

## Characteristics of LDPE Pyrolysis

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**Abstract**—Pyrolysis of low-density polyethylene (LDPE) was studied in order to relieve environmental pollution and recover the monomer or fuel. LDPE was thermally decomposed with and without catalyst. First, efficiency of oil production was analyzed according to the variation of reaction conditions such as reaction temperature, types of additives and catalyst, and contacting method. In non-catalytic LDPE pyrolysis, isothermal reaction was almost similar to non-isothermal reaction. Light oil was produced with low reaction temperature (430 °C) in the isothermal reaction, but low heating rate caused light oil production in the non-isothermal reaction. When pyrolyzed polyethylene (PE oil) was applied as an additive, no significant effect showed in the isothermal reaction. In catalytic LDPE pyrolysis (10%NiO/S-A) with additives, efficiency greatly increased especially with polystyrene (PS) addition. It was also found that the molecular weight distribution of product oil could be controlled by applying different additives. When a catalytic reactor was used, the amount of the low molecular weight compound increased as flow rate of thermally decomposed gas was lowered.

Key words: Low Density Polyethylene (LDPE), Pyrolysis, Catalysts, Additives, Catalytic Reactor

### INTRODUCTION

Disposal of used consumer plastics has increased according to the increase of its consumption with industrial development [Kim, 1999; Jeong et al., 2001]. In 1995, the regulation on disposal was established to control the amount of waste disposal in Korea, and the amount of domestic waste was reduced by 30% compared to 1992 [Lee, 2000; Rader, 1995; Fouhy, 1993]. However, generation of waste plastic was increased, reaching 4 million tons in the year 2001 [Lee, 2000; Korea Petrochemical handbook, 2001]. This tendency will likely be maintained in the future. There are six main plastics in Korean municipal solid waste: high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), and polyethylene tere-

phthalate (PET). However, LDPE and HDPE make up over 29% of the total plastic content of municipal solid waste as shown in Table 1 [Lee, 2000].

Waste plastic can cause considerable environmental pollution. When plastic is incinerated, a vigorous exothermic reaction can damage the incineration facility and produce harmful gases such as HCl, HCN, NO<sub>x</sub>, and dioxin. Waste plastic may not be used in a land fill because of its non-biodegradable nature and the lack of such sites in Korea.

Recycling of waste plastics is thus an important issue, and it has been researched worldwide. As a result, the technical recycling method has been widely diversified in the present [Fouhy et al., 1993; Kim, 1996]. Three kinds of recycling methods for waste plastic have been proposed. First, energy is recovered from the waste plastics by conversion into fuel oils. Second, waste plastic is recycled by material recycling or mechanical process. This method, however, may not be a long-term solution to the present problem [Williams, 1993; Song and Hyun, 1999]. The third method is called chemical recycling. Waste plastics are converted into the corresponding monomer or advanced chemical, which then is re-synthesized. Among these three methods, chemical recycling is the most economically sound. Converted fuels or chemicals could be merged into standard petrochemical or petroleum refining industry operation [Shelley et al., 1992; Ide, 1984]. In fact, DuPont has developed techniques to decompose waste PET into ethylene glycol and dimethyl terephthalate, which can be used for the reproduction of pure PET resin [Hirose, 1998].

Among the six main plastics, low density polyethylene (LDPE) is used in various fields such as in plastic grocery bags, water hoses, garbage cans, film, containers, etc. LDPE is also known as a very difficult plastic to pyrolyze, but the amount of waste LDPE generation is increasing with its use. In this study, pyrolysis of low density polyethylene (LDPE) was studied [Songip, 1993]. LDPE was

**Table 1. Tendencies of the plastic production in Korea**

(Unit: 1,000 t)

Type \ Year	LDPE	HDPE	PP	PVC	PS	ABS	Sum
1994	996	1,309	1,611	791	801	384	5,891
1995	1,195	1,235	1,613	898	842	465	6,249
1996	1,253	1,342	1,737	996	923	536	6,787
1997	1,394	1,551	2,081	1,085	950	560	7,621
1998	1,429	1,569	2,265	1,093	939	596	7,891
1999	1,657	1,695	2,361	1,161	971	763	8,608
2000	1,550	1,670	2,347	1,187	1,041	878	8,673

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<sup>\*</sup>This paper is dedicated to Professor Wha Young Lee on the occasion of his retirement from Seoul National University.

