CHAPTER II
BACKGROUND AND LITERATURE SURVEY

2.1 Polyethylene

Polyethylene or polyethene is one of the simplest and most inexpensive polymers. It is a waxy, chemically inert, rather soft plastic. The name of this type of polymer is obtained by the polymerization of ethylene (ethene). It is also known as polythene–a contraction of the name–and PE for the abbreviation. The molecule of ethene is consisted of two molecules of CH_2 connected together with a double bond.
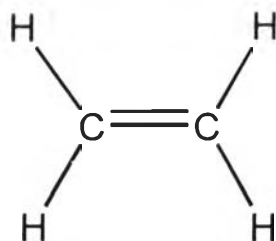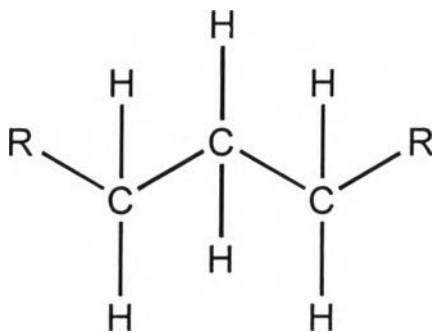

Figure 2.1 Chemical structure of ethane.

When the polymerization process is occurred, the double bond is broken to let an additional single bond to form, so the macromolecule is generated.

($R-CH_2-CH_2-CH_2-R$)

R indicates that the chain consists of the same compound of CH_2 groups

Figure 2.2 Chemical structure of polyethylene.
(www.encyclopedia4u.com)

2.2 Pyrolysis

Pyrolysis process is thermal degradation of a substance in the absence of oxygen/air. Plastic pyrolysis is for disposal of plastic wastes with recovery of valuable range of hydrocarbons. In pyrolysis, plastic materials are heated to high temperatures, so their heavier molecules are broken down into smaller molecules, and a variety of hydrocarbons are formed (Figure 2.3). On the other hand, for combustion, plastic materials are burnt at high temperatures with oxygen gas in the atmosphere. The products of reaction are water and carbon dioxide with carbon monoxide in some cases occurred from incomplete combustion (Figure 2.4).
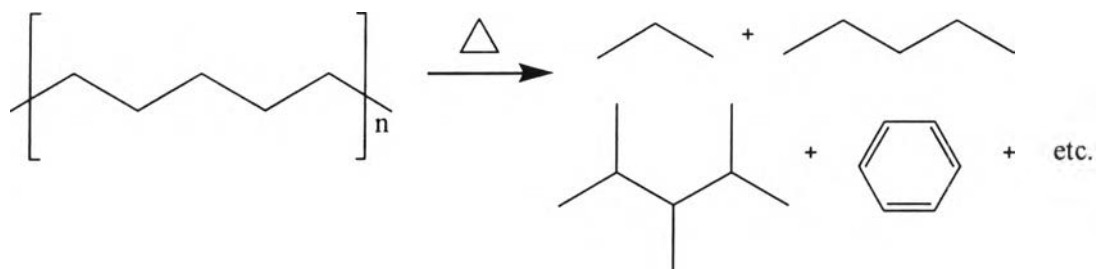

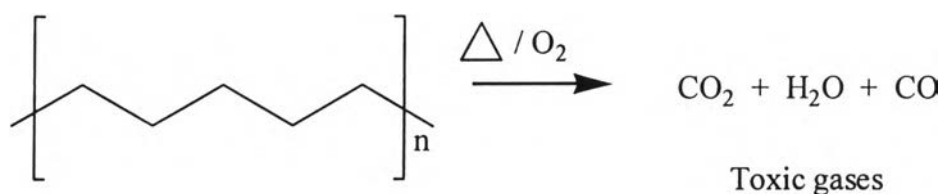**Figure 2.3** Pyrolysis reaction of polyethylene.

Figure 2.4 Combustion reaction of polyethylene.

2.3 Literature Survey

Researching on pyrolysis of plastic wastes to produce valuable chemical products have been accomplished, not only simply thermal degradation but also addition of some catalysts in order to improve the quality of products, decrease the cost, and make pyrolysis become an alternative way to recycle useless plastics.

