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PYROLYSIS OF PLASTIC WASTES USING THE NON-CATALYTIC HAMBURG-PROCESS AND A CATALYTIC PROCESS USING THE CYCLED-SPHERES-REACTOR

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Abstract : Mixed waste plastics from the DSD (Duales System Deutschland) were degraded by the Hamburg-Process using a fluidized-bed. The experiments purposed to obtain oils and heat-providing gas. Experimental results from the laboratory-scale- and pilot-scale- Hamburg Process were compared and analyzed. The most important products were BTX and styrene. On the other hand, a commercially available sample of polyethylene was decomposed over zeolites in the cycled-spheres-reactor. In the experiments, Y-type zeolites showed lower activity and higher deactivation than H-ZSM-5. H-ZSM-5 and Y-type zeolite of higher module showed less deactivation, but lower activity than those of lower module.

Key Words : Pyrolysis, BTX-aromatics, Zeolite, Fluidized-bed, Cycled-Spheres-Reactor

INTRODUCTION

Waste plastics, which have been usually disposed on landfill sites or utilized energetically, for instance, incineration, have caused so many problems. In order to solve such problems, many researchers have carried out intensive researches.[1-2] Modern Society, however, requires reasonable alternatives to cope effectively with needs for energy- and environmental conservation. Researchers consider the pyrolysis of plastic wastes to be an alternative. By the pyrolysis, plastic wastes can be converted into chemical feedstock which can be used to produce new valuable products such as oils and gases of high caloric value. Thermal degradation (pyrolysis) process can be divided into non-catalytic and catalytic. Non-catalytic process has some merits in relation to construction, operation and cost, although it has the disadvantage of high-energy demand. Therefore in this study I will compare experimental results from the non-catalytic Hamburg Process with those from a catalytic process using the cycled-spheres-reactor in relation to the product spectrum and energy consumption. Some reactors have been used in the non-catalytic pyrolysis of waste plastics[3-5], such as vessels, autoclaves, rotary kilns and fluidized bed. The Hamburg-Process uses a fluidized-bed reactor, and main research purposes of the process have been to obtain BTX, waxes and other petrochemicals.[6] This paper will show some experimental results using the laboratory-scale- and pilot-scale Hamburg-Process. The experimental results will show the

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characteristics of the non-catalytic pyrolysis of waste plastics. The goal of the experiments was to maximize the yield of oils, especially BTX, from mixed waste plastics with low amount of polyvinylchloride (PVC) from German household waste plastics which was supplied by the DSD. These experiments, especially the pilot experiment, would be a cornerstone to the way to commercializing the process.

Other aspect of the pyrolysis of waste plastics is the catalytic process. In relation to the catalytic process, fundamental research programs have been actively conducted in the United Kingdom and Japan.[7,8] In this paper, results from laboratory scale catalytic experiments with the cycled-spheres-reactor, which can be a further step to realize the chemical recycling of plastic wastes, are reported. The cycled-spheres-reactor is a new type of reactor for the treatment of waste plastics and is tested in these experiments to estimate whether this reactor can be applied in the catalytic pyrolysis of waste plastics, or not.

EXPERIMENTAL

Hamburg-Process for Non-catalytic Pyrolysis and the Laboratory Plant for Catalytic Process

Non-catalytic experiments were carried out in the laboratory scale- and the pilot- scale plant of the Hamburg-Process. Parameters of the experiments are listed in Table 1. In order to capture HCl produced during the experiments, lime was fed.

Figure 1 shows the flow scheme of the pilot plant of the Hamburg Process. Because the laboratory plant of the Hamburg Process is in

Table 1. Parameters of the experiments

Experiments	Lab.1	Lab.2	Lab.3	Tec. 1
Temperature ((C)	685	710	716	690
Residence time in reactors (s)	3	3	2	8
Amount of input (kg)	1.19	1.27	1.23	321
Duration (h)	2.83	2.67	2.3	22
Feed rate (kg/h)	0.42	0.47	0.53	14.6
Input of absorbent (g)	45	47	46	12000

