



CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Polypropylene

Polypropylene (PP) is a thermoplastic material that is produced by polymerizing propylene molecules, which are the monomer units, into very long polymer molecules or chains (Harutun, 1999).

2.2 Polypropylene Films (Harutun, 1999)

Polypropylene is used for a huge variety of applications for examples: automotive, fibers and fabrics, strapping, sheet or thermoforming, injection molding, blow molding and films. One of the most important applications of PP is films. Films can be gently divided into two broad classes: oriented film and casted film.

2.2.1 Biaxial Oriented Polypropylene (BOPP) Film

Tubular or bubble process is widely used for producing BOPP film by using the homopolymer of about 3 g/10 min. melt flow rate (MFI). Films typically range in thickness from 0.25 to 2 mm. The main applications for BOPP film is in flexible packaging.

2.2.2 Casted Film

In film casting process, polypropylene is extruded through a die onto a chill roll, and the resulting film is eventually taken up on winding equipment. Casted film is essentially unoriented but still fairly clear because of the quench cooling that occurs. Film thickness usually ranges between 1 to 4 mm.

Casted film is processed to products that include bags for clothing article such as pocket-pages for photographs and as the outer nonporous sheet on disposable diapers.

2.3 Pyrolysis

Pyrolysis is defined as the breakdown of a macromolecule by heat under the absence of oxygen atmosphere (Probstein *et al.*, 1985).

Pyrolysis of plastics to produce valuable chemical products has been continuously studied and gained more interest due to its applicability. By pyrolysis, the macromolecule can be thermally or catalytically degraded.

2.3.1 Thermal Degradation

In thermal degradation of polyolefins, many hydrocarbons having a wide distribution of carbon atom numbers are formed through an intramolecular free-radical transfer mechanism. The effects of temperature (Ishihara *et al.*, 1993) and kinetics (Dawood and Miura, 2001, Cardona and Corma, 2002) on product yields and distribution have been investigated on pyrolysis of PP. These studies proved their great possibility to produce chemical feed stock. However, the process was energy excessive, causing the concern about the economics of investment. Moreover, product selectivity can not be controlled and manipulated. Catalytic conversion of plastic wastes has been more attractive in the past decade.

2.3.2 Catalytic Degradation

In this case, catalytic degradation is referred to applying catalysts in any step of pyrolysis process. The oils produced by the catalytic degradation are known to contain a relatively narrow distribution of hydrocarbons which undergoes through an ionic mechanism.

2.4 Effect of Catalysts on Pyrolysis

Zhao *et al.*, (1996) studied the effects of zeolites on the degradation temperature of PP. It was found that the degradation temperature of PP strongly depended on the type of zeolites used, not only the zeolite framework structure but also its composition. The amount added was also an important factor in determining the degradation temperature. Some zeolites did not change the structure of the products, but narrowed the product distribution to smaller molecule region, while the HY zeolites led to hydrocarbons with cyclic structures.

Using non-acidic mesoporous silica as a catalyst (FSM: Folded sheet material) in catalytic degradation of polyolefinic polymers, such as PE and PP, was carried out (Uddin *et al.*, 1998) at atmospheric pressure by batch operation at 430°C and 380°C. This study showed that the FSM accelerated the initial rate of degradation of plastic polymers (PE, PP), increased the liquid product yield, and promoted degradation into lower molecular weight products, as compared with thermal degradation. In addition, the mesopores surrounded by the silica sheet acted as a radical flask. The radical species in these so-called radical flasks remained active for a long time and accelerated the degradation of plastics. These findings provided new insight into the degradation of plastic polymers over non-acidic mesoporous silica catalysts.

By working with USY zeolites with different unit cell sizes, it has been proven that neither the total amount nor the strength of acid sites was the most determinant factors for cracking PP. It has found that the first cracking event of PP occurred at or close to the external surface. Then, the formation of mesopores in the zeolite strongly improved the cracking activity. This has been supported by the results obtained with a Y zeolite synthesized with smaller crystallite sizes (Cardona and Corma, 2000).

Hwang *et al.*, (2002) investigated the performance of several differently, naturally treated zeolites in the degradation of PP. The degradation was carried out with a mixture of polypropylene and catalysts at 400°C and five types of natural zeolite (NZ), different in pre-treatment procedures, were used to test their catalytic performances in the degradation of PP. The clinoptilolite natural zeolites, either proton-exchanged (H-NZ) or further treated by boric acid (B-H-NZ) or phosphoric acid (P-H-NZ), were efficient catalysts for the conversion of PP to gasoline-range chemicals. These two acid-treated catalysts showed an increase in surface area and pore volume, as compared to H-NZ. For the degradation of PP, the acidic property of a catalyst was necessary for the formation of carbenium ion, and pore volume was another important character for further cracking of initially degraded fragments. The composition of degradation products, especially liquid fractions resulted over studied catalysts was compared to understand the role of catalysts. The liquid products from the catalytic degradation of PP were distributed in a narrower range of carbon

numbers compared with those obtained by thermal degradation. In addition, they found that high degradation temperature offered lighter hydrocarbons by accelerating the cracking reactions.

In 2002, Kim *et al.*, found that the clinoptilolite zeolites, either proton-exchanged (H-SCLZ4.4) or further treated by hydrochloric acid (H-SCLZ12.0 and H-SCLZ20.3), were efficient catalysts for the conversion of PP to gasoline-range chemicals. For the degradation of PP, the acidic sites of medium acid strength seemed necessary for formation of carbenium ion and cracking of carbon chains. Pore volume was another important factor for the further cracking of initially degraded fragments.

In the presence of silica-alumina catalyst with 13 wt% alumina content (Ishihara *et al.*, 1993), the formation of gas was resulted from catalytic decomposition of PP. The catalytic decomposition of PP proceeds from polymer to degraded polymer, oligomer, liquid, and gas, respectively. Gas composition and mechanisms were also examined. Gas was produced from the chain-ends of the liquid fraction and its components were primarily isobutane and isopentane. The most important elementary reaction in the decomposition was intramolecular rearrangement taking place via a six-membered transition state to inner tertiary carbon atoms (back-biting reactions). The main gas components were produced by the decomposition of the C9 fraction formed by back-biting.

In summary, the discovered effects of catalysts are: (1) reduction of operation temperature (Zhao *et al.*, 1996), (2) acceleration of the degradation rate (Uddin *et al.*, 1998; Dawood and Miura, 2002), (3) improvement of controllable product selectivity and yields (Uddin *et al.*, 1998; Cardona and Corma, 2000; Dawood and Miura, 2002), (4) lower range of desirable hydrocarbon products (Hwang *et al.*, 2002; Kim *et al.*, 2002) and (5) less residue production (Uddin *et al.*, 1998; Dawood and Miura, 2002; Kim *et al.*, 2002).

Furthermore, most researchers often used zeolites as acid catalysts, for example, ZSM-5 (Zhibo *et al.*, 1996), HY zeolite (Zhao *et al.*, 1996), HNZ (Kim *et al.*, 2002), and FCC catalyst (Cardona and Corma, 2000), in their studies on catalytic decomposition of PP. In contrast, no studies have been performed using solid superacid catalysts to affect the degradation process of polypropylene. Therefore,

solid superacid catalysts were investigated for the influence of the catalyst on the pyrolysis of PP films.