ELSEVIER

Chemical Engineering Journal 82 (2001) 173–181

Chemical Engineering Journal

www.elsevier.com/locate/cej

Chemical recycling of mixture of waste plastics using a new reactor system with stirred heat medium particles in steam atmosphere

Takao Masuda [a,*], Tatsuhiko Kushino [a], Toshihiro Matsuda [a],
Shin R. Mukai [a], Kenji Hashimoto [a], Shu-ichi Yoshida [b]

[a] *Division of Chemical Engineering, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan*
[b] *R&D Section, NGK Insulators Ltd., Maegata-cho, Handa, Aichi 475-0825, Japan*

Received 14 June 2000; accepted 9 October 2000

Abstract

A new reactor system was developed for recovery fuels from the waste plastic mixture in steam atmosphere. Firstly, the degradation mechanisms of eight kinds of plastics, two polyolefins (polyethylene and polypropylene), two polyamide resins (nylon-6 and nylon-6,6), polystyrene and three polyesters (polycarbonate, poly(butylene terephthalate) and poly(ethylene terephthalate), were investigated both in nitrogen and steam as the carrier gas. Plastics except for polyesters were degraded without any influences of the kinds of the carrier gas, leaving negligibly small amount of carbonaceous residue. Polyesters, which were degraded with producing large amount of the residue in nitrogen, were succeeded to be hydrolyzed at high reaction rates in steam with producing hardly the carbonaceous residue. Secondly, a mixture of the waste plastics was continuously degraded to produce heavy oil in steam atmosphere by using a new reactor system. This system was composed of three kinds of reactors connected in series. One was a reactor filled with stirred heat medium particles, which enabled the high heat transfer rate, the high holdup and the good contact of the melted plastics with steam. The second was a tank reactor. The last one was a fixed bed reactor with FeOOH catalyst particles, which showed the catalysis in steam for the decomposition both of a wax and sublimate materials generated by the degradation of plastics. Furthermore, the oil produced from the proposed reactor system was continuously upgraded to produce gasoline and kerosene over Ni-REY catalyst in steam atmosphere.

Keywords: Mixture of waste plastics; Chemical recycle; Iron catalyst; Fuels; Zeolite catalyst; Reactor system

1. Introduction

The amount of waste plastics discarded each year is constantly increasing and is causing serious pollution problems. If this material can be chemically recycled, this material will become a cheap and abundant source for useful chemicals and energy. Among various recycling methods, the chemical method which converts waste plastics to useful hydrocarbons, has been recognized as a promising approach. Presently, about half of the waste is generated from factories as specific plastics, such as polyolefins, polystyrene (PS), poly(ethylene terephthalate) (PET) and poly(vinylchloride) (PVC). Therefore, several studies on the individual degradation of each type of waste plastics have been reported. PS can be easily decomposed to yield aromatics [1–4]. There are many studies on the pyrolysis of PVC [2,3,5–9]. PET can be easily degraded by the hydrolysis in steam atmosphere, yielding an amount of pure terephthalic acid predicted from the chemical formula of PET [10,11]. The produced terephthalic acid could be reused as monomers for PET synthesis. Polyolefins, such as polyethylene (PE) and polypropylene (PP), were thermally pyrolyzed above 683 K, yielding hydrocarbons with carbon numbers ranging from 1 to 30 [2,3,12–14]. The obtained oil was mainly composed of aliphatic hydrocarbons, and can be converted to high quality gasoline over rare earth metal exchanged Y-type zeolite catalysts (REY) and Ni supporting REY [15–18].

Thus, on the basis of elemental technologies described above, the process could be designed for the chemical recycling of the specific waste plastics which are generated from factories.

The remaining half of the waste plastics is generated from household in the forms of a mixture of plastics and the waste containing kitchen refuse. Kaminsly et al. [19,20] reported that mixed plastics collected from the “Duales System Deutchland” with different contents of polyolefins, polyesters and polystyrene were pyrolyzed by use of a

---

* Corresponding author.
E-mail address: tako@cheme.kyoto-u.ac.jp (T. Masuda).

1385-8947/01/$ – see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S1385-8947(00)00347-8

Nomenclature

a	heating rate in the thermogravimetric analysis ($K\,min^{-1}$)
F	mass flow rate of feedstock ($kg\,h^{-1}$)
N6	nylon-6
N6,6	nylon-6,6
P_W	partial pressure of steam (Pa)
PBT	poly(butylene terephthalate)
PC	polycarbonate
PE	polyethylene
PET	poly(ethylene terephthalate)
PP	polypropylene
PS	polystyrene
T	reaction temperature (K)
W	mass of catalyst (kg)
x_A	conversion of feed oil
X	conversion of plastic resin
Y_B	yield of gasoline fraction
Y_G	yield of gaseous compounds
Y_C	yield of coke

fluidized bed to obtain aromatics in the temperature range from 958 to 1011 K. The yield of aromatics was 21 wt.%. However, a large amount of gaseous products was produced and the carbonaceous residue was left by 5.2–6.4 wt.%, because of the high reaction temperature. Bockhorn et al. [2,3] proposed the stepwise pyrolysis of waste plastics containing PVC to recover useful chemical. First, PVC was dechlorinated at 603 K, then remaining melted plastics were successfully pyrolyzed at 653 and 713 K by use of the circulated-spheres reactors.

