

Thermal and Catalytic Degradation of Waste High-density Polyethylene (HDPE) Using Spent FCC Catalyst

Kyong-Hwan Lee[†], Sang-Gu Jeon, Kwang-Ho Kim, Nam-Sun Noh, Dae-Hyun Shin, Jaehyeon Park, Younghwa Seo*, Jurng-Jae Yee** and Geug-Tae Kim***

Clean Energy Research Department, Korea Institute of Energy Research, 71-2 Jang dong, Yusong ku, Daejeon 305-343, Korea

*Dept. of Environmental Engineering, Suwon Science College, Suwon 445-742, Korea

**Faculty of Architectural Design & Engineering, Dong-A University, Busan 604-714, Korea

***Dept. of Chemical and Polymer Engineering, Hannam University, Daejeon 306-791, Korea

(Received 27 November 2002 • accepted 28 February 2003)

Abstract—Thermal and catalytic degradation using spent fluid catalytic cracking (FCC) catalyst of waste high-density polyethylene (HDPE) at 430 °C into fuel oil were carried out with a stirred semi-batch operation. The product yield and the recovery amount, molecular weight distribution and paraffin, olefin, naphthene and aromatic (PONA) distribution of liquid product by catalytic degradation using spent FCC catalyst were compared with those by thermal degradation. The catalytic degradation had lower degradation temperature, faster liquid product rate and more olefin products as well as shorter molecular weight distributions of gasoline range in the liquid product than thermal degradation. These results confirmed that the catalytic degradation using spent FCC catalyst could be a better alternative method to solve a major environmental problem of waste plastics.

Key words: Thermal & Catalytic Degradation, Spent FCC Catalyst, Waste HDPE, Liquid Product Distribution

INTRODUCTION

The consumption of various plastic materials has been growing continuously due to their versatility and low cost. Accordingly, the waste arising from this expanding use of waste is enormous [Patel et al., 1998]. However, the recycling of waste plastics is a small percentage, whereas the large majority is landfilled or incinerated, causing a severe environmental problem due to their chemical inertness. Their impact on the environment needs to be mitigated. Adequate alternative methods for recycling of waste plastics are needed for producing higher value products. The thermal and catalytic degradation processes of waste plastics are accepted alternative methods, both economically and environmentally [Walendziewski, 2002; Bockhorn et al., 1998].

Pyrolysis of waste plastics could be proposed to produce the oil feedstocks in the petroleum industry as a feed for a petroleum refinery catalytic cracker and steam cracker in the production of gasoline and various alkenes. This method is a simple thermal process in which polymers at high temperature are melted and broken down to smaller molecules as the mixture products of gaseous, liquid and solid hydrocarbons [Pinto et al., 1999]. However, these products are not good as fuels due to their low quality. Consequently, the interesting method of polymer utilization is catalytic degradation. This is to convert the melted polymer to light carbon derived materials, constituting high quality components, in the presence of degradation catalysts [Bagri and Williams, 2002; de la Puente et al., 2002; Jeong et al., 2001; Lee and Shin, 2003; Park et al., 2002]. For appli-

cation processes, acidic catalysts such as zeolite Y, ZSM-5, silica-alumina and mordenite mainly produce C₅-C₁₂ light hydrocarbon for the range of gasoline, whereas the thermal process with use of non-acidic catalysts produces C₁₂-C₂₂ compounds with the range of kerosene+diesel [Walendziewski, 2002; Buekens and Huang, 1998; Sakata et al., 1999; Park et al., 2002]. Also, the combination of pyrolysis and catalytic reforming was known as a more efficient method for processing large amounts of waste plastics [Songip et al., 1993].

In this study, thermal and catalytic degradations using spent FCC catalyst of waste HDPE, which can easily produce the low quality components, are compared. Spent FCC catalyst used in the catalytic degradation process is thrown away from the commercial FCC process in Korea as a few ten thousand tons per year, although it has high activity. It means that this catalyst can be reused in the liquid-phase cracking process. Accordingly, spent FCC catalyst with a low cost is utilized in the catalytic degradation process for waste plastics into oil recovery. FCC catalyst, which is mainly composed of zeolite and matrix such as alumina and silica-alumina, is prepared by spray drier to make a strong fine powder type. Catalytic degradation enables lowering of reaction temperature as well as boiling temperature range, compared to thermal degradation. In the product distributions for the two processes, the yields, accumulative product amount, PONA distribution and molecular weight distribution are discussed.

