

## 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 four parts : (i) catalyst preparation (ii) polymerization (iii) characterization of polymer products and (iv) characterization of catalysts. The details of the experiments were discuss below.

#### 4.1 CHEMICALS

Chemicals used in this experiment were 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 reactors.

Ultra high purity nitrogen gas ( $N_2$ , 99.999% vol.) was supplied from TIG Trading Limited (Thailand) and was purified by passing through the column packed with molecular sieve 3A° to remove traces of moisture.

Hexane ( $C_6H_{14}$ ) polymerization grade used for the preparation of catalyst and polymerization was received from Esso Chemical Co. Ltd. (Thailand). It was purified by passing through  $CaCl_2$  and molecular sieve packed column and was distilled from sodium to remove traces of moisture and stored under nitrogen gas.

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

Titanium tetrachloride ( $TiCl_4$ ) was used as received from Carlo Erba Co., Ltd. (Italy) without further purification.

Triethylaluminum ( $\text{Al}(\text{C}_2\text{H}_5)_3$ , ca. 300 mmol/l in hexane) was used as received from Bangkok Polyethylene Co., ltd. (Thailand) without further purification.

Anhydrous Magnesium Chloride ( $\text{MgCl}_2$ ) from Aldrich (Germany) ) was used as received without further purification.

Diethyl phthalate ( $\text{C}_{12}\text{H}_{14}\text{O}_4$ ) was used as internal electron donor as received from Fluka Chemical Industries Limited (Germany) without further purification.

2-ethyl-hexanol ( $\text{C}_8\text{H}_{18}\text{O}$ ) was used as received from Fluka Chemical Industries Limited (Germany) without further purification.

Phthalic anhydride ( $\text{C}_8\text{H}_4\text{O}_3$ ) was used as received from Fluka Chemical Industries Limited (Germany) without further purification.

Decane ( $\text{C}_{10}\text{H}_{22}$ ) was used as received from Fluka Chemical Industries Limited (Germany) without further purification.

Tetraethoxysilane ( $\text{Si}(\text{OC}_2\text{H}_5)_4$ , TES), Methyltriethoxysilane ( $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$ , MTES), Dimethyldiethoxysilane ( $(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$ , DMDES), Trimethylethoxysilane ( $(\text{CH}_3)_3\text{SiOC}_2\text{H}_5$ , TMES) and Phenyltriethoxysilane ( $\text{C}_6\text{H}_5\text{Si}(\text{OC}_2\text{H}_5)_3$ , PTES) 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 3 parts : catalyst preparation equipments, polymerization equipments and characterization equipments

### 4.2.1 Catalyst Preparation Equipment

All of catalyst preparations were carried out in ultrahigh purity nitrogen atmosphere by using equipment as follows :

4.2.1.1 Schlenk double tubes as shown in figure 4.1 for vacuum and nitrogen lines.

4.2.1.2 250 cm<sup>3</sup> two-necked round bottom flask with 1 septum was used as a catalyst preparation flask as shown in Figure 4.2

4.2.1.3 As shown in Figure 4.3, a glove bag was used for transferring chemicals.

#### 4.2.2 Polymerization Equipment

Polymerization equipment consists of 4 parts as shown in Figure 4.4 as follows :

##### 4.2.2.1 Polymerization Reactor and Controller

As shown in Figure 4.5 and 4.6 the polymerization reactor which was a batch stirred autoclave model 4522 equipped with controller model 442 both from Parr Instrument Company (USA). The reactor consisted of 2,000 cm<sup>3</sup> stainless steel 316 cylindrical bomb, bomb head, a bomb heater, a stirrer and a cooling coil. The controller can control the pressure range of 0-1,900 psig, the temperature range of 0-350 °C and the stirring speed in the range of 0-1,600 rpm.

##### 4.2.2.2 Cooling System

The system as shown in Figure 4.7 was divided into 2 parts, one for cooling the reaction in cylindrical bomb and another for cooling the system of the reactor. 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 desired temperature so the cooling system was added. Another part of this cooling system was used to remove the friction heat from the mechanical stirring system.

##### 4.2.2.3 Gas Distribution System

As shown in Figure 4.8, the system consisted of an ultrahigh purity nitrogen and propylene feeding lines made of stainless steel pipe with diameter of ¼ inch.

#### 4.2.2.4 Catalyst Feeding Unit

1,000 cm<sup>3</sup> glass bottle with 2 arms and 1 stopcock on the neck, 1 arm at the bottom and a septum cap for injection through at the middle was used as the catalyst feeding unit as shown in Figure 4.9. 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 and some chemicals were introduced into the reactor by injection through the septum.

#### 4.2.3 Characterization Equipment

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

4.2.3.1 Soxhlet-type reactor with boiling heptane shown in Figure 4.10 was used for determining the isotactic content. Polypropylene product was weighed in cellulose thimble about 2.0-2.2 g. then was extracted in Soxhlet-type reactor 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.

$$\% \text{ II} = \frac{\text{Insoluble weight of polypropylene}}{\text{Total weight of polypropylene}} \times 100$$

4.2.3.2 Scanning Electron Microscope (SEM) model JEOL at Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University, as shown in Figure 4.11., 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.

