A comparative study of liquid product on non-catalytic and catalytic degradation of waste plastics using spent FCC catalyst

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Abstract–Non-catalytic and catalytic degradation of waste plastics (high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP) and polystyrene (PS)) using spent fluid catalytic cracking (FCC) catalyst into liquid product were comparatively studied with a stirred semi-batch reactor at 400 °C, under nitrogen stream. Liquid product characteristics were described by cumulative distribution as a function of lapse time of reaction, paraffin, olefin, naphthene and aromatic (PONA) composition, and also carbon number distribution on plastic type of reactant. For degradation of waste PE with relatively high degradation temperature, the effect of adding spent FCC catalyst greatly appeared on cumulative distribution of liquid product with a reaction lapse time, whereas those for waste PP and PS with low degradation temperature showed a similar trend in both non-catalytic and catalytic degradation at 400 °C. In PONA and carbon number distribution of liquid product, the characteristics of waste PS that was mainly degraded by end chain scission mechanism were not much altered in presence of spent FCC catalyst. However, waste polyolefinic polymer that was degraded by a random chain scission mechanism significantly differed on PONA and carbon number distribution of liquid product with or without spent FCC catalyst. The addition of spent FCC catalyst in degradation of polyolefinic polymer, which economically has a benefit in utilization of waste catalyst, significantly improved the light olefin product by its high cracking ability and also the aromatic product by cyclization of olefin as shape selectivity in micropore of catalyst.

Key words: Non-catalytic Degradation, Catalytic Degradation, Spent FCC Catalyst, Waste Plastic Type, Characteristics of Liquid Product

INTRODUCTION

The recycling of waste polymer by non-catalytic and catalytic degradation processes can be an important source of producing alternative fuel oils from an economical aspect as well as from contributing to environmental protection as an environmental aspect [Lin et al., 2004]. Waste polymer mainly consists of PE (polyethylene), PP (polypropylene) and PS (polystyrene) in a plastic type as a thermoplastic material [Serrano et al., 2003], which can be degraded to oil product by non-catalytic and catalytic degradation processes. Non-catalytic degradation is a method for upgrading waste plastic into liquid product at a temperature of 400-600 °C in the absence of oxygen [Marcilla et al., 2003; Miskolczi et al., 2004; Cha et al., 2002]. However, this process has high-energy consumption, due to the low thermal conductivity of waste plastic and to an endothermic reaction by degradation of waste plastic. Thus, in order to decrease the temperature of this process, a catalyst has been added in this process. This catalytic degradation process can be conducted at low temperature and also result in a high quality product, compared to non-catalytic degradation [Ding et al., 1997; Aguado et al., 2002].

Spent FCC catalyst used in this study is thrown away from commercial FCC process in Korea in the range of tens of thousands of 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. This method has a great advantage economically for producing high quality oil and simultaneously for environmental reuse of spent FCC catalyst.

This paper is aimed at comparing non-catalytic and catalytic degradation processes on the characteristic of liquid product for plastic type. The characteristics of liquid product over two processes are discussed with cumulative distribution, carbon number distribution and PONA composition.

EXPERIMENTAL

The waste plastic samples were palletized 1/8 inch (O.D.) X a few mm (L), which was obtained from a recycling company (Daeshin Co.) in Korea. The reactants used in this experiment were pure waste plastics of four types (HDPE, LDPE, PP and PS); their properties are presented in Table 1. Spent FCC catalyst that was supplied by

Table 1. Physical properties of various waste plastics

Items	Mn[a]	Mw[b]	Mw/Mn
HDPE	22600	367500	16.3
LDPE	21000	212800	10.1
PP	57600	281700	4.9
PS	73900	171000	2.3

[a]Number average molecular weight.
[b]Weight average molecular weight.

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Table 2. Physical properties of spent FCC catalyst

Items	Surface area (m²/g)			Pore volume (cm³/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.

SK Oil Co. (in Korea) consisted of a few ten-micrometer sizes and 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 by using the T-plot method. Its physical properties are presented in Table 2.

The degradation experiment was carried out in a stirred semi-batch reactor (volume 1.1 liter) at 400 °C under atmospheric pressure [Lee and Shin, 2003]. The experiment conditions were as follows: a reactant amount of 200 g, a nitrogen stream of 20 cc/min, a speed of 200 RPM and heating rate of about 9 °C/min. The gas products were vented after cooling by a condenser to 7 °C. The liquid products were measured by weight, as a function of lapse time of reaction. Each component of the liquid product was quantified and qualified by gas chromatography, using FID and MS detectors. For this analysis method, a detailed explanation was described previously [Seo et al., 2003].