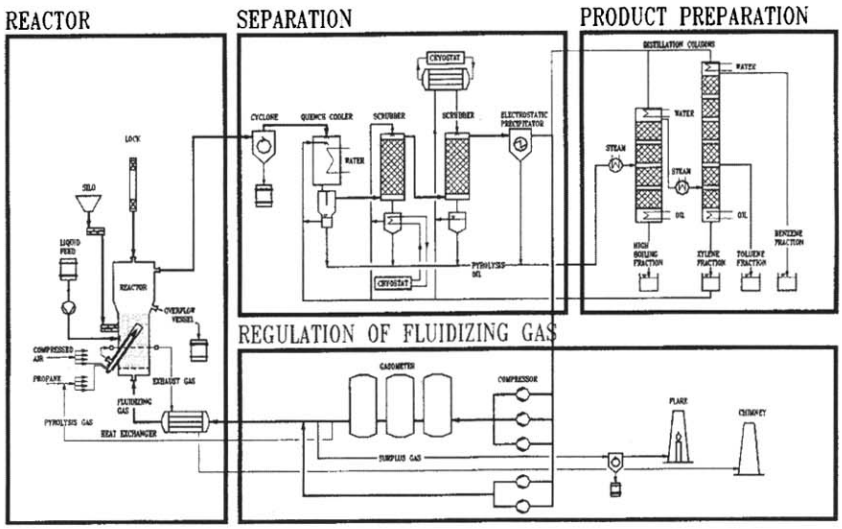

Figure 1. Pilot scale Hamburg-Process.

principle similar to the pilot plant, the flow scheme of the laboratory plant is omitted here. The Hamburg Process is composed of four parts, reactor, separation, gas regulation and product separation. The reactor is made of stainless steel and composed of three parts. The lower part has a diameter of 0.45 m and a height of 0.65 m. The middle part has an overflow vessel connector. Diameter and height of the upper part are 0.6 m and 1.08 m, respectively. The separation section contains a cyclone, quench coolers, scrubbers and electrostatic precipitator. After product gas is quenched into oils, the remaining gas is circulated into the reactor by a compressor.

A schematic diagram of the laboratory plant for the catalytic process is shown in Figure 2.

The main part of this apparatus is the cycled-spheres-reactor with a volume of 1.5 l. Spheres circulating in the reactor provide a good heat transfer to plastics and high viscous molten plastics, which enables chemical reactions to take place in thin films on the surface of spheres.

In the experiments, 150 g of granulated PE was fed into the reactor where 5 g of catalyst were charged before the experiments and metal spheres (200-500 pieces) were circulated by a rotating conveyor screw. And then reactions took place at a temperature of 440°C. Reaction time lay between 20 (with catalyst) and 60 (without catalyst) minutes. Product gas was quenched by a series of quencher. Product gas was quantitatively analyzed on-line by a GC and qualitatively by a GC-MS system. Product oils were distillated, and then were analyzed by a GC and a GC-MS system. N_2 as an inert gas was fed continuously.

Feed Materials and Catalysts

In the Hamburg Process, a fraction of mixed waste plastics from the DSD was fed. The composition is listed in Table 2.

A commercially available pure sample of middle density polyethylene granule, diameter of which was about 4 mm, was used in the catalytic experiments.

Table 3 describes the catalysts applied in the experiments. From Alsi-Penta Zeolite, H-ZSM-5 was supplied, and Y-type zeolites from Degussa AG

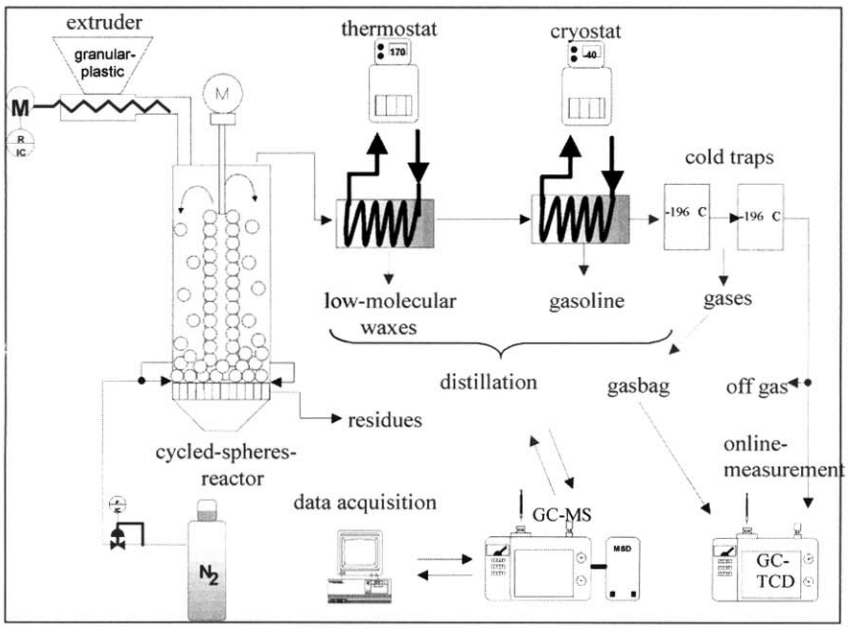

Figure 2. Schematic diagram of the experimental set-up.

