

Thermal Degradation of Plastics into Fuel Oil by a Continuous Flow-Carberry Reactor

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Introduction

Catalytic degradations of plastics (polyethylene, polypropylene and polystyrene) were carried out in a continuous flow stirred tank reactor in the presence of silica-alumina to investigate the effect of catalyst on the product distribution and the volatilization rate.

Plastics were fed into the reactor, in which a catalyst cage is installed, by using an extruder in the range of feed rate 0-1.5 kg/h. This reactor system was able to attain a steady state without any appreciable accumulation of residual substance.

It was found that the silica-alumina catalyst had a remarkable effect on the product distributions, while not on the volatilization rate of plastics.

Experimental

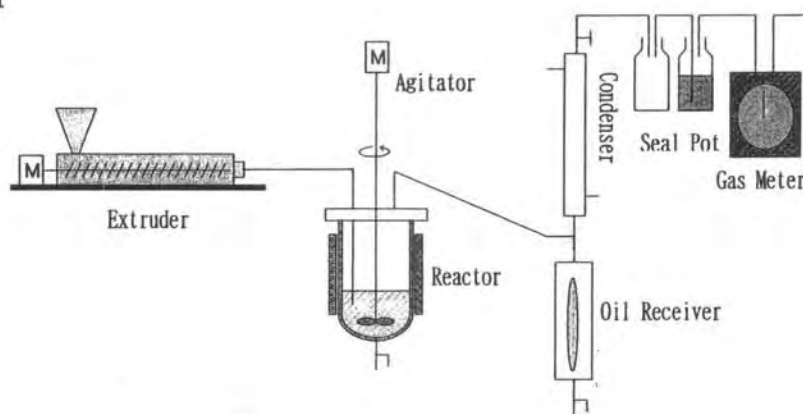


Fig.1 Experimental Setup

Fig.1 shows the experimental apparatus for thermal degradation of plastics.

Plastics are fed into the reactor by using a extruder in the range of feed rate 0-1.5 kg/h. Fig.2 shows the catalyst cage which is installed in the reactor. This reactor system can attain a steady state without any appreciable accumulation of residual substance.

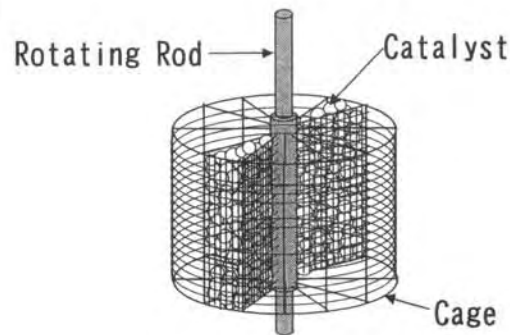


Fig.2 Catalyst Cage

Results and Discussion

Gaseous Product :

Fig.3 and 4 show the yield and the average molecular weight of the gaseous product from the thermal degradation of PE. As can be seen , both of them increase linearly with the amount of catalyst charged in the reactor.

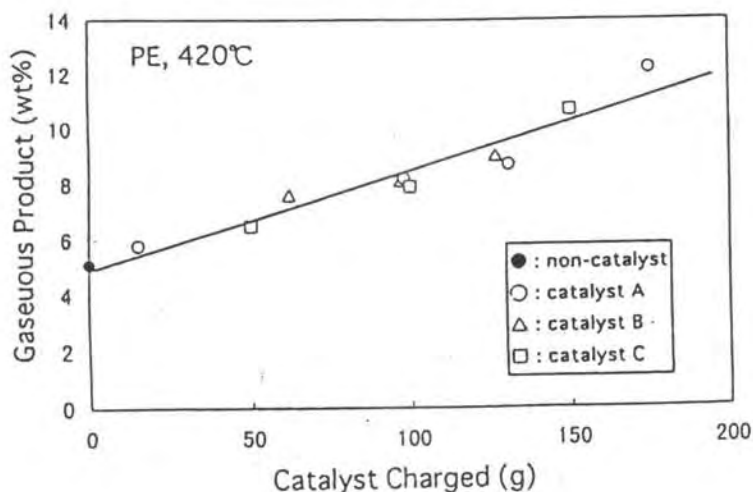


Fig.3 Yield of Gaseous products

The carbon number distributions of the gaseous products (Fig.5) shows that the profile shifts to the higher carbon number side with increasing the amount of catalyst. The gaseous products from the thermal degradation of PE are mainly C3 (propane and propylene), C2 (ethane and ethylene) and a small amount of C4 (butane and butene) component. In catalyst degradation, the content of C2 and C3 decreases and that of C4 and C5 increases significantly.