RESULTS AND DISCUSSION

1. Cumulative Distribution

In order to understand the characteristics of thermal degradation for waste plastic type, the normalized weight loss of reactant using
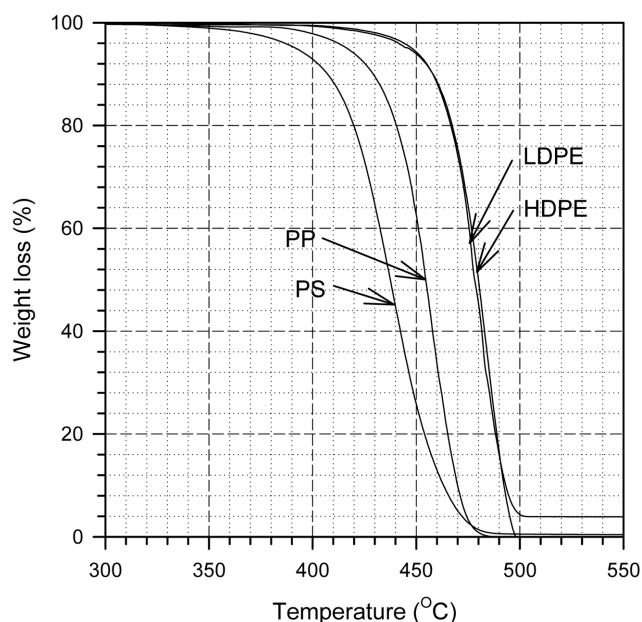

Fig. 1. Thermogram curves of various waste plastics at a heating rate of 10 °C/min under nitrogen stream.

TGA analyzer was relatively compared with a function of temperature, as shown in Fig. 1. Thermal degradations of all plastics occur between 350 and 500 °C. One of the degradation characteristics in the type of plastic is the level of temperature at which the degradation takes place. The temperature levels of thermal degradation of the reactants were in the following order: waste PS<waste PP<waste LDPE, HDPE. Also the degradation temperatures at which a weight loss of 50% (T_{50}) takes place were about 440 °C for waste PS, about 455 °C for waste PP, and about 480 °C for waste HDPE and LDPE, respectively. One can see that waste PS with polycyclic structure was easily degraded at the lowest temperature among all the plastics and also waste PP in polyolefinic polymer was degraded at lower temperature than waste PE. Thus, the reaction temperature in this study was 400 °C, where the weight loss of all samples using TG analyzer was below 10%.

The non-catalytic and catalytic degradations of four waste plastic samples (HDPE, LDPE, PP and PS) using spent FCC catalyst were carried out under the same experimental conditions. The influence of plastic type and also the comparison of both non-catalytic and catalytic processes on the characteristic of oil product were discussed in detail. Moreover, the possibility of application of spent FCC catalyst in the degradation of thermoplastics to produce the alternative fuel oil was described.

Fig. 2 shows the cumulative distributions of liquid products obtained from non-catalytic and catalytic degradation of waste LDPE (a), HDPE (b), PP (c) and PS (d) at 400 °C, as a function of lapsed time of reaction. In case of waste PE (LDPE and HDPE), the cumulative distributions of liquid product obtained over non-catalytic and catalytic degradation processes clearly showed a different pattern. the non-catalytic degradation process showed a slow increase of the cumulative amount of liquid product as a function of reaction lapsed time, whereas the catalytic degradation process showed a large cumulative amount of liquid product at relatively short reaction lapsed time. According to the addition of spent FCC catalyst in the pyrolysis process, the production of liquid product was accelerated by more cracking of waste polymer into light hydrocarbons. From the comparison of 50% liquid product yield (Y_{50}), the reaction lapse time in the catalytic degradation process needs around 100 min, but the case of non-catalytic degradation process showed a lapse time of about 400 min, as a great difference in the reaction lapse time of two processes. These results show that the addition of spent FCC catalyst in pyrolysis of waste PE had a good effect on the cumulative distribution of liquid product as an economical aspect by productivity.