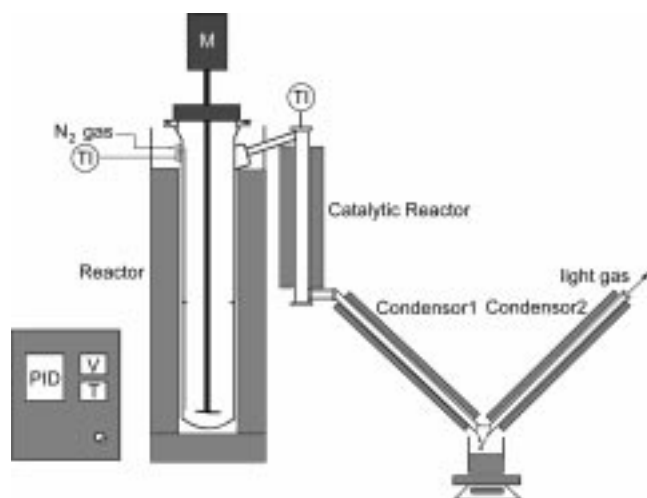


Fig. 1. Schematic diagram of the pyrolysis.

thermally decomposed to recover oil. First, efficiency of oil production was analyzed according to the variation of reaction conditions such as reaction temperature, types of additives, types of the catalysts, and the contacting method of sample and the catalysts. Second, oil composition was analyzed and compared for each reaction condition.

## EXPERIMENTAL

LDPE was used in this experiment to produce light oil through pyrolysis. A reaction schematic diagram includes, as shown in Fig. 1, the main reactor, catalytic reactor, temperature controller, agitator, and condenser. An 800 ml semi-batch reactor (SUS material) with agitator was used as the main reactor, and the mixing rate was maintained at 100 rpm. Amount of sample was varied from 50 to 200 g. Reactor was heated with 3 kw capacity molded type electric heater from 0 °C to 520 °C. PID temperature controller (KT-1130, Korea CHINO Co.) was used to maintain constant heating rate (7 °C/min) and to observe isothermal reaction conditions. N<sub>2</sub> gas (≤10 ml/min) was used as carrier gas to prevent oxidation and reformation of thermally decomposed gases. The first condenser was maintained at 70 °C to prevent wax formation by immediate condensation while the second condenser was kept at 4 °C to condense low boiling point hydrocarbons (H.C. range C<sub>5</sub>-C<sub>8</sub>).

Silica-Alumina (Sigma-Aldrich Co.) and NiO/S-A(10 wt% Ni impregnated) were used as catalysts. Pelletized catalyst (5 mm) was also used in the gas-contact pyrolysis. Produced oil was analyzed by SIMDIS-GC(HP-6890 series) by using mixed n-paraffin standard (Standard carbon C<sub>5</sub>-C<sub>44</sub>, Sigma-Aldrich Co.)

## RESULTS AND DISCUSSION

### 1. Non-Catalyst Pyrolysis with Temperature Variation

Effect of temperature was studied without catalyst. Isothermal pyrolysis was observed in the range of 440-500 °C, and non-isothermal reaction was studied from 0 to 440 °C with 7 °C/min elevation (Table 2). For non-isothermal reaction, retention time increased in the low temperature region, but the ratio of low molecular weight

Table 2. Effect of the reaction temperature on the pyrolysis

Reaction temperature (°C)	Reaction time (min)	Yield (wt%)	≤C <sub>11</sub> (wt% <sup>a</sup> )	Yield of ≤C <sub>11</sub> (wt%)
440	132	84.0	29.0	24.4
450	90	83.0	26.0	21.6
460	95	86.7	20.0	17.3
470	61	90.5	21.0	19.0
500	40	94.3	15.0	14.2
0-440 (7°C/min)	166	76.0	31.0	23.6

<sup>a</sup>Carbon analysis by using ASTM, D-2887; ≤C<sub>11</sub>, yield (wt%) of the carbon number below 11.

oil increased and the product oil showed brighter color. As reaction temperature increased, reaction time was shortened and the ratio of low molecular weight oil decreased. At 440 °C, the highest product yield (84.0 wt%) and low molecular weight hydrocarbon (≤C<sub>11</sub>, 24.4 wt%) was achieved with retention time of 132 min. For isothermal reaction, ratio of low molecular weight compound within the product oil increased as temperature was lowered. Thus, isothermal reaction in the low temperature region showed the same pattern with the non-isothermal reaction with low heating rate. SIMDIS-GC was used to analyze carbon numbers in the oil product, and the carbon distribution is shown in Fig. 2. Most carbon numbers are concentrated from 5 to 50. Fig. 2(a) and (e) are most desirable since low molecular weight compounds are abundant. Here again, isothermal

