feeding lines.

4.2.6 Catalyst Preparation Unit

A glass cylinder with two stop-cocks at both ends, a septum cap for injection through at the middle, and 500 cm^3 capacity was used as the catalyst preparation unit as shown in Figure 4.7. By means of the closed system to prevent air and moisture, it 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.

4.2.7 Characterization Instruments

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

Soxhlet-type extractor with a boiling heptane shown in Figure 4.8 was used for determining the isotactic content. Polypropylene product was weighed in cellulose thimble about 2.0-2.2 g. then extract in Soxhlet-type extractor for 6 hrs. 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.

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

Modified Ubbelohde viscometer as shown in Figure 4.9 was used to determine intrinsic viscosity (limiting viscosity number) that related to molecular weight of the polypropylene products.

Scanning electron microscope (SEM) model as shown in Figure 4.10 was employed to investigate the polymer morphology.

4.3 POLYMERIZATION PROCEDURE

Propylene polymerization was carried out in the 2000 cm^3 autoclave reactor, which was equipped with all parts described above and several valves for gas feeding, catalyst dosing, and gas releasing as shown in Figure 4.1

Before starting up the reaction, the system was checked for leaks by pressurizing with high-pressure ultra high purity nitrogen gas for an hour. 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 cm^3 suspension of catalyst was prepared in such a studied manner of catalyst compositions by the reaction of titanium tetrachloride and triethylaluminum in the glass cylinger under nitrogen atmosphere and introduced into the reactor.

Then the reaction contents were heated to 50°C and hydrogen stream was introduced at 1 bar partial pressure. The reaction temperature was gradually increased at a rate 2°C per minute to 70 °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 70 °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. The 10-20 cm^3 of acidic methanol was poured into the polymerization mixture for a while to deactivate the catalyst and remove $TiCl_3$ residues from the polymer particle[79] 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 titanium tetrachloride - triethylaluminum catalytic 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:

4.3.1 Effect of Catalyst 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 70 °C, 4 bar of total pressure, C_3H_6/H_2 ratio of 3, and 90 minutes of polymerization time.

4.3.2 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 4.3.1. The following is the experimental conditions for the polymerization.

$TiCl_4$ concentration = 8.936 mmol liter^{-1}
Temperature = 70 °C
Polymerization time = 90 minutes
n-hexane = 500 cm^3

4.3.3 Effect of total pressure

During the study, the total pressure was varied but propylene/hydrogen mole ratio as the best selected from part 4.3.2 and others parameters were kept constant.

4.3.4 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 others parameters were kept constant.

4.3.5 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/Ti .

4.3.6 Effect of external electron donor concentrations

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

4.4 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 involving chemicals and physical structure have become increasingly important. In this work the polypropylene products were characterized by the following methods.

4.4.1 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 [1]. 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 4.7 shows 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 $[\eta] = 0.1\text{-}0.8$ dl/g, would be considerably more soluble in hot solvent than one that had $[\eta] = 2\text{-}4$ dl/g, even though both had identical isotacticity. High molecular weight polymers might show lower solubility due to higher solution viscosity. [1]

4.4.2 Morphology

The term of morphology was referred to the shape , texture, or form of such a polypropylene. The polymer samples were coated with gold plate by ion sputtering device in Figure 4.10. Scanning Electron Microscope (SEM) technique was the effective method to investigate these morphologies