PVC could be remove from the mixture of the waste by utilizing the higher density of PVC than other plastics. There are, however, some problems for realizing the chemical recycling of the mixture of remaining waste plastics. One is that each kind of plastics shows different pyrolytic properties, the other is that a large amount of terephthalic acid, which is sublimate material (sublimation point is equal to about 573 K) is produced from some plastics, such as PET. This is precipitated as hard solid body around valves and pipelines where temperature is below 573 K. One of similar materials to terephthalic acid is a thermoplastic, which is included in PVC.

We reported that PET can be successfully degraded by the hydrolysis in steam atmosphere, yielding an amount of pure terephthalic acid predicted from the chemical formula of PET, and leaving carbonaceous residue less than 1% [10] at 773 K. This result suggests that there is a possibility to make pyrolytic properties with a uniform reaction rate among oxygen-containing plastics and to degrade the plastics with minimal carbonaceous residue by changing the decomposition mechanism from the random scission of the main chain in nitrogen into the hydrolysis in steam. Phthalic acid produced by the hydrolysis would be successfully converted to fuels over FeOOH catalyst in steam atmosphere at 773 K [11]. Furthermore, from economical and energetic viewpoints, it is cheap and easy to employ steam as the carrier gas in chemical recycling plants.

The main objective of this study is to propose a chemical recycling method of the mixture of waste plastics. Firstly, the possibilities were examined to make pyrolytic properties with a uniform reaction rate among oxygen-containing plastics and to degrade the plastics with minimal carbonaceous residue. Secondly, a new pyrolytic reactor was proposed to realize the high holdup, the high heat transfer and the good contacting of melted plastics with steam for accelerating the hydrolysis. Using this reactor, a mixture of the waste plastics was degraded and understood further decomposition over FeOOH catalyst. Finally, the obtained oil was upgraded to fuels, such as gasoline and kerosene over Ni-REY catalyst [18]. On the basis of the experimental data, the validity of the proposed chemical recycling method was examined.

2. Experimental

2.1. Plastics

Eight kinds of plastics were used: PE (Mitsubishi Rayon Co. Ltd.), PP (Mitsui Chemicals), polycarbonate (PC) (Sumitomo Dow Ltd.), PET (Mitsubishi Rayon Co. Ltd.), poly(butylene terephthalate) (PBT) (Mitsubishi Engineering-Plastics Co.), PS (Electronic Chemicals Industry), nylon-6 (N6) and nylon-6,6 (N6,6) (Ube Kosan). Almost these plastics were obtained as particle with 2–3 mm in diameter. These particles were cut into particles of 1 mm in diameter, and used in the experiments.

2.2. Catalysts

FeOOH catalyst was found to show high activity for converting sublimate materials, such as terephthalic acid in steam atmosphere [10], and Ni-supporting rare-earth metal exchanged Y type zeolite (Ni-REY) effectively cracked heavy oil in steam atmosphere [18]. Therefore, these catalysts were employed in this work.

FeOOH (Nacalai Tesque Co. Ltd.) was pelletized, crushed and sieved to yield catalyst particles of 0.21–0.25 mm in size, followed by treating it at 773 K in steam atmosphere. REY catalyst was prepared from a NaY type zeolite (JRC-Z-Y4.8 supplied by the Catalysis Society of Japan) by a conventional ion-exchange technique using a solution of rare-earth metal chloride. Nickel was supported on the prepared REY by the ion-exchange technique using a solution of nickel chloride, yielding Ni-REY catalysts. The zeolite catalyst was pelletized, crushed and sieved to obtain particles with a size of 0.33 mm in diameter, before usage in the further experiments.

Physical and chemical structures of these samples were analyzed by X-ray diffraction apparatus (XD-610, Shimadzu Ltd.), a scanning electron microscope (S-510, Hitachi) and

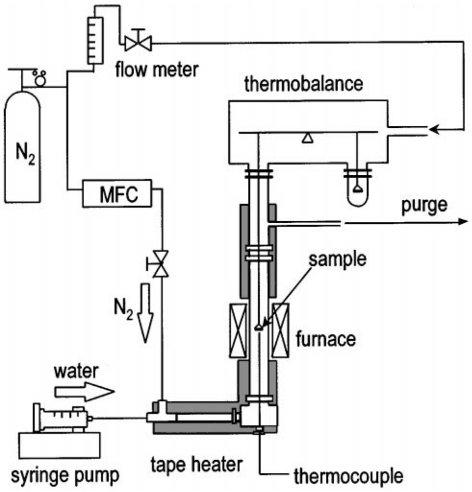

Fig. 1. Setup of thermogravimetric apparatus.

FT-IR (FTIR-8200P, Shimadzu Ltd.). Pores of these samples were observed using a transmission electron microscopy, TEM (JEM-1010, JEOL). The nickel content of Ni-REY was measured using an inductively coupled plasma analysis (ICPS1000, Shimadzu Ltd.), and was found to be 0.5 wt.%. The crystal sizes of the prepared catalyst samples were measured. The numbers of strong acid sites of the sample were measured by a new ammonia TPD method (*ac*-TPD), where the desorption of ammonia proceeds under complete adsorption equilibrium conditions [21].