Table 1. Physical properties of waste HDPE

Items	Mn ^a	Mw ^b	Mw/Mn
Values	22550	367534	16.3

^aNumber average molecular weight.

^bWeight average molecular weight.

[†]To whom correspondence should be addressed.

E-mail: khwanlee@kier.re.kr

*This paper is dedicated to Dr. Youn Yong Lee on the occasion of his retirement from Korea Institute of Science and Technology.

Table 2. Physical properties of spent FCC catalyst

Items	Surface area (m ² /g)			Pore volume (cm ³ /g)			BJH* desorption average pore diameter (Å)
	Total	Micro-	Meso-	Total	Micro-	Meso-	
Values	151	76	75	0.2533	0.0303	0.2230	39.95

*BJH means the Barrett, Joyner and Halenda method.

EXPERIMENTAL

Waste HDPE used as raw material was palletized 1/8 inch (O.D.) X a few cm (L) and its physical properties are presented in Table 1. Spent FCC catalyst of a few ten-micrometer sizes was treated with air stream during 4 h at 400 °C, before being used in this experiment. The surface area and pore volume of this catalyst were obtained from nitrogen adsorption isotherms measured at liquid-nitrogen temperature (Micromeritics, ASAP-2000). Total surface areas were determined by using the BET equation within a relative pressure of 0.2, and a distinction between micropores and mesopores was made using the T-plot method. Its physical properties are presented in Table 2.

The degradation experiment of waste HDPE was carried out in a stirred semi-batch reactor at 430 °C under atmospheric pressure [Lee et al., 2001]. Waste HDPE of 200 g and catalyst of 10 g were charged in the reactor. After charging, it was purged with a nitrogen flow of 20 cc/min. The temperature of the reactor increased up to 430 °C with a heating rate of about 7 °C/min and maintained at 430 °C for 4 h. The impeller speed was 200 RPM. Gas products were vented after cooling by condenser to 7 °C. Liquid products, as a function of lapse time, were measured by weight. Each liquid product was quantified and qualified by gas chromatography, using FID and MS detectors [Lee et al., 2002]. Residue yield was determined after the reaction was finished and defined as the ratio of the solid amount produced to the initial reactant amount. Gas yield was calculated from the difference between 100 and total yield of liquid and solid products.

RESULTS AND DISCUSSION

1. Product Yield

Table 3 shows the product yields obtained from thermal and catalytic degradation using spent FCC catalyst of waste HDPE at 430 °C. In the case of product distribution of catalytic degradation, the yield of gaseous products did not differ from that of thermal degradation, but the yield of oil products was increased to about 80% whereas that of residue was reduced to about 1%. These results indicate that the heavier residues were decomposed into lighter oil product by catalytic degradation.

2. Accumulative Amount of Liquid Product

Fig. 1 shows the accumulative amount distribution of liquid prod-

uct, as a function of lapse time, for thermal and catalytic degradation of waste HDPE at 430 °C. In the case of thermal degradation, the liquid product did not appear until the reaction temperature reached 430 °C. After the lapsed time passed 30 min at constant temperature of 430 °C, the initial liquid product appeared. On the other hand, the catalytic degradation produced initial liquid product at a reaction temperature of about 350 °C. From these results, an application of spent FCC catalyst for the degradation of waste plastic shows much faster liquid products in comparison with the thermal degradation in the absence of catalyst, due to more degradation of heavy molecules by the active sites of catalyst. In addition, the catalytic degradation showed much higher rate of oil product than thermal degradation. If waste plastic in the degradation process is conducted with short residence time in a continuous stirred tank reactor, more partial degradation of plastic can occur by thermal degradation, while the rest of the feed can be built heavy oil like wax. It is necessary to notice that the heavy oil obtained by the partial degradation of plastic is similar to coke.