As shown in Fig. 2(c) and (d), the case of waste PP and PS over non-catalytic and catalytic degradation processes showed a different pattern as a comparison of waste PE (Fig. 2(a) and (b)). In case of waste PP and PS, both non-catalytic and catalytic degradation processes showed roughly a similar trend for the pattern of cumu-
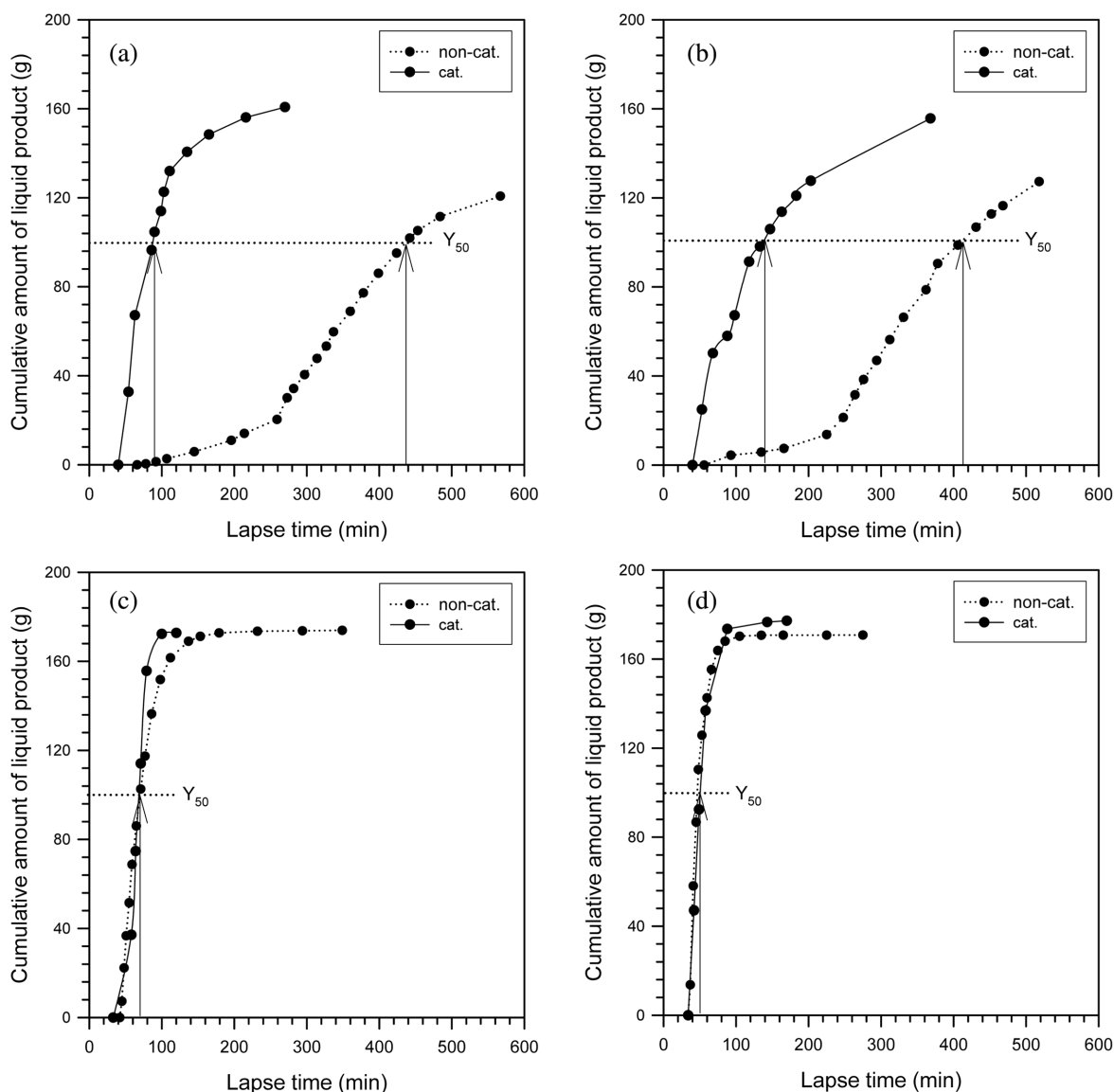
Fig. 2. Cumulative distribution of liquid product as a function of reaction lapse time on non-catalytic (dotted line) and catalytic (solid line) degradation of LDPE (a), HDPE (b), PP (c) and PS (d) at 400 °C.