#### 4.2.3.3 CO adsorption instrument

CO adsorption instrument at Petrochemical Engineering Research Laboratory, Chulalongkorn University, as shown in Figure 4.12., was used to determine the active sites of the catalyst.

#### 4.2.3.4 Fourier Transformed Infrared Spectrophotometer (FT-IR)

Nicolet FT-IR Impact 400 spectrophotometer at Petrochemical Engineering Research Laboratory, Chulalongkorn University, as shown in Figure 4.13., was employed to study the microstructure of polypropylene products.

#### 4.2.3.5 Differential Scanning Calorimetry (DSC)

Differential scanning calorimeter model 2910 TA at the Polymer Engineering Research Laboratory, Chulalongkorn University, was applied to determine the melting temperature ( $T_m$ ) of the polypropylene products.

#### 4.2.3.6 BET Surface Area

BET surface area analyzer model ASAP 2000 from Micromeritics (USA) at the Analysis Centre of Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, as shown in Figure 4.14., was used to determine the surface area of catalyst and support. The surface area were measured by the B.E.T. method, with nitrogen as the adsorbate at liquid-nitrogen boiling point temperature.

#### 4.2.3.7 X-ray Diffractometer

X-ray diffractometer (XRD) at Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University was used for phase analysis of the catalysts and support.

#### 4.2.3.8 Inductively Couple Plasma Emission Spectrometer

Inductively Couple Plasma Emission Spectrometer (ICP) model Perkin-Elmer PLASMA-1000 at Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University, was applied to determine percentage of metals in the catalysts.

### 4.3 CATALYST PREPARATION PROCEDURE

Supported Ziegler-Natta catalyst was prepared follow the patent which was claimed by Kioka et al.[49]. The details of the preparation procedures are as followed:

Anhydrous magnesium chloride 0.476 g, 2.5 ml of decane and 2.34 ml of 2-ethyl hexyl alcohol were reacted at 130 °C for 2 hours to form a uniform solution. Decane added as a medium for the reaction and 2-ethyl hexyl alcohol used as a solvent to dissolve MgCl<sub>2</sub> [49]. Phthalic anhydride 0.11 g was added to the solution to react together with diethyl phthalate which was added in the next step to prevent the recrystallization of MgCl<sub>2</sub> [121,125]. The mixture was stirred at 130 °C for 1 hour to dissolve phthalic anhydride. The resulting uniform solution was cooled to room temperature, and wholly added dropwise over the course of 1 hour to 20 ml of titanium tetrachloride kept at -20 °C. After the addition, the mixture was heated to 110 °C over the course of 4 hours. When the temperature reached 110 °C, 0.26 ml of diethyl phthalate was added and had a function as an internal electron donor together with phthalic anhydride [121,125]. The mixture was maintained at this temperature for 2 hours. After the reaction for 2 hours, the solid portion was collected from the reaction mixture. The solid portion was again suspended in 20 ml of titanium tetrachloride for cleaning the catalyst and fixed again on the MgCl<sub>2</sub> surface that the first loading can not occupied [124,125] and again reacted at 120 °C for 2 hours. After the reaction, the solid portion was again collected, washed with decane at 120 °C, and hexane 3 times. The resulting solid titanium catalyst prepared was stored as a slurry in hexane.

### 4.4 POLYMERIZATION PROCEDURE

Propylene polymerization was carried out in the 2,000 cm<sup>3</sup> reactor, which was equipped with all parts described above and several valves for gas feeding 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 ultrahigh purity nitrogen gas for an hour and looked

whether pressure dropped or not. The reactor was dried at 110 °C for an hour, ultrahigh purity nitrogen gas was purged and alternately vacuumed for 3 times. After cooling to 25 °C, the 500 cm<sup>3</sup> of hexane was introduced into the mixer and then triethylaluminum, prepared catalyst and external electron donor was injected to the mixer by glass syringes under nitrogen atmosphere and introduced into the reactor.

The reaction temperature was gradually increased to 85 °C and propylene gas was consequently introduced and kept at 100 psi. During 90 minutes for polymerization, propylene was continuously supplied at a constant 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 then applied.

This study of propylene polymerization emphasized on the effect of internal electron donor that was diethyl phthalate and external electron donor which were varied, the following was the experimental conditions for propylene polymerization which was reported in previous studies [114] to be the best conditions for propylene polymerization by using supported Ziegler-Natta catalysts.

Al/Ti ratio = 167  
total pressure = 100 psi  
temperature = 90 °C  
external electron donor / Ti ratio = 0.05

#### 4.5 CHARACTERIZATION OF THE POLYPROPYLENE

Polypropylene has remarkable chemical inertness, particularly at ordinary temperature to most chemicals, including acids and alkalies. For this 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 Isotacticity

The isotacticity 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 [120]. For isotactic polypropylene, boiling heptane was commonly used. The fraction of the whole polypropylene unextracted  $\times 100$  was as a percent index of isotacticity. Figure 4.10 showed an 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 comparison. 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 [120].

#### 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.

#### 4.5.3 Activity

The term of catalytic 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).



