CHAPTER IV

EXPERIMENT

In the present study of the ethylene polymerization on high-activity Ziegler-Natta supported catalyst, the experiments divided into three parts:

1. High activity Ziegler-Natta supported catalyst preparation,
2. Ethylene polymerization on the catalyst prepared,
3. Characterization of the polyethylene prepared.

The details of the experiments would explain in the following.

4.1 CHEMICALS

Ethylene gas (98.5% pure) was supplied by Union Carbide (Thailand) Limited. A column that packed with molecular sieve 5 ^{0}A size 1 1/6 mm. was used to remove traces of moisture from ethylene .

Ultra high purity hydrogen (UHP H_2) gas with oxygen and moisture contents both less than 3 ppm was used as the effective chain transferring agent.

Ultra high purity oxygen free nitrogen gas with oxygen and moisture contents both less than 3 ppm used to purge the reactor and the glove box. Both gases were supplied by Thai Industrial Gas Co. LTD. They were purified by passing through the column packed with molecular sieve 5 ^{0}A to remove moisture.

The n-hexane, the polymerization grade, that used as the polymerization media and in catalyst preparation media obtained from Shell (Thailand) Co. LTD. It was kept over sodium metal flakes.

Titanium tetrachloride($TiCl_4$) from Wake Pure Chemical Industries Limited was used as received without any purification.

Triethylaluminum ($AlEt_3$, TEA), ca.15 % in n-hexane from Tokyo Kasei, was used as received without any purification.

Magnesium dichloride($MgCl_2$), anhydrous grade from Aldrich, was kept in a Schlek tube to prevent from moisture. This method is an effective to store the salt.

Iron(III) oxide (Fe_2O_3) with purity 99.99% from Aldrich was kept in a vial inside the glove box. It had to be kept in the oven overnight before use.

Ethyl alcohol, absolute AR, from Merck was transferred to a vial and capped firmly. It was also stored in the glove box.

4.2 Equipment

All experiments, carried out in the polymerization reactor set, which consisted of six parts; the characterizations were conducted by instruments as follows:

4.2.1 Polymerization Reactor set

As shown in Figure 4.1, the reactor of ethylene polymerization was a batch stirred autoclave model 4521 from Parr Instrument Company consisted of 2000 cm^3 stainless steel 316 cylinder, a bomb head, a bomb heater, a propeller and a spiral cooling coil. The reactor was controlled by the automatic temperature controller.

4.2.2 Automatic Temperature Controller

The set of automatic temperature controller as shown in Figure 4.2 consisted of a magnetic contactor joined with a variac, an RKC model PF-8BIC-M temperature controller and a digital temperature indicator of Eurotherm model type 141. It obtained the signals from a thermocouple installed in a thermowell inside the bomb head to provide a temperature read-out. A dial setting established a setpoint at the polymerization temperature.

4.2.3 Adjustable Speed Motor Controller

The controller used as shown in Figure 4.3 was 64 EEEN model from Parr Instrument Company. The stirring speed was adjusted in the range of 0-1,000 rpm. It could stir two directions, forwards and backwards.