lative distribution of liquid product as a function of lapse time and also the lapse time of reaction to obtain a 50% yield of liquid product (Y_{50}). Here, the cumulative amount of liquid product over two cases was fast increased at relatively short lapse time of reaction, and also the effect of spent FCC catalyst addition in pyrolysis process appeared slightly, because of a sufficient low degradation temperature of reactants in the degradation of waste PP and PS, respectively. From the weight loss by TGA analyzer as shown in Fig. 1, waste PP and PS showed much lower degradation temperature than waste PE. The yield of liquid product over waste PP and PS showed above 80% in both the non-catalytic and catalytic degradation process. However, in the range of lapse time above 50% yield of liquid product, the catalytic degradation of waste PP showed much more cumulative amount of liquid product at the same lapse time than that of non-catalytic degradation. Also, waste PS had a little higher yield of liquid product in catalytic degradation than non-catalytic degradation. This implies that waste PS and PP by using spent FCC catalyst

was more cracked into liquid products from heavy intermediates like residue, which remained in the reactor after a sufficient reaction time.

2. PONA Distribution

Fig. 3(a) and (b) show PONA distributions of liquid products over non-catalytic and catalytic degradation processes of waste PE (HDPE and LDPE) at 400 °C. Generally, the main products were paraffin and olefin components, which were produced through random-chain scission of straight hydrocarbons [Demirbas, 2004]. However, the naphthene and aromatic products with cyclic structure show relatively low fraction in liquid product. As a comparison of non-catalytic and catalytic degradation processes, the catalytic degradation process showed more olefin and aromatic products than the non-catalytic degradation process. The addition of catalyst in pyrolysis process had an increase of light olefin products by more cracking of straight hydrocarbon intermediates, as was produced by β-scission mechanism of straight hydrocarbons, and also much more aromatic prod-
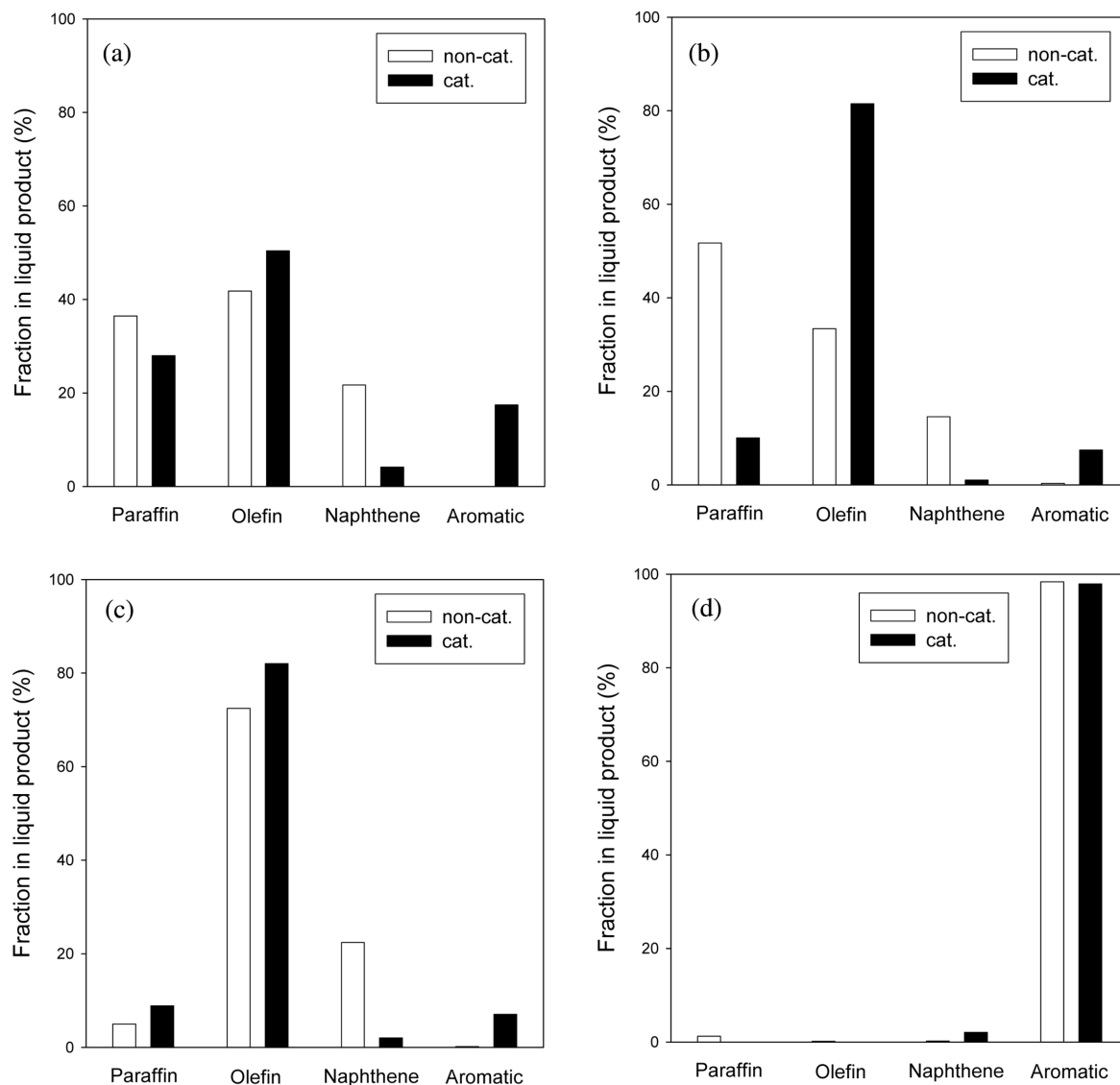
Fig. 3. PONA composition of liquid product on non-catalytic (white) and catalytic (black) degradation of waste LDPE (a), HDPE (b), PP (c) and PS (d) at 400 °C.