4.4.3 Molecular Weight

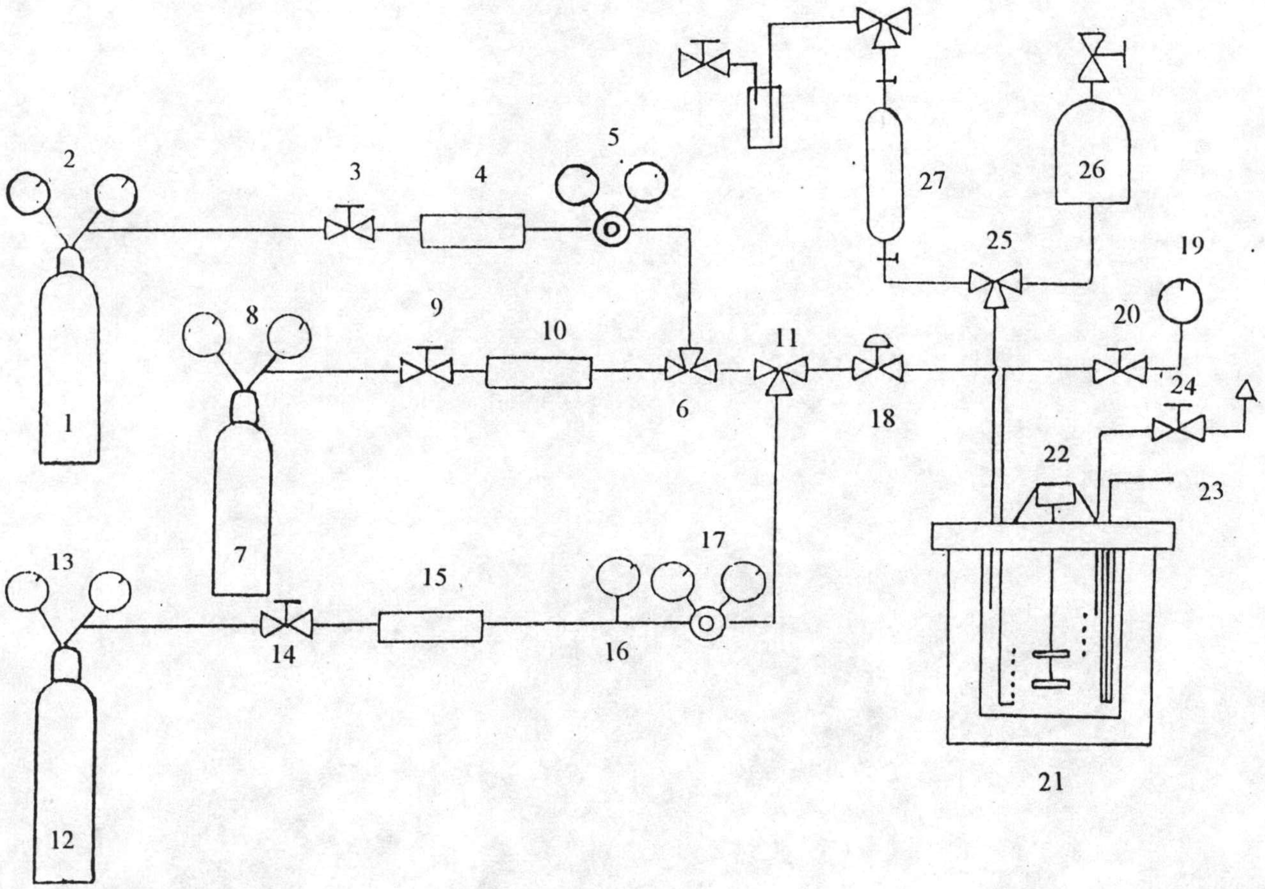
The viscosity of polypropylene solution has a relationship to its viscosity-average molecular weight. The method of Test for Dilute-Solution Viscosity of propylene polymer ; ASTM D 1601 , is specified in this work which employs decahydronaphthalene as a solvent. In terms of intrinsic viscosity ([η]), the viscosty-average of molecular weight ($\overline{M}_V$) of polymer is obtained by the Mark-Houwink equation.

$$[\eta] \quad = \quad K\overline{M}_V{}^{\alpha}$$

where the value of K and α are 2.38×10^{-4} and 0.725, respectively, for determinations in decahydronaphthalene at 135 °C. [ ]

4.4.4 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).