Previously, we have reported [1] that the decrease of C2 component and the increase of C4 component in the gaseous product is a special feature of the solid -acid -catalyst degradation of PE.

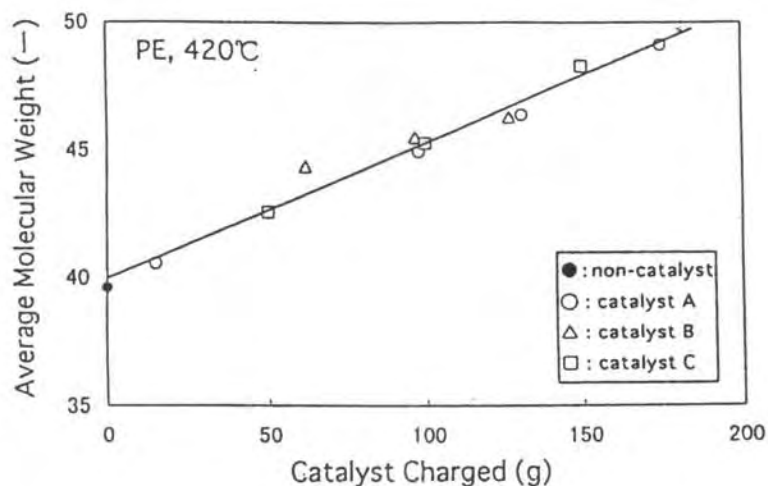


Fig.4 Average Molecular Weight of Gaseous Product

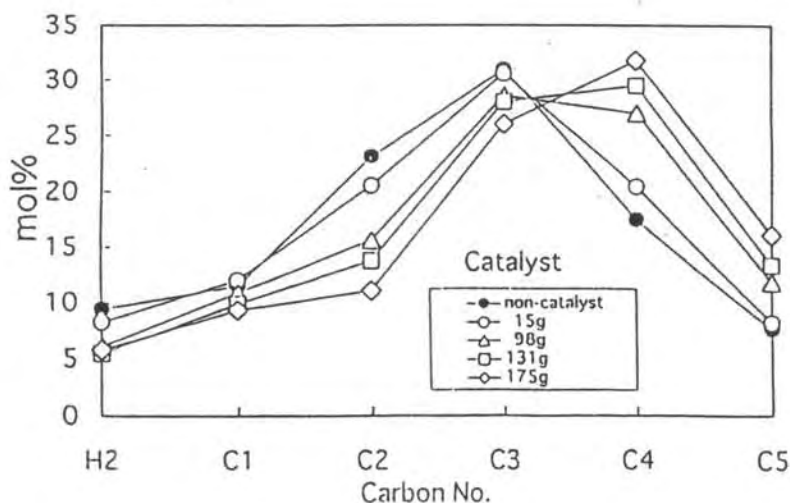


Fig.5 Carbon Number Distribution of Gaseous Products, PE/420°C

Liquid Product :

The average carbon number of the liquid products is shown in Fig.6 and the carbon number distributions of the liquid products from PE degradation in Fig.7.

For the thermal degradation of PE, the liquid products are distributed over wide range of carbon number (C4-C30), which is equivalent to boiling point ranges of 36 to 370°C. In the case of catalyst degradation over silica-alumina, the weight fraction of lighter hydrocarbons (C4-C10) increased and that of heavier hydrocarbons (>C12) decreased. As a result, the average carbon number of liquid products decreases with the amount of catalyst.