3. PONA Distribution for Liquid Product

The PONA distribution of liquid product obtained from thermal and catalytic degradation of waste HDPE at 430 °C is shown in Figs. 2 and Fig. 3, respectively. In Figs. 2, 3, 4 and 5, the fraction in the Y-axis means the fraction of weight percentage. In the case of thermal degradation, paraffins and olefins as the main products consisted of around 40%, both, and naphthenes show around 15%, and also aromatic compounds hardly appeared in the liquid product. This tendency is not changed, although the lapse time of reaction is

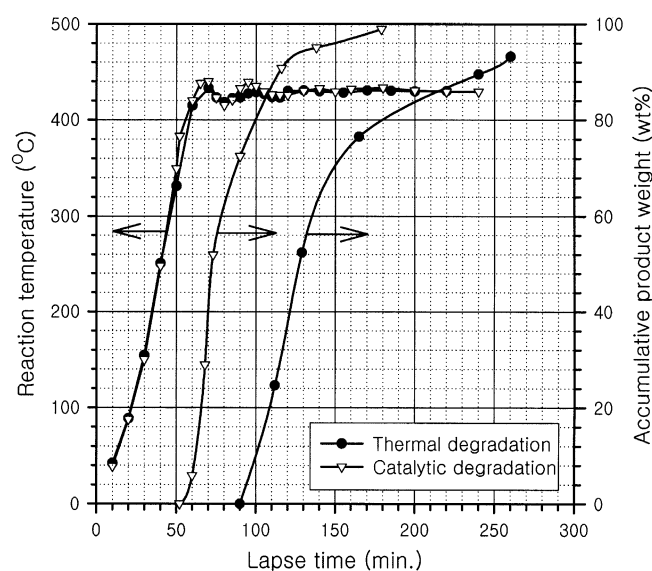


Fig. 1. Accumulative amount of liquid products obtained from thermal and catalytic degradation using spent FCC catalyst of waste HDPE at 430 °C.

Table 3. Yields of gas, liquid and residue obtained from thermal and catalytic degradation of waste HDPE at 430 °C

	Gas (%)	Liquid (%)	Residue (%)
Thermal degradation	20.0	75.5	4.5
Catalytic degradation	19.4	79.7	0.9

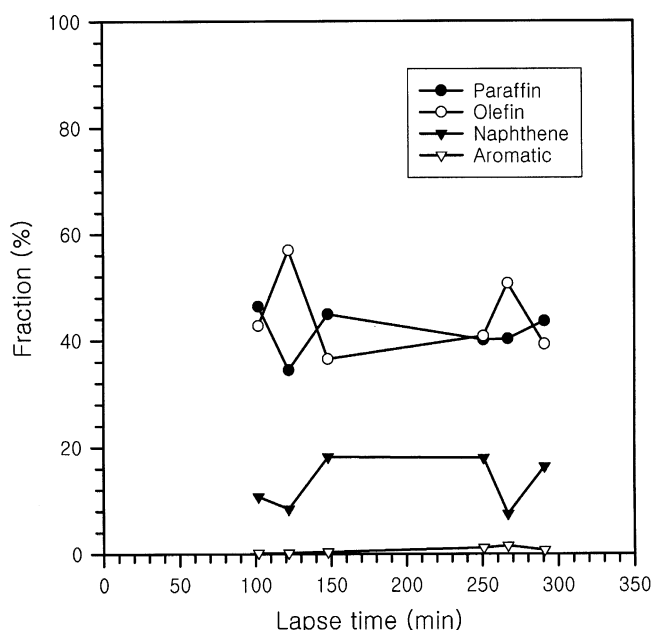


Fig. 2. Fractions of paraffin, olefin, naphthene and aromatic products obtained from thermal degradation of waste HDPE at 430 °C.

