

# Catalytic Degradation of Waste Polyolefinic Polymers using Spent FCC Catalyst with Various Experimental Variables

Kyong-Hwan Lee<sup>†</sup> and Dae-Hyun Shin

Clean Energy Research Department, Korea Institute of Energy Research, Daejeon 305-343, Korea  
(Received 3 October 2002 • accepted 28 November 2002)

**Abstract**—Liquid-phase catalytic degradation of waste polyolefinic polymers (HDPE, LDPE, PP) over spent fluid catalytic cracking (FCC) catalyst was carried out at atmospheric pressure with a stirred semi-batch operation. The effect of experimental variables, such as catalyst amount, reaction temperature, plastic types and weight ratio of mixed plastic on the yield and accumulative amount distribution of liquid product for catalytic degradation was investigated. The initial rate of catalytic degradation of waste HDPE was linearly increased with catalyst amount (4-12 wt%), while that was exponentially increased with reaction temperature (350-430 °C). Spent FCC catalyst in the liquid-phase catalytic degradation of polymer was not deactivated fast. The product distribution from catalytic degradation using spent FCC catalyst strongly depended on the plastic type. The catalytic degradation of mixed plastic (HDPE : LDPE : PP : PS=3 : 2 : 3 : 1) showed lower degradation temperature by about 20 °C than that of pure HDPE.

Key words: Catalytic Degradation, Spent FCC Catalyst, Catalyst Amount, Reaction Temperature, Deactivation of Catalyst, Plastic Type

## INTRODUCTION

Waste plastics are mostly landfilled or incinerated; however, these methods are facing great social resistance because of environmental problems such as air pollution and soil contamination, as well as economical resistance due to the increase of space and disposal costs [Bueken and Huang, 1998]. Accordingly, recycling has become an important issue worldwide. This method can be classified as energy recovery, material recycling and chemical recycling. Among them, one of the prevalent alternative methods is the production of converted fuel and chemicals by means of the thermal or catalytic degradation of polymers [Walendziewski, 2002; Sakata et al., 1997; Bockhorn et al., 1998; Songip et al., 1993]. These products could be changed into valuable raw material by the petroleum refining industry. Furthermore, hydrocarbon production from polymer has a great advantage on the catalytic degradation process rather than thermal degradation process, due to the hydrocarbon products with high-quality and low energy requirement operating at low temperature [Jeong et al., 2001; Lee et al., 2001, 2002; Park et al., 2002].

The main objective of this study was to investigate the effect of catalyst amount, reaction temperature, plastic type and weight ratio of mixed plastic, and also the deactivation of catalyst in the catalytic degradation of waste plastics using spent FCC catalyst with a semi-batch reactor, based on the results of yields and yield distributions of liquid product as a function of lapsed time.

## EXPERIMENTAL

The waste plastic samples (supplied by Duck Shin Co., Daejeon)

<sup>†</sup>To whom correspondence should be addressed.

E-mail: khwanlee@kier.re.kr

<sup>‡</sup>This paper is dedicated to Professor Baik-Hyon Ha on his retirement from Hanyang University.

Table 1. Molecular weights of various waste plastics

Reactant type	Mn <sup>a</sup>	Mw <sup>b</sup>	Mw/Mn
HDPE	22600	367500	16.3
LDPE	21000	212800	10.1
PP	57600	281700	4.9
PS	73900	171000	2.3

<sup>a</sup>Number average molecular weight.

<sup>b</sup>Weight average molecular weight.

used in this study were palletized to a form of 1/8 inch (O.D.) X a few mm (L); their molecular weights are presented in Table 1. Spent FCC catalyst, supplied by SK Co. Ltd., is received as a fine powder form with the size of a few ten-micrometers. Before being used in this experiment, spent FCC catalyst was treated with air stream for 4 h at 400 °C. The BET surface area of this catalyst was 151 m<sup>2</sup>/g, which consisted of micropore area of 76 m<sup>2</sup>/g and mesopore area of 75 m<sup>2</sup>/g.