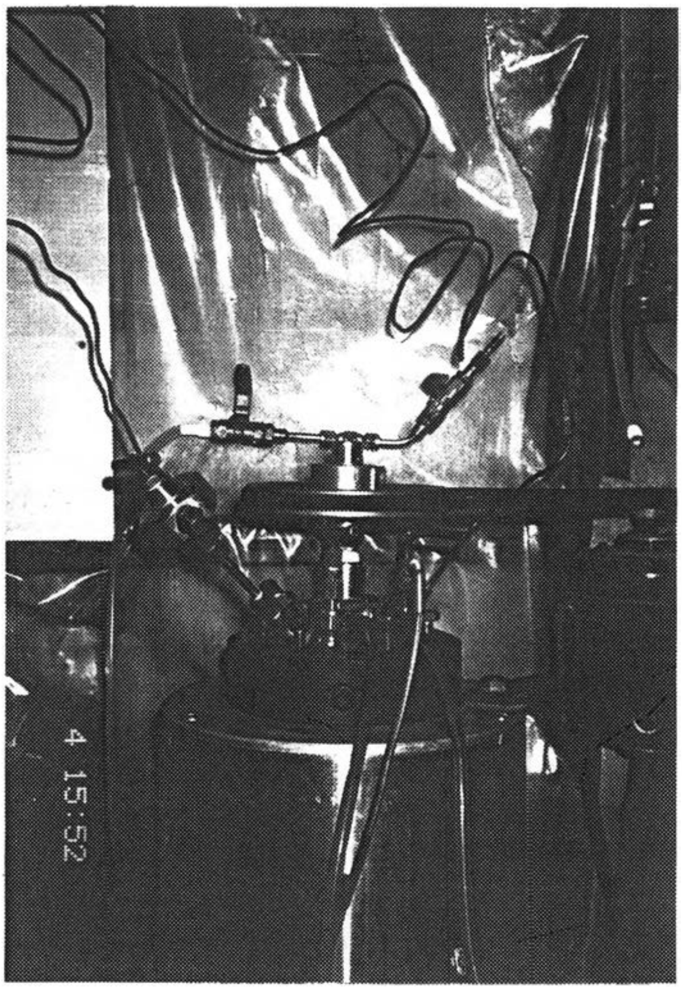

Figure 4.1 The polymerization reactor

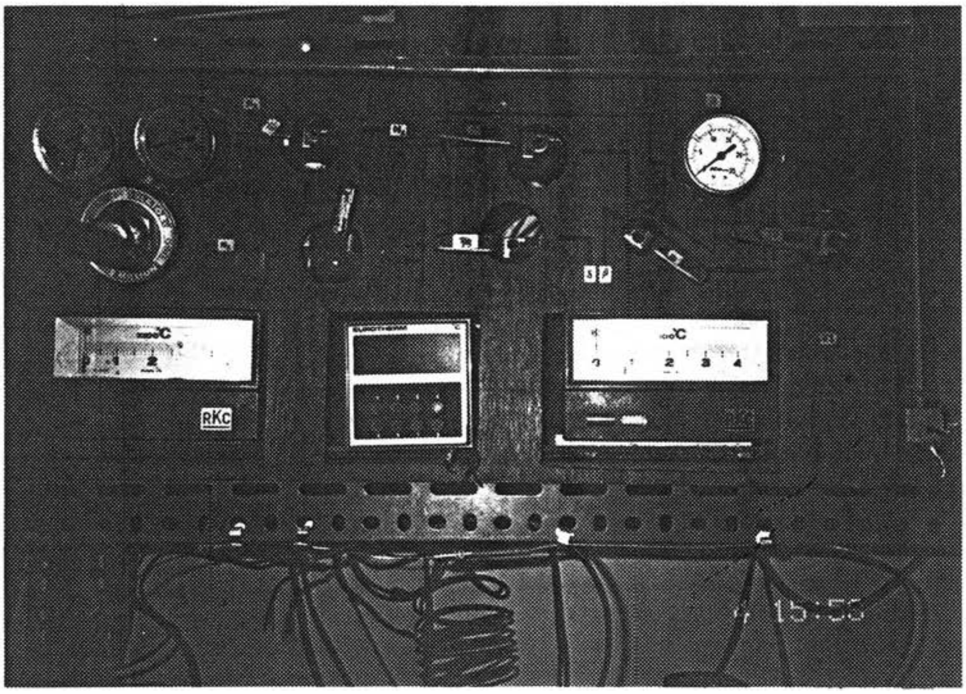

Figure 4.2 Automatic Temperature Controller

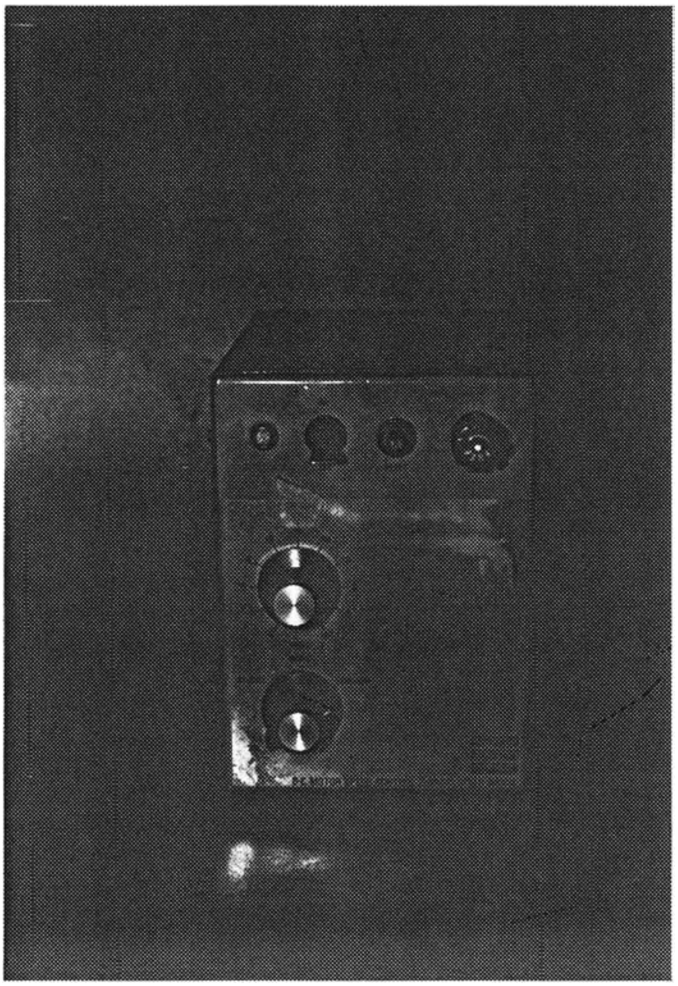

Figure 4.3 Adjustable Speed Motor Controller

4.2.4 Cooling system

The system as shown in Figure 4.4 was divided into two parts, one for cooling coil and another for cooling the stirring system. The rapid rate of polymerization at the beginning occurred because of the fast reaction, and the reaction temperature increased immediately . The automatic controller of temperature could not maintain the setpoint value sufficiently. The spiral cooling coil was immersed to overcome this problem. The other cooling system supplied by Eyela cooling bath was utilized to remove the frictional heat from the mechanical stirring system at the bomb head.

4.2.5 Gas Contribution System

Figure 4.5 is the flow diagram of the polymerization system. The system consisted of: a hydrogen line and an oxygen-free nitrogen feeding line and an ethylene feeding line. To investigate ethylene consumption rate, a storage ethylene tank was used and connected to the line of the ethylene cylinder. The storage tank was equipped with a pressure gauge to measure the amount of ethylene consumed during the polymerization. A pressure gauge (0-400 psig) was used for indicating the reaction pressure and two on-off valves were used for gas feeding and releasing.