Pyrolysis of high-density polyethylene without catalysts in a fluidized bed reactor was studied by Mastral *et al.* in 2001.They pyrolyzed the plastic and studied the influence of temperature and residence time on product distribution and gas composition. The results showed the effects of those operating parameters on the production and composition of gases, oil and waxes. Temperature and residence time had great influences on the pyrolysis product distribution. At 640° C the main product obtained was a waxy creamed coloured material rich in aliphatic hydrocarbons up to C_{30}. At higher temperatures, the product distribution changed drastically; the higher gas yield was obtained at 780° C.

In 1999 Milne *et al.* performed non-catalytic pyrolysis of low density polyethylene (LDPE) by using an internally circulating fluidized bed (ICFB) at temperatures ranging from 780 to 860 °C and residence time of 400-600 ms. They have found that this type of reactor allowed high temperature operation at short residence time, conditions favorable for conversion of waste plastic to olefins. They can obtain the gas yield of more than 90 wt% and the total olefin yields as high as 75 wt%.

Demirbas (2004) pyrolyzed waste plastics consisting of polystyrene, polyethylene and polypropylene without a catalyst in a stainless steel reaction vessel. He had found that under pyrolysis conditions, plastic wastes could be decomposed into three fractions: gas, liquid and solid residue. Liquid products from the pyrolysis can be separated as a mixtures of heavy naptha (C_7-C_{10}), gasoline (C_8-C_{10}) and light gas oil (C_{10}- C_{20}) fractions. The gaseous product contained C_1-C_4 parafinic hydrocarbons with some olefins. He has concluded that most of the liquid products formed should undergo further processing in a petrochemical refinery, and the gas can be used directly as fuels.

For thermal degradation, the analysis of products derived from the fast pyrolysis of plastic wastes was studied by Elizabeth *et.al* (1997). Mixture of LDPE, HDPE, PP, PS, PVC and PET were used as a feed for studying the influence of temperature and composition on product yields, which are gas and oil. They have found that as temperature was increased the amount of aromatic compounds in the oil increased and gas was produced at all temperatures with its concentration increasing at higher temperatures.

Although non-catalytic pyrolysis can convert plastic wastes to petrochemical feedstock, but the quality of products can not be controlled, and the heat in this reaction is very excessive, so the investigations of adding catalysts into the system are of the interest.

Catalyst addition in polyethylene thermogravimetric pyrolysis was studied by Marcilla *et al.* in 2001.They studied the effect of type and concentration of different catalysts on the thermal decomposition process of low density polyethylene. They proved that MCM-41 had more effectiveness in reducing temperature of the LDPE decomposition than the zeolitic catalysts, USY and ZSM-5. They applied a kinetic model concerning two pathways, catalytic and non-catalytic ones, and concluded that the non-catalyzed pathway was much slower than the catalyzed one.

Thermal and catalytic cracking of both high and low-density polythylene under mild conditions were investigated in order to study the properties of the obtained solid waxy product (Grieken *et al.,* 2001). The catalysts employed were n-HZSM-5 and HY zeolites, amorphous silica-alumina, activated carbon, Pd charcoal powder and mesoporous aluminosilicate material (MCM-41), with and without impregnated Pd. The best results achieved in the LDPE degradation with regard to stability and homogeneity of the waxy product were obtained using MCM-41 as a catalyst. The high BET surface area, uniform mesoporosity and medium acid strength of this catalyst promoted the polymer cracking according to a random scission mechanism, as well as, the development of hydrogen transfer reactions, which reduced the olefinic character of the solid product. On the other hand, the product obtained from HDPE had a higher homogeneity than that from LDPE, leading to a waxy product with better quality for potential applications.

In 2001 Seddegi *et al.* studied the catalytic cracking of high-density polythylene in a glass batch reactor by using all-silica MCM-41 as a catalyst because this catalyst can crack HDPE through the carbenium ion mechanism by the silanol groups on the surface of the catalyst. The authors have proposed that the formation and stabilization of carbenium ion in the pores of the catalyst were due to the adsorption of the polyethylene on the surface of the channels, increasing the basicity of the hydrocarbon fragment, and the protonation occured by the silanol groups.

