

## CHAPTER II

### THEORETICAL CONSIDERATIONS

#### 2.1 Polyethylene[6-8]

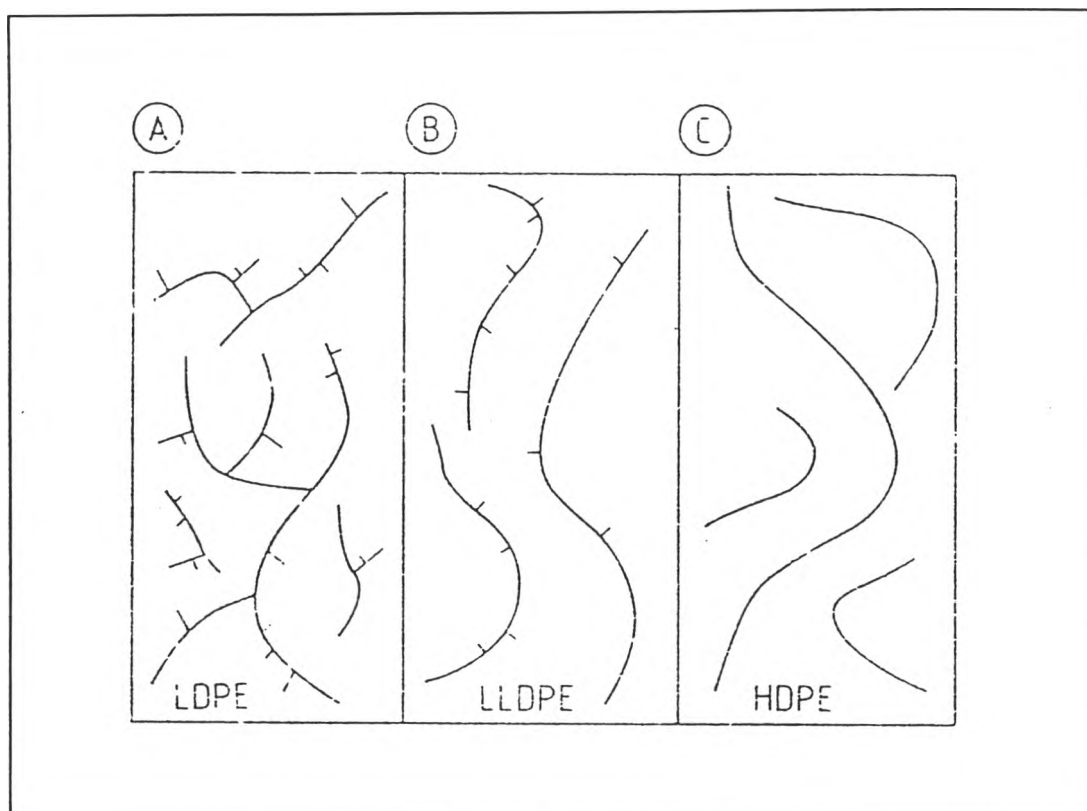
Polyethylene is a thermoplastic, the designation for polymers that soften when exposed to heat and return to their original condition when cooled to room temperature.

Polyethylene makes up about 63% of plastic used in packaging. High-density polyethylene (HDPE) is made up of unbranched long chains used for rigid container applications such as milk jugs and motor oil bottles. Low-density polyethylene (LDPE) is used mainly for wrapping films and bags. Polyethylene films is the most widely used of all plastic films in flexible packaging end uses. One of the significant factors about polyethylene film is that its growth as a packaging material has been in two directions. First, it has competed directly with cellophane and paper for existing applications. Second, it has opened up entirely new packaging markets for itself and is used on products that were previously either not packaged or were packaged in larger aggregations. Examples are the use of films for fresh produce, meat, and textile products packaging. Polyethylene is used also as a laminated material and as a liner for barrels, drums, and shipping sacks.