4.2.6 Catalyst Loading Unit

A glass cylinder with two stopcocks at both ends and a thread adapter for the catalyst and cocatalyst injection was set in the middle as shown in Figure 4.6. By means of the closed system avoiding air and moisture, it was attached to the polymerization reactor and the n-hexane storage. A prepared suspension of transition metal catalyst components was transferred to the reactor by the stream of UHP oxygen-free nitrogen stream through this glass cylinder.

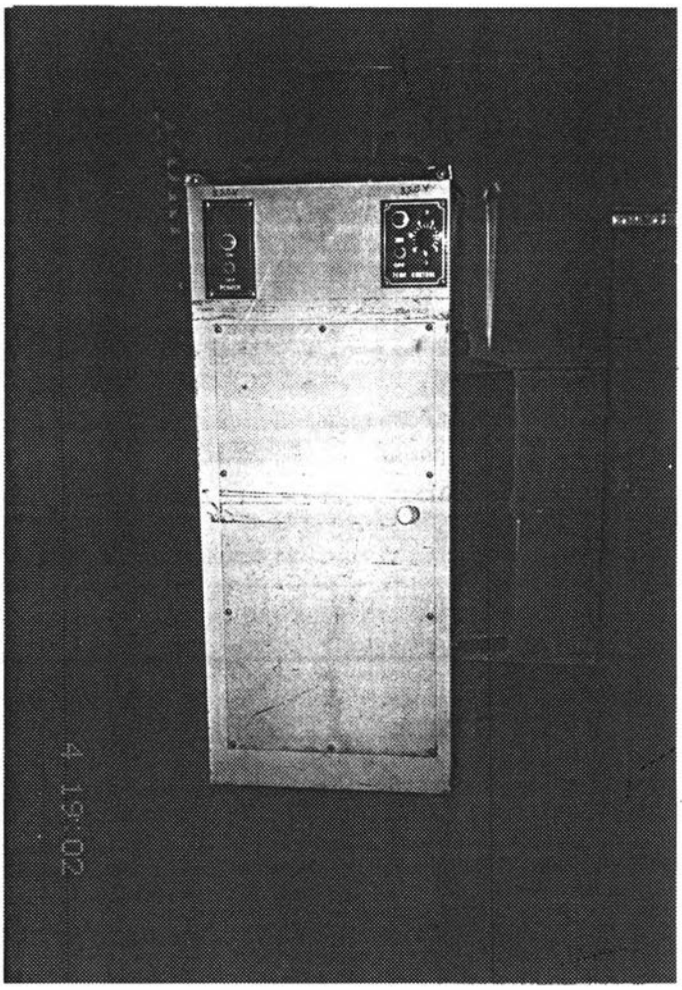

Figure 4.4 Cooling System

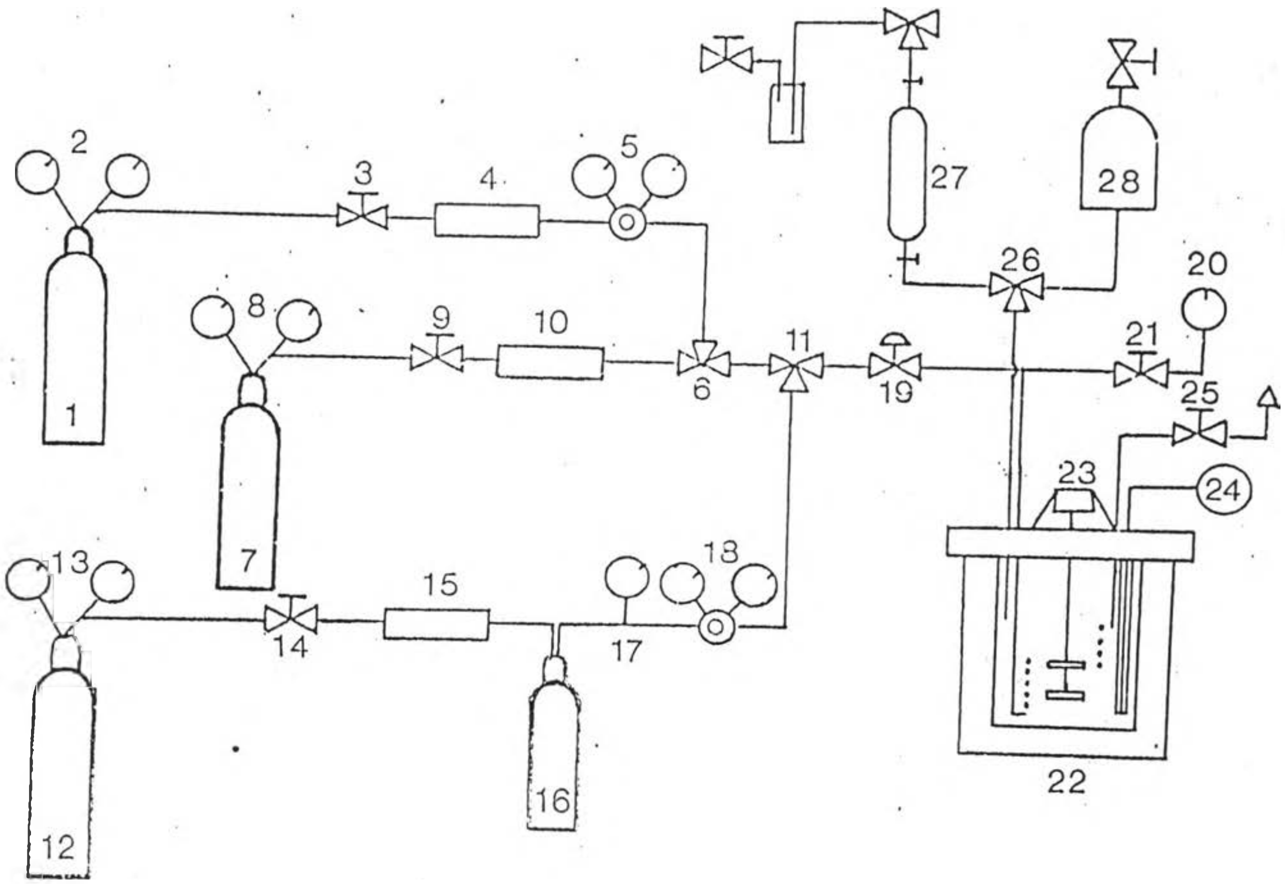

Figure 4.5 Flow Diagram of the Polymerization System

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_2H_4 cylinder
13. Pressure regulator
14. On-off valve
15. Moisture removal unit
16. C_2H_4 storage cylinder
17. Pressure gauge
18. Pressure regulator
19. On-off valve
20. Pressure guage
21. On-off valve
22. Reactor
23. Adjustable speed motor
24. Thermocouple
25. On-off valve
26. Three-way valve
27. Catalyst preparation unit
28. Hexane storage

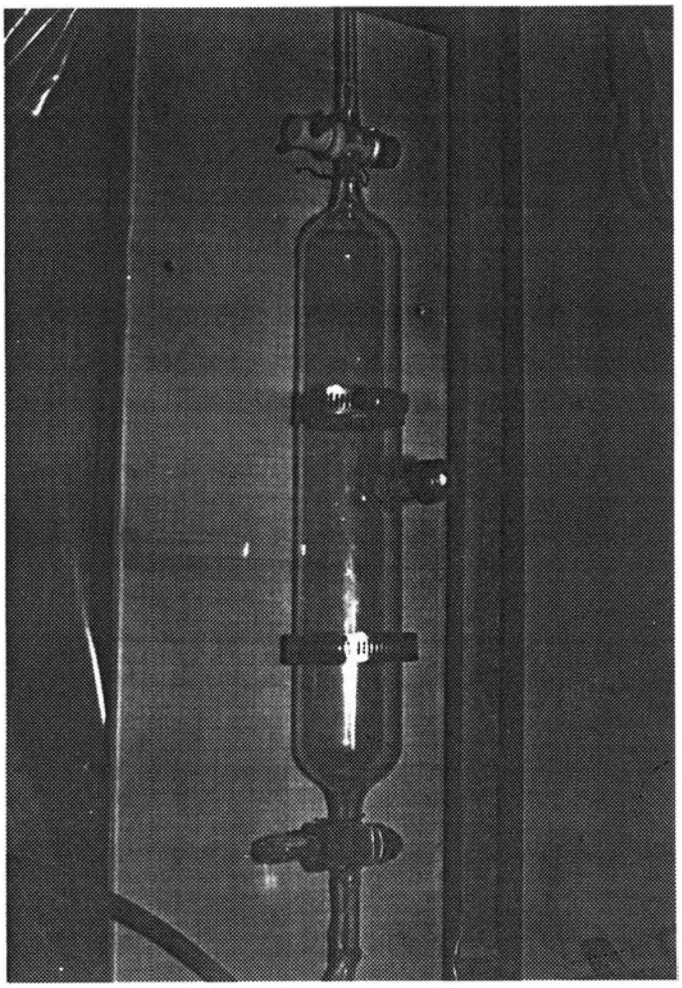

Figure 4.6 Catalyst Loading Unit

4.2.7 Characterization Instruments

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

(a) Scanning Electron Microscope (SEM) applied to investigate the morphology of the polyethylene particles in Figure 4.7. The ion sputtering device was used to gold coat the polyethylene samples.

