

# CHAPTER 1

## INTRODUCTION

### 1.1 Background

The world demand for energy has increased dramatically in the past century. It will grow even stronger in the future. The resources are non-renewable such as coal, natural gas, and crude oil, etc. Crude oil is the most demanded resource for the last few years. The prices for crude oil have been rising dramatically. The demand is increasing while there is less crude oil available. Therefore the alternative energy has been considered such as hydropower (water), solar, wind, geothermal, biomass, and plastic wastes. Recycling of plastic waste into fuel oil has gained attention because plastic consumption has grown tremendous rate over the past decades. The world's annual consumption of plastic materials has increased from 5 million tons in 1950s to nearly 100 million tons today. 35 Percent of total plastic is used for packaging was shown in Figure 1.1.

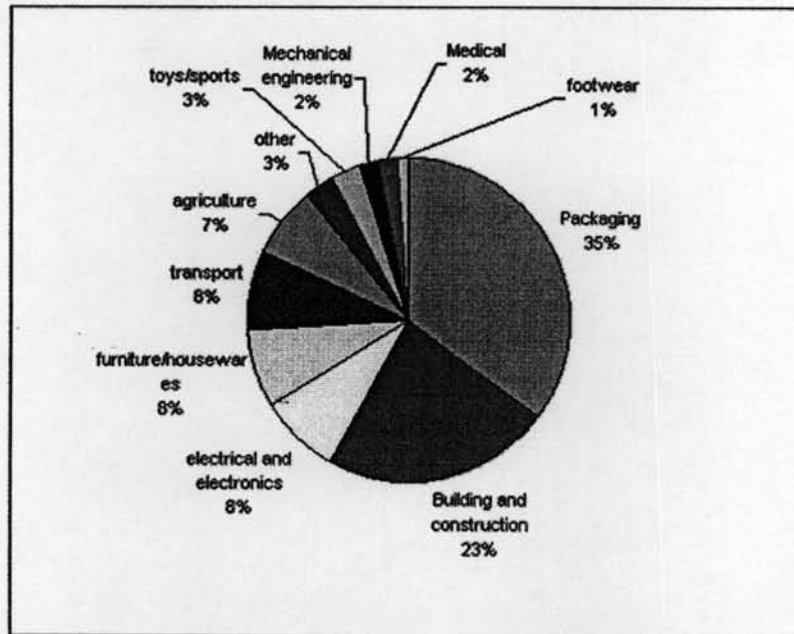


Figure 1.1 Plastic applications. [1]

There are six main plastics in municipal solid waste: high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), poly(vinyl chloride) (PVC), and polyethylene terephthalate (PET)[2]. These plastics have been traditionally disposed as follows;

(1) Mechanical reprocessing of used plastics to form new products. This method is not generally applicable because the quality of new products is low and the purity of waste-plastic streams is required.

(2) Incineration of the plastics to generate heat. This method produces toxic gaseous compounds and only shifts a solid waste problem to air pollution. In many countries incineration of plastic waste is forbidden and politically prohibited.

(3) Thermal or catalytic degradation of plastic waste to fuels or chemicals. These methods are the most promising cost-effective process for solving the environmental problem of plastic waste disposal. The products from pure thermal degradation show a wide range of carbon numbers. That requires further process for upgrading its quality [3]. In contrast, catalytic degradation allows the reaction to be performed at lower temperature. The product distribution can be controlled by a right selection of catalyst type. A number of acid porous solids, such as amorphous silica-alumina, zeolites, and ordered mesoporous materials have been used as catalysts. For example ordered mesoporous materials such as Al-MCM-41 and Al-HMS, yield hydrocarbons within gasoline and gas oil fractions. ZSM-5 and beta zeolite produce light products, mainly gaseous and aromatic hydrocarbons [4]. However, the low acidity of mesoporous catalyst and the restriction of large molecules to access micropores catalyst are disadvantages.