Polyethylene (PE) will continue to be the dominant plastic in flexible packaging in coming years. The basic resin technology is well established, production methods are well developed, and equipment is readily available, Additional factors to support PE in its dominant position will be the

appearance of new types of polyethylene films for packaging applications-oriented films for shrink packaging and crosslinked films for meats and other products requiring special characteristics. Furthermore, polyethylene will be the most popular substrate or prime segment material of structured or layered film combinations. The greatest volume will continue to be in monolithic form, however. PE has enjoyed rapid growth in both food and non-food packaging. Bulk shipping containers (bags, sacks, barrels, pallet buns, etc.) are also often lined with polyethylene.

Polyethylene is produced by the polymerization of ethylene ( $C_2H_4$ ) using heat, pressure, and various catalysts. Copolymers produced by polymerizing ethylene and lesser quantities of other monomers (comonomer) are also generically known as polyethylene. The plastics industry trends to separate the types of polyethylene into two broad designations based on density. Polymers having densities between 0.915 and 0.940  $g/cm^3$  are referred to as low-density polyethylene (LDPE); those with densities above 0.940  $g/cm^3$  are called high-density polyethylene (HDPE). During the 1980s, the production and use of a new type of polyethylene, called linear low-density polyethylene (LLDPE), became widespread. The name for this new family of polyethylene derives both from its molecular structure, which resembles the structure of HDPE, but its density range is identical to that of LDPE.



**Figure 2.1** Schematic molecular structure A) Low-density polyethylene  
B) Linear low-density polyethylene C) High-density polyethylene

Figure 2.1 shows schematic structures for the three polyethylene, with the main features exaggerated for emphasis. LDPE has a random long branching structure, with branches on branches. The short branches are not uniform in length but are mainly four or two carbon atoms long. The ethyl branches probably occur in pairs and there may be some clustering of other branches. The molecular mass distribution (MMD) is moderately broad.

LLDPE has branching of uniform length which is randomly distributed along a given chain, but there is a spread of average concentrations between chains, the highest concentrations of branches being generally in the shorter chains. The catalysts used to minimize this effect generally also produce fairly narrow MMD.

HDPE is essentially free of both long and short branching, although very small amounts may be deliberately incorporated to achieve specific product targets. The MMD depends on the catalyst type but is typically of medium width.

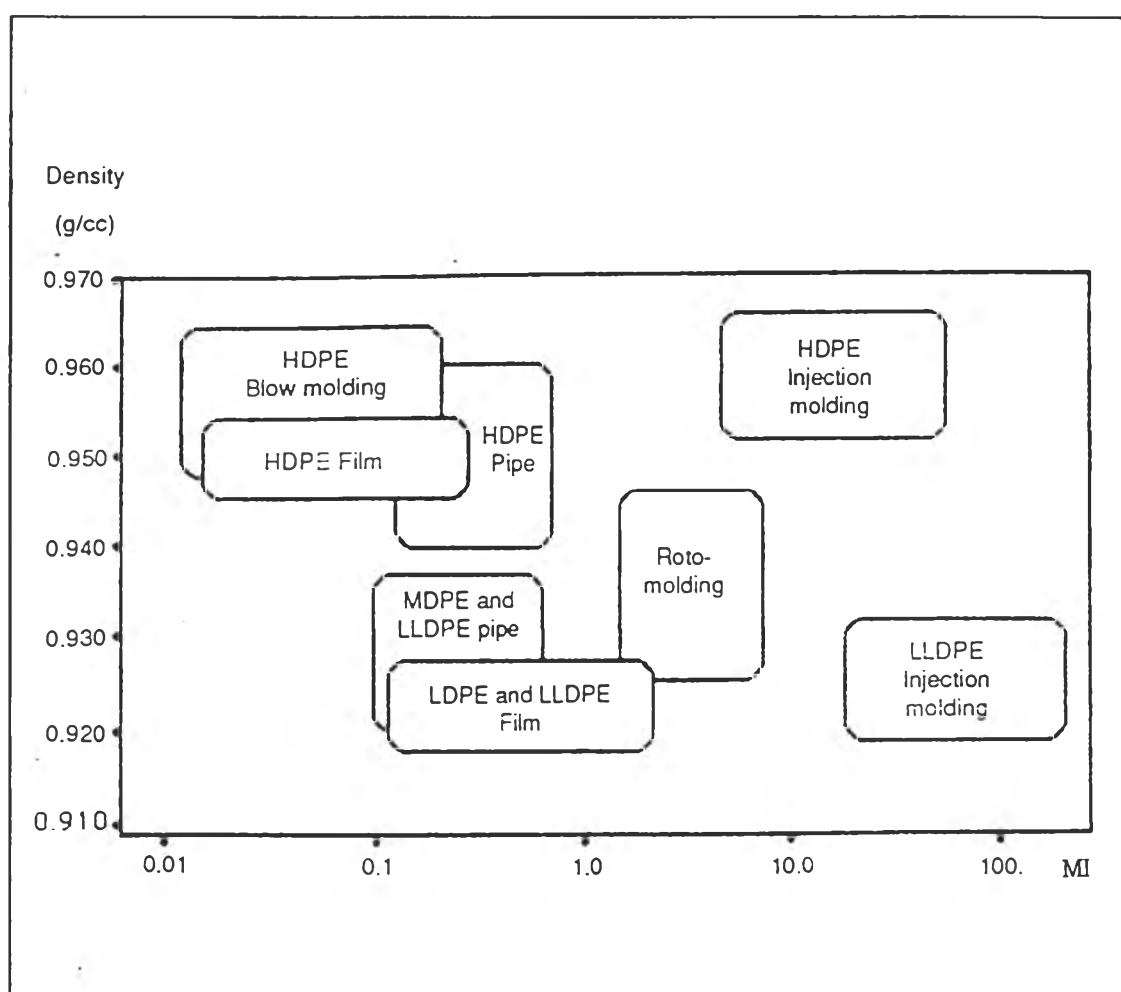
Properties that combine excellent toughness, chemical resistance, flexibility, processability, and sealability, as well as its optical, moisture barrier, and electrical properties, enable polyethylene to be the material of choice in thousands of plastics products applications. Polyethylene's final end-use properties can be controlled and predictably varied by changing the density, average molecular weight, and molecular weight distribution through manipulation of process variables.

