

CHAPTER III EXPERIMENTAL



3.1 Materials

3.1.1 Polypropylene Sources

- Polypropylene Homopolymer Resin HP520M (PW-583) was supplied by HMC POLYMERS COMPANY LIMITED with a reported density of 0.90 g / cm^3 (ASTM D 792B) and used as starting material (virgin PP) for polymer reprocessing. The melt flow rate was 8 g/10 min (ASTM D1238).
- Commercial polypropylene films were purchased from High Land Industrial Company Limited.

3.1.2 The Chemical Reagents for Catalyst Preparations

- Zirconium oxide (ZrO_2) was used as catalysts and catalyst supports. It was purchased from Riedel-deHaën.
- Ammonium sulfate (NH_4SO_4) was purchased from Asia Pacific Specialty Chemical Limited.

3.1.3 The Carrier Gas Used in Pyrolysis Study

- High purity nitrogen was purchased from Thai Industrial Gas Co., Ltd., (TIG).

3.1.4 Gas Sampling Bag

- Dual-Valve Tedlar PVF Gas Sampling Bags of size (3.8 Liters) were purchased from Cole-Parmer.

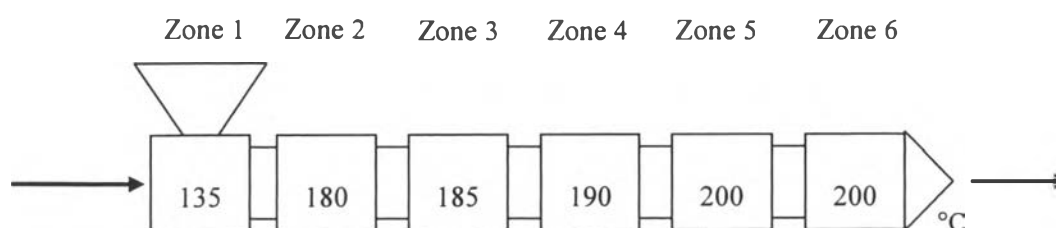
3.1.5 Standard Fluids for GC Calibrations

- Refinery gas test sample (Agilent P/N 5080-8755) was supplied from Agilent Technologies (manufactured for Agilent by Scott Special Gasses), and
- 99.0% n-pentane (C_5H_{12}) and 99.0% n-hexane (C_6H_{14}) were supplied from Lab-Scan, Analytical Reagent, with 0.626 g / cm^3 and 0.659 g / cm^3 density, respectively.
- ASTM Method D2887 Column Test Mixture was provided by ULTRA Scientific. This ULTRAstandard (TM) solution was gravimetrically prepared, and the analyte concentrations were verified using high resolution gas chromatography and/or high performance liquid chromatography.

3.2 Film Processing

3.2.1 Preparation of Reprocessed PP Pellets

Reprocessed PP pellets were obtained from virgin PP pellets using a COLLIN intermeshing self-wiping co-rotating twin screw extruder ZK-25 with the following conditions:



Screw speed = 35 rpm.

The extrudate was cooled in the water ($\sim 25 \text{ }^\circ\text{C}$) and cut into a pellet form by a Planetrol 075D2 pelletizer. The 1st generation PP pellets were taken back into the hopper for the next pass and reprocessed with the same condition. The cycle was repeated for four times, making four generations of reprocessed PP pellets. The pellets from each generation were kept for preparing four generations of films.

3.2.2 Preparation of PP Films

Virgin PP film with approximately 1.0 mm. film thickness was prepared from virgin PP pellets by using chill-roll cast film technique. Four generations of PP films with the same thickness were casted from each corresponding generations of reprocessed pellets by using the same technique. The preparation procedure is illustrated in Figure 3.1;