#### 4.5.4 Melting Temperature ( $T_m$ )

The measurement of the melting temperature of polypropylene samples was performed on a Differential Scanning Calorimeter (DSC). The DSC heater and the sample cells are shown schematically in Figure 4.15. Each composition of the reference and the polypropylene samples was weighted to as close to  $15 \pm 2$  mg as possible. It was then placed in the DSC aluminium pan. The sample was heated from  $30^\circ\text{C}$  to  $180^\circ\text{C}$  at a constant heating rate of  $10^\circ\text{C}/\text{min}$ . A DSC scan of the specific energy against the temperature was obtained. The critical point of DSC curve showed the melting temperature of the polypropylene products.

#### 4.5.5 Microstructure Determination

Infrared spectroscopic technique is suited for the determination of microstructure of polymer.

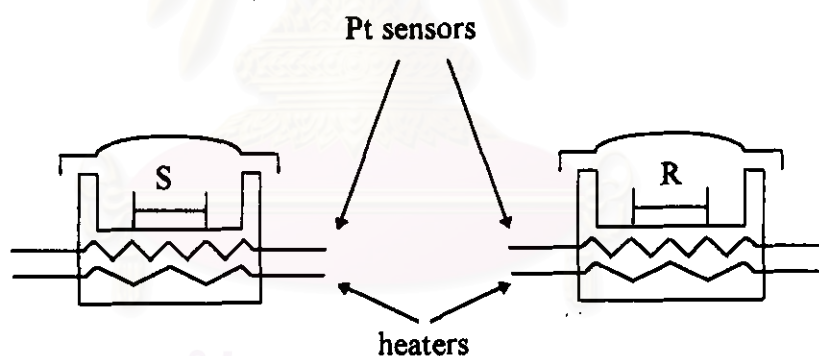


Figure 4.15 The DSC sample cell consists of a sample pan (S) and a reference pan (R)

## 4.6 CATALYST CHARACTERIZATION

### 4.6.1 Chemical Analysis

Percentage of metal in catalyst was analyzed by Inductively Couple Plasma (ICP) method. The catalyst was dissolved by the following procedure.

A certain amount of catalyst was digested by digesting solution containing solution of 5 ml of conc.  $H_2SO_4$  and 2.5 ml of 65%  $HNO_3$ . The mixture was heated up and  $H_2O$  had to be added into the mixture during heating step to maintain the volume of mixture. Until the solution became clear, the volume of the solution was made up to 100 ml by adding distilled water.

The titanium and magnesium of the prepared solution was analyzed by Inductively Couple Plasma (ICP) at the Scientific and Technological Research Equipment Centre, Chulalongkorn University.

### 4.6.2 Active Sites Measurement

Active sites of the prepared catalyst were determined by CO adsorption instrument. The 99.99% helium was used as a carrier gas. The carbon monoxide was used as an adsorbed gas and a standard gas. The amount of CO adsorbed was measured by the thermal conductivity detector.

Operation condition of TCD gas detector

Carrier gas and flow : He 30 ml/min

Temperature of detector : 80 °C

Detector current : 80 mA

### 4.6.3 X-ray Diffraction

In this study, catalysts were sent to analyze their lattice structures using x-ray diffraction pattern. Conventional cells were used in which the solids were covered with a non-absorbent film, to protect them from air and water. Sample preparation for x-ray diffraction analysis was all carried out under an inert atmosphere inside a glove bag.

#### 4.6.4 Infrared Spectroscopy

IR spectra of the catalysts was recorded on a thin wafer that hold between KBr plates. The wafer was prepared by grinding sample with KBr powder and then pressed. The preparations were carried out in a dry and inert atmosphere inside a glove bag. The spectra so obtained weve therefore referenced to instrumental background and blank KBr plates.

#### 4.6.5 Surface Area Measurement

BET surface area method was a physical adsorption of  $N_2$  on surface of catalyst to find the specific surface area. The sample was heated and placed under vacuum to remove traces of moisture and other contaminants before analysis and then automatically analyzed. The amount of  $N_2$  gas needed to form a monolayer on the surface of sample could be determined from measurements of the volume of gas adsorbed.

Preparation of sample for BET surface area analysis was carried out under dry and inert atmosphere in a glove bag.

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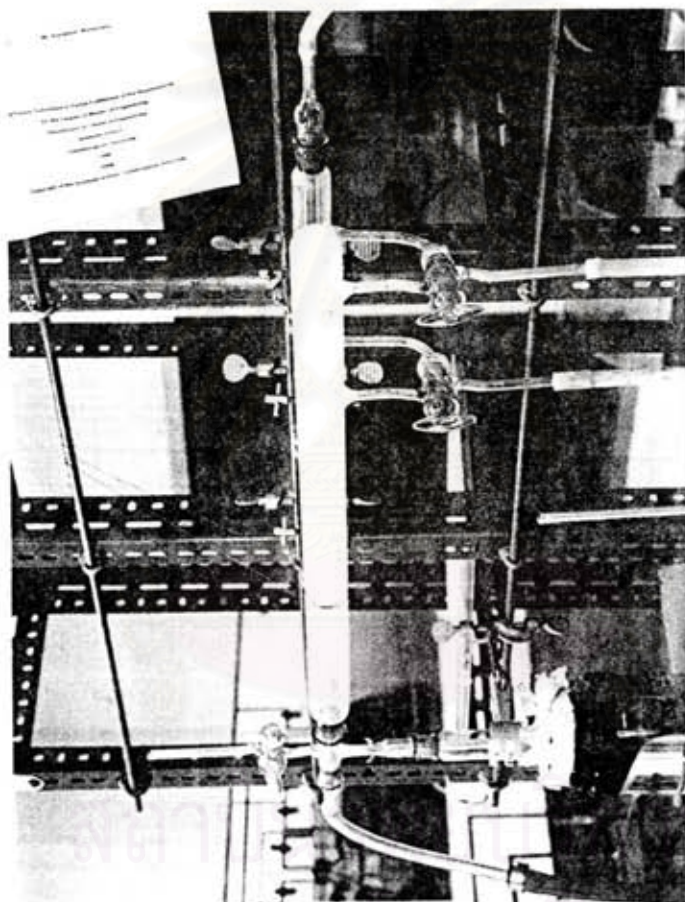