Jalil (2002) studied catalytic degradation of polyethylene at atmopheric pressure under batch conditions at 420 °C, and the MCM-41 was added as a catalyst. The result showed that the pore sizes of MCM-41 had an influence to the product distribution. Smaller pore size gave lighter hydrocarbon number. After that the larger pore size was further studied by using as a support for tungstophosphoric acid (HPW/MCM-41) and impregnation of water and methanol. The gas products obtained from water/methanol- impregnated HPW/MCM-41 had lower molecular weight of hydrocarbons than HPW/MCM-41 only. A large amount of isobutane was obtained on thermal degradation , but not HPW/MCM-41.

The study of thermal decomposition of several PEs with different properties was reported by Marcilla *et al.* in 2002. The result showed that no significant differences were found at any temperature of the thermal process. Contrarily, a decrease of 60-79° C in the thermal decomposition temperature was observed when about 9% of catalyst MCM-41 was added to the polyethylene.

Catalytic degradation of polyethylene was studied by Fernandes *et al.* (2002). In this study, they have used silicoaluminophosphate (SAPO-37) as a catalyst because the presence of specific Bronsted and Lewis acid sites in its structure. The thermogravimetric study showed that using the catalyst, the activation energy in degradation of polyethylene decreased from 290 KJ/mol to 220 KJ/mol. The results from GC/MS have indicated that the range of hydrocarbons in non-catalytic degradation was C_5-C_{25}, but after SAPO-37 was added, the range of hydrocarbons decreased to C_1-C_{12}.

Bagri *et al.* (2002) investigated the catalytic pyrolysis of polyethylene by studying the influence of zeolite catalytic upgrading of the pyrolysis gases.The yield and composition of the derived hydrocarbon gases and oils were investigated in terms

of the temperature of the catalyst. Polyethylene was pyrolysed in a fixed bed reactor, and the pyrolysis gases were passed to a secondary reactor containing Y-zeolite or zeolite ZSM-5 catalyst. After catalysis there was a marked increase in the concentration of aromatic compounds in the oil, which further increased in concentration as the temperature of catalysis was raised. The single ring compounds consisted of mainly toluene, ethylbenzene and xylenes, and the two and three ring compounds were mainly, naphthalene and phenanthrene and their methyl derivatives. Also they found that the Y-zeolite produced significantly greater concentration of aromatic hydrocarbons in th derivatived oils as compared to when zeolite ZSM-5 catalyst was used.

Seo *et al.*(2003) studied the catalytic degradation of waste high-density polyethylene to hydrocarbons by ZSM-5, zeolite-Y, mordenite and amorphous silica-alumina were carried out in a batch reactor.They investigated the cracking efficiency of catalysts by analyzing the oily products including paraffins, olefins, naphthenes and aromatics. It was found that both all zeolite and silica-alumina increased olefin contents in the oil product. Particularly, ZSM-5 and zeolite-Y enhanced the formation of both aromatics and branched hydrocarbons suddenly. ZSM-5 showed the greatest catalytic activity on cracking of heavy hydrocarbons to small gases hydrocarbons and formation of aromatics. Amorphous silica-alumina showed a great activity on cracking heavy hydrocarbons. It generated a pronouncedly high yield of lighter olefin due to strong acidity, but was inferior to zeolites in the formation of aromatics and branched hydrocarbons because of amorphous structure.

From the literature reviews above, most of the researchers used zeolites as catalysts in catalytic pyrolysis, but the zeolysts also have disadvantage because they are quite expensive. Therefore, this work is concerned about investigating catalysts that have high efficiency but low price. The series of superacid (sulfated zirconia) and superbasic (potassium zirconia) were chosen as catalysts in this work.