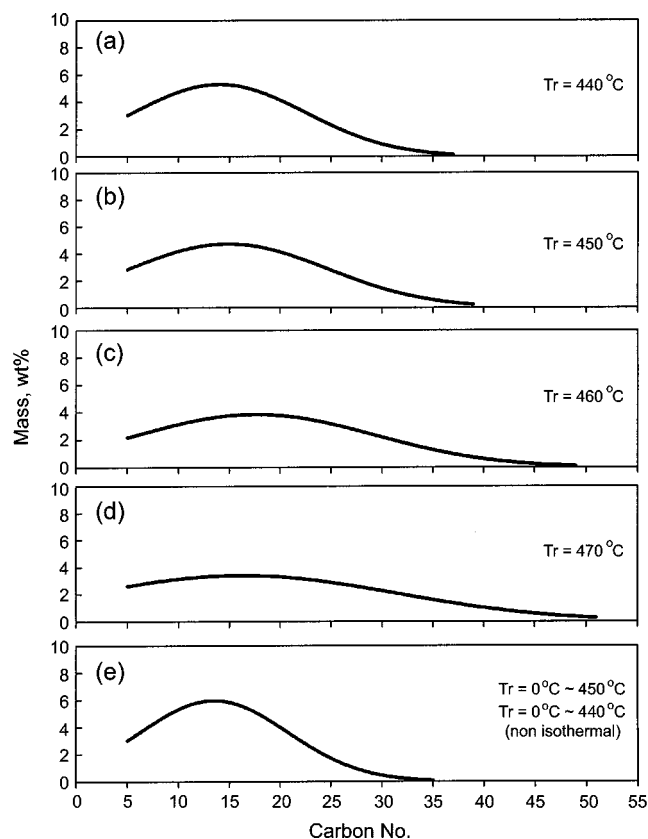


Fig. 2. Molecular weight distribution of product oil by thermal degradation.

**Table 3. Effect of the additive on the pyrolysis**

Raw material	Additive	Yield (wt%)	Appearance	$\leq C_{11}$ (wt%)	Yield of $\leq C_{11}$ (wt%)
LDPE	none	84.4	Waxy	22	18.6
LDPE	PE oil (10%)	73.5	Oil (9.0%)+waxy (91.0%)	27	19.9
LDPE	PE oil (20%)	76.7	Cream (27.5%)+waxy (72.5%)	37	28.4
LDPE	PE oil (30%)	78.6	Oil (22.8%)+cream (77.2)	36	28.3
LDPE	NiO/S-A	71.7	Oil	66	47.3

reaction in the low temperature region (Fig. 2a) showed the same pattern with the non-isothermal reaction with low heating rate (Fig. 2e).

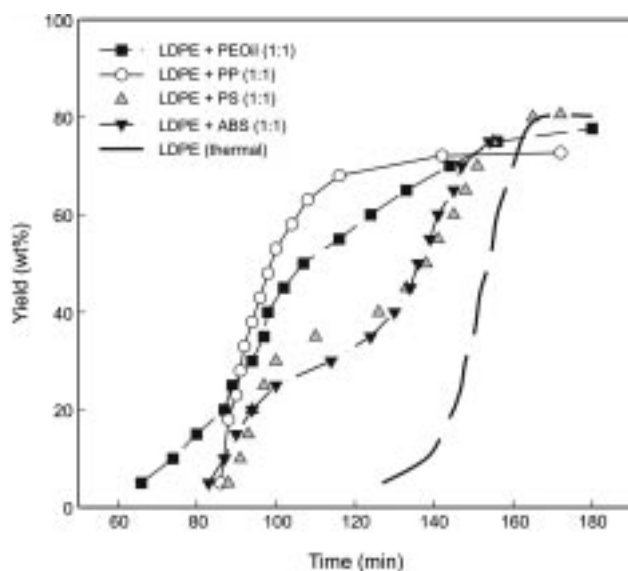
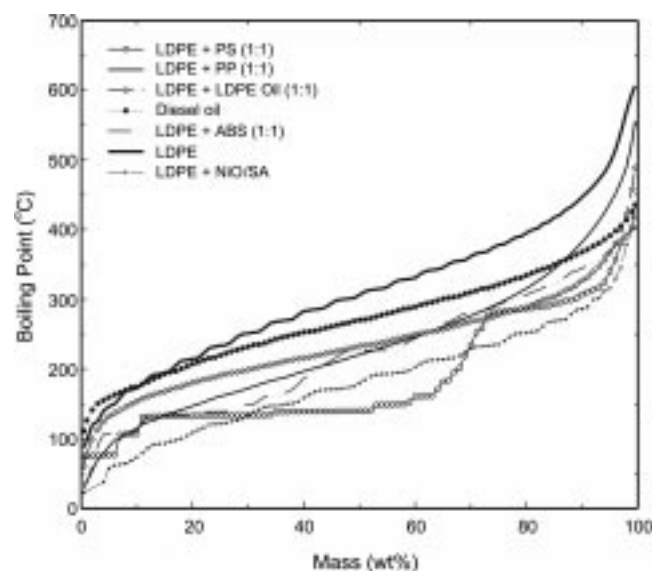
## 2. Non-Catalyst Pyrolysis with Additives (PE Oil)