Density is usually measured in grams per cubic centimetre and is a function of the length and number of side-chain branches on the main polymer chains. Increasing the density increases the crystallinity, stiffness, tensile strength, abrasion resistance, softening point, barrier properties, and hardness of the polyethylene product. Decreasing the density increases the tear strength, clarity, permeability, impact resistance, and heat seal range. Commercially available grades of polyethylene have densities that generally range from 0.910 to 0.960 g/cm<sup>3</sup>.

Commercial grades of polyethylene have melt index (MI) that generally range from 0.01 g per 10 min to over 100 g per 10 min, representing a weight-average molecular weight range from about 300,000 to about 30,000. Increasing the molecular weight (lower MI) increases impact strength, tear strength, and environmental stress crack resistance but lowers the brittleness temperature. Increasing molecular weight also increases melt viscosity, which causes the resin to be harder to process into finished products.

Compromises must usually be made between conditions that give the best end-use properties and those conditions that give the best processability

of the product on customers' fabrication equipment. The ability to vary the properties of polyethylene over a wide range has resulted in a multitude of product applications for the material. This ability in combination with fabrication know-how has resulted in the definition of major end-use markets by density versus molecular weight, as shown in Fig. 2.2



**Figure 2.2** Definition of major polyethylene market applications by density and melt index.

## 2.2 Hydrocracking Reaction and Dual Function Catalyst[9,11]

Hydrocracking is a catalyst cracking process that takes place in the presence of hydrogen. Cracking of long chain compounds and hydrogenation of the cracked products are the main reactions that take place. The hydrocracking reaction could be simply represented as:-



The primary process is dehydrogenation of the absorbed paraffin with formation of the respective olefin; the secondary process is the addition of a proton from the acid centre of the catalyst and formation of a carbonium ion. The ion formed is either split or isomerised to the thermodynamically most stable tertiary ion. The isomerised ion is again either split or, it transfers the proton over to the catalyst. An isoolefin is formed which, on hydrogenation, forms the isomer of the initial substance. The composition of the reaction product will therefore depend on the mutual ratio of reaction rates of the individual processes and, therefore, on the reaction conditions, activity and selectivity of the catalyst employed.