Table 3. Specifications of catalysts

Type of zeolite	Trade name	Module (Si/Al)	Crystallite size [μm]	Pore size[Å]
H-ZSM-5	SM 27[1)]	22	1-3	5.4×5.6
H-ZSM-5	SM 55[1)]	46	3-5	5.4×5.6
H-Y	HY 8	5.9	≈0.5	7.4
H-Y	HY 26[2)]	26	≈0.5	7.4, mesopores

1) prepared without template
2) steamed HY zeolite

Table 2. Composition of the mixed waste plastics from the DSD (wt%)

Composition	wt%
Polyolefines	65
Polystyrene	14
PVC	3.8
Polyester/paper	7.2
Other plastics	2.0
Water	4.0
Fillers, metals	4.0

Analysis

In each experiment gas, oil and solid residue were obtained as products. A representative sample of oils was distilled in a bench-scale apparatus (210°C, 13.3 kPa in the case of non-catalytic product oil and 170°C, 10 kPa for catalytic product oil) to obtain a light fraction of oil and a distillation residue. The gases and oils were analyzed by a GC and a GC-MS system. All the products obtained in the experiments were subjected to elemental analysis. In addition, the content of metal and chlorine were determined.

RESULTS AND DISCUSSION

Non-catalytic Pyrolysis Experiments

Non-catalytic pyrolysis experiments have been carried out with the Hamburg Process. The mass balance is shown in Table 4, referring to the total organic input. The amount of product oil reaches up to 48wt%. The sum of BTX is about 20wt%. In the laboratory experiments, the amount of gas is increased with the reaction temperature. In Lab.3, the reduced amount of gas can be explained by the shorter residence time. The effect of residence time can be seen by the comparison between the laboratory-scale- and the pilot-scale-experiment. Under longer residence time, the amount of thermodynamically stable components, such as methane and hydrogen, increases in the product gas. This tendency appears also, as the reaction temperature goes higher. Product gas consists chiefly of methane, ethane and propene. Plastics containing oxygen element, such as polycarbonate and PET, is likely to contribute to the production of carbon monoxide and carbon dioxide. The gas produced in the experiments has a caloric value between 45 and 50MJ kg^{-1}.

The main product was pyrolysis oil. The amount of pyrolysis oil and BTX increases, as reaction temperature goes up. However, styrene concentration decreases, as reaction temperature rises. Styrene is formed mainly from polystyrene. As a whole, the amount of highly aromatized compounds goes higher at higher reaction temperatures. The effect of residence time on the production of oil can be seen from the comparison between Lab. 1 and Tech. 1, although the reaction temperature between two experiments are a little different. The residence time in Lab. 1 was 3.2 seconds and that in Tech. 1 was 7.9 seconds. As the residence time in the reactor increases, aliphatic components are subject to split into small molecules, therefore into gases. In the gas products, thermodynamically stable components prevail. In addition, the longer residence time in the pilot plant leads to higher condensed aromatics.