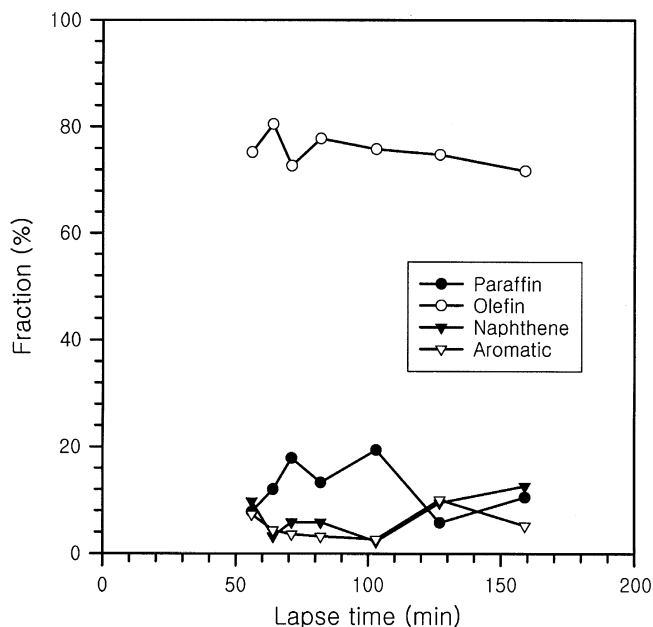


Fig. 3. Fractions of paraffin, olefin, naphthene and aromatic products obtained from catalytic degradation of waste HDPE on spent FCC catalyst at 430 °C.

increased to about 240 min. On the other hand, the catalytic degradation as shown in Fig. 3 produced much more olefins, which consisted of around 80% as a main product. For the catalytic reaction mechanism, the interaction between the active sites of acidic catalyst and the hydrogen atoms from linear polyethylene makes the carbenium ions and then undergoes β -scission to form the olefin products [Seddegi et al., 2002]. The paraffin fraction in the catalytic degradation process was decreased to about 15%, whereas aro-

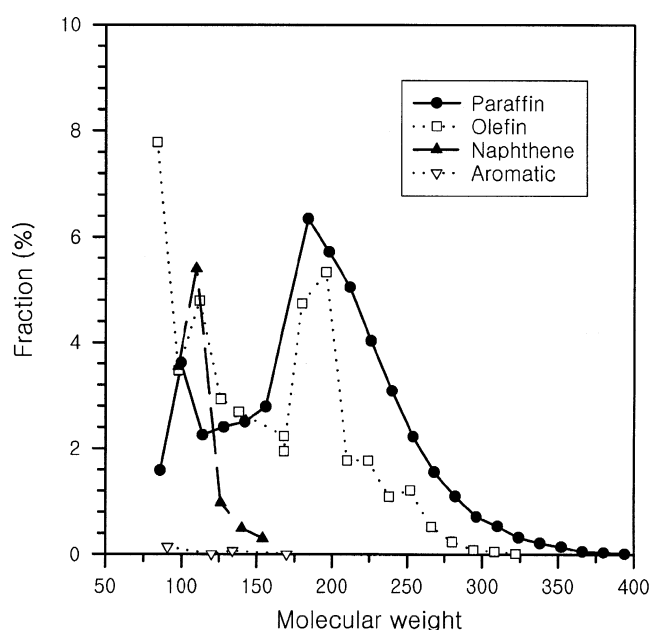


Fig. 4. PONA distributions of liquid products obtained from thermal degradation of waste HDPE at 430 °C (lapse time=102 min).

matic compound fraction was increased to about 5% by the aromatization of olefin in the cracked product. The spent FCC catalyst used as a degradation catalyst of waste HDPE markedly increased the fraction of olefin and aromatic components with comparatively high octane number in the liquid products, due to the olefin product from the primary cracking of high molecular weight polyethylene and the aromatic product from the cyclization of olefin intermediates within pores of catalyst as shape selectivity [Lee et al., 1998].

4. Molecular Weight Distribution for Liquid Product

Characteristics of molecular weight distribution of liquid product obtained by the thermal degradation of waste HDPE at a lapse time of 102 min are presented in Fig. 4. Both paraffin and olefin, as a main liquid product, were distributed in a wide range of molecular weight ranging between 80 and 400, due to the random-chain scission of long hydrocarbon molecules. They showed a similar type of molecular weight distribution with bimodal structure. On the contrary, naphthene products that were obtained by the cyclization of carbonium ion intermediates from paraffin and olefin components showed a narrow molecular weight distribution and one modal structure, which are the light oil products below 150 of molecular weight with the single ring derivatives.