In recent years, several authors have reported a new class of porous materials combining the properties of both zeolites and ordered mesoporous aluminosilicates [5, 6]. These catalysts promote the cracking activity and produced some more hydrocarbons with higher market value. Some literatures are discussed as follows;

R. A. Garcia *et al.* [4] reported the catalytic cracking of HDPE over hybrid ZSM-5/MCM-41 and compared with Al-MCM-41 and HZSM-5 at 380°C for 2 hours. The hybrid catalyst showed higher conversion of polyolefins than both Al-MCM-41

and HZSM-5. The product distributions obtained from HDPE cracking over the hybrid materials were similar to that over HZSM-5 zeolite. It mainly contains light hydrocarbons. Moreover, the products present a high content of C<sub>3</sub>–C<sub>5</sub> olefins, which is an interesting result regarding its possible use as raw chemicals.

Y.-H. Lin *et al.* [7] also studied catalytic cracking of HDPE over various catalysts using a fluidized-bed reactor operating isothermally at ambient pressure. The reaction temperature was 360°C with N<sub>2</sub> rate at 570 ml/min. HZSM-5 catalyzed cracking resulted much larger amounts of volatile hydrocarbons compared with cracking over MCM-41 and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (SAHA). When an HZSM-5 was used as a cracking addition in MCM-41/HZSM-5 and SAHA/HZSM-5 mixed catalysts, the solid mixed catalysts produced less gas and a higher gasoline than HZSM-5. MCM-41 with large mesopores and SAHA with weaker acid sites produced a highly olefinic product and gave rise to the broadest hydrocarbon in the range of C<sub>3</sub>-C<sub>7</sub>. For HDPE cracking over MCM-41 at temperatures in the range of 290°C-430°C, liquid and residue fractions decreased with increasing reaction temperature. Both SAHA and MCM-41 materials allowed bulky reactions to occur leading to coke formation and subsequently deactivation of the catalyst.

George Manos *et al.* [8] explored the catalytic cracking of HDPE over ultrastable Y, Y, zeolite beta, mordenite, and ZSM-5 at 360°C. The structure of zeolite framework has shown a significant influence on the product distribution. Over large-pore USY, Y, and zeolite beta, alkanes were the main products with less amounts of alkenes and aromatics and very small amounts of cycloalkanes and cycloalkenes. Medium-pore mordenite and ZSM-5 gave alkenes as major products. The hydrocarbons formed with medium-pore zeolites were lighter than those formed with large-pore zeolites. A similar order was found regarding the bond saturation:

(more alkenes) ZSM-5 < mordenite < zeolite beta < Y < USY (more alkanes)

J. Aguado *et al.* [9] investigated a mesoporous HMCM-41 type material and a nanosized HZSM-5 (n-HZSM-5) as catalysts for the conversion of plastic mixture consisting of PP, LDPE, and PE. Both materials presented high conversion for polyolefin mixture as the temperature was increased from 375 to 450 °C or as the P/C ratio was varied from 200 to 4. The product distributions obtained with these two

catalysts were completely different, suggesting prevailing cracking mechanism. n-HZSM-5 zeolite with high external surface area and strong acid sites promotes end-chain scission reactions of the polymers. Light hydrocarbons with 80-90% of the products in the range C<sub>3</sub>-C<sub>6</sub> were obtained. In contrast, heavier products (C<sub>5</sub>-C<sub>12</sub> and C<sub>13</sub>-C<sub>22</sub>) were found over HMCM-41, indicating a random scission mechanism as a result of large pores and mild acidity of this material. Changes in reaction temperature and/or P/C ratio over the HMCM-41 catalyst allowed the optimization of selectivity toward gasoline and middle distillate fractions up to 90%.

Y. Sakata *et al.* [10] reported catalytic cracking of PE and PP using FSM, silica-alumina, ZSM-5, silicalite, and silica-gel in batch operation at 430°C and 380°C. Compared with thermal degradation, FSM catalyst accelerated the initial rate of degradation, increased the liquid product yield and promoted degradation into lower molecular weight products. Silicalite and silica-gel had very negligible effects on polymer degradation. When the batch reaction was repeated four times using FSM catalyst, the extent of the decline in the degradation rate was lower for PE than PP. Compared with silica-alumina and ZSM-5, which turned completely black in the case of both PE and PP, the deposition of coke on the used FSM catalyst was extremely slight. It seems likely that catalytic effect of FSM for polyolefinic polymer degradation is related more to the hexagonal pore structure system of FSM.