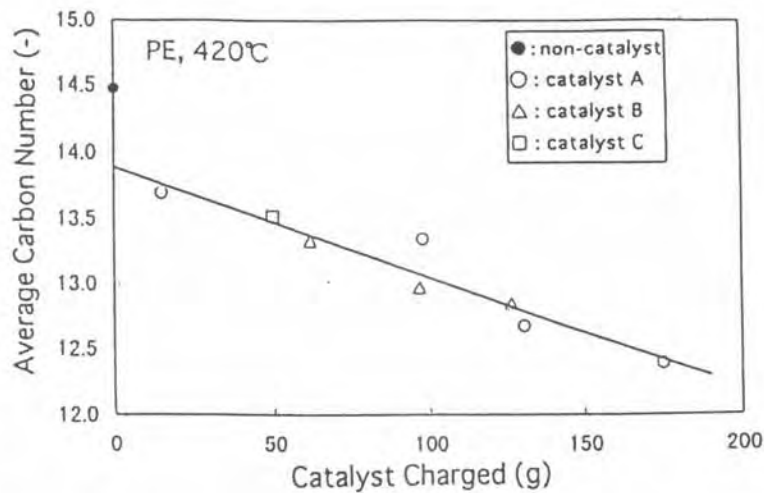


Fig. 6 Average Carbon Numbers of Liquid Products

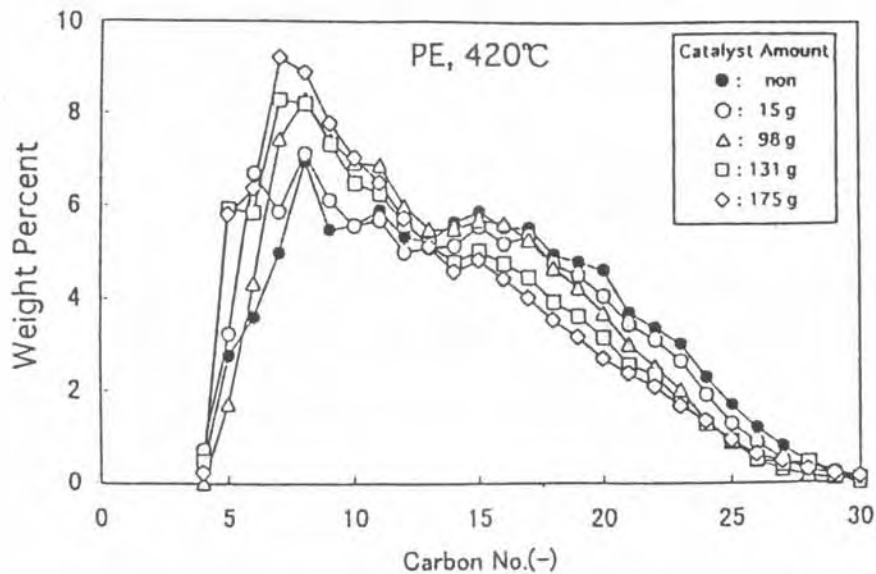


Fig.7 Carbon Number Distributions of Liquid Products

Reaction Rate :

The rate of volatilization of PE degradation at 420°C are shown in Fig.8 for various amount of the catalyst charged.

Surprisingly, the silica-alumina catalyst does hardly affect the rate of volatilization, even though it has an remarkable effect on the product composition for PE degradation.