Elemental analysis of distillation residues was

Table 4. Mass balance of the experiments

Experiment	Lab.1	Lab.2	Lab.3	Tech.1
Temperature (°C)	685	710	716	690
Residence time (sec.)	3.2	3.0	2.3	7.9
Total Gases	**41**	**44**	**43**	**43**
Hydrogen	0.4	0.5	0.6	0.5
Carbon monoxide	4.6	5.5	6.0	4.7
Carbon dioxide	2.0	2.5	1.7	2.2
Methane	10.9	12.3	16.2	14.2
Ethene	8.6	8.9	10.1	10.7
Ethane	4.0	3.9	3.3	4.5
Propene	6.3	6.0	3.2	4.5
others	4.2	4.4	1.9	1.8
Total Oils	**48**	**44**	**45**	**41**
Aliphatic oils	8.0	6.5	2.7	3.3
C5-C6 Hydrocarbon	5.7	4.9	2.2	2.9
C7-C9 Hydrocarbon	2.3	1.6	0.5	0.4
BTX-aromatics	16.8	17.5	19.3	18.7
Benzene	9.5	10.8	14.0	11.6
Toluene	6.7	6.1	4.8	5.9
Xylene	0.6	0.6	0.5	1.2
Other aromatics	14.5	13.8	18.3	15.4
Ethylbenzene	0.9	1.0	0.9	0.8
Styrene	9.0	7.9	6.8	6.4
Methylstyrene	1.4	1.1	1.5	1.2
Indene	0.6	0.8	2.1	1.1
Naphthalene	0.8	1.2	4.2	2.8
Methylnaphthalenes	0.3	0.4	0.5	1.1
others	1.5	0.6	2.3	2.0
Nitrogen compounds	0.02	0.1	0.01	0.01
Oxygen compounds	0.1	0.3	0.01	1.1
Other compounds	8.1	5.8	5.0	2.4
Distillation residue	**5.4**	**5.6**	**6.3**	**10.8**
Soot	**5.2**	**6.4**	**5.7**	**4.8**

conducted. The C/H ratio lay between 0.7 and 1.1. It shows that a highly aromatic character of a residue can be obtained, as reaction temperature rises, and therefore that product oils can contain more aromatic compounds, including BTX at higher temperature. The distillation residue in Tech. 1 showed more aromatic characteristics than that in Lab. 1, which can explain the formation of higher condensed aromatic components at longer residence time in the reactor, in spits of a little higher reaction temperature in Tech. 1.

In order to avoid the corrosion by chlorine during pyrolysis, the amount of chlorine in products, especially in product oils, must be low. The demand from petrochemical industries on the chlorine content of product oils is under 10 ppm. In order to capture HCl generated from PVC in the mixed waste plastics, lime was fed with plastic wastes. Lime conducts a reaction as follows:

$$CaO + 2\ HCl \rightarrow H_2O + CaCl_2(\downarrow)$$

Table 5. Distribution of chlorine over the products in Tech.1

Experiment	Tech.1 (m%)
Plastic wastes (input)	1.90
Oil	1.75 E-03
Dist. Residue	0.02
Soot	11.30
Bed material	0.28
Water	1.00 E-03

Table 5 shows the distribution of content of chlorine in products for Tech.1. Most of chlorine was found in the distillation residue and soot, which can easily be separated and disposed. The product oil contains about 18ppm of chlorine. This is not far from the demand from petrochemical industries. One method to use the pyrolysis oil will be the mixing of the oil with fresh oils. The distribution of chlorine in products and the content of chlorine in product oils in the laboratory experiments were almost the same as those in Tech.1.

Product oils should be free of heavy metals, in order to avoid the deactivation of catalysts used in further treatments of product oils in petrochemical industries. In the experiments, they were found mainly in soot and sand bed. Product oils and even distillation residues were almost free of them.

Catalytic Pyrolysis Experiments using the Cycled-spheres-reactor

Experiments using catalysts were carried out at a weight ratio of 30:1 (plastics to catalyst) and at 440°C, and one non-catalytic experiment was performed at the same temperature using this system. The feed material was virgin polyethylene. The generation of oil- and wax product started 3-4 times earlier in the catalytic reactions than the non-catalytic reaction, which explains the reduction of activation energy by using catalysts.

Figure 3 shows the product distributions in the catalytic- and non-catalytic pyrolysis.

After degradation only small amount of reaction residue (under 0.5wt%) was found due to the pure PE which contains no filler and no pigments. In the non-catalytic pyrolysis, the main product was a wax fraction, the amount of which reached up to 66wt%. In the case of the catalytic pyrolysis, oil fraction was mainly obtained at the expense of wax fraction. H-ZSM-5 was more active than Y-type catalysts producing higher yield of lower molecules. This is mainly due to the stronger acidity of H-ZSM-5. The activity of the catalysts with lower module is higher than those with higher module. A lower module means a higher number of active acid