Molecular weight distributions of liquid product obtained from the catalytic degradation of waste HDPE at a lapse time of 82 min are shown in Fig. 5. For each product group, molecular weight distributions clearly show a different tendency with those of thermal degradation process as shown in Fig. 4. More light oil products in the range of gasoline were obtained by the catalytic degradation. Spent FCC catalyst as a cracking catalyst improved the conversion of heavy reactant to obtain the light oil with high quality product. This means that the molecular weight distribution of liquid product can be easily controlled by pore size distribution in the spent FCC catalyst, including the micropore of zeolite and the mesopore of

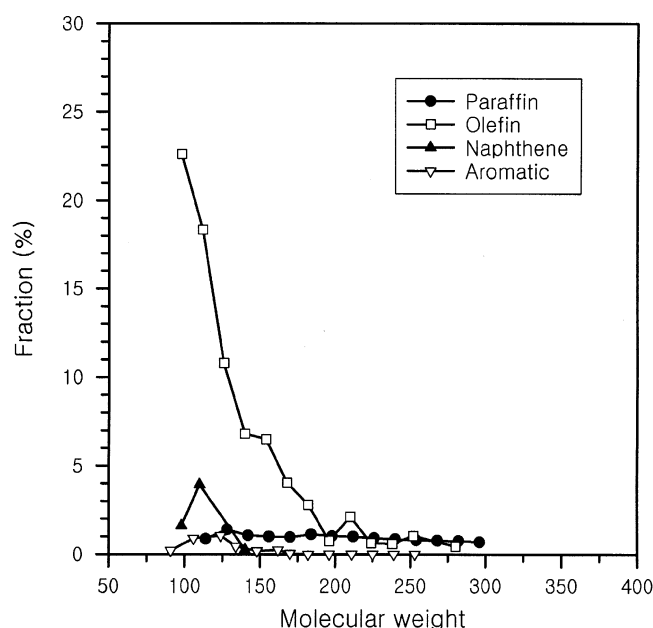


Fig. 5. PONA distributions of liquid products obtained from catalytic degradation of waste HDPE at 430 °C (lapse time=82 min).

silica-alumina [Lee et al., 1998]. Accordingly, the improved accessibility of the heavy reactant into the mesopore and also that of the cracked intermediates into the micropore may increase the reaction rate. This result suggests that the large molecule reactants were firstly cracked to small intermediates on external surface of catalyst or within mesopores of silica-alumina and then the cracked intermediates were broken down to smaller product in micropore of zeolite. The main product was olefin components, which is the light oil product with molecular weight below 200 in the range of gasoline. Among the olefin products, the C_7 components showed a maximum fraction of above 20%. The fraction of olefin products sharply decreased with the increase of the molecular weight. Other components produced a little fraction. This result led to the conclusion that the catalytic degradation using spent FCC catalyst showed a better result on the production of light oil from waste plastic.

CONCLUSIONS

Both thermal and catalytic degradation using spent FCC catalyst were compared for the liquid-phase reaction of waste HDPE in a stirred semi-batch reactor at 430 °C.

1. Thermal and catalytic degradation of waste HDPE convert it to fuel oil with over 75% yield. However, the catalytic degradation process produces much less residue content than that from thermal degradation.

2. In comparison to the thermal degradation process, the catalytic degradation process results in lowering of the degradation temperature of waste HDPE as well as the boiling temperature in the liquid product. Furthermore, the faster rate of oil product is obtained from the catalytic degradation process.

3. In the liquid product distribution, the catalytic degradation process produced mostly the products below 150 of molecular weight like the components of gasoline range and much higher olefin frac-

tion with about 80%, while the thermal degradation process showed the bimodal product distribution and also higher paraffin as well as olefin fraction.

ACKNOWLEDGMENTS

This work was performed with the financial assistance of Industrial Waste Recycling R & D Center (Project No. A-A-1), which is 21 C Frontier Projects of Korea Ministry of Science and Technology.