(b) X-ray diffraction (XRD) method was carried to compare the crystallinity of the two polyethylene. The samples were used in powder form.

(c) Fourier-Transformed Infrared Spectroscopy (FT-IR spectrum) was used to effectively identify the characteristic band of the polyethylene samples.

(d) The viscosity was measured from the aliquot of diluted solution of polyethylene by Ubbelohde viscometer shown in Figure 4.8. The solvent of the polyethylene was decahydronapthalin or called as decalin. The flowtime of the solvent and the solution of polyethylene was carried out in the oil bath. The molecular weight (Mv) of the polyethylene was determined by viscometry from Mark-Houwink-Sakurada Equation.

(e) Kayness Extrusion plastometer Model D-2050 was used to determine the melt flow index of polyethylene. The polyethylene particles were molten inside the pistol of the plastometer at the 135 ^{0}C.

(f) Gradient column containing a solution of p-Xylene in carbon tetrachloride as liquid gradient which was prepared in ten proportions of density range was employed to determine the density of the product.

(g) Differential Thermal Analysis(DTA) technique was carried out to determine the melting temperature of polyethylene.

(h) Gel Permeation Chromatography(GPC) technique was carried out to determine the number-average molecular weight (Mn) under high temperature. This technique had the trustful result for molecular weight.