When a sufficiently high temperature is employed or, the hydrogenolytic activity of the catalysts is sufficient intensive, splitting of ions take place in the  $\beta$ -position of the carbonium ion and lower olefins are formed which, on hydrogenation, convert to lower paraffins (or isoparaffins). Alternatively, they are re-protonated and undergo secondary splitting in this form or after preliminary isomerisation. Some alkylation reactions may also take part as side reactions. The hydrocracking rate of n-paraffins differs greatly with lower hydrocarbons.

Dual function catalysts are used in the hydrocracking processes. These catalysts are characterized by providing cracking sites and hydrogenation/dehydrogenation sites. The hydrogenation/dehydrogenation

components are usually cobalt, nickel, chromium, tungsten, vanadium or their oxides. These catalysts are usually presulfided before operation and the combination of two or more metals is normal practice.

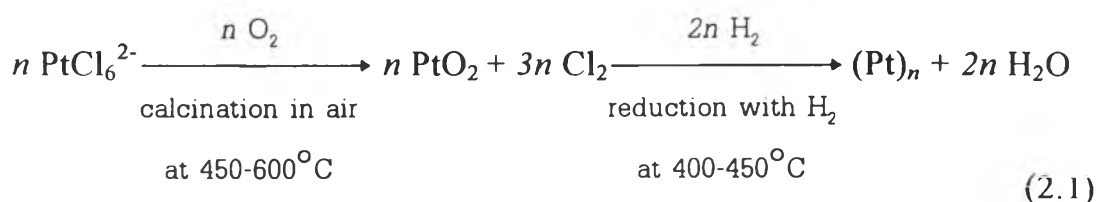
Cracking sites, on the other hand, are provided by silica/alumina combinations or zeolites. Zeolites not only possess higher activity than amorphous silica/alumina.

### **2.2.1 Preparation and Structure of Dual Function catalyst[12-28]**

Alumina-supported platinum is one of the most frequently used catalysts in isomerization, hydrogenation and dehydrogenation processes. Platinum is the metal of choice because it is the only one that has activity for the desired reactions without being more than moderately active for undesired reactions such as hydrogenolysis of paraffins. Alumina is the support of choice because it is inexpensive, and easily forms the aggregates with platinum to maintain a high metal dispersion.

One common method of preparing the bifunctional catalysts involves impregnation of alumina with an aqueous solution of chloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ). The catalyst typically contains from 0.1-5.0 %wt metal, preferably 0.1-1.1 %wt metal, and most preferably 0.2-0.6 %wt. After impregnation the samples are usually dried and then calcined at temperatures in the range of 450 to 600 °C. Other catalysts have been considered. Among these are certain metal oxides on alumina e.g. chromia (chromium oxide) and molybdena (molybdenum oxide) on alumina. However, these catalysts are much less active than the platinum on alumina catalyst.

Preparation of platinum metal impregnated on alumina received from chloroplatinic acid solution can be represented as the hexachloroplatinate ion being the precursor which does not react with the support (equation 2.1)



### 2.2.2. Metallic Component[13,16]

On the metallic component (usually platinum), hydrocarbons can undergo hydrogenation or dehydrogenation reactions in the presence of hydrogen pressure ( $\text{H}_2$ ). It is however evident that platinum catalysts are more active in hydrogenation-dehydrogenation reactions. Table 2.1 gives a comparison of the activities of some catalysts in the dehydrogenation of cyclohexane.

**Table 2.1** Rate of the Dehydrogenation of Cyclohexane over different catalysts (temperature  $427^\circ\text{C}$ , Pressure 7 atm)[13]

Catalyst	Dehydrogenation activity, mmoles benzene / g of catalyst $\times \text{sec}^{-1}$
34% $\text{Cr}_2\text{O}_3$ on $\text{Al}_2\text{O}_3$	0.5
10% $\text{Mo}_2\text{O}_3$ on $\text{Al}_2\text{O}_3$	3
5% Ni on $\text{Al}_2\text{O}_3$	13
5% Co on $\text{Al}_2\text{O}_3$	13
0.5% Ir on $\text{Al}_2\text{O}_3$	190
1% Pd on $\text{Al}_2\text{O}_3$	200
5% Ni on $\text{SiO}_2$	320
1% Rh on $\text{Al}_2\text{O}_3$	890
0.5% Pt on $\text{Al}_2\text{O}_3$	1,400-4,000