2.3. Gravimetric analysis

The pyrolytic properties of plastics were investigated using a thermogravimetric apparatus equipped with a thermobalance (TG-31, Shimadzu Ltd.) as shown in Fig. 1. Plastic particles, weighing about 20 mg, were placed in a basket hanging from a thermobalance, and a mixture of steam and nitrogen was introduced as a carrier gas. The fraction of steam in the carrier gas was varied from 0 to 100%. Plastic particles were heated up to 900 K at different heating rates of 2.5, 5 and 10 K min^{-1}. The weight loss of plastics was continuously measured. In order to investigate the chemical structure of the plastics during degradation, when the conversion of the plastics reached 55%, the sample was cooled to room temperature. The chemical structure of the sample was then measured by FT-IR (FTIR-8200PC, Schimadzu Ltd.).

2.4. Continuous conversion of plastic mixture to fuels

2.4.1. Degradation of plastics

When the mixture of waste plastics was degraded by accelerating the hydrolysis of the plastics with steam and by decomposing the generated sublimate materials over FeOOH catalyst, the following reaction conditions are needed:

1. A good contact of melted plastics with steam to accelerate the hydrolysis of plastics.
2. Large rate of the heat transfer to heat plastics up to a desired temperature.
3. High holdup of plastics in a reactor to achieve an enough reaction time for degrading plastics.
4. Contact of vapor of sublimate materials with FeOOH catalyst to decompose the materials.

Bockhorn et al. [2,3] proposed the circulated-spheres reactors for the pyrolysis of waste plastics. This reactor enabled to remove gaseous products from the reaction zone and to achieve high heat transfer rates, namely the condition (2) described above. The concept of this circulated-spheres reactor has a possibility to attain the conditions (1) and (3) by improving the reactor.

In order to realize the above all requirements (1)–(4), a new type of reactor called pyrolytic reactor system with stirred heat medium particles was made, as shown in Fig. 2. This system is composed of three kinds of reactors in series. One is the reactor with stirred heat medium particle (reactor 1), the second is a tank reactor (reactor 2) and the remaining one is a fixed bed reactor (reactor 3). Reactor 2 was located under reactor 1, and was separated from reactor 1 by stainless steel net. The expected reaction behavior is described below.

In the reactor 1, plastic particles are fed to the top of the bed of glass beads as the heat medium particles, melted and adhered to the particles. Glass beads are stirred slowly by two equipped impellers, one is the propeller type and the other is the anchor type located of the bottom of the glass beads bed. The propeller type impeller is turned to lift the particles. In this manner, glass beads on the top layer of the glass beads bed are replaced continuously by another beads

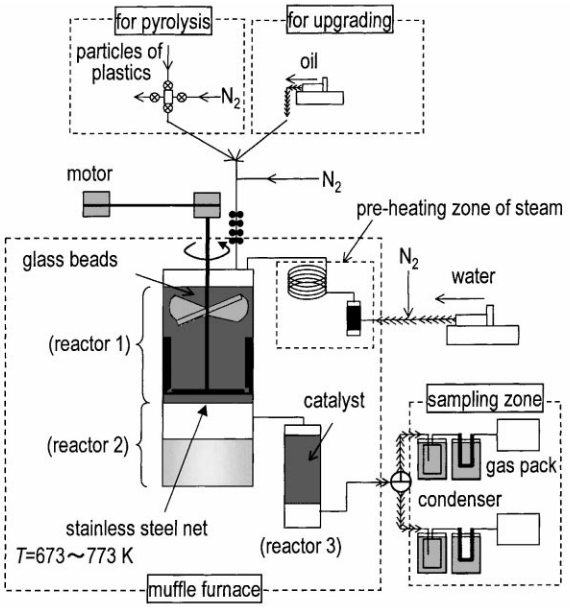

Fig. 2. Schematic view of proposed reactor system for chemical recycling of plastics.

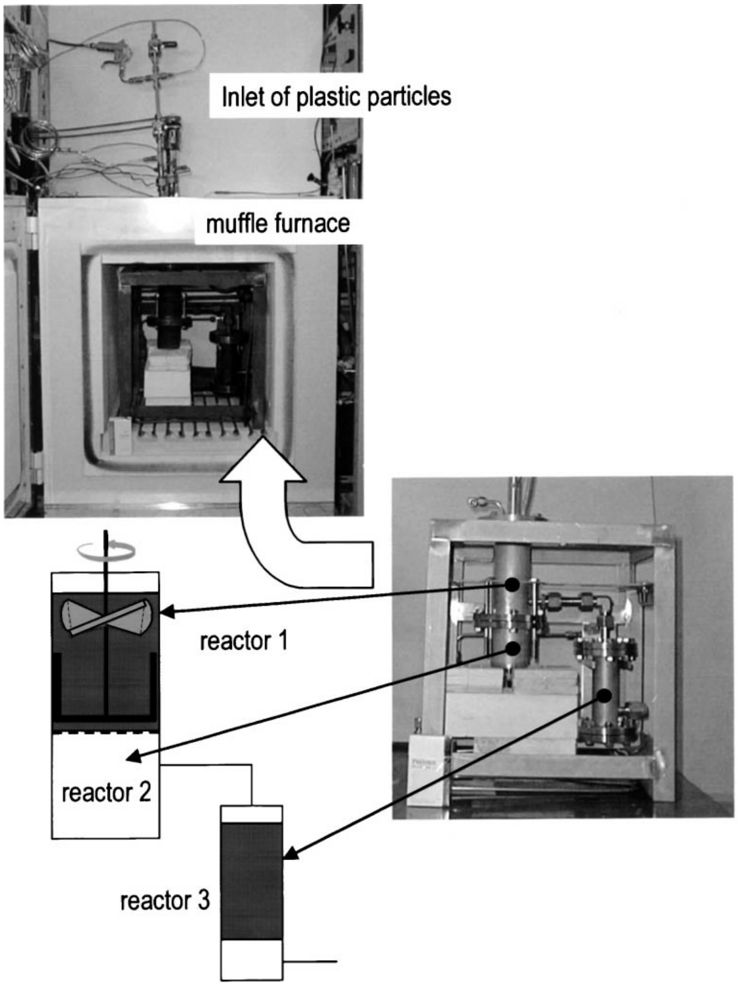

Fig. 3. Photograph of proposed reactor system.