The degradation experiment of waste plastics was carried out in a stirred semi-batch reactor (volume 1.1 l) at 400 °C under atmospheric pressure [Lee et al., 2002]. The experimental conditions were as follows: reactant of 200 g, catalyst of 10-25 g, nitrogen stream of 20 cc/min, impeller speed of 200 rpm, heating rate of about 7 °C/min and reaction temperature of 350-430 °C. Gas products were vented after cooling by condenser to 7 °C. Liquid products were collected in a reservoir over a period of lapsed time and were measured by weight. Solid yield was determined by dividing the solid amount produced by the initial reactant amount. Accordingly, gas yield was measured by the difference between initial reactant amount and the total amount of liquid and solid products after reaction.

## RESULTS AND DISCUSSION

### 1. Effect of Catalyst Amount

To investigate the effect of catalyst amount on the catalytic degradation of waste HDPE using spent FCC catalyst, the catalytic degradations in the range of 4-12 wt% catalyst amount were performed under the same experimental conditions. Spent FCC catalyst used in this study was fine powder type, which was the catalyst regenerated after use in the fluid catalytic cracking (FCC) process. Reaction temperature was changed from room temperature to 400 °C with 7 °C/min of heating rate and then maintained at that temperature for a few hours. Fig. 1 shows the yield distributions of liquid product for each catalyst amount as a function of lapsed time.

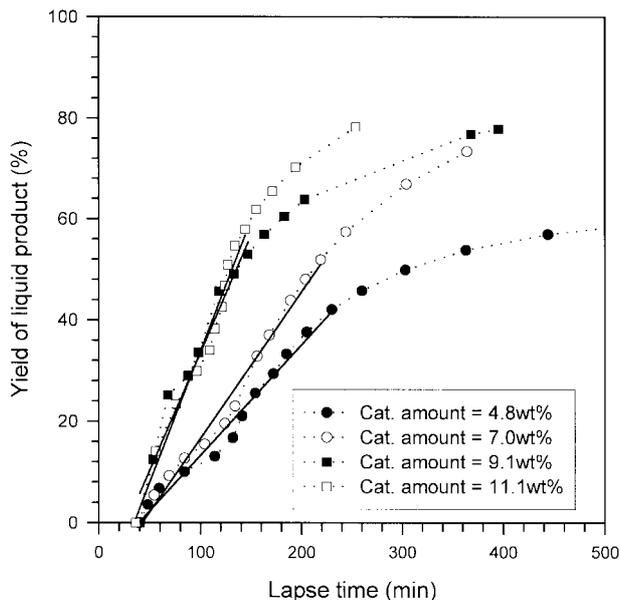


Fig. 1. Yield of liquid product as a function of lapsed time for catalytic degradation of waste HDPE using spent FCC catalyst at different catalyst amounts, 400 °C.

In the range of initial lapse time the yield distribution of liquid product changed with catalyst amount. The initial rate of degradation of waste HDPE calculated from Fig. 1, as a function of catalyst amount, is shown in Fig. 2. Here the initial rate of degradation is defined as the slope of accumulative amount of liquid product versus the initial lapsed time. Here the accumulative amount of liquid product multiplies the yield of liquid product by 2. In the range of 4-12 wt% catalyst amounts, the initial rate of degradation of waste HDPE linearly increased from 0.4 g/min to 1.1 g/min with the increase of catalyst amount. It means that the initial rate of degradation of poly-