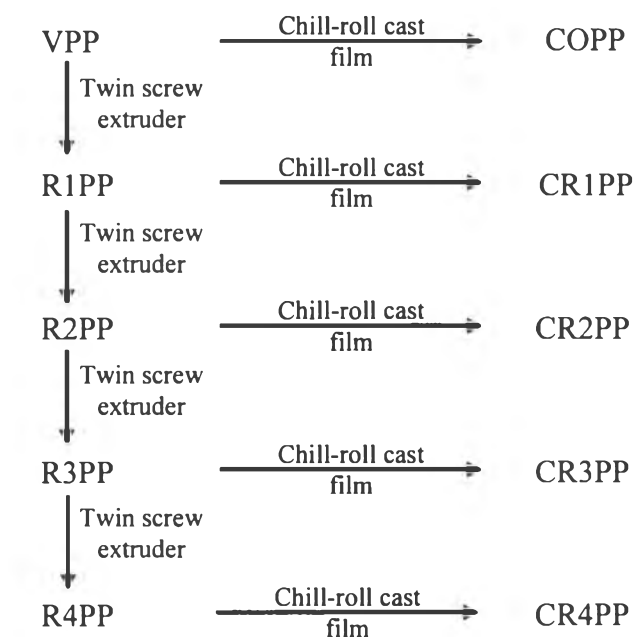


Figure 3.1 Preparation scenario of pellets and films.

where	VPP	=	Virgin PP pellets
	R1PP	=	1 st generation reprocessed PP pellets
	R2PP	=	2 nd generation reprocessed PP pellets
	R3PP	=	3 rd generation reprocessed PP pellets
	R4PP	=	4 th generation reprocessed PP pellets
	COPP	=	Virgin PP film
	CR1PP	=	1 st generation reprocessed PP film
	CR2PP	=	2 nd generation reprocessed PP film
	CR3PP	=	3 rd generation reprocessed PP film, and
	CR4PP	=	4 th generation reprocessed PP film.

3.3 Catalyst Preparation

The solid superacids $\text{SO}_4^{2-}/\text{ZrO}_2$ was easily prepared by impregnating ZrO_2 with $(\text{NH}_4)_2\text{SO}_4$ solution followed by calcination at 550°C for 2 hours in a furnace. The amounts of SO_4^{2-} in $\text{SO}_4^{2-}/\text{ZrO}_2$ was varied from 0 to 8 wt%.

3.4 Pyrolysis Studies

Small pieces (approx. 1mm^2) of 0.5 gram PP film sample were loaded into a semi-batch reactor with or without catalyst. In a typical run, after the reactor was set up, air remaining in the reactor was purged with nitrogen gas at a flow rate of 30 ml/min. for half an hour. The reactor was then heated from room temperature to 500°C at a heating rate of $10^\circ\text{C}/\text{min}$. held at 500°C for 1 hour. (See reactor and reactor system in Figure 3.2). The degradation products were classified into three groups: gases (products which were not condensable at ice-NaCl cooling temperature), liquid hydrocarbons and residues. The amount of gaseous products was calculated by subtracting the weight of liquid products, residues and catalyst from the total weight of PP film sample and fresh catalyst initially loaded to the reactor. Pyrolysed gas products were characterized via Gas Chromatograph in an Agilent Technologies HP 6890N gas chromatograph equipped with FID and a capillary column, HP-PLOT Q with $20\ \mu\text{m}$ coating thickness, 0.32 mm i.d. and 30 m length, using refinery gas (gas mixtures) for calibration. The temperature program of the GC column used was as follows: temperature constant at 70°C for the first 8 min and increased to 200°C with a heating rate of $20^\circ\text{C}/\text{min}$ and kept at this temperature for 20 min. Pyrolysed liquid products were performed by Simulated Distillation Gas Chromatography (DGC) (ASTM-D 2887) in a Varian CP-3800 gas chromatograph equipped with FID and a capillary column, WCOT fused silica 15 m long \times 0.25 mm i.d., using ASTM Method D2887 Column Test Mixture for calibration. The temperature program of the GC was as follows: the initial temperature at 30°C and increased to 320°C with a heating rate of $20^\circ\text{C}/\text{min}$ and kept at 320°C for 8.50 min.