1. H_2 cylinder
2. Pressure regulator
3. On-off valve
4. Moisture removal unit
5. Pressure regulator
6. Three-way valve
7. N_2 cylinder
8. Pressure regulator
9. On-off valve
10. Moisture removal unit
11. Three-way valve
12. C_3H_6 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 4.1 Flow Diagram of Polymerization Procedure

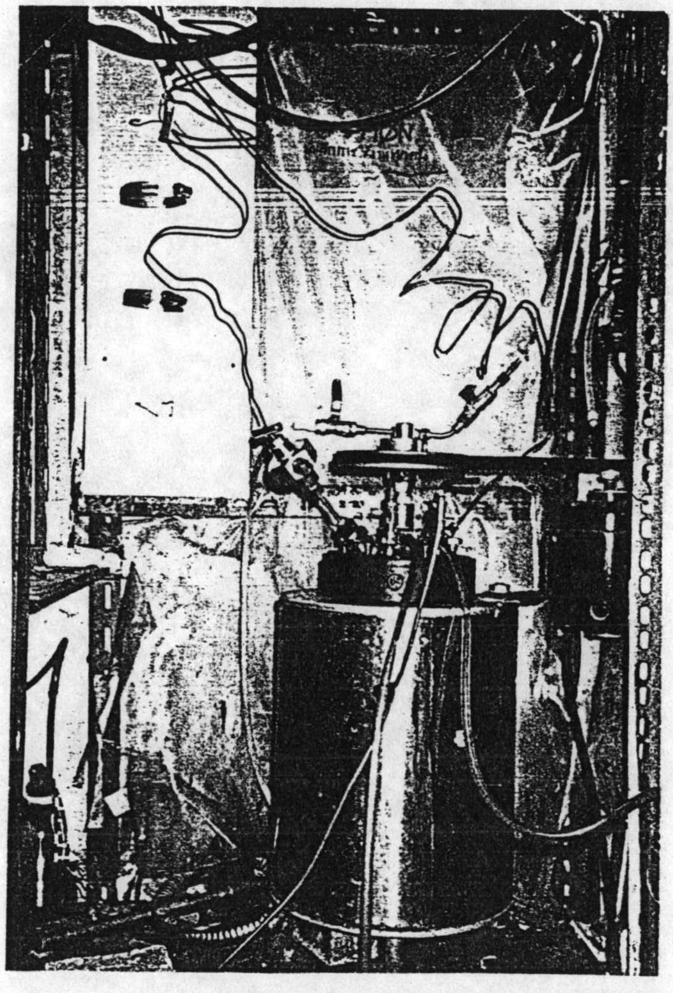


Figure 4.2 Polymerization Reactor

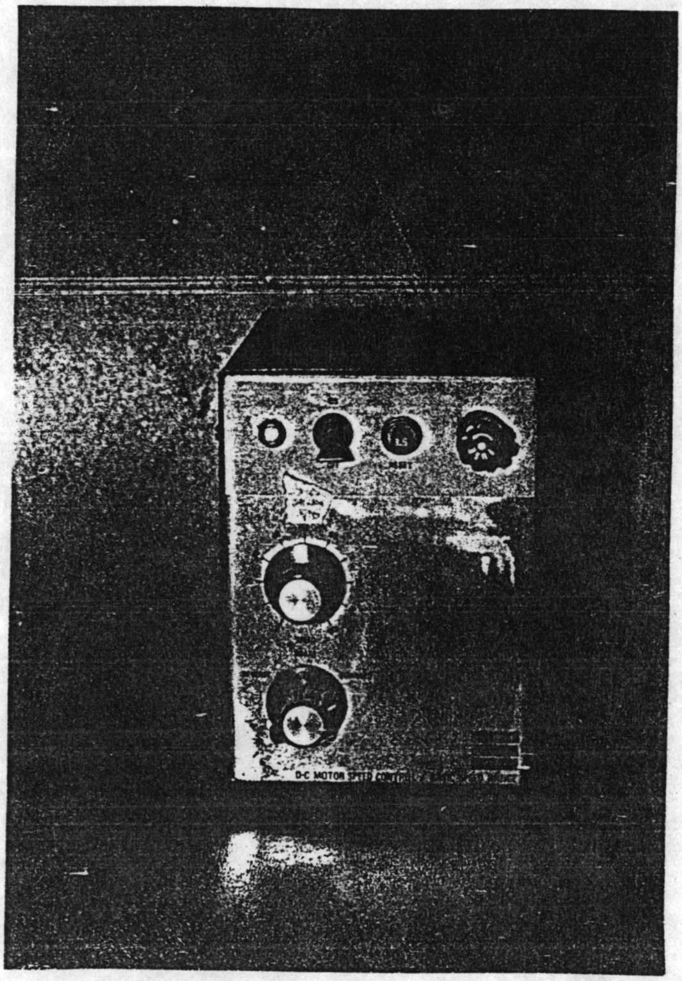