Oil produced from the LDPE pyrolysis was used as additive and mixed with LDPE sample, and non-isothermal reaction was carried out from 0 °C to 520 °C with steady temperature elevation of 7 °C/min. 10 wt%, 20 wt%, and 30 wt% of product oil was mixed with LDPE sample to make up the total of 200 g for non-catalyst pyrolysis while the reactor was packed with 10% NiO/S-A catalyst. Oil yield decreased as shown in Table 3, but  $\leq C_{11}$  increased a little. Thus, the effect of oil addition in the non-catalyst reaction was so small that it may be ignored. On the other hand,  $\leq C_{11}$  increased almost 30% with catalytic pyrolysis. However, if the cost of catalyst and impracticality of catalyst regeneration is taken into consid-

eration, non-catalytic pyrolysis is preferable.

## 3. Other Additives (PE Oil, PS, ABS, PP) with Catalyst

LDPE sample (100 g) was mixed 1 : 1 ratio with additives such as LDPE oil, polystyrene (PS), acrylonitrile-butadiene-styrene (ABS), and polypropylene (PP). Non-isothermal reaction was carried out from 0 °C to 520 °C (heating rate of 7 °C/min), and (10%NiO)/S-A catalyst was mixed with sample in the reactor. Fig. 3 shows the differences in reaction kinetics of non-catalytic and catalytic pyrolysis. In non-catalytic pyrolysis, thermal decomposition is slower than the catalytic pyrolysis, but the rate of thermal decomposition is much faster. However, as the rate of thermal decomposition increased, the amount of high molecular weight compounds increased and appeared as wax form (Table 4). Each additive has its own characteristics (thermal decomposition rate); thus, it is possible to control the

**Fig. 3. Effects of the additives on catalytic degradation.****Fig. 4. Analysis of catalytic pyrolysis oil product by using NiO/S-A.****Table 4. Effect of the additive (50 wt%) on the pyrolysis with the catalyst (NiO/S-A)**

Raw material	Additive	Yield (wt%)	RT (75%) (min)	$\leq C_{11}$ (wt%)	Yield of $\leq C_{11}$ (wt%)
LDPE	Non-catalyst	84.4	36	22.0	18.6
LDPE	PS	81.3	67	69.0	56.1
LDPE	PP	64.7	above 86	47.0	30.4
LDPE	ABS	75.0	72	45.0	33.8
LDPE	PE oil	76.3	90	37.0	28.23

RT (75%); the time to achieve 75 wt% oil product.