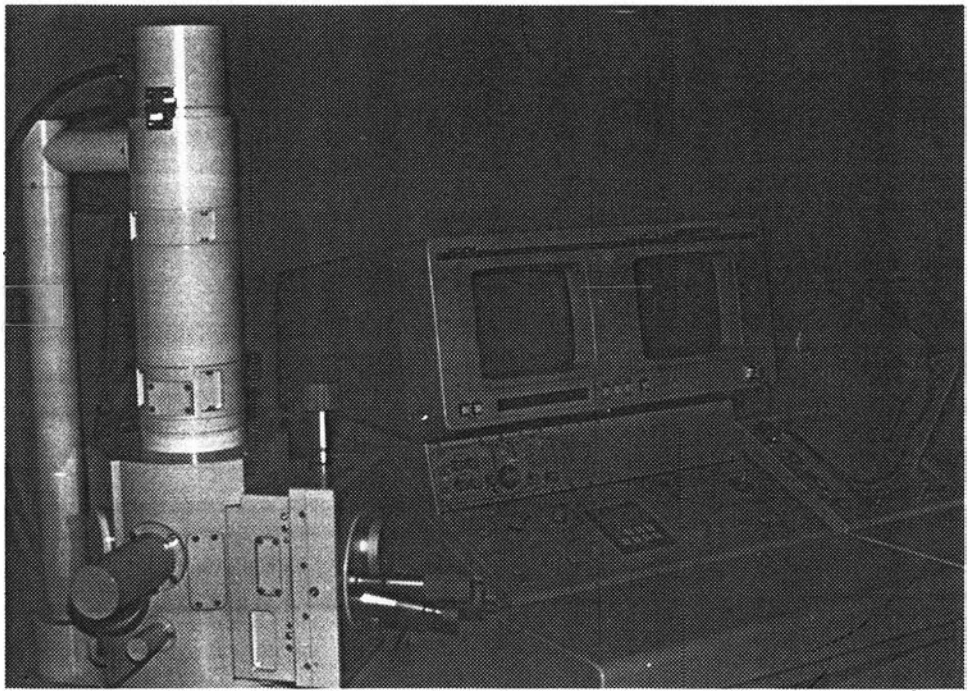

Figure 4.7 Scanning Microscope

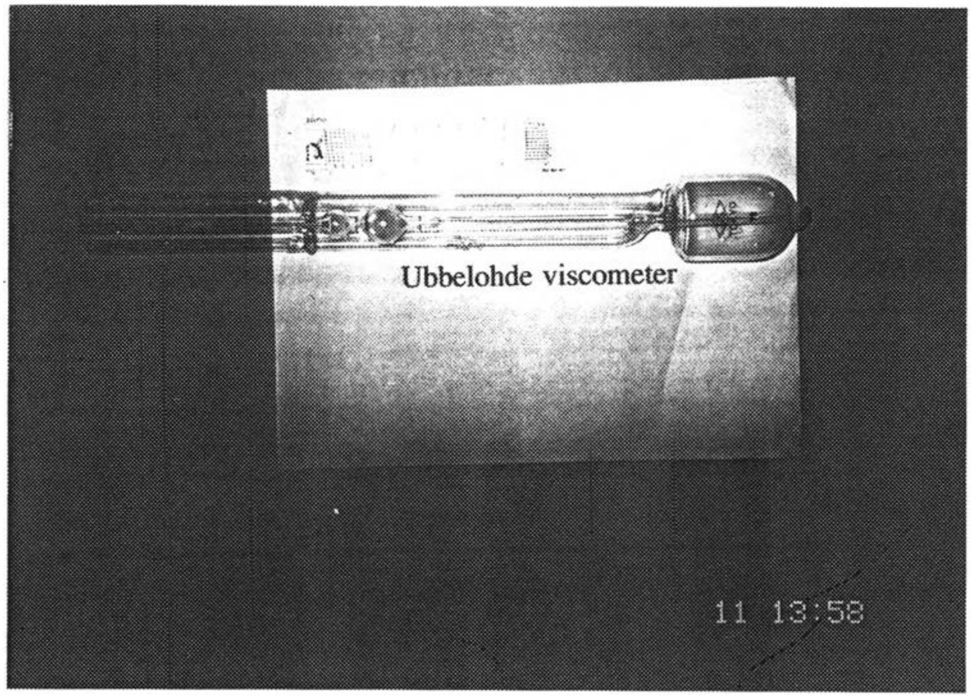

Figure 4.8 Ubbelohde viscometer

4.3 Procedure

4.3.1 High Activity Ziegler-Natta Supported Catalyst Preparation

The anhydrous $MgCl_2$ stored in the Schlek tube shown in Figure 4.9 was transferred to the test tube in the glove box. The amount of the ethanol added in 8 moles per mole of $MgCl_2$. The ethanol was added dropwise at room temperature over a period of 30 minutes under vigorous stirring. After ethanol addition, the content was stirred until it became nearly slurrry. The alcohol adduct was obtained.

$$\frac{[\text{Ethanol}]}{[\text{Magnesium dichloride}]} = 8.0$$

The alcohol adduct was then reacted with triethylaluminum(TEA). When it was especially desired to prepare a catalyst having high activity, TEA was used in such that the quantity of the ethyl group of the triethylaluminum was preferably 0.5 to 1.0 mole per mole of the alcoholic hydroxy group of the alcohol adduct of $MgCl_2$. In the study, this ratio used was 0.75.

$$\frac{[\text{-Et}]\text{triethylaluminum}}{[\text{-OH}]\text{ethanol}} = 0.75$$

The determined amount of TEA was added dropwise within 30 minutes, and afterwards then the content was stirred vigorously for 2 hours. The product in this step was called the reaction product.