D.P. Serrano *et al.* [11] reported catalytic cracking of polyolefin mixture consisting of 46.5 wt% LDPE, 25 wt% HDPE, and 28.5 wt% PP at 400°C over a variety of acid solids as catalysts. The activity order was found as follows:

n-HZSM-5>H beta>HMCM-41>>SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>>HZSM-5>HY>thermal degradation

The activity order found for the different catalysts was related to their respective properties and the nature of the polyolefin mixture. HMCM-41 led to a high conversion because of its large pore size, which promotes the access of polymer molecules to acid sites. In the case of n-HZSM-5 and H-beta, the presence of high external surface area enhanced its cracking activity because the external acid sites are not sterically hindered for the conversion of the bulky polyolefin molecules. Significant differences were observed in the product distribution: n-HZSM-5 showed the highest selectivity toward C<sub>1</sub>-C<sub>4</sub>(50 wt %), H beta led mainly to liquid hydrocarbon C<sub>5</sub>-C<sub>12</sub>(60 wt %), whereas HMCM-41 yielded both C<sub>5</sub>-C<sub>12</sub> (54 wt %) and

C<sub>13</sub>-C<sub>30</sub>(32 wt %) fractions. Regarding the selectivity by carbon atom number in all cases C<sub>4</sub> fraction was the major products, its value changes widely depending on the catalyst.

J. Aguado *et al.* [12] investigated catalytic degradations of PP, LDPE, and HDPE over different samples of zeolite beta. Zeolite beta synthesized by the fluoride method had low activity for cracking of polyolefins. It was related to its large crystal size (12  $\mu\text{m}$ ) and poor aluminium incorporation. In contrast, zeolite beta synthesized from amorphous xerogels consisted of small crystallites ( $\leq 200$  nm). Polyolefins degraded with high conversion (40-60%) and good selectivity towards C<sub>5</sub>-C<sub>12</sub> hydrocarbons (60-70%), while heavier products were hardly obtained (< 6%). The incorporation of titanium into the BEA structure enhanced the catalytic activity, as denoted by the highest conversion per Al atom obtained with the Ti-Al-beta sample compared to Al-beta.

S. Chaianansutcharit *et al.* [13] studied degradations of PP and PE over pure hexagonal mesoporous silica and aluminum-containing hexagonal mesoporous silica catalysts in a fixed bed catalytic reactor at 380 and 430°C, respectively. The liquid products were widely distributed in hydrocarbons with boiling point ranges of 36–405°C. By adding a small amount of aluminum to the hexagonal mesoporous material, aluminium-containing hexagonal mesoporous silica exhibited good performance in cracking heavy molecular weight hydrocarbons into light hydrocarbons. High liquid yields and less coke deposits were obtained in liquid-phase-contact reaction with increasing aluminum content. The liquid products were mainly composed of C<sub>5</sub>-C<sub>10</sub> hydrocarbons with boiling points of 36–174°C, and propene, butene, and butane were main components in gaseous products.

This research was aimed to demonstrate the successful catalytic cracking of polyolefin over catalyst mixture between zeolite beta and Al-HMS. The large pore size, high surface area, and moderate acid strength of Al-HMS allow plastic wastes to be degraded with high conversion activity. While ordered microporous zeolite beta directs the catalytic cracking products towards light hydrocarbons. In addition, this work also developed a NH<sub>4</sub>Cl treatment method to improve the cracking activity of

Al-HMS and zeolite beta/Al-HMS mixed catalysts in HDPE and PP cracking reactions.

### **Objectives**

1. To prepare Al-HMS catalyst and study the effect Si/Al ratios.
2. To study the optimal condition for  $\text{NH}_4\text{Cl}$  treatment of Al-HMS.
3. To synthesize nanoparticles zeolite beta catalysts.
4. To investigate the efficiency of zeolite beta/Al-HMS mixed catalysts for cracking of high density polyethylene and polypropylene.
5. To study the activity of regenerated zeolite beta/Al-HMS mixed catalysts.