REFERENCES

- Bagri, R. and Williams, P. T., "Catalytic Pyrolysis of Polyethylene," *J. Anal. Appl. Pyrol.*, **63**, 29 (2002).
- Bockhom, H., Hornung, A. and Hornung, U., "Stepwise Pyrolysis for Raw Material Recovery from Plastic Waste," *J. Anal. Appl. Pyrol.*, **46**, 1 (1998).
- Buekens, A. G. and Huang, H., "Catalytic Plastics Cracking for Recovery of Gasoline-range Hydrocarbons from Municipal Plastic Wastes," *Res. Con. Recycl.*, **23**, 163 (1998).
- de la Puente, G., Klocker, C. and Sedran, U., "Conversion of Waste Plastics into Fuels: Recycling Polyethylene in FCC," *Appl. Catal. B*, **36**, 279 (2002).
- Jeong, S.-W., Kim, J.-H. and Seo, G., "Liquid-phase Degradation of HDPE over Alkali-treated Natural Zeolite Catalysts," *Korean J. Chem. Eng.*, **18**, 848 (2001).
- Lee, K.-H., Ha, B. H. and Lee, Y. W., "Catalytic Cracking of Vacuum Gas Oil on the Dealuminated Mordenites," *J. Catal.*, **178**, 328 (1998).
- Lee, K.-H., Ha, B. H. and Lee, Y. W., "Catalytic Cracking of Vacuum Gas Oil over the Modified Mordenites and Y-type Zeolites Mixed with Alumina," *Ind. Eng. Chem. Research*, **37**, 1761 (1998).
- Lee, K.-H., Kim, S.-K. and Shin, D.-H., "Catalytic Decomposition of Waste HDPE over Zeolite, in a Semi-batch Reactor," *J. Korean Solid Wastes Eng. Soc.*, **18**(5), 442 (2001).
- Lee, K.-H., Noh, N.-S., Shin, D.-H. and Seo, Y. H., "Comparison of Plastic Types for Catalytic Degradation of Waste Plastics into Liquid Product with Spent FCC Catalyst," *Polym. Degrad. Stab.*, **78**, 539 (2002).
- Lee, K.-H. and Shin, D.-H., "Catalytic Degradation of Waste Polyolefinic Polymers Using Spent FCC Catalyst with Various Experimental Variables," *Korean J. Chem. Eng.*, **20**, 89 (2003).
- Patel, M. K., Jochem, E., Radgen, P. and Worrell, E., "Plastics Streams in Germany-an Analysis of Production, Consumption and Waste Generation," *Res. Con. Recycl.*, **24**, 191 (1998).
- Park, J. J., Park, K. N., Park, J.-W. and Kim, D. C., "Characteristics of LDPE Pyrolysis," *Korean J. Chem. Eng.*, **19**, 658 (2002).
- Park, J. R., Yoon, J. H. and Park, D. W., "Catalytic Recycling of the Mixture of Polypropylene and Polystyrene," *Polym. Degrad. Stab.*, **76**, 61 (2002).
- Pinto, F., Costa, P., Gulyurtlu, I. and Cabrita, I., "Pyrolysis of Plastic Wastes. 1. Effect of Plastic Waste Composition on Product Yield," *J. Anal. Appl. Pyrol.*, **51**, 39 (1999).
- Sakata, Y., Uddin, M. A. and Muto, A., "Degradation of Polyethylene and Polypropylene into Fuel Oil by Using Solid Acid and Non-acid Catalysts," *J. Anal. Appl. Pyrol.*, **51**, 135 (1999).
- Seddegi, Z. S., Budrthumal, U., Al-Arfaj, A. A., Al-Amer, A. M. and Bari, S. A. I., "Catalytic Cracking of Polyethylene over All-silica

- MCM-41 Molecular Sieve," *Appl. Catal. A*, **225**, 167 (2002).
- Songip, A. R., Masuda, T. and Kuwahara, H., "Test to Screen Catalysts for Reforming Heavy Oil from Waste Plastics," *Appl. Catal. B*, **2**, 153 (1993).
- Walendziewski, J., "Engine Fuel Derived from Waste Plastics by Thermal Treatment," *Fuel*, **81**, 473 (2002).