The reaction product formed between the alcohol-adduct of $MgCl_2$ and TEA reacted directly with a titanium compound. The product after reaction was called as the transition metal catalyst component. The herein titanium compound was $TiCl_4$. The transition metal catalyst component prepared from this step was the titanium catalyst component. The molar ratio of TEA to $TiCl_4$ used is 1:0.176 or 5.70. This reaction was done at room temperature for 6 hours.

$$\frac{[\text{TEA}]\text{preparation}}{[\text{titanium tetrachloride}]} = 1:0.176$$

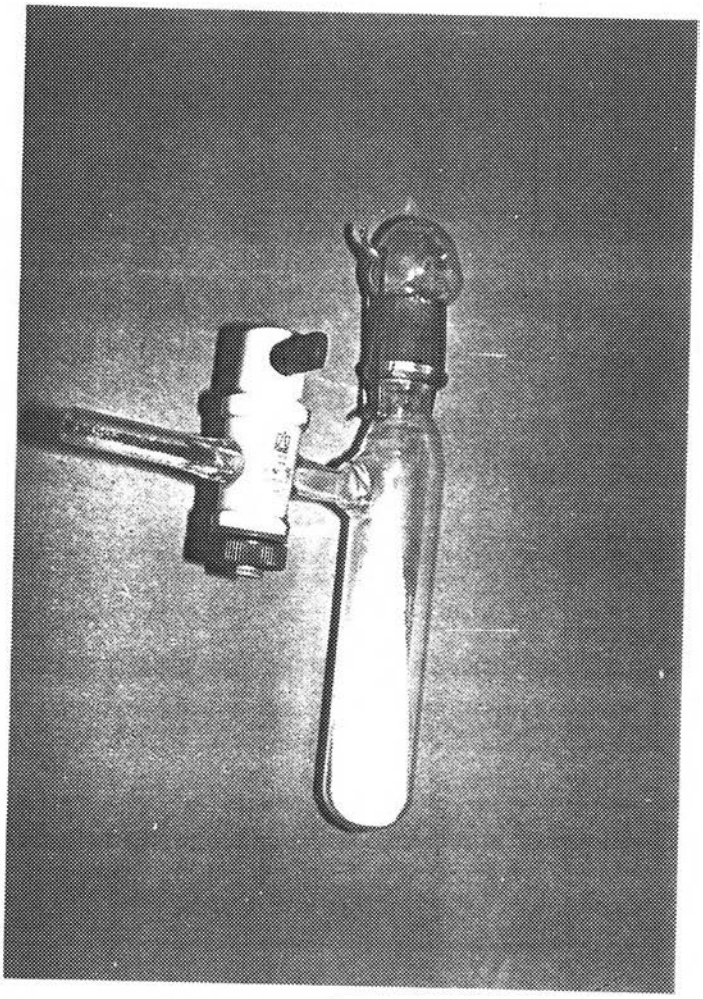

Figure 4.9 Schlek Tube

The titanium catalyst component diluted by n-hexane to seven-fold. The titanium catalyst component after dilution was called as catalyst suspension. The catalyst suspension was 0.01780 mole Ti/l

4.3.2 Ethylene polymerization on the prepared catalyst

The polymerization of ethylene using the catalyst suspension was preferably carried out under inert solvent, n-hexane. The amount of TEA for the activation in the polymerization was 160 moles per mole of the titanium catalyst components calculated as the titanium atom.

$$\frac{[\text{TEA}]\ \text{activation}}{[\text{Titanium}]\ \text{in titanium catalyst component}} = 160$$

The catalyst suspension, 3.0 cm^3, was transferred to the glass cylinder and filled with n-hexane to 250 cm^3. The TEA was calculated in the above condition and injected into the glass cylinder. The color of catalyst suspension changed from white to yellowish brown. Then it introduced into the reactor and another 250 cm^3 of n-hexane transferred to the reactor. The catalyst loading was carried out at 18-23^oC.

The polymerization reactor with the premixed catalyst was heated from the catalyst loading temperature to 50^oC (130 V). When the temperature attained 40^oC, the hydrogen feed line was set at the desired pressure. The temperature reached 50^oC and the adjustable resister was reduced to 60 V. The hydrogen introduced to the reactor. During this interval, the temperature was gradually increased. At 75^oC, the ethylene feed line had been readily set at the desired pressure. As soon as the polymerization temperature was 85^oC, the ethylene was suddenly introduced. The reaction time from this point was 1.5 hr.

After the reaction finished, the mixture of catalyst and polyethylene was filtered by Buchner funnel. The n-hexane which was used as the solvent was removed from polyethylene particles. The obtained polyethylene was dried in an oven at 110^oC for 12 hours, and kept to characterize its properties latter.

The study of ethylene polymerization on high-activity Ziegler-Natta supported catalyst was divided into two parts. Firstly, the suitable polymerization conditions and their effects on the ethylene polymerization were carried on the $MgCl_2$/EtOH/TEA/$TiCl_4$-TEA catalyst system. When the optimum condition obtained, the effect of iron(III) oxide(Fe_2O_3) addition was examined latter. The investigation of the conditions and effects on the polymerization were conducted as follows:

4.3.2.1 The effect of ethylene partial pressure

The polymerization was carried out to investigate the effect of ethylene partial pressure on the catalytic activity by constant value of TEA/Ti molar ratio, $TiCl_4$ concentration, temperature, polymerization time and volume of solvent. The partial pressure of ethylene was varied from 1 to 3 atm whereas the partial pressure of hydrogen was 1 atm. The following is the experimental condition for the polymerization.