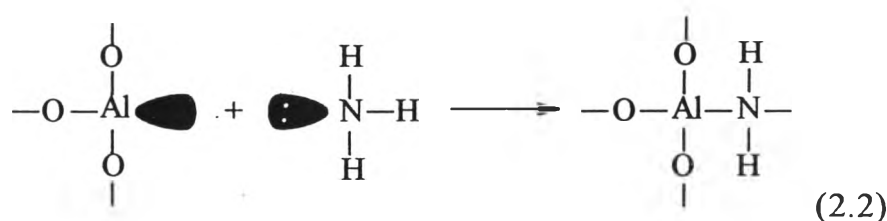
While the Pt-alumina catalysts were an outstanding success, they had to be regenerated at rather frequent intervals, every three months or so. Thus, the introduction in the late 1960s of a platinum-rhenium catalyst that could remain on-stream for a period of a year or even longer led to a second revolution in naphtha reforming. The Pt-Re-alumina catalyst had to be activated and brought on stream using a rather lengthy procedure that usually involved poisoning the catalyst with sulfur during a break-in period. Today, with the potential for a naphtha reforming process utilizing continuous catalyst regeneration, other bimetallic catalysts which do not require complex activation procedure must be utilized; Pt-Sn-alumina appears to be an attractive catalyst for this process.

Many of the explanations for the superior properties of the bimetallic catalysts are based on a structural point of view. Many argue that the bimetallic components form an alloy which has better catalytic properties than Pt alone. For example, alloy formation could influence the d-band electron concentration, thereby controlling selectivity and activity. On the other hand, the superior activity and selectivity may be the result of high dispersion of the active Pt component, and the stabilization of the dispersed phase by the second component.

### **2.2.3 Acidic Component[17-22]**

The alumina support used in dual catalysts have been shown to be acidic in nature. The acidic properties are really demonstrated by the affinity of these solids for adsorption of basic compounds, such as ammonia, trimethylamine and pyridine. In the case of structure, the aluminium atom is not complete co-ordinated. It is bonded to three oxygen atoms instead of four. The aluminium atom has six valence electrons instead of the maximum eight. It therefore has the potential of accepting a pair of

electrons from another species to complete a stable octet. To illustrate the interaction of alumina and a basic compound, can be represented in which a molecule of ammonia could bond with the aluminium atom. The ammonia molecule donates a pair of electrons to the electron deficient aluminium atom, thus completing a stable octet of electrons in structure of equation 2.2



Treatment of alumina with halogens, such as chloride or fluoride tends to make the acidic properties of alumina more pronounced, in the sense that it increases the activity of alumina for the catalysis of typical acid catalyzed reaction, such as the skeletal isomerization and various cracking reactions of hydrocarbons. The enhancement of acidic properties is then attributed to the halogens having higher electron affinity than oxygen, thus causing the residual hydrogen atoms on the surface to become more acidic.

### 2.3 General Characteristics of Gasoline Fuels[29-32]

Gasoline is still in great demand as a major product from petroleum. Gasoline is essentially a complex mixture of hydrocarbons that boils below 180 °C (355 °F) or, at more, below 200 °C (390 °F). The hydrocarbon constituents in this boiling range are those that have 4-12 carbon atoms in their molecular structure. The hydrocarbons of which gasoline is composed fall into three general types: paraffins (including the cycloparaffins and branched materials), olefins and aromatics. Highly branched paraffins,

which are particularly valuable constituents of gasoline, are not usually the principal paraffinic constituents of straight-run gasoline.

There are several basic requirements of a gasoline;

### 2.3.1 Specific Gravity

Specific gravity (ASTM D 1298) is defined as the ratio of the mass (weight) of a given volume of product to the mass of an equal volume of water, usually at 60 °F for each. The density is the absolute value and can be expressed as lb/gal or lb/ft<sup>3</sup> in Imperial units or as kg/m<sup>3</sup> in the SI system of units.