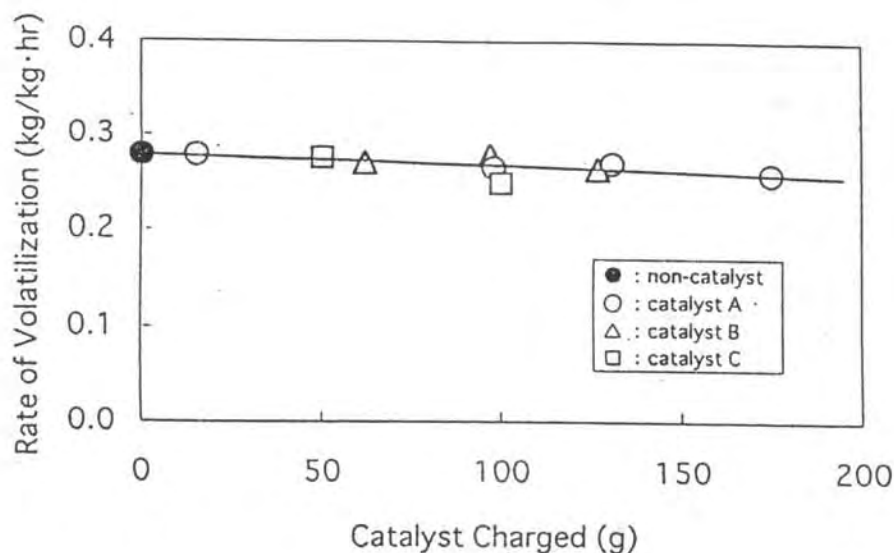


Fig.8 Rate of Volatilization, PE/420°C

Mechanismic Consideration of Polymer Degradation in the Presence of Catalyst :

The silica-alumina catalyst has a remarkable effect to change the carbon number distributions of gaseous and liquid products, while it does not increase the volatilization rate in the thermal degradation of PE. These results suggest that two kinds of scission occur simultaneously in the thermal degradation of polyethylene. One is non-catalytic random scission and the other is catalytic chain end scission.

Almost same results were found in the case of thermal degradation of polypropylene and polystyrene.

It should be concluded from Fig. 9 that the silica-alumina catalyst in the molten-degrading polymer accelerates the rate of chain end scission, but not that of random scission. As a result, the rate of volatilization can be controlled.

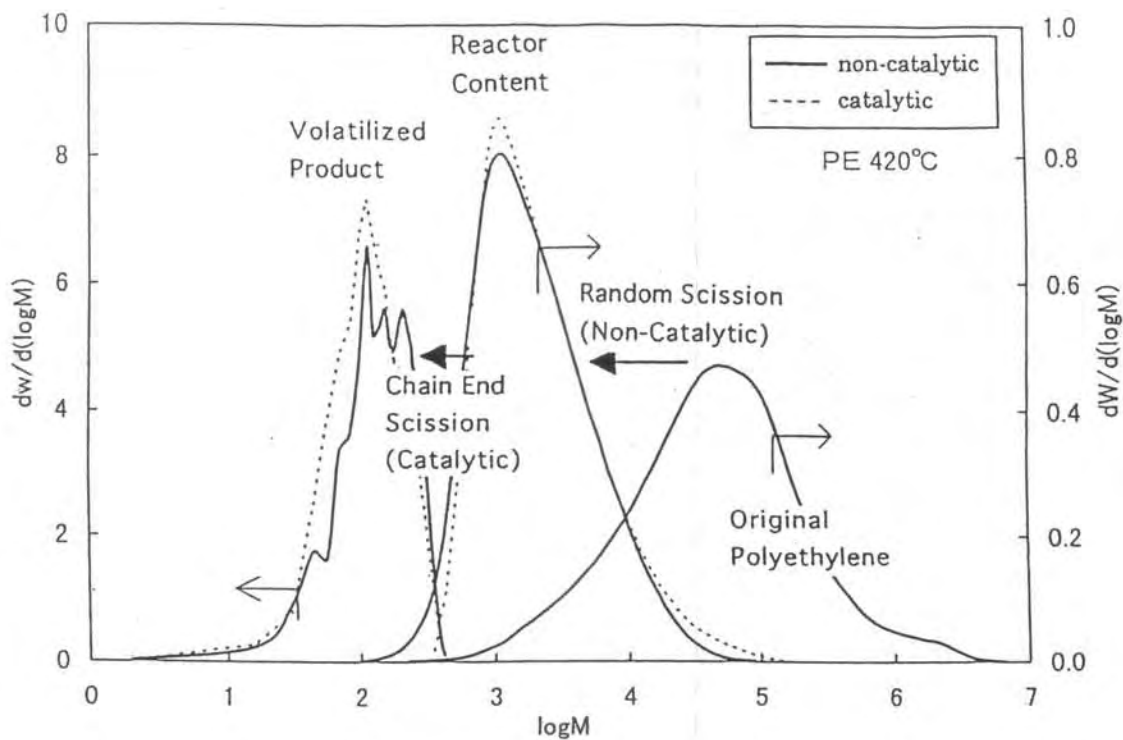


Fig.9 Molecular Weight Distributions of Original Polyethylene and its Degradation Products