Sulfted zirconia is classified as a superacid catalyst famous in the petrochemical field for the development of the gasoline in order to improve the octane number. The superacid character in this catalyst is obtained from the nature of zirconia itself, which is an the amphoteric oxide, so it can be Lewis acid, Bronsted acid and Bronsted base.

$$\text{Bronsted Acid}: \quad \text{ZrOH} + \text{OH}^- \longleftrightarrow \text{ZrO}^- + \text{H}_2\text{O}$$

Brosted Base:

$$\text{Lewis Acid} \quad : \quad \text{Zr(OH)}_2 + {}^-\text{OOCR} \longleftrightarrow \text{ZrOOC-R} + \text{H}_2\text{O}$$
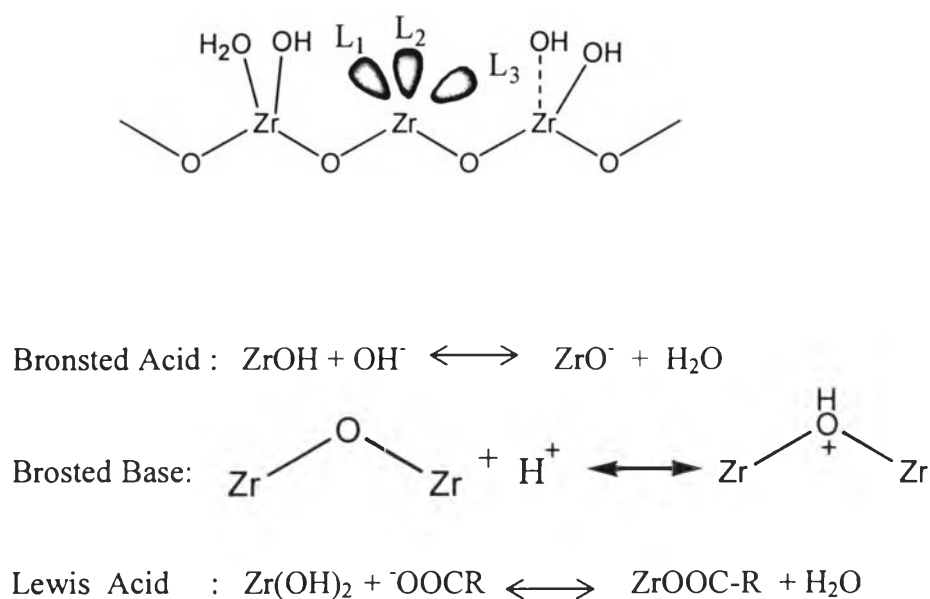
Figure 2.5 Nature of zirconia's surface (Zhang, 1999).

When sulfate is added onto the surface of zirconia, it will make this catalyst a superacid catalyst by increasing the H_0 value to -16.1, which is stronger than 100 % of sulfuric acid having $H_0 = -12.1$ (Arata, 2003). The change is occurred because the sulfate group is the electron-withdrawing group that can withdraw electron from zirconia, making zirconia have higher characteristic of Bronsted acid and Lewis acid.
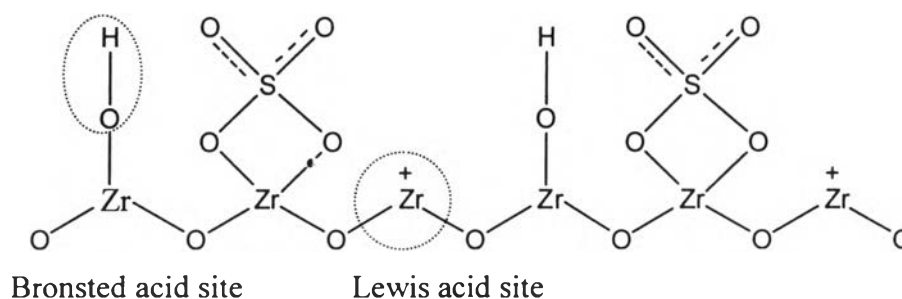

Bronsted acid site   Lewis acid site

Figure 2.6 Sulfated zirconia (M.Reddy , 2002).

For the superbasic type of catalyst, Wang *et al.* (2000) generated the super basic catalyst by impregnating the KNO_3 onto the surface of the zirconia to obtain KNO_3/ZrO_2 that possessed the basic strength of H. = 26.5 which is the characteristic of solid superbase. The activity of this type of catalyst also investigated which had a high activity in both dehydrogenation of isopropanol at 400°C and isomerization of cis-but-2ene at 0°C.