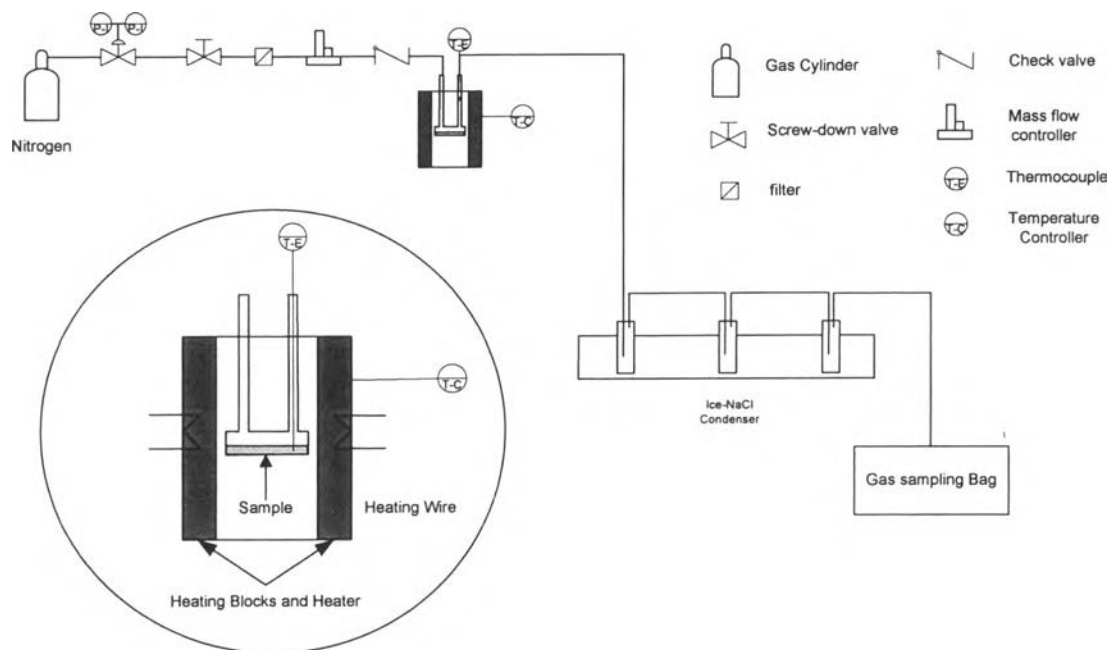


Figure 3.2 Schematic diagram of reactor and reactor system.

There are two parts of pyrolysis studies:

- Effect of film reprocessing on pyrolysis products, and
- Effect of catalysts on pyrolysis products

3.5 Testing and Characterization

3.5.1 PP Film Testing and Characterization

3.5.1.1 *Tensile test*

Tensile tests were carried out on Instron Universal Testing Machine, Model 4206, according to ASTM D638 test procedure. Ten specimens were tested and the results were averaged to obtain a mean value of tensile strength.

3.5.1.2 *Viscosity measurement*

Viscosity of samples was measured via Melt Rheometer Model RSI Orchestrator V 6.4.3. The test was performed on parallel plates with 25 mm. diameter under steady state.

3.5.1.3 Differential scanning calorimetry (DSC)

Differential Scanning Calorimetry (DSC) was carried out on a Perkin Elmer Model DSC 7. A sample of 8-12 mg was prepared in an aluminum sample pan. The chamber was purged with dry nitrogen at flow rate of 25°C/min. The temperature was programmed with the heating rate of 10 °C / min. from 30° to 200°C. The melting temperature (T_m), heat of fusion (ΔH_f) and degree of crystallinity were determined from the thermogram. The area under the melting peak is the heat of fusion which can be converted to the percentage of crystallinity, as shown in the Appendix A.

3.5.1.4 Thermal stability

Thermogravimetric analysis (TGA) of PP films was performed on Dupont TGA machine Model 2950. 10-20 mg of a sample was loaded on a platinum pan. The sample was heated in 30-800°C temperature range under N_2 flow with the heating rate of 10°C/min.

3.5.2 Catalyst characterization

3.5.2.1 Thermal stability

Thermogravimetric analysis (TGA) of catalysts was performed with the same procedure as it was accomplished on PP films by using Dupont TGA machine Model 2950.

3.5.2.2 Crystal structure

Crystal structure of catalysts was characterized using a D/MAX-2200H Rigaku diffractometer with $CuK\alpha$ radiation on specimens prepared by packing sample powder into a glass holder. The diffracted intensity was measured by step scanning in the 2θ range from 5° to 90°.

3.4.2.3 Surface area and pore size distribution

Specific surface area, nitrogen adsorption-desorption, and pore size distribution were determined using an Autosorp-1 gas sorption system (Quantachrome Corporation) via the Brunauer-Emmett-Teller (BET) method. Nitrogen was used to calibrate the analyzer, and also as the adsorbate at liquid nitrogen temperature. Samples were first outgassed for 3 hours under vacuum at 280°C. Twenty-two-point adsorption and desorption isotherms were obtained, from

which BET surface area (taken at $P/P_0 \sim 0.3$), total pore volume (P/P_0 close to unity), and pore size distribution (BJH method) were calculated.