beneath the top layer. These stirred beads increases the heat transfer rate. Followed the glass beads, the melted plastics are transported over the glass beads bed, resulting in a high holdup of plastics in the reactor and contacting well with steam as the carrier gas. Melted plastics on the glass beads are decomposed by the hydrolysis with steam and the random scission of C–C bonds. A part of the melted plastics on glass beads, which are carried to the bottom of the glass beads bed, would be dripped onto the reactor 2 (tank reactor). In the reactor 2, the unreacted plastics undergo the further decomposition, yielding gaseous compounds. The reactor 3 is filled with FeOOH catalyst. The gaseous compounds including the vapors of sublimate materials are passed through the FeOOH catalyst bed by undergoing the catalytic degradation.

Fig. 3 shows the photograph of a setup of the reactor system described above. This reactor system was consisted of stainless steel tubes connected in series; the first one corresponded to the reactors 1 and 2, and was 223 mm length and 60 mm i.d. The stainless steel net was located at the middle of the tube. The second tube was 130 mm length and 39 mm i.d. (Kyoto Takaoshin Ltd.) in which FeOOH catalyst of $0–3.0\times10^{-2}$ kg diluted with glass beads of 2.0×10^{-2} kg was filled up. This system was set in a muffle furnace with preheating section of steam, and was heated to 773 K. Water was fed to the preheating section to generate steam, which was used as the carrier gas. A mixture of PE and PET, which was a model mixture representing actual waste plastics, was intermittently fed to the reactor at the average feed rate of 2.0×10^{-2} kg h^{-1}. The mass ratio of PE/PET was adjusted to 15/2, which is the ratio of the amounts of the two plastics discarded in Kyoto city of Japan.

The reaction products were separated into liquid and gas fractions through a series of two condensers, respectively, cooled with ice and dry ice. The gas was collected using a sampling bag at timed intervals. Chemicals in the condensers were recovered by extraction using dichloromethane. Two phases were observed in thus recovered oil; one the phase of water solution, and the other dichloromethane solution. The total amount of hydrocarbons in the water phase was found to be negligibly small by the analysis using a Karl–Fisher moisture titrator apparatus (MKC-210, Kyoto Electronics Ltd.).

Therefore, chemicals contained in the water phase were ignored in the measurement and analysis of the products. The analysis of liquid products was conducted using a GC-MS (QP-5000, Shimadzu Ltd.), and a capillary gas chromatograph (GC-17A, Shimadzu Ltd.). The compositions of the gaseous were measured using a gas chromatograph equipped with columns of activated carbon and Porapak-Q (GC-12A, Shimadzu Ltd.). All of catalyst particles and glass beads were collected after the reaction. A part of them was burned using a thermogravimetric apparatus (shown in Fig. 1) in air stream at 823 K. Using the weight changes of the catalyst and glass beads prior to and after the burning experiment, the amount of carbonaceous residue, coke, formed in the degradation of plastics was calculated.

2.4.2. Upgrading of oil obtained by degradation of plastics

The apparatus used in the degradation of plastics was used by replacing the feed port of plastic particles with a syringe pump, which was used to feed the oil obtained in the degradation of plastics described above. Ni-REY catalyst of 6.0×10^{-3} kg was loaded in the second reactor tube (reactor 3). In experiments, the time factor *W*/*F* and the reaction temperature were set to 1 h and 673 K, respectively, where *W* is the mass of catalyst and *F* the feed rate of reactant (oil). The compositions of products and the coke amount were analyzed by the same way as the degradation of plastics.

3. Results and discussion

3.1. Degradation properties in nitrogen and in steam using thermogravimetric apparatus

Fig. 4(a) and (b) show the remarkable changes in the fractions of unreacted PBT and PC, respectively, as the molar fraction of steam in the carrier gas was varied. The similar result was also observed for PET [10]. For the case of PC, when a pure nitrogen stream (steam molar fraction = 0%) was used, the degradation of PC was initiated at about 680 K and was terminated at about 800 K, leaving about 23% carbonaceous residue. When the carrier gas contained steam, the fraction of carbonaceous residue was drastically reduced from 23% (100% nitrogen) to almost 0% (100 mol% steam). Furthermore, the initiation temperature for pyrolysis decreased by about 80 K. The similar result was also observed for PET, in which the initiation temperature was decreased by 50 K [10]. On the other hand, there were not any influences of steam on the pyrolytic properties for other plastics used in this work. Thus, the acceleration of the decomposition by steam was observed for PC, PBT and PET which have main chains of ester bonds. These bonds would be easily hydrolyzed in steam atmosphere, yielding monomers corresponding to each plastic resin, such as terephthalic acid for PET and PBT, and bis-phenol A for PC.