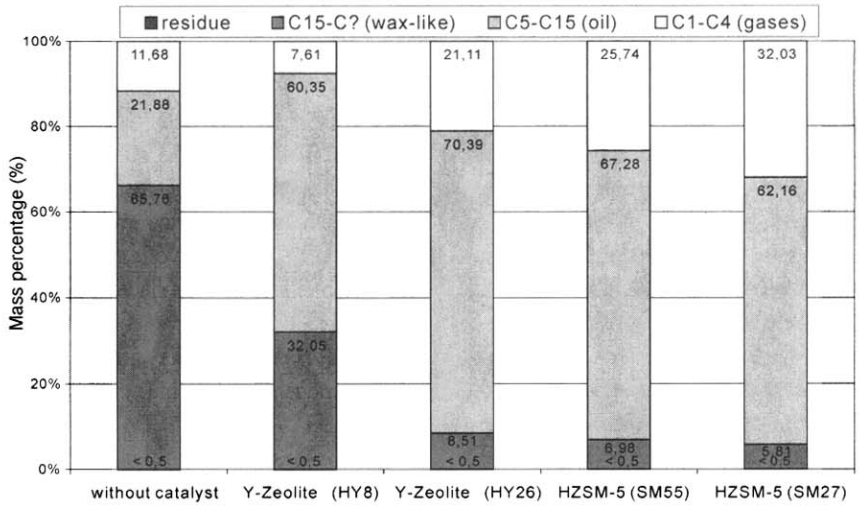

Figure 3. Product distribution over various catalysts at 440°C.

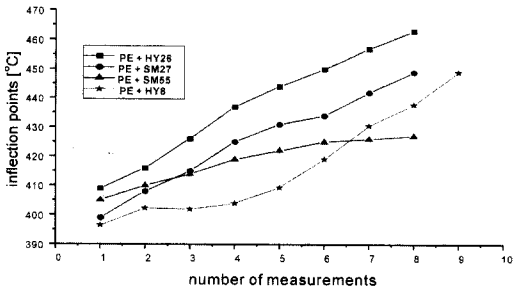

Figure 5. Deactivation behavior of several catalysts.

sites. Lower module of the catalyst has a positive influence on the production of gases. HY 26 was found the best based on the oil production, and the yield of oils sums up to 70wt%. Fig. 4 shows the deactivation behavior of several catalysts.

The inflection point is where the degradation of plastics begins. Y-type catalysts are apt to be coked due to their cage-type structure. In contrast, in the case of H-ZSM-5, which has a channel-like structure, there is not so much possibility of the trapping of cokes in the catalyst. Module has also an effect on the deactivation behavior of catalysts. If a catalyst has a small module, site density becomes large, and coke molecules can be formed more easily. Therefore the high yield of waxes with HY 8 results from its rapid deactivation.

GC-MS analysis of liquid products showed that catalytic pyrolysis produced a spectrum of lower carbon numbers. In the non-catalytic pyrolysis, the product spectrum was broad. Oils obtained by the pyrolysis with H-ZSM-5 were distributed predominantly between C5 and C6. The module of H-ZSM-5 seems to have little influence on the product distribution.

CONCLUSIONS

Non-catalytic and catalytic experiments were carried out to examine the possibility of the production of valuable chemicals (gases and oils) from post-consumed plastice. H-ZSM-5 was less deactivated, due to its channel-like structure. Catalytic pyrolysis revealed its advantage on the reaction temperature, and a specific spectrum could be obtained. By setting-up of the catalytic process, however, there were some problems, for instance, feeding of catalysts and process control. Non - catalytic process had advantage on such points.

The non-catalytic- and the catalytic process have their own merits and at the same time they are competitive. They can be applied in the pyrolysis of waste plastics, according to desired product spectrum.

REFERENCES

1. Menges, G., Recycling von Kunststoff, Hanser Verlag, Munchen, 1992.
2. Sutter, H., Erfassung und Verwertung von Kunststoff, EF-Verlag, Berlin, 1993.
3. Baumgaertel, G.J., *J. Anal. Appl. Pyrolysis* **27** (1993) 15.
4. Shelley, S., Fough, K., Moore, D., *Chem. Eng.* **7** (1992) 30.
5. Kaminsky, W., *Angew. Makromol. Chem.* **232** (1995) 151.
6. Kim, J. S., Ph. Thesis, D., University of Hamburg 1997.
7. Garforth, A. A., Lin, Y.-H., Sharrat, P. N., Dwyer, J., *Applied Catalysis A: General 169* (1998) 331.
8. Sakata, Y., Uddin, M. A., Muto, A., Kanada, Y., Koizumi, K., Murata, K., *J. Anal. Appl. Pyrolysis* **43** (1997) 15.