Figure 4.1 Schlenk tubes

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Figure 4.2 250 cm<sup>3</sup> two-necked round bottom flask

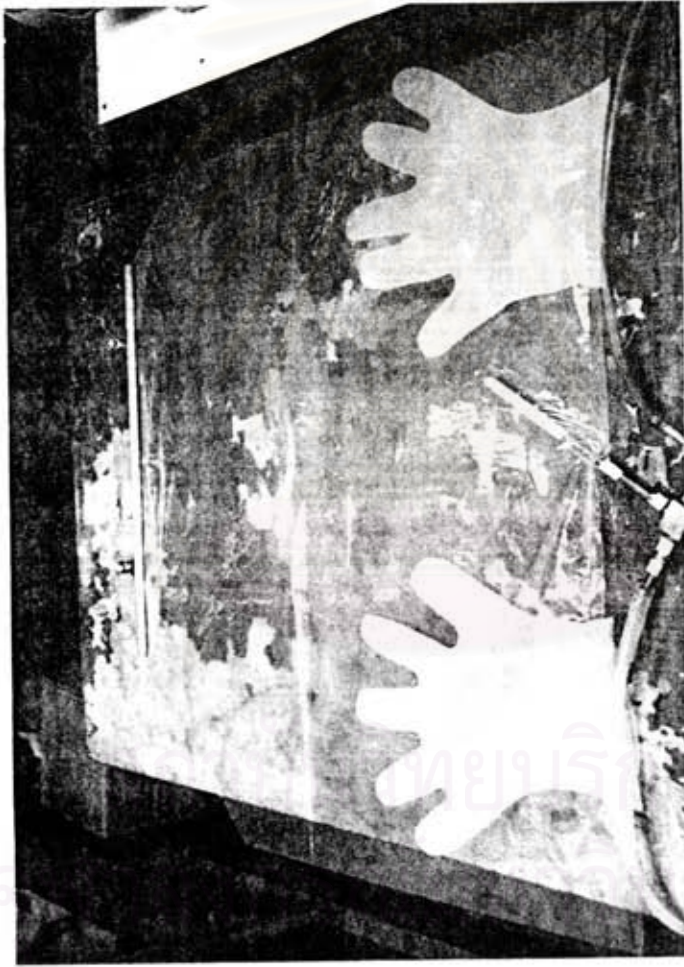


Figure 4.3 glove bag

มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี

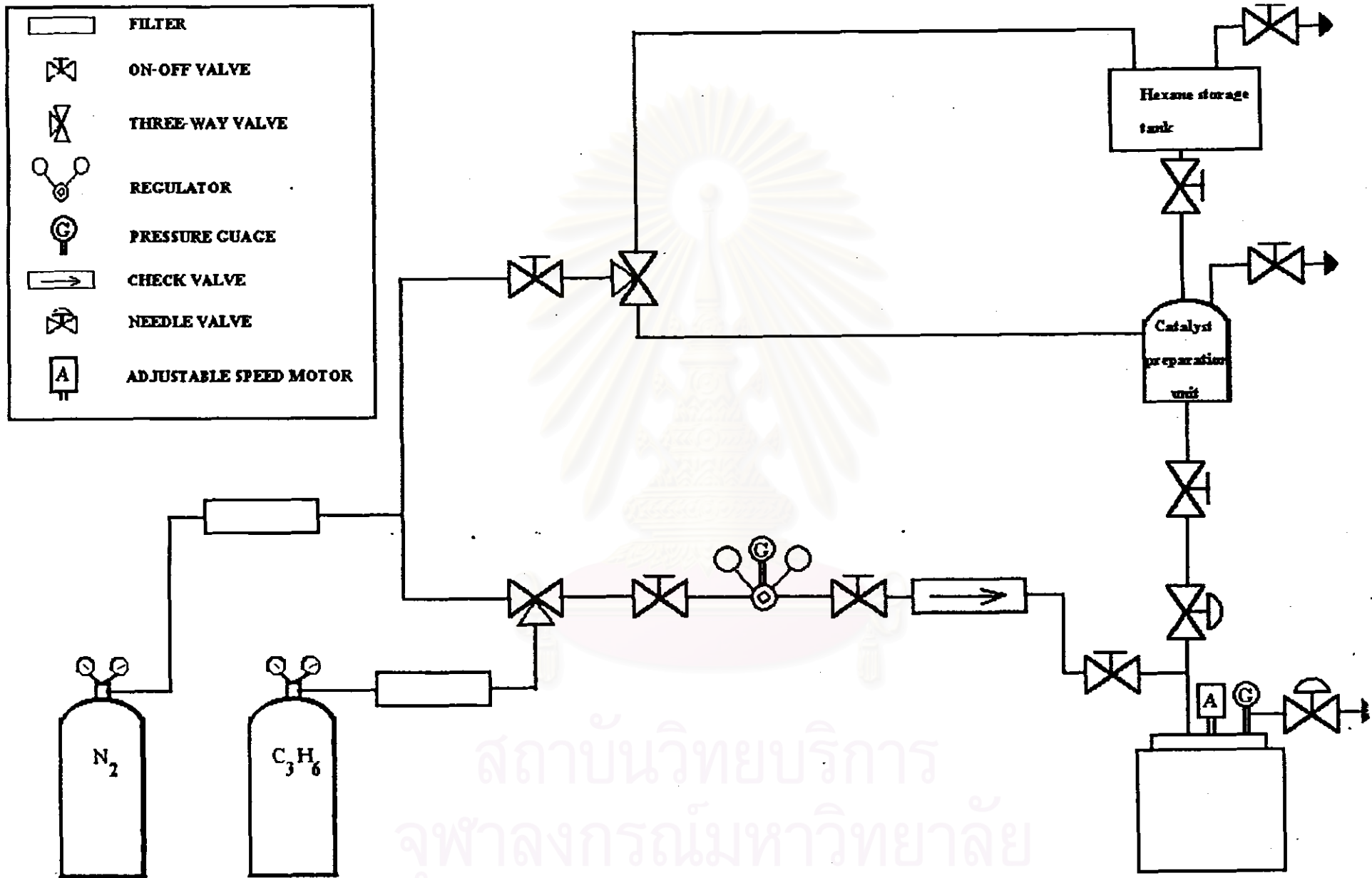


Figure 4.4 Polymerization Equipment

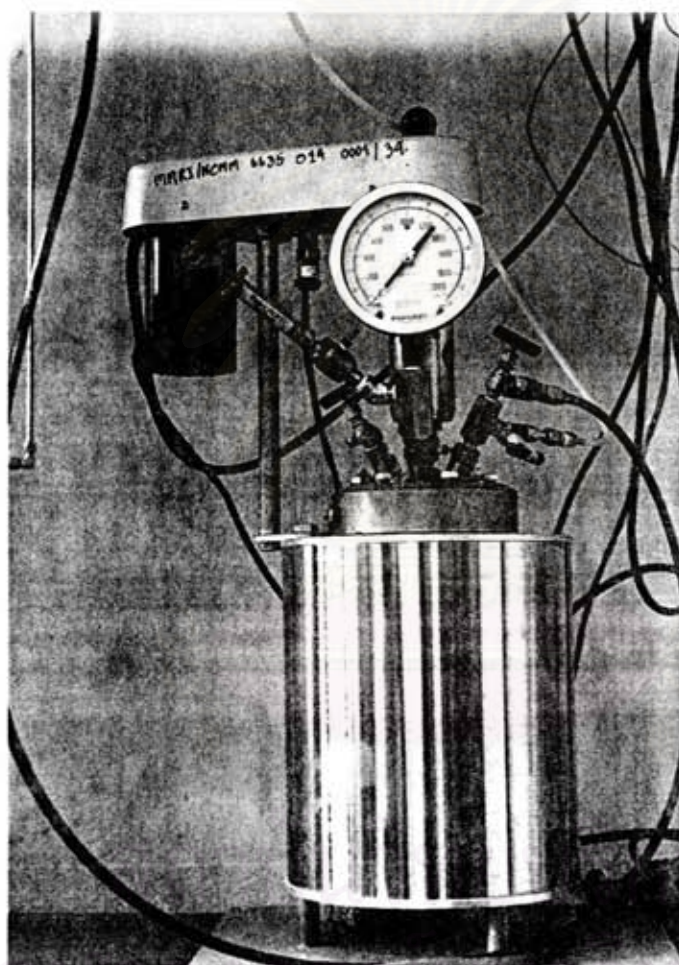


Figure 4.5 Polymerization reactor





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Figure 4.6 Automatic Temperature Controller