ucts by steric reaction within micropore of spent FCC catalyst [Vitolo et al., 2001]. On the contrary, naphthene product was produced more on the non-catalytic degradation processes. This seems to be formed from the cyclization of paraffin and olefin intermediates that is mainly produced by pyrolysis of polyolefinic plastics [Lee and Shin, 2003]. Moreover, in case of waste HDPE (Fig. 3(b)) the catalytic degradation process showed much more olefin and less paraffin products than the non-catalytic degradation process. Here, the cracking reaction by using spent FCC catalyst was more accelerated into light olefin products from heavy straight hydrocarbon intermediates.

Liquid PONA distribution over waste PP is shown in Fig. 3(c). Among polyolefinic polymers, waste PP showed highest olefin fraction in the non-catalytic degradation at 400 °C by more cracking into light olefin product, due to the lowest degradation temperature in polyolefinic polymer as the result of the TGA analysis appearing in Fig. 1. This gave roughly a similar result to that of the catalytic degradation process. However, catalytic degradation showed a little higher fraction of liquid olefin and aromatic products than non-cat-

alytic degradation, like those of waste PE. Thus, the main reaction in the catalytic degradation of polyolefinic polymer using spent FCC catalyst seemed to be the following: straight hydrocarbons are cracked into olefin and paraffin products and moreover into light olefin products by more cracking of olefin and paraffin intermediates, and also the improvement of aromatics is caused by cyclization of straight intermediates.

In the case of waste PS with polycyclic structure as shown in Fig. 3(d), the liquid product over both non-catalytic and catalytic degradation was mostly the aromatic components with above 95% fraction in PONA distribution, whereas other components showed very low fraction with below 5%. It means that the degradation of PS by either non-catalytic or catalytic degradation was mostly cracked into aromatic components by means of end-chain scission mechanism. These tendencies in PONA distribution were clearly different from those of polyolefinic polymer described previously.