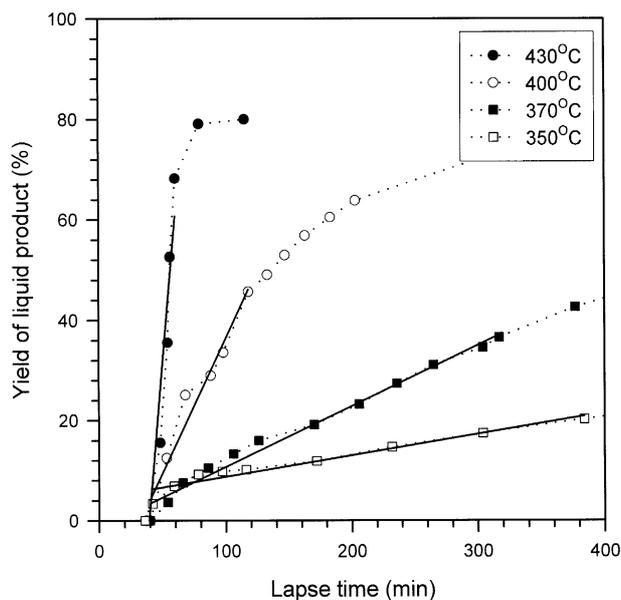


Fig. 3. Yield of liquid product as a function of lapse time for catalytic degradation of waste HDPE at different reaction temperature, 9.1 wt% catalyst amount.

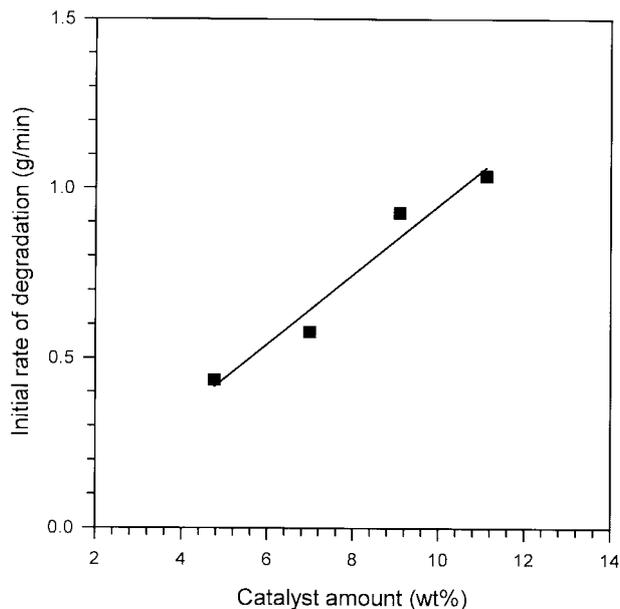


Fig. 2. Initial rate of degradation as a function of catalyst amount for catalytic degradation of waste HDPE using spent FCC catalyst at 400 °C.

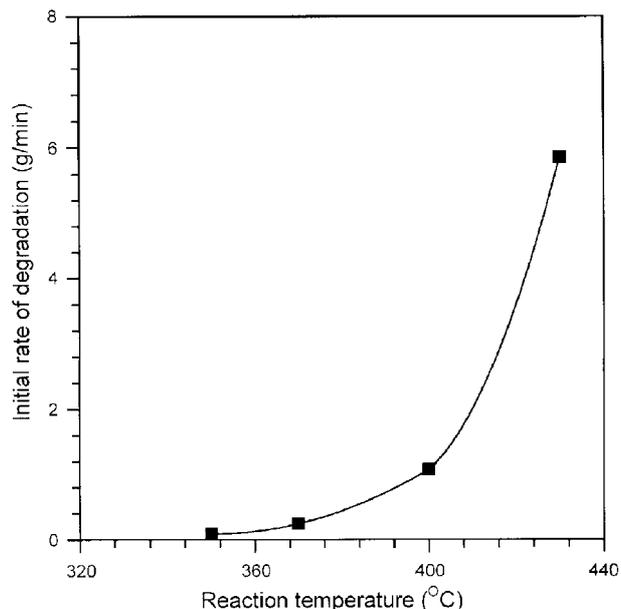


Fig. 4. Initial rate of degradation as a function of reaction temperature for catalytic degradation of waste HDPE using spent FCC catalyst at 9.1 wt% catalyst amount.

mer depended on the catalyst amount of spent FCC catalyst.