Figure 4.3 Adjustable Speed Motor Controller

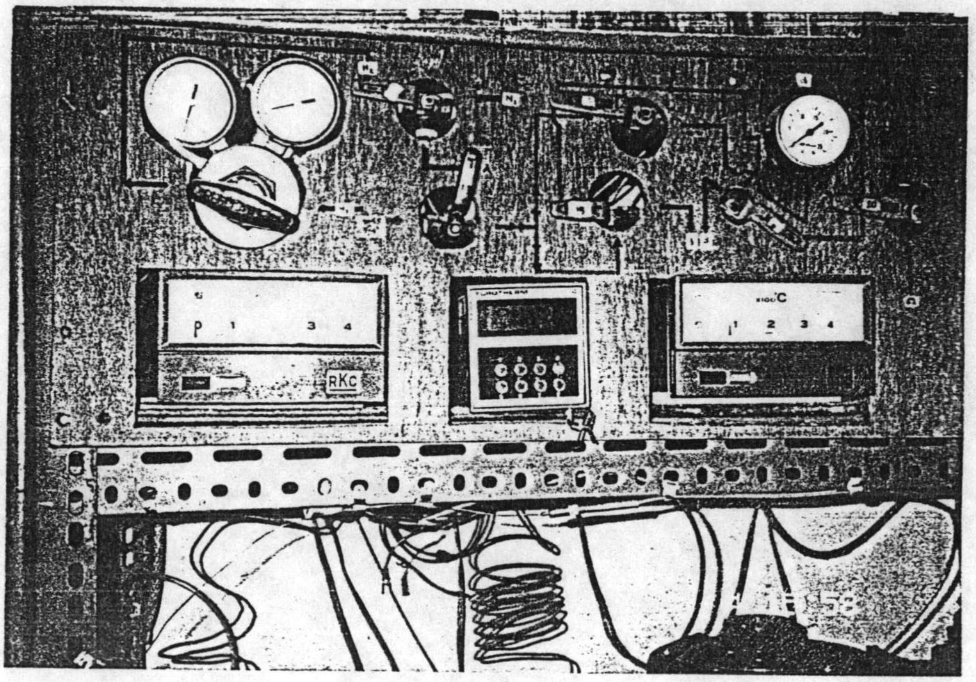


Figure 4.4 Automatic Temperature Controller

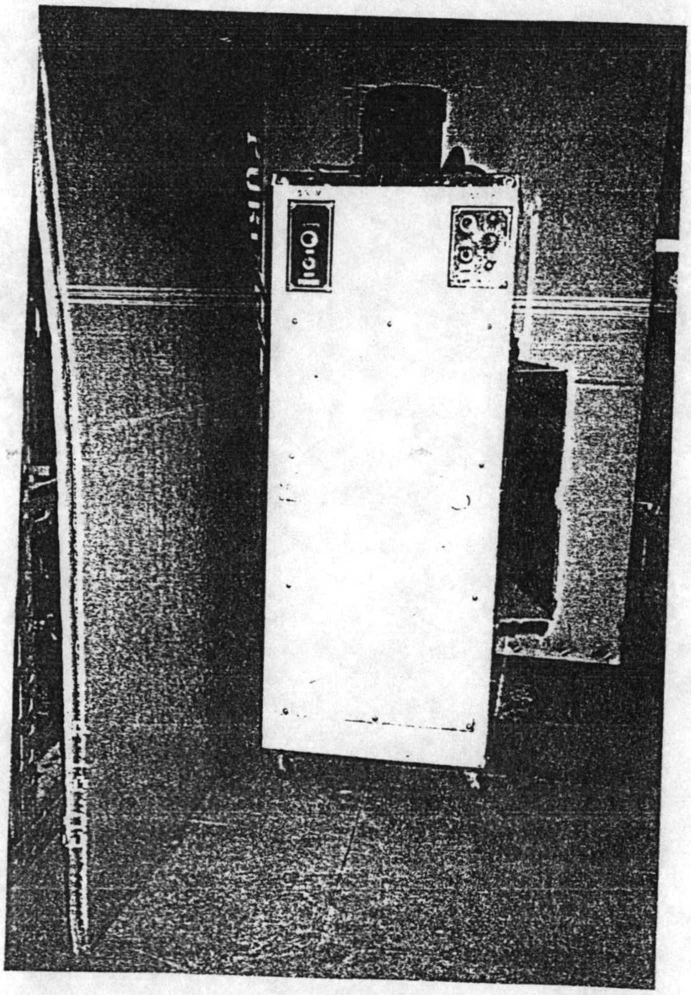


Figure 4.5 Cooling System