**Table 5. Effect of the reaction temperature on isothermal pyrolysis**

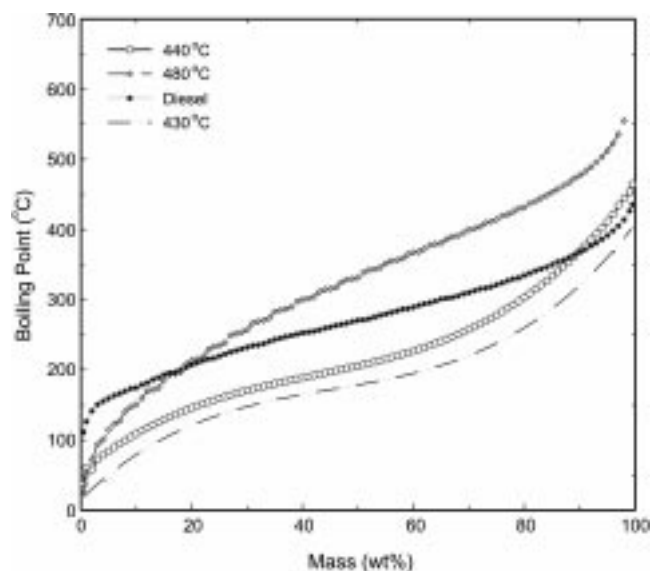
Rxn temp. (°C)	Catalyst	RT (min)	Yield (wt%)	Appearance	$\leq C_{11}$ (wt%)	Yield of $\leq C_{11}$ (wt%)
480	10% NiO/SA	41	68	Waxy	17.0	11.6
440	10% NiO/SA	97	63	Light oil	63.0	39.7
430	10% NiO/SA	186	60	Light oil	76.0	45.6

Reaction condition; temperature, 430 °C; catalytic reactor, 340 °C; feed, LDPE 50 g.

rate of thermal decomposition by adding the additives (PE oil, PP, PS, ABS). When PS is added, smaller than  $C_{11}$  in the product oil increased compared to non-catalytic pyrolysis (56.1 wt% vs 18.6 wt%). Fig. 4 represents the analysis of product oil from (NiO/S-A) catalyst+additives+LDPE pyrolysis. Boiling point of most compounds is below diesel oil except non-catalytic pyrolysis of LDPE. Thus, additives are very important in the pyrolysis process, especially PS. Liebman explained this phenomenon [Liebman, 1985]. Activation energy of styrene is lower than ethylene so that the thermal decomposition occurs at the lower temperature [Liebman, 1985; Bockhorn, 1998]. Therefore, low boiling point region increased, and molecular weight was further decreased when mixed with LDPE and pyrolyzed.

#### 4. Temperature Variation

Flow rate of thermally decomposed gases was decreased by using small amount of LDPE sample (50 g) without using catalyst. Isothermal reaction was carried out by maintaining the reactor temperature at 430 °C, 440 °C, and 480 °C before sample was added. Thermal decomposition rate was very fast at reaction temperature (480 °C), but the oil production (40 wt%) and the content of  $<C_{11}$  (11.6 wt%) were the lowest. On the contrary, the yield of oil and content of  $<C_{11}$  was 60 wt% and 45.6 wt%, respectively, at the reaction temperature of 430 °C. As a result, the content of  $<C_{11}$  was the best at the lowest reaction temperature (430 °C). For this experiment, thermally decomposed gas was passed through the catalytic reactor (fixed bed reactor) while the catalytic reactor was maintained at 340 °C. 10 g of 10% NiO/SA was pelletized (5 mm) and placed in the catalytic reactor. As the reaction temperature decreased, oil

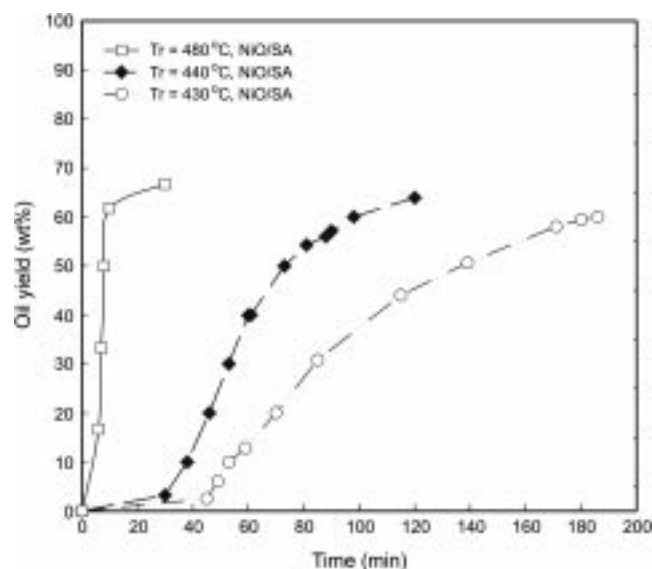
**Fig. 6. Analysis of pyrolysis oil product by using catalytic reactor (fixed bed reactor).**

yield decreased while reaction time increased (Table 5, Fig. 5). However, the amount of light oil (below  $C_{11}$ ) increased (Table 5), and the boiling point was lowered (Fig. 6) [Bamford, 1975]. Thus, the catalytic reactor showed better performance than other variables although only small amount of sample was used. It is thought that the catalytic reactor is the key for LDPE pyrolysis, and further study is needed for better performance and scale-up.