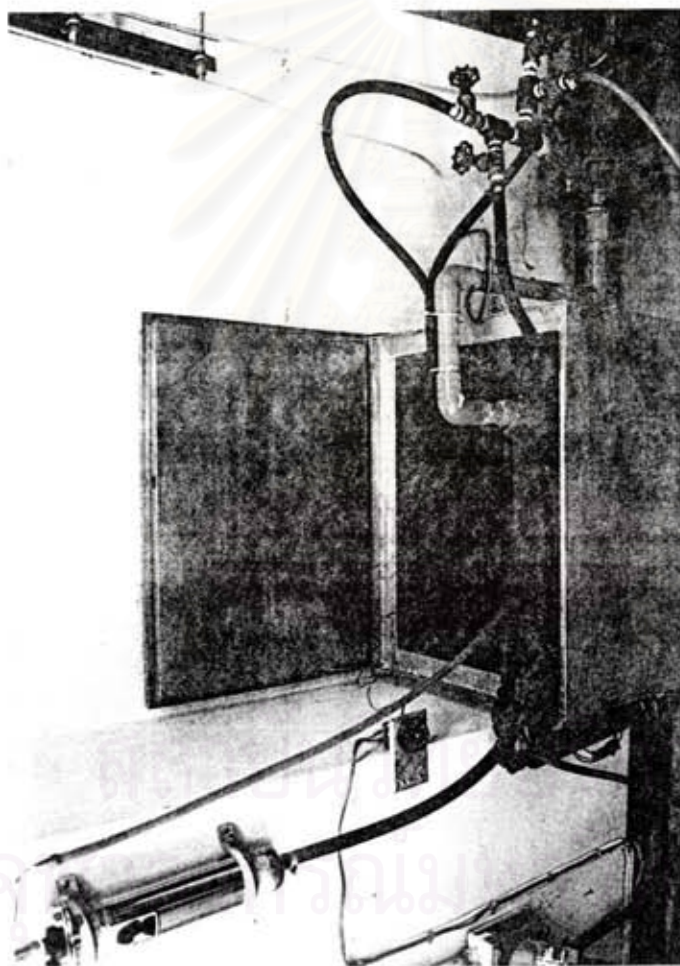


Figure 4.7 Cooling system

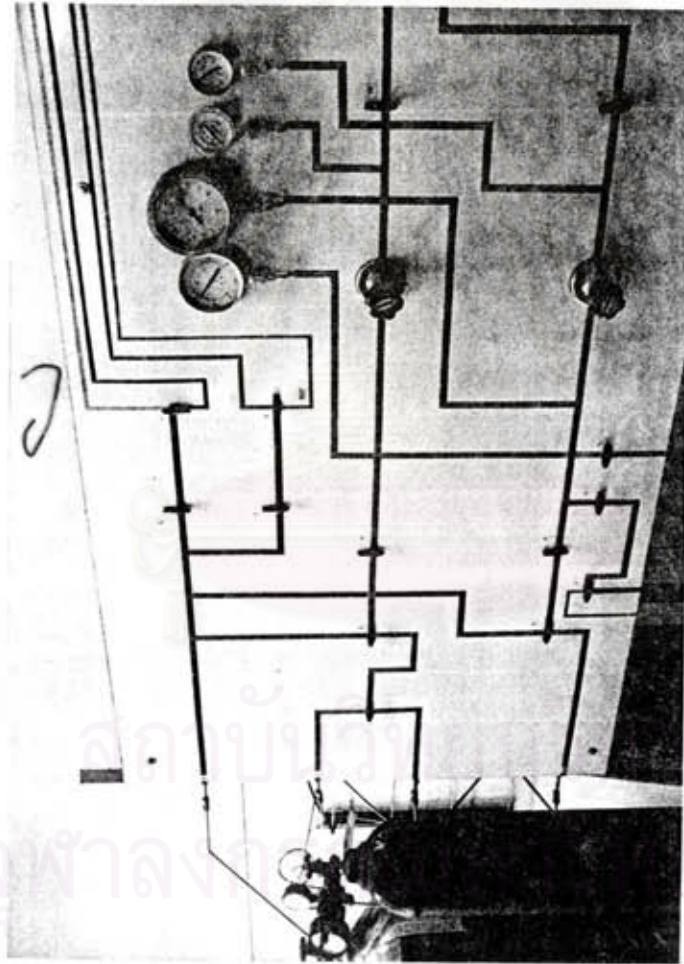


Figure 4.8 Gas distribution system.