In the petroleum industry the API gravity scale is almost universal used as the measure of the density of a petroleum product. API gravity is an arbitrary scale, calibrated in degrees and related to the specific gravity by

$$\text{API gravity (degrees)} = \frac{141.5}{\text{Specific gravity at } 60/60^{\circ}\text{F}} - 131.5$$

The higher the specific gravity or density, the lower the API gravity. Water, by definition, has an API gravity of 10°. The specific gravity (or API) is an important parameter which is sometimes used to indicate crude oil quality. A low density crude (high API) has a higher percentage of the more valuable light and middle distillates oils with a high sulfur content are less in demand than those with a low sulfur content hence lower density since fractions from the former oils have to be subjected to further treatment to remove these sulfur compounds.

### **2.3.2 Color Test**

The color test was performed by following the ASTM D 1500 method. It is a guide to the presence of contaminants or to the degree of deterioration in storage. It is also an indication of the intensity of refining. Absence of color (water white) is important in certain applications such as in textile machinery lubrication to avoid indelible staining of the textile. Absence of color is also important to uses of waxes, petrolatums, and white oils where extremely high purity is required.

### **2.3.3 Pour Point**

The pour point (ASTM D 97) of a fuel is an indication of the lowest temperature at which the fuel can be pumped. As the oil is chilled, it eventually reaches a point where it will no longer flow under the influence of gravity. The lowest temperature to which a fuel can be cooled without setting, fuel and in particular waxy fuels will in some circumstances flow below their tested pour point. This condition is brought about either by the thickening (more viscous) that always accompanies a reduction in temperature or by crystallization of wax dissolved in the oil, restricting the flow of the liquid portion.

### **2.3.4 Distillation**

Distillation characteristics are measured using a procedure (ASTM D 86) in which a sample of the fuel is distilled and the vapor temperatures are recorded for the percentages of evaporation or distillation throughout the range .

In general the distillation range should be as low as possible without adversely affecting the flash point, burning quality, heat content or viscosity of the fuel. If the 10 percent point is too high, poor starting may result. An excessive boiling range from 10 percent to 50 percent evaporated may increase warm-up time. A low 50 percent point is desirable in preventing smoke and odor. Low 90 percent and end points tend to ensure low carbon residuals and minimum crankcase dilution.

### **2.3.5 Lead Content**

Lead content is measured using a procedure (ASTM D 3116) in which a sample of the fuel is determined by Spectrophotometer, capable of measuring light adsorption at a wavelength of 520 nm. Grades of commercially gasoline commonly have a maximum of 0.013 g/l.

### **2.3.6 Sulfur Content**

A fuel sulfur content above 0.4 percent is generally considered as medium or high whereas fuel sulfur content below 0.4 percent is considered low. The presence of sulfur compounds in the fuel is undesirable because of their corrosive action, but the complete elimination of them is not practical. Sulfur burns to  $\text{SO}_2$  and  $\text{SO}_3$  which may react with water to form sulfurous or sulfuric acid. Acid formation is a more serious problem for engines operating either intermittently or at low temperature. Removal of sulfur compounds by chemical treatment increases the cost of the fuel. The production of straight-run fuels low in sulfur is limited by the availability of low sulfur crude.

## 2.4 Literature Reviews

Earlier studies on methods for converting polyethylene to higher value product can be formed in the following patent literature.

Coenen and Hagen [33] studied a process for the production of liquid hydrocarbons from old tires, cable wastes, polyethylene wastes and polypropylene wastes, by which the waste products, in pulverized form, were treated at a temperature of 150°-500°C and a pressure 20-300 bar with a solvent which was liquid at 1 bar and 20°C to form a solvent phase charged with liquid hydrocarbons and a residue phase.

Fukada, Saito, Suzuki, Sato and Hirota [34] converted plastic scrap, especially of polyolefin plastics to low pour point oils by thermal cracking (450°C ) in the liquid phase followed by catalytic conversion of the vaporous cracking product over an intermediate pore size zeolite such as ZSM-5 at a temperature 200°-340°C . The yield of hydrocarbon oil was 60.4%wt..