## CONCLUSIONS

Thermal decomposition of LDPE is very difficult but not impossible. Through the pyrolysis of LDPE, the following results were developed, and we may control the LDPE decomposition and reuse the oil as fuel or recover the monomer:

1. In non-catalytic LDPE pyrolysis, isothermal reaction in the low temperature region was almost similar to the non-isothermal reaction with the low heating rate. Thus, it is possible to produce low molecular weight compound with non-catalytic pyrolysis if the rate of thermal decomposition is controlled just like non-isothermal pyrolysis.
2. In non-catalytic LDPE pyrolysis, the effect of PE oil as an additive showed insignificant result.
3. In catalytic LDPE pyrolysis (10% NiO/S-A) with additives, efficiency greatly increased, especially with PS addition. Thus, molecular weight distribution of product oil can be controlled by using appropriate additives.

**Fig. 5. Reaction characteristics of isothermal pyrolysis.**

4. In the catalyst reactor, the amount of low molecular weight compound increased when flow rate of thermally decomposed gas was decreased.

## REFERENCES

- Bamford, C. H. and Tipper, C. F. H., "Comprehensive Chemical Kinetics; Degradation of Polymer," *Elsevier Science pub. Co.*, **14**, 44 (1975).
- Bockhorn, H., Hornung, A. and Hornung, U., "Stepwise Pyrolysis for Raw Material Recovery from Plastic Waste," *J. Analytical and Applied Pyrolysis*, **46**, 1 (1998).
- Fouhy, K., Kim, I., Moore, S. and Culp, E., "Plastics Recycling's Diminishing Returns," *Chem. Eng.*, **100**(Dec.), 30 (1993).
- Hirose, T., Takai, Y., Azuma, N., Morioka, Y. and Ueno, A., "Polystyrene Foams with Dispersed Catalyst for a Design of Recyclable Plastics," *J. Mater. Res.*, **13**(1), 77 (1998).
- Ide, S., Nanbu, H., Kuroki, T. and Ikemura, T., "Catalytic Degradation of Polystyrene in the Presence of Active Charcoal," *J. Analytical and Appl. Pyrolysis*, **6**, 69 (1984).
- Jeong, S. W., Kim, J. H. and Seo, S., "Liquid-Phase Degradation of HDPE over Alkali-Treated Natural Zeolite Catalysts," *Korean J. Chem. Eng.*, **18**, 848 (2001).
- Kim, S., "Pyrolysis of Scrap Tire Rubbers: Relationship of Process Variables with Pyrolysis Time," *Korean J. Chem. Eng.*, **13**, 559 (1996).
- Kim, Y. S., Hwang, G. C., Bae, S. Y., Yi, S. C., Moon, S. K. and Kumazawa, H., "Pyrolysis of Polystyrene in a Batch-Type Stirred Vessel," *Korean J. Chem. Eng.*, **16**, 161 (1999).
- KOREA PETROCHEMICAL HANDBOOK, *KOREA PETRO-CHEMICAL INDUSTRY ASSOCIATION*, 43 (2001).
- Lee, C. H., "State of the Art Report on Waste Recycling Technical Trend," *Ministry of Science & Technology*, 37 (2000).
- Liebman, S. A. and Levy, E. J., "Pyrolysis and GC in Polymer Analysis," *MARCEL DEKKER, INC.*, 156 (1985).
- Rader, C. P., Baldwin, S. D., Cornell, D. D., Sadler, G. D. and Stockel, R. F., "Plastics, Rubber, and Paper Recycling," *ACS SYMPOSIUM SERIES*, **609**, 62 (1995).
- Shelley, S., Fouhy, K. and Moore, S., "Plastics Reborn," *Chem. Eng.*, **99**(July), 30 (1992).
- Song, H. S. and Hyun, J. C., "An Optimization Study on the Pyrolysis of Polystyrene in a Batch Reactor," *Korean J. Chem. Eng.*, **16**, 316 (1999).
- Songip, A. R., Masuda, T., Kuwahara, H. and Hashimoto, K., "Test to Screen Catalysts for Reforming Heavy Oil From Waste Plastics," *Applied Catalysis B: environmental*, **2**, 2(2-3), 153 (1993).
- Williams, V., *preprint of Symposium of Waste Plastic Recycle, Tokyo*, 21 (1993).