3. Carbon Number Distribution

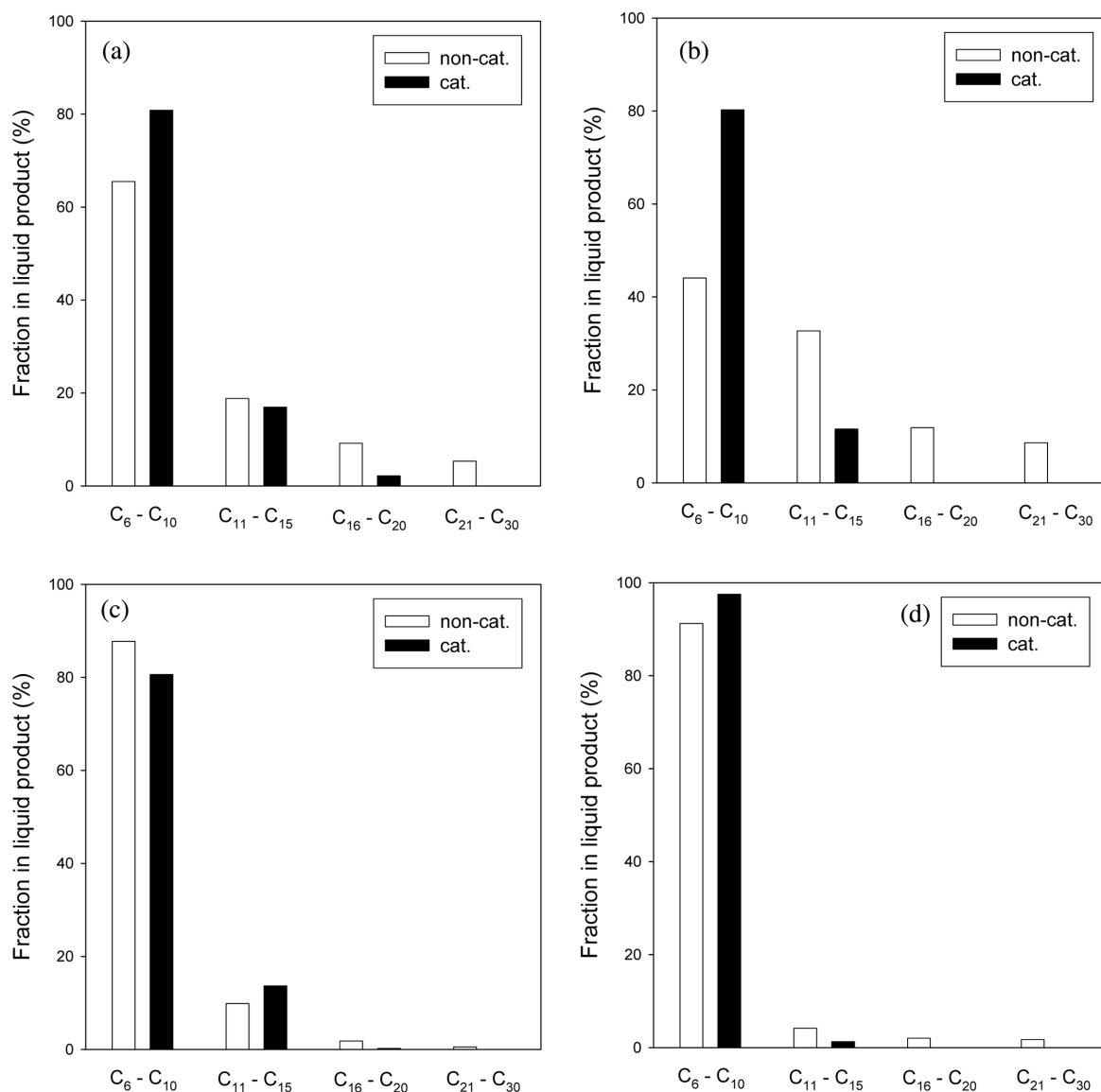Carbon number distributions of liquid products obtained from

Fig. 4. Carbon number distribution of liquid product on non-catalytic (white) and catalytic (black) degradation of waste LDPE (a), HDPE (b), PP (c) and PS (d) at 400 °C.

non-catalytic and catalytic degradation of waste plastics are shown in Fig. 4. Main products were gasoline-range products with below 10 of carbon number in whole range of carbon number. For a comparison of non-catalytic and catalytic degradation of waste LDPE (Fig. 4(a)), catalytic degradation showed much larger light liquid product and much less heavy liquid product than non-catalytic degradation. As the light liquid products, the gasoline-range products were increased from about 65% fraction in non-catalytic degradation to about 80% fraction in catalytic degradation. These indicated that catalytic degradation has a short carbon number distribution with below 20 of carbon number, whereas non-catalytic degradation has a wide carbon number distribution with up to 30 of carbon number. This tendency was very similar to the case of waste HDPE, as shown in Fig. 4(b), as long as the trend of carbon number distribution was considered. However, the gasoline-range products over waste HDPE were much increased from about 40% to about 80%, when spent FCC catalyst was added in the degradation process of

waste HDPE. It should be pointed out that the addition of spent FCC catalyst in the non-catalytic degradation process has a good effect on the carbon number distribution of liquid products for obtaining light liquid products with high quality. From the carbon number distribution, the degradation mechanism of both waste LDPE and HDPE was a similar random scission reaction, under either the catalytic or non-catalytic degradation process.