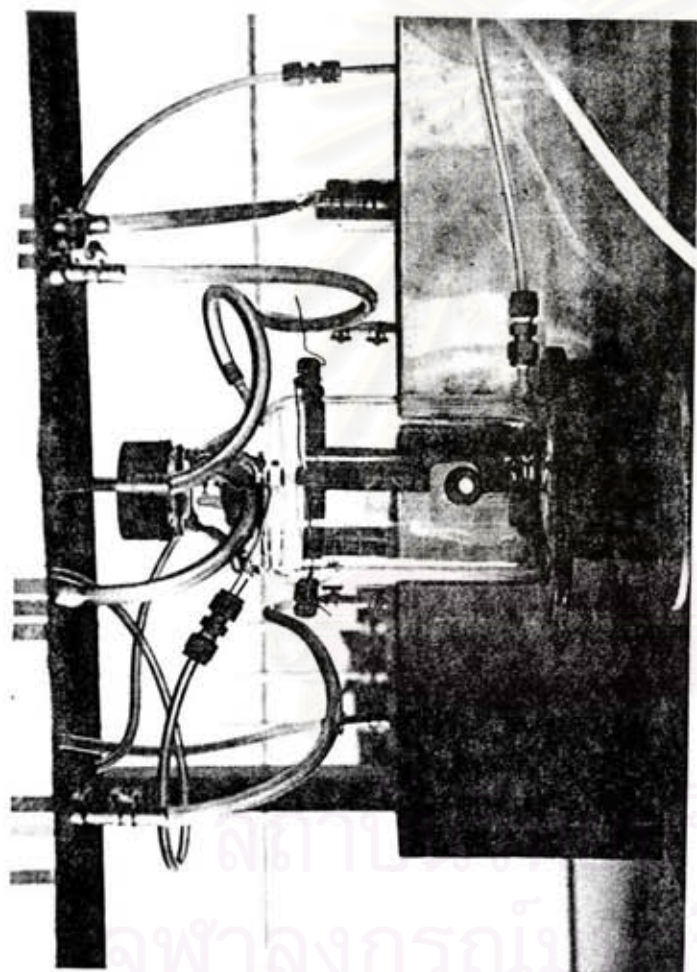


Figure 4.9 Catalyst Feeding Unit

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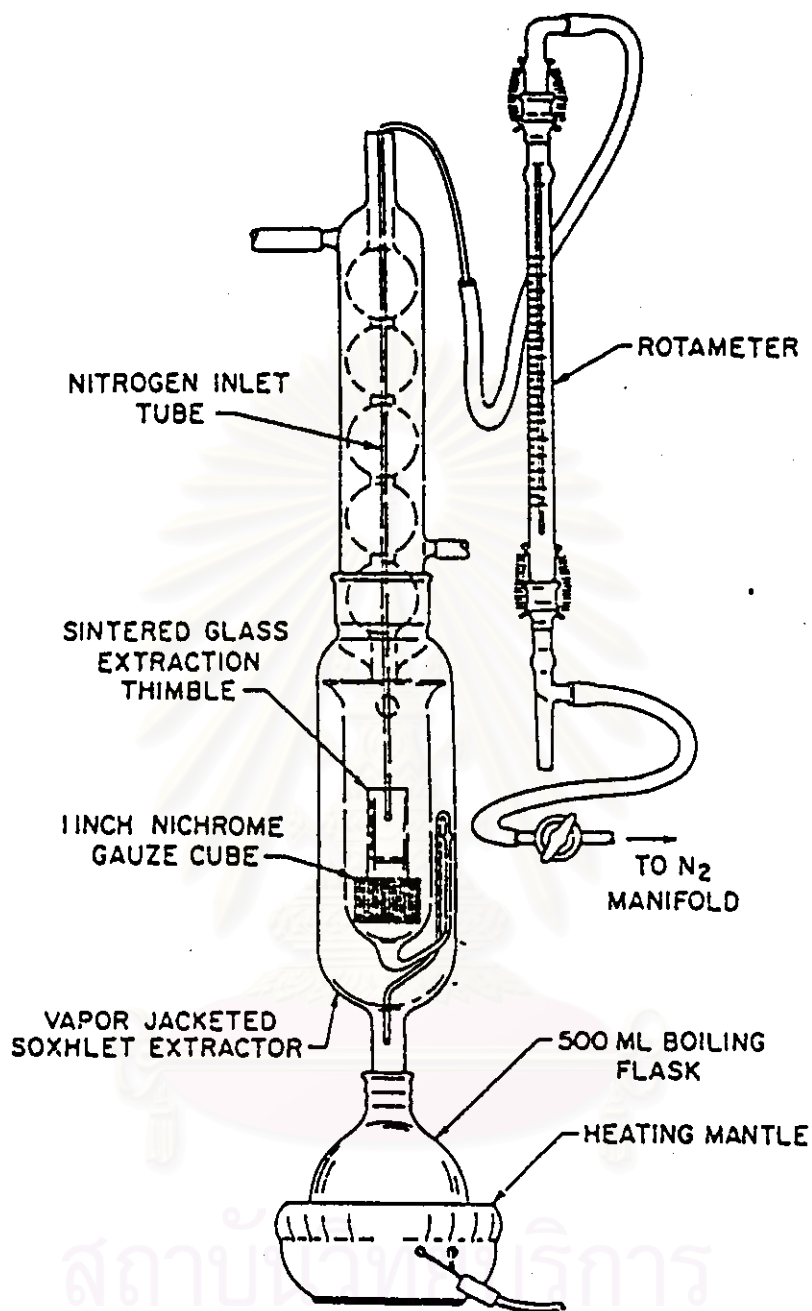


Figure 4.10 Soxhlet-type Extractor [120]