TEA/Ti = 160,
[$TiCl_4$] = 5.34X10^{-5} gmoleTi,
Temperature = 85 °C,
Polymerization time = 1.5 hr.,
n-hexane = 500 cm^3.

4.3.2.2 The effect of hydrogen partial pressure

The hydrogen partial pressure was varied but the composition of the supported catalyst system was not changed. The titanium metal catalyst component with 0.01780 moleTi/l was used 3.00 cm^3. Therefore, the titanium metal atom in the reaction system was 1.068x10^{-4} mole Ti/l with the TEA/Ti mole ratio of 160. The reaction temperature was 85°C and the polymerization time was 1.5 hr.

4.3.2.3 The effect of triethylaluminum/Ti ratio

The cocatalyst ratio was varied from 8 to 200. The high-activity Ziegler-Natta supported catalyst system was carried out in various TEA concentrations. The reaction temperature was 85°C and reaction time of 1.5 hr. The ethylene and hydrogen partial pressures were 1.0 atm. The Ti metal in the catalyst suspension was fixed at 1.068x10^{-4} mole Ti/l.

4.3.2.4 The effect of percentage mole ratio of Fe/Ti modification

The ethylene polymerization was further investigated by ferric(III) oxide modified high activity Ziegler-Natta supported catalyst at the suitable condition from the previous section. The amount of ferric(III) oxide added in the form of the ferric(III) oxide suspension was varied as the percentage mole ratio of Fe/ Ti. The suspension was 1.013×10^{-3} gFe_2O_3/cm^3 or 1.267×10^{-7} mole atom Fe/cm^3.

4.4 Characterization of the polyethylene product

This polyethylene product has remarkable chemical inertness, particularly at ordinary temperatures to most chemicals, including acids and alkalies. Chemical analysis used to characterize polyethylene was few. As a consequence of this, a quantitative measurements of physical properties and determinations of the involving chemicals and physical structure have been increased important. In this work the polyethylene products were characterized as the following.

4.4.1 Morphology

The high-activity Ziegler-Natta supported catalyst can uniquely replicate its morphology to that of the progeny polymer particles. The term of morphology was referred to the shape, texture, or form of such a polyethylene. The polymer samples were coated with gold plate by ion sputtering device in Figure 4.11. Scanning Electron Microscopic(SEM) technique was the effective method to investigate these morphologies.

4.4.2 X-ray diffraction (XRD) method

X-ray diffractometer, Philips Type PW 1730/10 was used to compare the crystallinity of the polyethylene. It used Cu tube as the target with Ni as the filter and the wavelength was 1.5405 nm. The diffraction followed the Bragg's Law of Diffraction. The diffraction pattern was plotted between the angle(2θ) and relative intensity.

4.4.3 Microstructure Determination

Infrared spectroscopic technique is the reliable indicator for the microstructure of polymer such as methyl groups, unsaturation and carbonyls. The correlation of infrared adsorption intensities to concentration values obey Beer-Lambert's

Law. Figure 4.10 shows the polyethylene spectrum. There are three very strong bands at about 2950, 1460, and 762/720 cm^{-1}. They were assigned to the CH_2/CH_3 stretching, CH_2/CH_3 bending and rocking modes of $-(CH_2)_n-$ groups, respectively. The presence of chain branching is present in polyethylene at 1378 cm^{-1}.

In addition to chain branching, there is a second type of defect structure as double bands. There are readily identified by the out-of-place deformtion modes. Polymers from the Phillips process have one end of each chain terminating by a vinyl group, which gives the sharp band at 910 cm^{-1}[67]. Low density polyethylene (LDPE) from high pressure process contained vinylidene groups, which absorbed at 890 cm^{-1}[67], while polyethylene prepared from a Ziegler-Natta catalyst has frequently a combination of three types of unsaturation, the two ones already mentioned together with trans CH=CH-, characterized by a band at 965 cm^{-1}.

4.4.4 Molecular Weight Determination by viscometry

The viscosity of polyethylene solution has a relationship to its viscosity-average molecular weight [80]. It can apply to a wide spectrum of polyethylene having densities from 0.940 to 0.970 g/cm^3. Elevated temperature about 135^0C is employed because polyethylene insolubility at room temperature. The method was in ASTM D1601-58T[68].

4.4.5 Flow properties of polyethylene

The plastometer was heated to 190 ^{0}C, then the polyethylene filled in the pistol and the exact weight loaded 325 g, 2160 g, respectively. The polyethylene melted and passed through the orifice during 10 min. The polyethylene molten was weighed to obtain melt flow index.