Cody and Brown [35] upgraded waxy distillates and raffinates by a process comprising the steps of hydrotreating the waxy oil under conditions which convert less than 20% of the feed into products boiling lower than the feed to reduce the sulfur and nitrogen content of the oil followed by hydroisomerizing the hydrotreated waxy oil to reduce the wax content and increase the viscosity index. Two catalysts were prepared. One was of low fluorine content and another was of high fluorine content. The results demonstrated that low fluorine level Al<sub>2</sub>O<sub>3</sub>-based catalysts are excellent “raffinate isomerization” catalysts. Preferred catalysts for raffinate isomerization, therefore, are Al<sub>2</sub>O<sub>3</sub>-based catalysts comprising Group VIII

metals or Group VIII/Group VI combinations and containing less than 2%F, preferably 0.2 to 1.5 wt%F. The preferred fluoridating medium is an aqueous ammonium solution.

Stapp [36] studied a method for converting municipal waste containing plastics to a high quality synthetic crude oil. The municipal waste was contacted in the reaction vessel with a gas atmosphere selected from hydrogen and mixtures of hydrogen and hydrogen sulfide. The municipal waste was heated in the reaction vessel to a temperature between 350°-450°C at a pressure between 750-3000 psig for a time in the range of 30 minutes to 8 hours. The yield of oil was 85.6 %wt.

Matsuzaki [37] studied waste plastic material, e.g. hard plastic waste constituted of vinyl chloride, polyethylene and foamed polystyrene, soft plastic waste, or other plastic waste containing metal fragments, immersed in a vegetable or mineral oil heated to 110°-180°C. The plastic material, in which quantities of the oil were entrapped, was mixed with a given dose of a neutralizing agent, e.g. calcium hydroxide, at a temperature of 200°-300° C. Then, the resultant mixture, in which a quantity of the oil was entrapped into a solid fuel product, or into a predetermined form disposable in a landfill.

Takahashi and Tanimoto [38] studied a method of producing a low boiling point hydrocarbon oil from waste plastic materials, comprising two steps. In the first step, waste plastics were heated so as to be thermally decomposed. This was performed at a temperature between 250°C and 450° C, thereby producing a vapor product. In the second step, vapor product was brought into contact with a solid lewis acid catalyst at a temperature

between 120°C and 250°C, thereby producing 30-40% of a low boiling point hydrocarbon oil.

Butcher [39] studied a method for depolymerizing polymeric materials by degradation of a polymeric material through the use of a molten basic material at a high temperature (250°C) and of copper oxide as catalyst. The yield of liquid hydrocarbon was 50 %wt.

Khan and Decanio [40] studied a process for converting scrap plastic material into high quality transportation fuel. The plastic material was liquefied in closed autoclave while in contact with 2700 psig of hydrogen gas at a temperature of 1500°F.

Zmuda [41] studied a method for obtaining liquid fuels from the polyolefins waste, and also from used products made of polyethylene, polypropylene, polystyrene and other polyolefins. The polyolefin raw materials were degraded in a purely thermal way at temperatures between 500°-600°C. On the other hand catalysts were introduced into the system in the form of aluminium oxide, aluminium silicate or aluminosilicates of alkali metals or alkali earth metals, in amounts of 1-5% by weight at temperatures between 400°-600°C. Small amounts of air can be introduced into a system. The obtained petrol type or diesel oil type fuels had good anti-knock properties.

Hardman, Leng and Wilson [42] studied a process for cracking a polymer into hydrocarbon products which comprises contacting a polymer with a fluidized bed comprising more particulate materials of quartz, sand, silica, ceramics, carbon black, refractory oxide and acidic catalyst although



the acidic catalytic component was suitably less than 40 %wt./wt. and at a temperature of 300°-600°C and under pressure (2-10 bar). The hydrocarbon products comprised 20 %wt. of C<sub>1</sub>-C<sub>4</sub> hydrocarbons and 10 %wt. of aromatic hydrocarbon.

Intarapeecha [6] studied a hydroisomerization reaction for converting high density polyethylene wax into hydrocarbon products comprising C<sub>11</sub>-C<sub>25</sub> and C<sub>11</sub>-C<sub>16</sub> as the main component. The reaction operated at 300°C, 300 psig hydrogen pressure, for 10 minute using 5% by wt. of Pt (0.3%) / F (0.5%) on alumina catalyst .