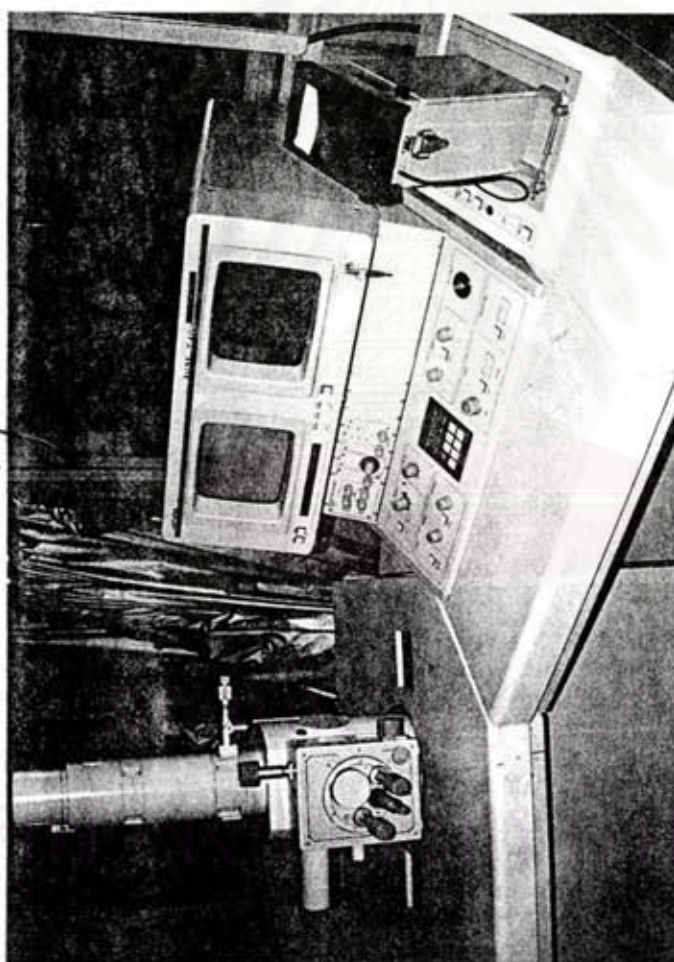


Figure 4.11 Scanning Electron Microscope

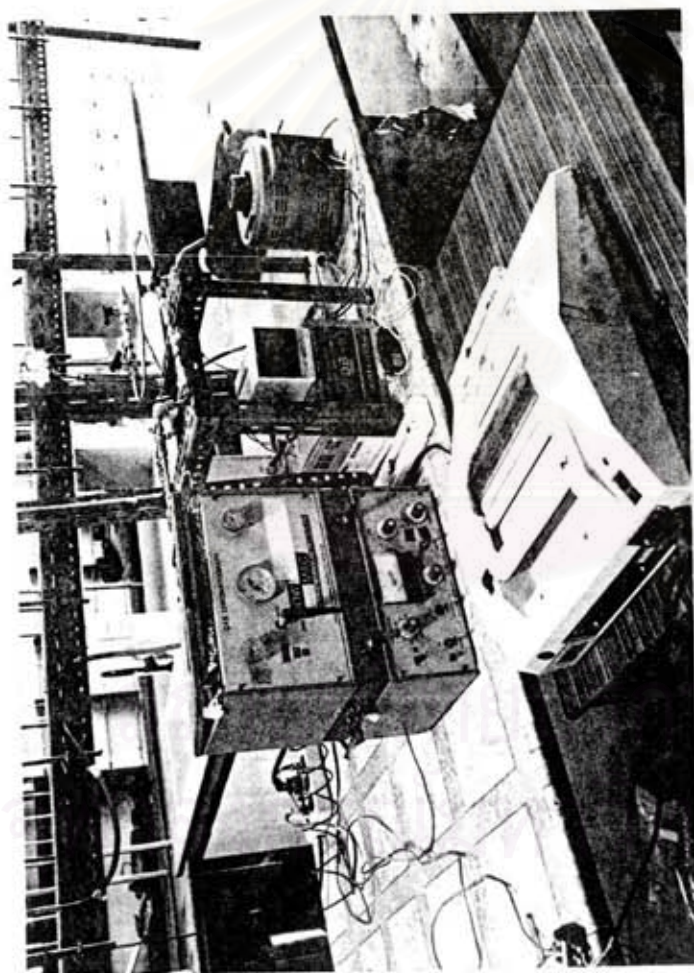
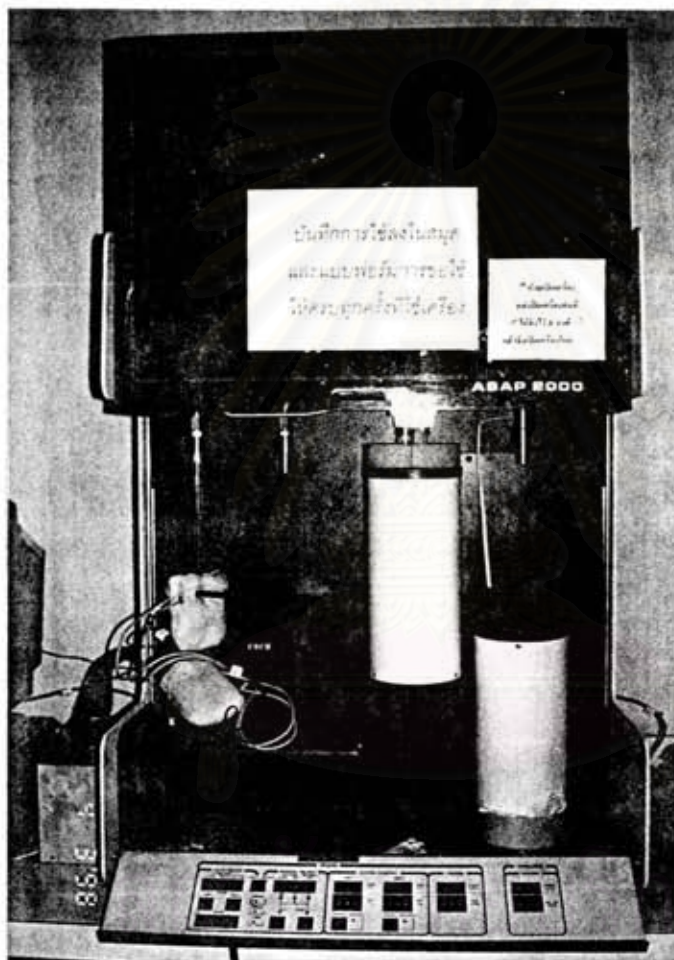


Figure 4.12 CO adsorption instrument



Figure 4.13 Fourier Transformed Infrared Spectroscopy





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Figure 4.14 BET surface area