4.4.6 Density

The method was carried out as according to ASTM D1505-57T[69] to determine the density of the polyethylene. Specimen for the determination may be chipped or cut before being dropped into the column. The variation of the column lengths

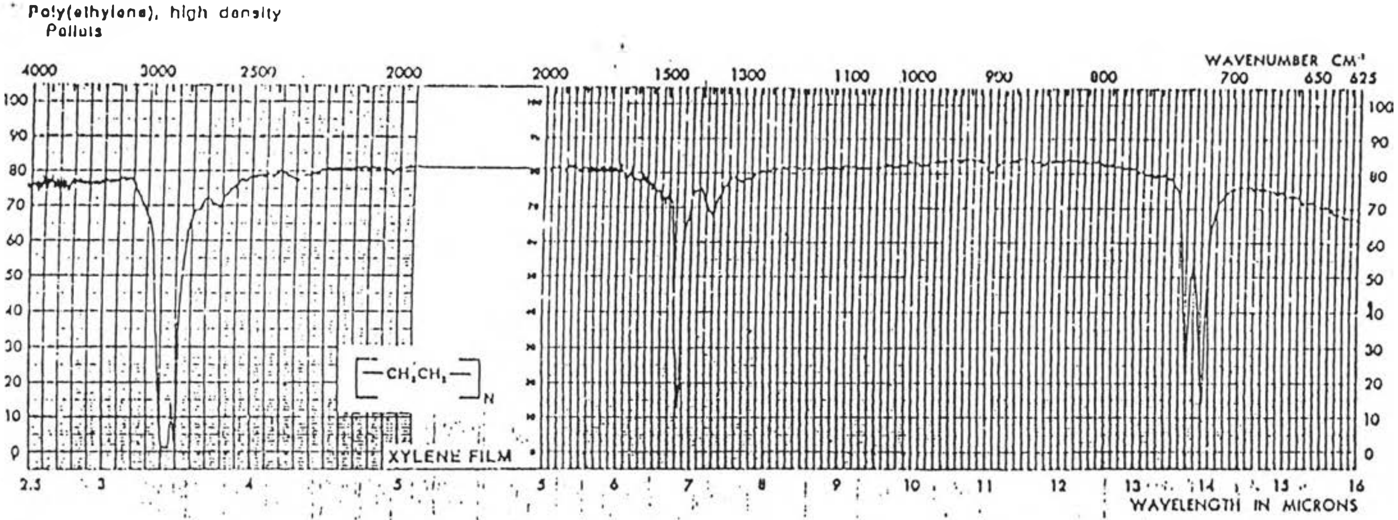

Figure 4.10 Infrared spectrum of high density polyethylene

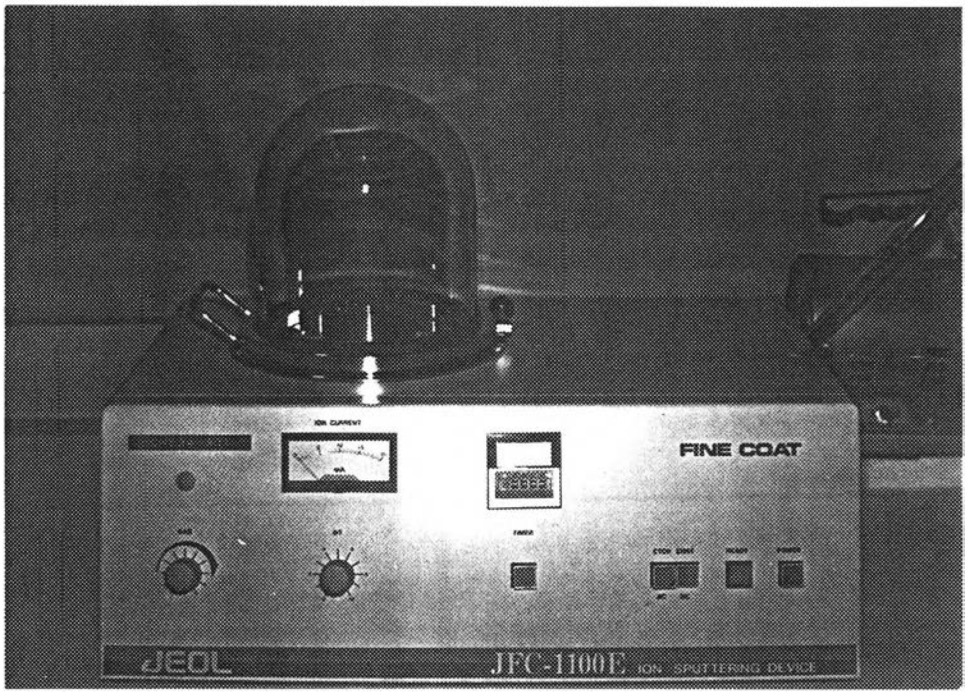

Figure 4.11 Ion sputtering device

was employed to obtain the range of density desired. The density of the polymer was reported in gram per cubic centimeter at 23^0C.

4.4.7 The Melting Temperature Determination

The polyethylene sample was weighed about 6.0 -7.0 mg. in Differential Theemal Analyzer (DTA) model DT-30. It was carried out to determine the melting temperature of polyethylene under static air by open pan techniques. The heating rate was 5 ^{0}C/min. and sensitivity ±50 µV. And the chart speed was 2.5 mm./min.

4.4.8 Gel Permeation Chromatography(GPC) of polyethylene

The whole procedure of Gel Permeation Chromatography (GPC) was carried out at Research Lab of Thai Polyethylene Co. The Gel Permeation Chromatography was Water 150-C ALC/GPC. The column was µStyragel HT with TCB (trichlorobenzene) as the eluent. The flow rate of eluent was 1.0 ml./min. at 135 ^{0}C.

4.4.9 Activity of the catalyst

The catalyst activity in this study is defined in gram of polyethylene produced per 1 gram of titanium atom per atm C_2H_4 per hr. The value is calculated from polyethylene yield after the polyethylene was dried for 12 hours at 100-110 ^{0}C.

4.4.10 Ethylene consumption

The amount of ethylene consumption during the polymerization time is expressed as a curve of gmole C_2H_4 consumed vs. polymerization time.