Fig. 5 shows the dependencies of the amount of carbonaceous residue remaining at 800 K on the molar fraction of steam in the carrier gas for PBT, PET and PC. All data lie on a single curve for each plastic resin, suggesting that the amount of carbonaceous residue depends only on the partial pressure of steam, not on the heating rate. The amounts of residue decrease with increases in the partial pressure of steam, and leave almost zero in a 100% steam carrier gas.

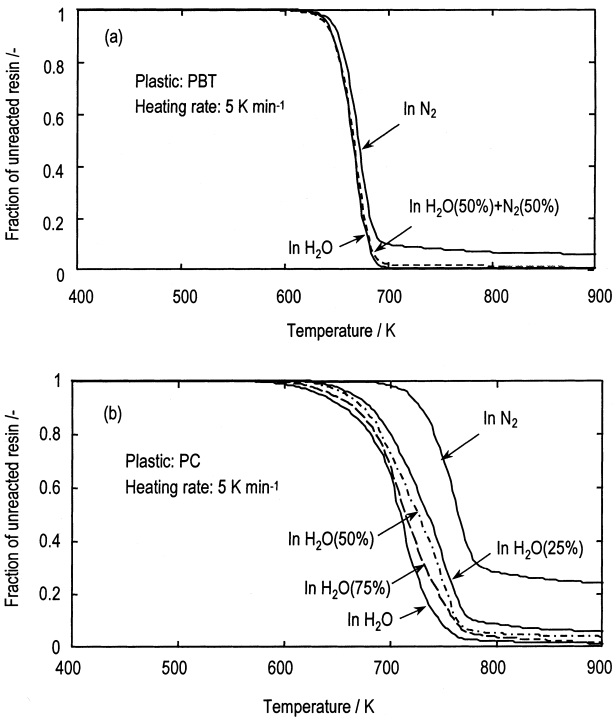

Fig. 4. Changes in the fractions of unreacted polyesters in nitrogen and steam at different molar fraction of steam in carrier gas: (a) poly(buthylen terephthalate) (PBT); (b) polycarbonate (PC). Heating rate: $5\,\mathrm{K\,min^{-1}}$.

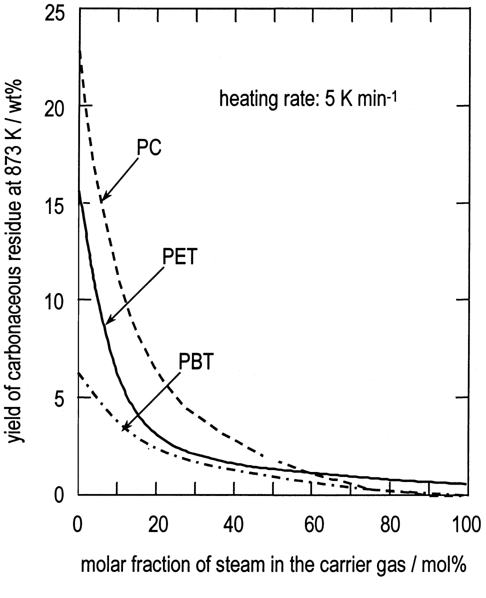

Fig. 5. Relationship between the molar fraction of steam in the carrier gas and the yield of residue produced from polycarbonate (PC), poly(buthylene terephthalate) (PBT) and poly(ethylene terephthalate) (PET) at 800 K.

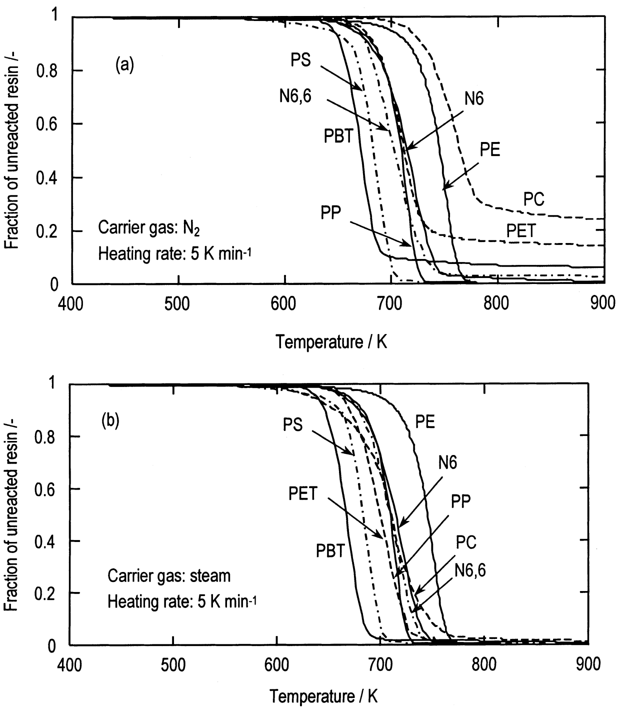

Fig. 6. Changes in the fractions of unreacted plastics used in this work at heating rate of 5 K $\min^{-1}$: (a) in nitrogen; (b) in steam.

