

CHAPTER I

INTRODUCTION

The amount of waste polymers is now recognized as a major environmental problem. The type of plastics in municipal wastes are shown in Figure 1.1. Plastic and rubber are undesirable components for landfilling, since they are not presently biodegradable. Their destruction by incineration poses air pollution problems due to the release of airborne particles and carbon dioxide into the atmosphere. Furthermore, the aromatics from plastics or foams can poison the soil. An alternative would be true recycling, i.e. conversion into monomers that can be reused [1]. However, most polymers do not depolymerize thermally with sufficient selectivity. On the other hand, waste plastics and rubbers can be regarded as a potentially suitable source for transportation fuels and useful industrial chemicals [2].

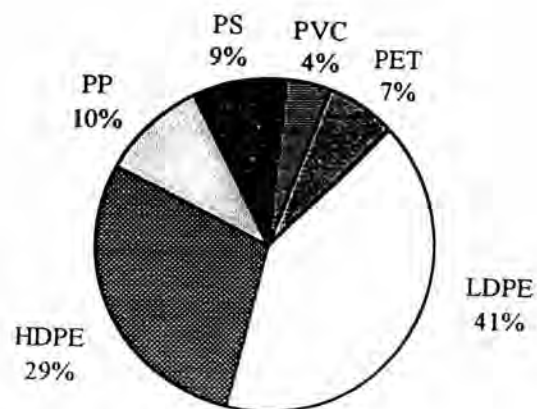


Figure 1.1 Plastic materials in post-consumer waste [3]

Limitation to recycling plastics include the high costs and difficulty of collecting and sorting recyclable plastics. So the purpose of this research focused on the recycling of polystyrene and trying to reduce costs. Polystyrene is widely used in the production of packaging. The increase of imported quantities between 1992 and 1996 are shown in Table 1.1 and 1.2 [3]. Much of the polystyrene is produced from styrene monomer which is, in turn, prepared from ethylbenzene. The quantities of imported and exported styrene monomer and ethylbenzene are shown in Table 1.3 and 1.4 [3]. Hence, a suitable recycling method should produce ethylbenzene for processes that use it as a starting material.

Table 1.1 Imported and exported expandable polystyrene in primary forms

Year	Import		Export	
	Quantity (Kg)	Value (Baht)	Quantity (Kg)	Value (Baht)
1992	5,435,658	162,495,829	571,500	12,232,148
1993	1,503,880	43,469,036	956,750	18,246,707
1994	5,113,841	156,760,133	2,530,850	62,676,505
1995	6,088,318	260,450,362	968,251	29,851,832
1996	7,611,190	226,852,801	65,000	1,592,643

Table 1.2 Imported and exported other polystyrene in primary forms.

Year	Import		Export	
	Quantity (Kg)	Value (Baht)	Quantity (Kg)	Value (Baht)
1992	44,602,485	1,196,253,135	16,030,780	254,181,102
1993	26,201,633	618,066,831	18,101,382	293,680,210
1994	57,388,291	1,440,423,995	18,858,198	390,599,550
1995	579,484,694	2,020,286,877	13,939,044	342,808,870
1996	33,934,135	1,041,664,263	-	-

Table 1.3 Imported and Exported styrene.

Year	Import		Export	
	Quantity (Kg)	Value (Baht)	Quantity (Kg)	Value (Baht)
1992	114,938,364	1,498,511,709	28,800	554,545
1993	62,501,010	746,070,083	100	16,824
1994	143,176,430	2,509,205,356	48,002	1,008,424
1995	150,404,461	3,604,282,646	16,040	296,094
1996	233,565,356	3,154,328,042	14,400	279,922

Table 1.4 Imported and exported ethylbenzene.

Year	Import		Export	
	Quantity (Kg)	Value (Baht)	Quantity (Kg)	Value (Baht)
1992	162,667	4,899,617	-	-
1993	149,306	4,477,637	-	-
1994	214,078	64,252,351	-	-
1995	125,546	3,873,016	-	-
1996	1,313,072	19,985,082	-	-

Literature Review

A number of early studies on the recycling of polystyrene have been patented.

Albright studied the cracking of thermoplastic polymers to valuable products, primarily their monomers, in a two steps process [5]. In the first step, the polymers were converted to a liquid or fluidized stage. In the second step, the product from the first step was mixed with a hot inert gas in a weight ratio of gas to polymer of about 1 to 8 ; the temperature was maintained in the range of 800°C to 1050°C and the residence time in the reaction zone was about 10 to 100 milliseconds. The products consisted of ethylene, propylene, butadiene, benzene, toluene, xylenes and others.

Zellerhoff was able to obtain aromatic hydrocarbons from polystyrene waste and liquid bituminous coal-tar [6]. The mixture was heated at a temperature between 300°C and 470°C at a pressure of 30 bar for 5 hours to 8 hours. The aromatic products consisted of benzene, toluene, ethylbenzene, cumene and other hydrocarbons. The yield of aromatic hydrocarbon was 29-41%wt.

Matsuzaki immersed 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, in a vegetable or mineral oil heated to 110°C-180°C[7]. 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°C-300°C. Then, the resultant mixture, in which a quantity of the oil was entrapped into a solid fuel product, or disposed of in a landfill.

Butcher depolymerized polymeric materials by degradation through the use of a molten basic material at a high temperature (250°C) in the presence of Cu(I) or Cu(II) catalyst [8]. The yield of liquid hydrocarbon was 50%wt.

Takahashi and Tanimoto devised a method of producing a low-boiling hydrocarbon oil from waste plastic materials, comprising two steps [9]. 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 gaseous product. In the second step, the gaseous 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 hydrocarbon oil.

Hardman, Leng and Wilson developed a process for cracking a polymer into hydrocarbon products [10]. A polymer in contact with a fluidized bed consisting of particulate materials of quartz, sand, silica, ceramics, carbon black, refractory oxide and acidic catalyst at a temperature of 300°C to 600°C and under pressure (2-10 bar) was converted to hydrocarbon products consisting of 20%wt of C1-C4 hydrocarbons and 10%wt of aromatic hydrocarbons.

Zmuda obtained liquid fuels from the polyolefin waste, and also from used products made of polystyrene, polyethylene, polypropylene and other polyolefins [11]. The polyolefin raw materials were degraded in a purely thermal way at temperatures between 500°C and 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°C and 600°C. Small amounts of air could be introduced into a system. The petrol type or diesel oil type fuels obtained had good anti-knock properties.

Leesuksan studied a hydrocracking reaction for converting polyethylene into hydrocarbon products (C10-C16). The reaction operated at 400°C, 600 psig hydrogen pressure, for 12 hours using 40% by wt of a Pt(0.6%)/Sn(0.15%)/Cl(1.21%)/F(0.5%) on alumina catalyst [12].

Objective and Scope of the Research

The principle objective of this research was to transform used polystyrene to hydrocarbons. This would be achieved by cracking with various catalyst types, catalyst concentrations, reaction temperatures, hydrogen pressures and reaction times. In addition, the hydrocarbon would be characterized by gas chromatography and NMR.