## 2. Effect of Reaction Temperature

Fig. 3 shows the yield distributions of liquid product by catalytic degradation of waste HDPE at each reaction temperature as a function of lapsed time. The catalyst of 20 g (9.1 wt%) was mixed with 200 g of reactant in the reactor. At different reaction temperatures the yield distributions of liquid product clearly differed. The slope of the accumulative amount of liquid product versus the initial lapsed time (defined as the initial rate of degradation) as a function of reaction temperature is shown in Fig. 4. Here the accumulative amount of liquid product multiplies the yield of liquid product by 2. In the range of reaction temperatures below 400 °C, the initial rate of degradation of waste HDPE was slowly increased with the increase of reaction temperature, while that was sharply increased from 1 g/min to 6 g/min with the increase of reaction temperature from 400 to 430 °C. This result showed a great effect of reaction temperature on the catalytic degradation of waste HDPE, compared to that of catalyst amount as shown in Fig. 2.

## 3. Deactivation of Catalyst

Fig. 5 shows the lapsed time for the accumulative amount of liquid product obtained on both catalytic degradation and thermal degradation as a function of yield of liquid product. The deactivation of catalyst in the liquid-phase catalytic degradation of waste HDPE at the reaction temperature of 430 °C and catalyst amount of 9.1 wt% can be explained by the difference of lapsed time between two processes. The reaction temperature programming of two processes is shown in Fig. 6. Here the maintenance for 3 hrs at 300 (catalytic degradation) or 350 °C (thermal degradation) involved melting the waste HDPE as the reactant and also partially deactivating the catalyst before the main reaction. At the main reaction of above 220 min lapse time, the reaction temperatures of two processes were conducted under the same conditions. In Fig. 5, the catalytic degradation process shows shorter lapse time at a constant yield of liquid product than the thermal degradation process, due to the high

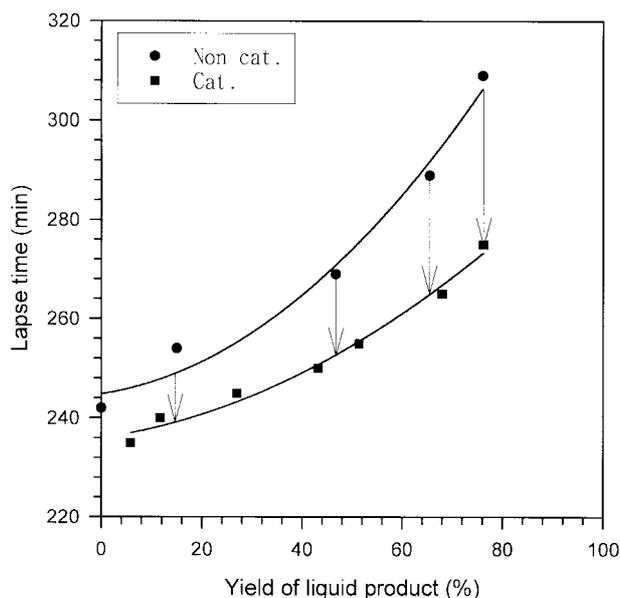


Fig. 5. Lapse time as a function of yield of liquid product for thermal degradation (●) and catalytic degradation using spent FCC catalyst (■) of waste HDPE at 430 °C.