3.2. Possibility for changing degradation mechanism by using steam as carrier gas

Fig. 6(a) and (c) show the thermogravimetric curves (TG-curves) for plastics used in this work at heating rate of 5 K $\min^{-1}$ in nitrogen and in steam, respectively. The TG-curves are remarkably different among the plastics used in this work in nitrogen stream, due to the difference of the main chain of the plastics. Furthermore, polyester resin, such as PC, PBT and PET, yielded large amounts of carbonaceous residue at 800 K due to the dehydration during the degradation in nitrogen. In steam atmosphere, the TG-curves of PC, PBT and PET were remarkably changed by shifting to lower temperature regions and by reducing the amount of carbonaceous residue, as compared with those in nitrogen. When the steam was used as the carrier gas, the degradation of the polyester resins was degraded by both of the thermal pyrolysis and the hydrolysis. We have reported the kinetic equation of the degradation of PET in steam atmosphere as follows [10]:

$$a\frac{\mathrm{d}X}{\mathrm{d}T} = 3.8\times10^{13}\,\mathrm{e}^{-2.0\times10^{5}/R_{\mathrm{g}}T}(1-X)^{0.5} + 8.0 \times10^{5}P_{\mathrm{w}}\,\mathrm{e}^{-1.6\times10^{5}/R_{\mathrm{g}}T}(1-X)^{0.5} \qquad (1)$$

where X is the conversion, a the heating rate (K $\min^{-1}$), T the temperature (K) and P_{w} the partial pressure of steam (Pa). The first term in the right hand side of Eq. (1) corresponds to the thermal pyrolysis and the second term is the hydrolysis. In steam atmosphere, the conversion rate of PET was well expressed by the second term, indicating that the degradation proceeded by the hydrolysis. These considerations lead that the degradation mechanisms of PC, PBT and PET are changed from the thermal pyrolysis to the hydrolysis by introducing steam into the carrier gas.

In nitrogen stream, PC shows the lowest degradation rate. On the other hand, the plastic resin with the lowest degradation rate is PE in steam atmosphere. Therefore, the size of the degradation reactor could be designed by considering only the degradation rate of PE. By the method proposed by Friedman [22] with the TG-curves of PE at different heating rates (0.5, 1, 2.5, 5 and 10 K $\min^{-1}$), the degradation rate of PE was found to be well expressed by Eq. (2):

$$a\frac{\mathrm{d}X}{\mathrm{d}T} = 3.7\times10^{17}\,\mathrm{e}^{-2.6\times10^{5}/R_{\mathrm{g}}T}(1-X) \qquad (2)$$

On the basis of Eq. (2), it was found that PE of above 98% could be degraded for a reaction time of 90 s at 773 K. Hence, the operation conditions of the reactor system shown in Fig. 2 should be decided to attain the residence time of above 90 s for plastics.

3.3. Cold model experiment of continuous degradation of plastics

Fig. 7 shows a typical result of a cold model experiment using a Pyrex glass tube with the same size as the reactor 1 shown in Fig. 2. The glass tube was filled with glass beads in the lower region, and with alumina ceramic bolls in the upper region to recognize visibly the movement of the particles followed by the rotation of the impellers equipped inside the tube. The propeller type and anchor type impellers were rotated at a rate of 8 rpm. Followed by the rotation of impellers, the particles were transported and were distributed over the bed after stirring time of 90 s. This result indicates that the melted plastics adhered to the glass beads have enough time to degrade at above 98% conversion.

3.4. Continuous degradation of a mixture of plastics using a reactor system with stirred heat medium particles

A mixture of PE and PET was used as a model mixture of the waste plastics. The ratio of PE/PET was 15/2, which is the ratio of the amounts of the two plastics discarded in Kyoto city of Japan.

After the continuous degradation with and without stirring glass beads, glass beads were collected from the reactor 1 (Fig. 2). When glass beads were not stirred, which corresponded to a trickle bed type reactor, massive carbonaceous residue with glass beads was left on the top of the glass beads bed. It is the reason that the heat transfer rate was low and the melted plastics could not well contact with steam. On the other hand, any massive residues were not observed and glass beads lightly colored yellow, when glass beads were stirred by rotating the impellers at 8 rpm. Furthermore, there were not any residue and oils in the reactor 2, tank reac-

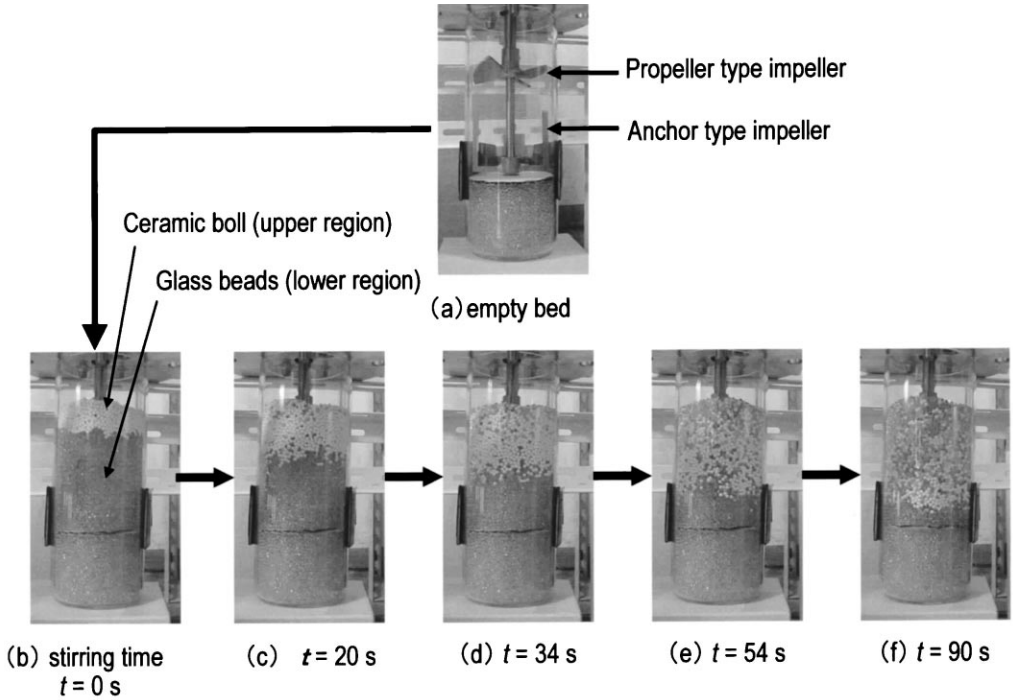

Fig. 7. Transportation manner of glass beads at 8 rpm rotation rate of impellers in cold model experiment for reactor 1 shown in Fig. 2.