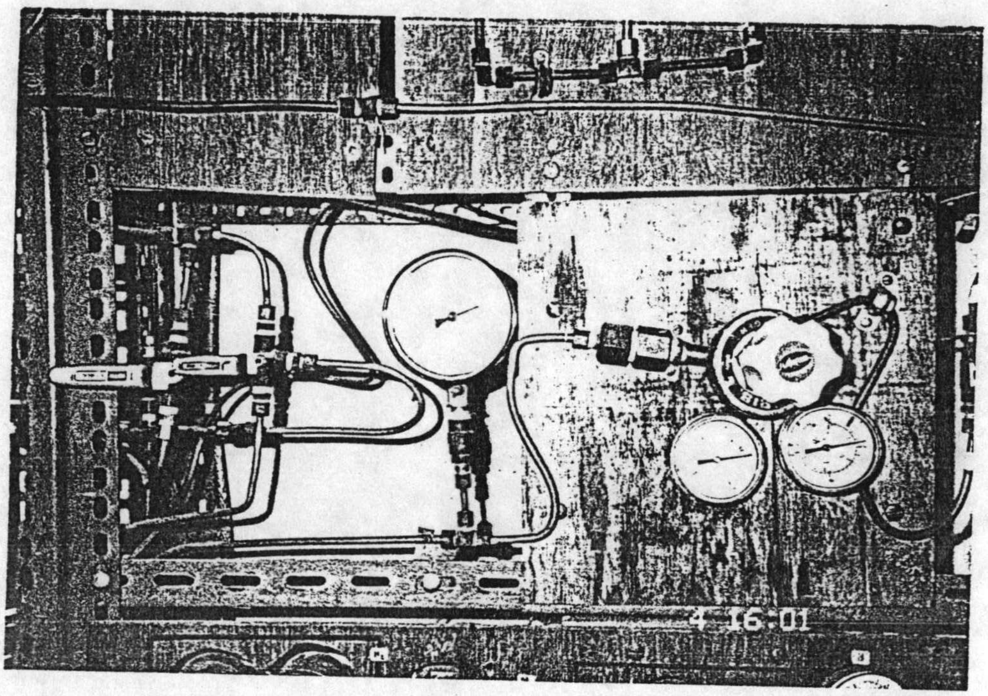


Figure 4.6 Gas Distribution System

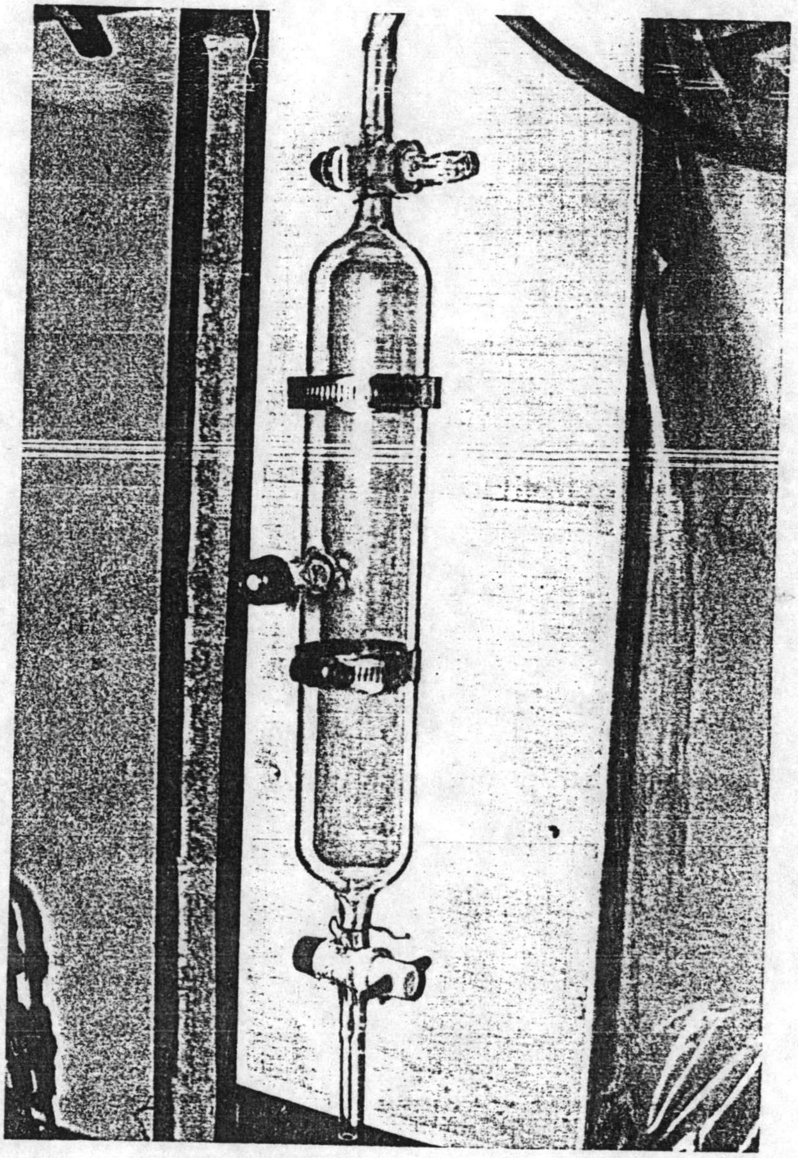


Figure 4.7 Catalyst Loading Unit

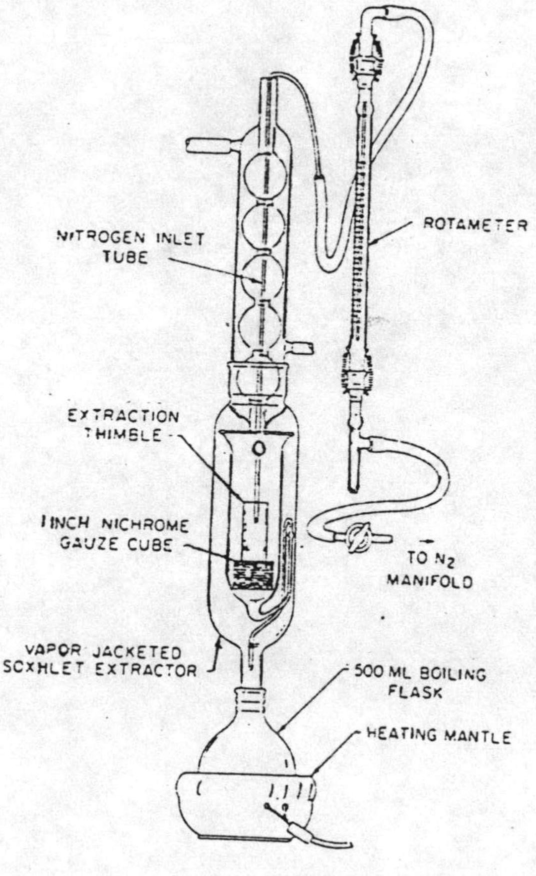