Also, Fig. 4(c) shows carbon number distribution of liquid products for non-catalytic and catalytic degradation of waste PP. Among polyolefinic polymers, PP showed clearly a difference in carbon number distribution of liquid products as a comparison of those of waste LDPE and HDPE. Liquid products over waste PP showed mainly a gasoline-range product with below 10 of carbon number in both the non-catalytic and catalytic degradation process. Their fraction showed above 80% in liquid product. Because waste PP had lowest degradation temperature in polyolefinic polymers as analyzed by TGA, it was easily degraded into light liquid product at

Table 3. Carbon number distribution of liquid products obtained on non-catalytic and catalytic degradation of PS at 400 °C

Carbon number	Non-catalytic process	Catalytic process
C_6	-	2.03
C_7	11.03	8.95
C_8	69.71	75.13
C_9	10.24	10.67
C_{10}	0.26	0.73
C_{11}	0.07	0.17
C_{12}	0.17	0.14
C_{13}	0.15	0
C_{14}	0.15	0.97
C_{15}	3.64	0
$>C_{16}$	3.79	0

degradation temperature of 400 °C under either the non-catalytic or catalytic degradation process. However, the catalytic degradation of waste PP using spent FCC catalyst showed much shorter carbon number distribution of liquid product up to 15 of carbon number than the non-catalytic degradation process. These indicated that spent FCC catalyst was suitable for catalytic degradation of polyolefinic polymer, in order to obtain light hydrocarbon products.

For waste PS with a polycyclic structure, the carbon number distribution of liquid product over non-catalytic and catalytic degradation processes is shown in Fig. 4(d). Their characteristics had a similar trend for gasoline-range products with above 90% fraction as a main product. Moreover, the fraction of C_8 components in liquid products showed high values with about 70% and 75% in the non-catalytic and catalytic degradation process, respectively. Thus, the monomer may be recovered from either the non-catalytic or catalytic degradation of waste PS, which occurred by the end-chain scission mechanism. However, a different trend was observed by two cases, i.e., producing much larger heavy product and lower fraction of C_8 components in the non-catalytic degradation process, as shown in Table 3, than the catalytic degradation process. This implies that non-catalytic degradation of PS with cyclic structure was much changed by the polymerization of one benzene ring intermediates into heavy products with above two benzene rings, as a high fraction of 3.64% C_{15} and 3.79% $>C_{16}$ components in the non-catalytic degradation process. However, in the case of the catalytic degradation process the heavy products that consist of C_{15} and $>C_{16}$ components scarcely appeared by more cracking of heavy intermediates. As followed, C_7 and C_9 components in two cases were present with about 10% selectivity, respectively.

CONCLUSIONS

The characteristics of liquid product obtained over the non-catalytic and catalytic degradation of waste plastics using spent FCC catalyst were investigated by using a stirred semi-batch reactor at 400 °C.

For the cumulative distributions of liquid products, waste PE (HDPE and LDPE) with relatively high degradation temperature by TGA analysis was fast degraded to the liquid product by high cracking ability in the presence of spent FCC catalyst, compared to

that of the non-catalytic degradation process. However, waste PP and PS with low degradation temperature did not find a great difference in both non-catalytic and catalytic degradation processes, due to sufficient degradation at 400 °C.

Compared with non-catalytic degradation, the catalytic degradation of polyolefinic polymer using spent FCC catalyst produced much more light olefin product (above 50% for LDPE, above 80% for HDPE and PP) with below 15 of carbon number by more cracking of heavy straight hydrocarbons, whereas the amount of paraffin and naphthene products was much decreased. Also, light aromatic products were improved by cyclization of light olefin as shape selectivity in micropores of spent FCC catalyst. However, for waste PS with cyclic structure, the characteristics of the liquid product produced by end chain scission mechanism in the degradation were not much altered with or without spent FCC catalyst, in which aromatic products with mainly one benzene ring were above 95% fraction. However, the C_8 aromatic components in catalytic degradation (about 75%) showed a little higher selectivity than that of non-catalytic degradation (70%). It is followed by C_7 and C_9 components with about 10% selectivity, respectively.

It is concluded that the utility of spent FCC catalyst in degradation process of waste polyolefinics has improved the rate and quality of liquid product, and moreover could significantly reduce the cost of catalyst, which leads to economically advantageous process.

ACKNOWLEDGMENT

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