tor (Fig. 2). These results indicate that the proposed reactor system is useful for the continuos degradation of plastics.

Fig. 8 shows the change in the product yields, which was collected at the outlet of the reactor 3 (see Fig. 2), as the ratio of the catalyst mass, *W*, to the feed rate of plastics, *F* (time factor), increased from 0 to 1.5 h. When the FeOOH catalyst was not loaded in the reactor 3, a large amount of a wax colored yellow was obtained. When the FeOOH catalyst was loaded in the reactor 3, the oil and carbon dioxide were produced. The amounts of carbon dioxide and gaseous hydrocarbons increased and the yield of oil decreased, as the loaded FeOOH catalyst increased. This suggests that the FeOOH catalyst has the catalysis for the decomposition of a wax through the oxidization with oxygen atoms from the lattice of FeOOH and/or from H_2O.

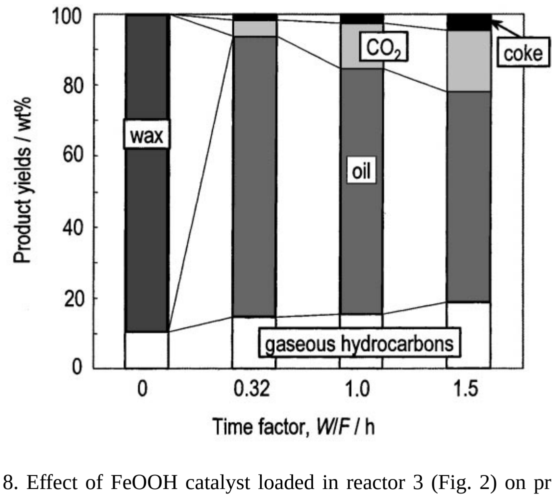

Fig. 8. Effect of FeOOH catalyst loaded in reactor 3 (Fig. 2) on product yield, temperature = 773 K, carrier gas: steam.

When a wax is decomposed through the oxidation with oxygen atoms from the lattice of FeOOH catalyst, the catalytic activity of the FeOOH catalyst would be decreased. Therefore, the gaseous product yields of the reaction under the conditions of temperature of 773 K and the time factor of 1 h were measured by sampling at different intervals. Main gaseous products were CO_2 (about 3 wt.% for 140 min), *n*-C_4H_{10} (2 wt.%), *n*-C_3H_8 (2 wt.%), C_2H_6 (0.5 wt.%), C_2H_4 (1.5 wt.%) and CH_4 (0.5 wt.%). Except for the beginning of the reaction, there were negligibly changes in the product yields. The amount of oxygen required for producing carbon dioxide during the reaction time of 140 min was evaluated, and was found to be larger than that generated through the phase change of iron from Fe_2O_3 to Fe_3O_4. These results suggested that a wax was decomposed by a reaction with H_2O over FeOOH catalyst, and the catalytic activity of the FeOOH catalyst was stable in steam atmosphere.

Fig. 9 shows the carbon number distribution of the product obtained under the conditions of temperature of 773 K and the time factor of 1 h. Produced oil is considered to be corresponding to heavy oil in view of the carbon number distribution. Therefore, it is needed to upgrade this oil.

3.5. Continuous upgrading of oil derived from a mixture of PE and PET

The catalytic cracking of the oil derived from a mixture of PE and PET was conducted using the same reactor system as in the degradation of the plastics by replacing FeOOH

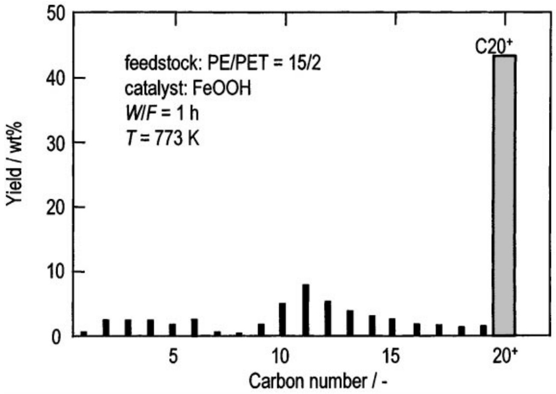

Fig. 9. Carbon number distributions of produced heavy oil of degradation of a mixture of polyethylene (PE) and poly(ethylene terephthalate) (PET), weight ratio of PE/PET = 15/2, temperature = 773 K, time factor $W/F = 1$ h, carrier gas: steam.

catalyst to Ni-REY catalyst (see Fig. 2). In this experiment, the reactors 1 and 2 were regarded as the preheating zone of the oil and steam, and the glass beads in the reactor 1 were not stirred.