Figure 4.8 Soxhlet-type Extractor

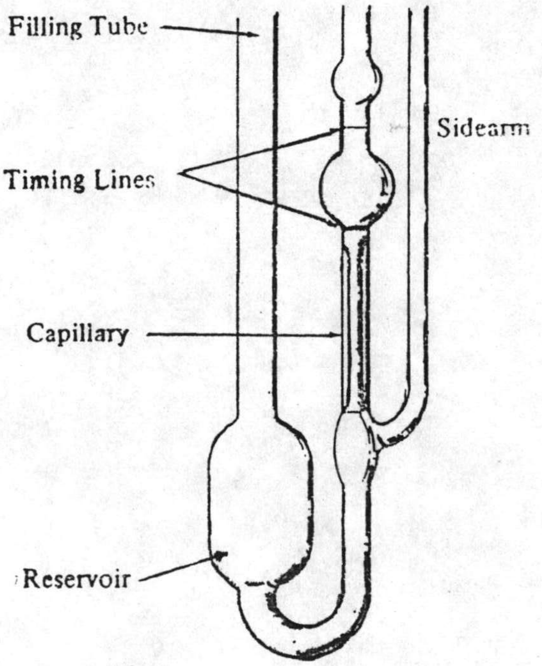


Figure 4.9 Ubbelohde Viscometer

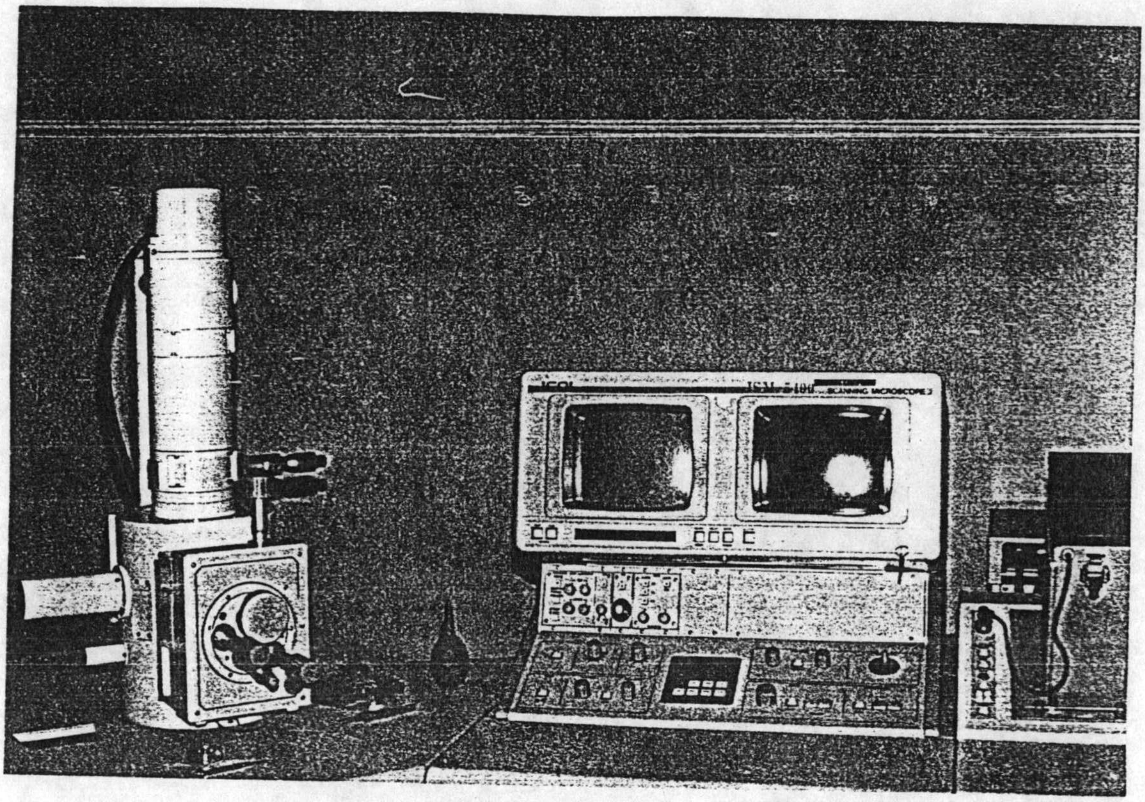


Figure 4.10 Scanning Electron Microscopy

Figure 4.11 Ion Sputtering Device