References

1. M.A.Uddin, K.Koizumi, K.Murata and Y.Sakata, *Polym. Degrad. Stab.*, **56**, 37(1997)

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Smart and Tender-to-nature Oil-production from Waste Plastics via Novel System ; KTO

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To establish the stable, tender-to-nature and economical oil-production from waste plastics by means of thermal decomposition, we are now developing the novel system <KTO>. Firstly, the main reactions are set simpler. Melting waste plastics, de-hydrochlorination and decomposition proceed stepwise in only one vessel. The waste plastics are heated by the hot reactor content, by hot flow through the shell-heat-exchanger and by hot gas injected. The appropriate reaction field is prepared by the reactor content left in the vessel. The stepwise (not continuous) reactions in one vessel, the milder heating method and the appropriate reaction field are smart and effective to process the mixed plastics. Secondly, the process flow and the heating method in the decomposition are nicely developed. The ejector is the simple and effective apparatus to draw off the product gas and to inject it into the atmospheric-pressure still. The boiling-point width of the light product oil is so narrow to be easily heated to gas and to be easily over-heated with no coke formation in the furnace tubes. The over-heated gas heats the reactor content for the decomposition reaction without any liquid formation by heat-release, as a result that the system in the reactor is kept stable in the decomposition reaction. Thirdly, the whole process is set simpler. It works well to process the mixed waste plastics including some contaminant, to prevent coke formation and to avoid plugging-up troubles, with the result that the stable, safer and economical oil-production is attained. Lastly, no chlorine is purged out to nature or to the products. The chlorine is mainly removed in the reaction vessel and is recovered as hydrochloric acid. The chlorine left in the product flows is removed by alkaline solution and by the newly developed catalyst. We believe that these improvements in the main reaction, the process flow, the heating methods and the dechlorination will give us the smart and tender-to-nature oil-production from waste plastics.

Introduction

The stable, tender-to-nature and economical oil-production from waste plastics by means of thermal decomposition is useful to preserve natural resources and to keep nature clean. To realize this desire, we are now developing the novel oil-production system <KTO>.

Materials and Methods

Many test units were constructed. Samples (plastics pellets or waste plastics) with the small size of 5~20 Kg were thermally decomposed. Modified reaction schemes and/or new catalysts were tested.

Results and Discussions

Novel oil-production system. We are now developing the novel oil-production system <KTO>, as shown in the following figure.

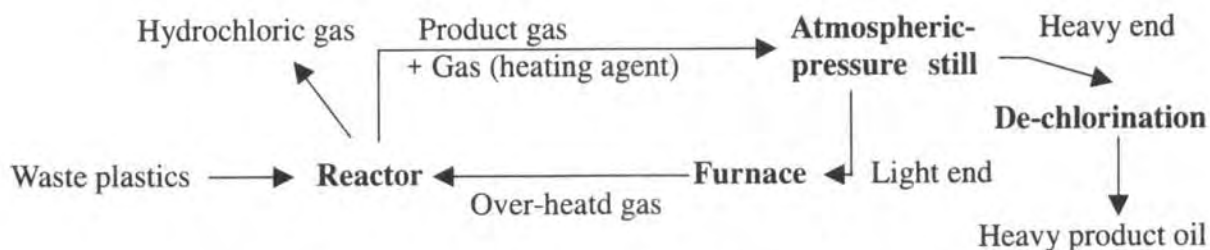


Figure 1 Flow diagram of the novel oil-production from waste oil

Main reactions. The preparatory step is leaving the hot reactor content. The hot ($\sim 400^{\circ}\text{C}$) reactor content of larger volume is left in the vessel after finishing the previous batch. The first step is melting waste plastics. The charged waste plastics are heated by the hot reactor content left and are melted in the vessel. The second step is heating for de-hydrochlorination. The reactor content ($200\sim 250^{\circ}\text{C}$) is heated by hot flow through the shell-heat-exchanger up to 300°C . The third step is de-hydrochlorination. The chlorine in the reactor content is removed as hydrogen chloride. The fourth step is heating for decomposition. The light product oil is heated by the furnace and is converted to the over-heated gas. The reactor content is heated by the hot-gas injection up to $420\sim 450^{\circ}\text{C}$. The last step is decomposition. The reactor content is decomposed and is converted to the gas, where the temperature is kept by the hot-gas injection.