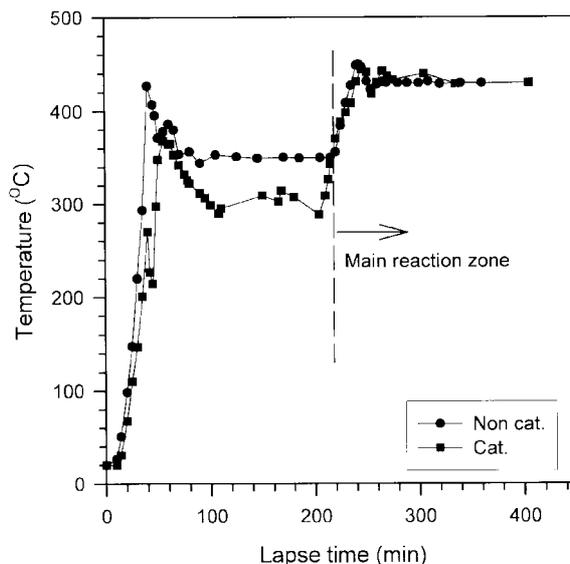


Fig. 6. Reaction temperature programming as a function of lapsed time for thermal degradation (●) and catalytic degradation using spent FCC catalyst (■) of waste HDPE at 430 °C.

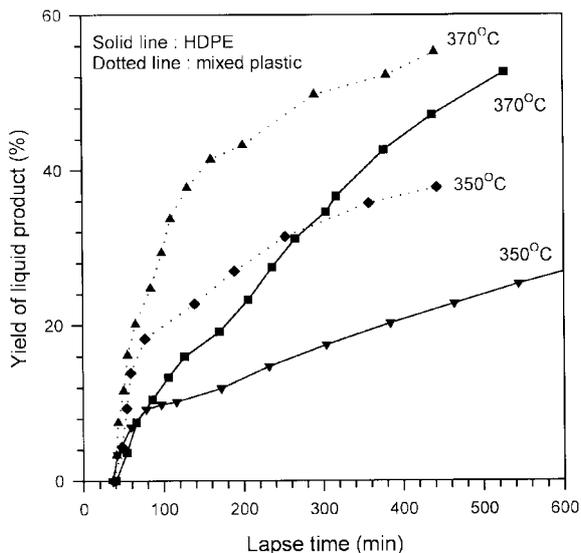
activity of spent FCC catalyst in the catalytic degradation. According to the increase of yield of liquid product, the lapse time of thermal degradation was sharply increased, whereas that of catalytic degradation was smoothly increased by the slow deactivation of catalyst. If the catalyst is deactivated fast on the catalytic degradation, its curve pattern of lapse time as a function of yield of liquid product will be similar to that of thermal degradation. However, the difference of lapse time of both thermal degradation and catalytic degradation was gradually increased with the increase of yield of liquid product. This can be explained as the spent FCC catalyst included in the catalytic degradation process not deactivating fast according to the progress of reaction.

## 4. Effect of Plastic Type

In the catalytic degradation of polyolefinic polymers (HDPE, LDPE, PP) using spent FCC catalyst (9.1 wt%) at 400 °C, the yields of individual samples are shown in Table 2. In all cases, the yields of liquid products were more than 80%. Furthermore, the total yields of gas and liquid product that can be used as a fuel were about 99%. Among various plastics, waste PP showed higher liquid yield and lower gas yield than waste PE (HDPE, LDPE). The initial rates of waste LDPE and PP were about two times and three times faster than that of waste HDPE. According as thermal degradation in the type of plastic occurred at lower temperature, a higher initial rate of catalytic degradation of waste plastics conducted under the same reaction temperature programming was obtained [Lee et al., 2002]. We thus know that the catalytic degradation for various plastics was

Table 2. Product distribution for catalytic degradation of waste polyolefinic plastics on spent FCC catalyst at 400 °C

Reactant type	Liquid (wt%)	Gas (wt%)	Solid (wt%)	Initial rate of degradation (g/min)
HDPE	82.0	17.0	1.0	1.077
LDPE	80.4	19.1	0.5	1.867
PP	86.4	13.1	0.5	3.308



**Fig. 7.** Yield of liquid product as a function of lapse time for catalytic degradation using spent FCC catalyst of waste HDPE and mixed plastic (HDPE : LDPE : PP : PS=3 : 2 : 3 : 1) at 350 and 370 °C, respectively.

significantly influenced by the characteristics of the plastic.