Improvements in the main reactions. The main reactions are designed to keep the high efficiency and to avoid any process troubles, where the three improvements are introduced. <Stepwise (not continuous) reactions in one vessel> Continuous treatments in serial vessels work well for many processes. However, the process fluctuations can be amplified, and the fatal damages can be resulted in the continuous reactions of the oil-production. So, stepwise (not continuous) reaction in one vessel is applied for our system. Melting of waste plastics, de-hydrochlorination and decomposition proceed continuously in our system. As a result, any fluctuations are not amplified and any trouble are avoided. <Applying the milder heating methods> The charged waste plastics are heated mildly because of the smooth heat transfer from the liquid (= the reactor content). The larger heat-flux was given to the reactor content mildly by the hot-gas injection. Any coke-deposition troubles are avoided by the milder heating methods. <Preparing the appropriate reaction field> Some troubles (plugging-up, etc) can occur in the main reactions (de-hydrochlorination and decomposition), where the higher temperature and the larger heat-flux are necessary. In our improved scheme, the main reactions are conducted in not-so-viscous liquid, which is the reactor content left in the vessel. As a result, the reactions are smoothly conducted and any troubles are avoided.

Process flow and heating method in the decomposition. The decomposed product gas flows through the ejector into the atmospheric-pressure still. The light product oil is heated by the heat-exchangers and the furnace, and is converted to the gas, which is injected into the reactor to heat the reactor content for the decomposition reaction.

Improvements in the process flow and the heating method. The ejector is the simple and effective apparatus to draw off the product gas and to inject it into the atmospheric-pressure still. The product gas flows so fast to minimize the time of the chlorine recombination. The boiling-point width of the light product oil is so narrow to be easily heated to gas and to be easily over-heated with no coke formation in the furnace tubes. The over-heated gas heats the reactor content for the decomposition reaction without any liquid formation by heat-release because of its narrow boiling-point width, as a result that the system in the reactor is kept stable in the decomposition reaction.

Process flow. The whole process is set simpler. The number of the vessels, the lines and the others are cut to the minimum. They are simply designed. The feeder, the reaction vessel and the outlet ejecting the reactor content (to keep the coke content in the not-so-high level) are designed with the highest simplicity. Especially, the outlet is carefully designed to avoid the plugging-up troubles.

Improvements in the process flow. The simplified process flow works well to process the mixed waste plastics including some contaminant and to avoid any coke-depositions or any plugging-up troubles. As a result, the stable, safer and economical oil-production is attained.

Dechlorination. Three-step dechlorination is conducted. (1) The chlorine in the reactor content is mainly removed as hydrogen chloride in the reaction vessel and the hydrogen chloride in the gas flow is removed by alkaline solution. (2) The product gas is quickly cooled by alkaline solution. As a result, the time of the suitable temperature for the hydrogen chloride recombination is cut to the minimum. In the same time, the hydrogen chloride in the flow is removed by the alkaline solution. (3) The little chlorine in the product is removed by the newly developed catalyst.

Careful treatments in the dechlorination. The oil-production in KTO has no oxygen in the reaction atmosphere, producing no dioxin. No chlorine is purged out to nature, which is kept clean. No chlorine is purged out to the product fuels, which are burned without any pollution. These are nicely tender to nature and to our lives.

Conclusions

We believe that these improvements in the main reaction, the process flow, the heating methods and the dechlorination will give us the smart and tender-to-nature oil-production from waste plastics. We are now planning to construct the actual plants of this novel system <KTO> until March, next year.