### 5. Comparison of Pure HDPE and Mixed Plastic

Fig. 7 shows the yield distributions of liquid product, as a function of lapsed time, for catalytic degradation of waste HDPE and mixed plastic (HDPE : LDPE : PP : PS=3 : 2 : 3 : 1) at 350 and 370 °C, respectively. Here the ratio in the mixed plastic is average weight ratio of individual plastics generated in Korea. In the range of initial lapsed time, the mixed plastic showed much higher rate of the yield of liquid product than that of pure HDPE. Furthermore, at the same lapsed time the yield of liquid product was more produced on the catalytic degradation of mixed plastic than that of pure HDPE. This explains why PS and PP polymers in mixed plastic had lower degradation temperature by TGA analysis than HDPE polymer [Lee et al., 2002]. Therefore, it can be concluded that the catalytic degradation of mixed plastics lowered the reaction temperature by about 20 °C in comparison with that of pure HDPE.

### CONCLUSIONS

The initial rate of degradation of waste HDPE was linearly increased with catalyst amount, while that was exponentially increased with reaction temperature. The reaction temperature had a great influence on the initial rate of degradation of waste plastics using spent FCC catalyst than the catalyst amount.

According to the progress of reaction, spent FCC catalyst in the liquid-phase degradation of polymer was not deactivated fast.

Waste polyolefinic polymers (PP, PE (HDPE, LDPE)) were de-

graded to liquid products with over 80% yield and also solid product with below 1% yield. In the type of plastic, waste PP showed higher liquid yield and lower gas yield than waste PE (HDPE, LDPE). The initial rates of degradation of waste LDPE and PP were about two times and about three times faster than that of waste HDPE.

The initial rate of degradation of mixed plastic (HDPE : LDPE : PP : PS=3 : 2 : 3 : 1) was much higher than that of pure HDPE, and also the catalytic degradation of mixed plastic occurred at lower reaction temperature by about 20 °C than that of pure HDPE plastic, because plastics of low degradation temperature were included in the mixed plastic.

### ACKNOWLEDGEMENTS

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

- Bockhorn, 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 Plastic Cracking for Recovery of Gasoline-Range Hydrocarbons from Municipal Plastic Wastes," *Res. Con. Recycl.*, **23**, 163 (1998).
- 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., Jeon, S.-G., Kim K.-H., Noh, N.-S., Shin, D.-H., Yun, W.-L. and Seo, Y.-H., "Liquid-Phase Catalytic Degradation of Waste Plastics Using Spent FCC Catalyst," The 2nd Intl Conf. On Combustion, Incineration/Pyrolysis and Emission Control, 571 (2002).
- Lee, K.-H., Kim, S.-G. and Shin, D.-H., "Liquid-Phase Degradation of Waste HDPE over Amorphous Acid Catalysts with Mesoporous Structure," *J. KSWE*, **18**(5), 451 (2001).
- Lee, K.-H., Noh, N.-S., Shin, D.-H. and Seo, Y.-H., "Comparison of Plastic Types for Catalytic Degradation of Waste Plastic into Liquid Product with Spent FCC Catalyst," *Polym. Degrad. Stab.*, **78**, 539 (2002).
- Park, J. J., Park, K. N., Park, J.-W. and Kim, D. C., "Characteristics of LDPE Pyrolysis," *Korean J. Chem. Eng.*, **19**, 658 (2002).
- Sakata, Y., Uddin, M. A., Muto, A., Kanada, Y., Koizumi, K. and Murata, K., "Catalytic Degradation of Polyethylene into Fuel Oil over Mesoporous Silica (KFS-16) Catalyst," *J. Anal. Appl. Pyrol.*, **43**, 15 (1997).
- 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).