Fig. 10 represents the carbon number distribution of the products of the reaction over Ni-REY in a steam atmosphere under the conditions of temperature of 673 K and the time factor of 1 h. By comparing Fig. 9 with Fig. 10, the fraction of heavy oil with carbon number above 20 was completely converted to gasoline and kerosene, indicating that the Ni-REY could be used for the upgrading of the oil derived from the mixture of PE and PET. The ranges of the carbon numbers of gasoline and kerosene were obtained by measuring those of commercial ones. This high activity of Ni-REY is due to the hydrogenation over Ni of Ni-REY in a steam atmosphere [19].

The results in the degradation of the plastic mixture and the upgrading of the plastic-derived oil indicate that the mixture of the waste plastics can be effectively converted to useful fuels by the proposed reactor system with FeOOH and Ni-REY catalysts in steam atmosphere.

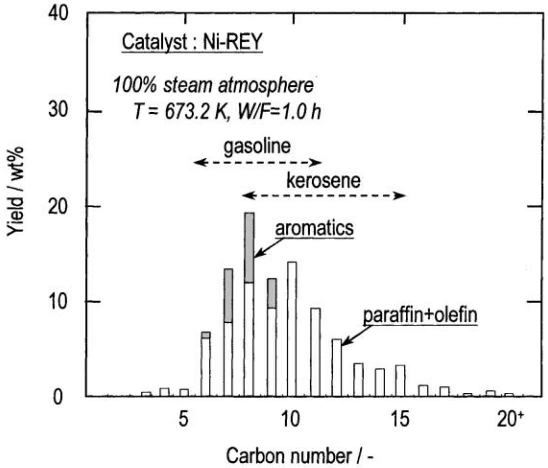

Fig. 10. Carbon number distribution of products obtained by upgrading heavy oil shown in Fig. 9 over Ni-REY zeolite catalyst, temperature = 673 K, time factor $W/F = 1$ h, carrier gas: steam.

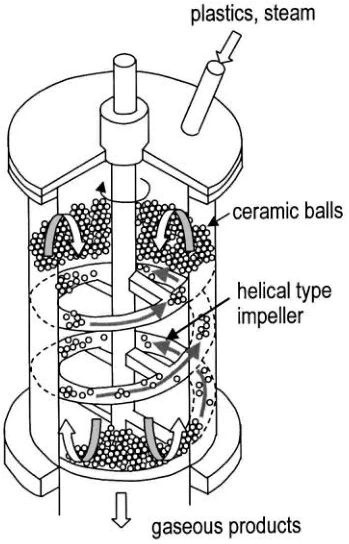

Fig. 11. Schematic diagram of pyrolytic reactor used in a pilot plant.

3.6. Recovery of oil from waste plastics in a pilot plant

On the basis of the results described in the previous sections, a pilot plant for continuous conversion of waste plastics was built. As it is difficult to stir heat medium particles (ceramic balls) in the reactor 1 (Fig. 2) by using propeller type and anchor type impellers in the case of an industrial plant, an helical type impeller was employed, which was shown in Fig. 11. Ceramic balls located near the reactor wall were lifted, and the balls located centrally on the top of the bed came down to the bottom of the reactor. By this movement, ceramic balls were transported wholly in the reactor.

Beads of waste plastics were fed to the top of the ceramic ball bed. Plastics were melted and were transported according to the movement of the ceramic balls by undergoing reaction in steam atmosphere. Products, such as sublimate materials and wax, reacted during passing the reactor filled with FeOOH catalyst producing heavy oil. This oil was cracked in the reactor with Ni-REY catalyst yielding lighter fuels. The product yields were as follows: gaseous hydrocarbons (C1–C4) with carbon number from 1 to 4 were 13.5 wt.%; fuel (C5–C19) was 52.4; heavy oil (C20+) was 33.9 wt.% and others 0.2 wt.%. The yield of fuel can be increased by recycling heavy oil.

These results indicate that the proposed reactor system is useful to recover fuels continuously from the waste plastics.

4. Conclusions

1. The dominant degradation mechanisms of polyester resins, such as polycarbonate, poly(butylene terephthalate)

and PET, were changed from the thermal pyrolysis to the hydrolysis by introducing steam into the carrier gas. This mechanism change leaded to leaving negligibly small amount of the carbonaceous residue. Furthermore, the initiation temperature of the degradation was found to be decreased by 50–80 K, when polyester resins were degraded by the hydrolysis in steam atmosphere. On the other hand, the degradation properties of other plastics were not changed in steam atmosphere, as compared in nitrogen stream.

2. A new reactor system was proposed for the degradation of a mixture of the waste plastics. This system was composed of a reactor with stirred heat medium particles, a tank reactor and a fixed bed with FeOOH catalyst which were connected in series. This reactor system realized the high heat transfer rate, the high holdup of the melted plastics and the good contact of the plastics with steam. A mixture of PE and PET was succeeded to be continuously degraded to yield oil without any sublimate materials.
3. FeOOH catalyst showed a stable activity for the decomposition of a plastic-derived wax through the oxidation in steam atmosphere. A part of oxygen species was found to be supplied from steam.
4. The oil obtained by the degradation of a mixture of PE and PET could be effectively upgraded to gasoline and kerosene over Ni-REY zeolite catalyst in steam atmosphere.
5. The waste plastics were successfully converted to fuels in the pilot plant with the new reactor system and the catalysts proposed in this work.

References

[1] D.A. Anderson, E.S. Freeman, The kinetics of the thermal degradation of polystyrene and polyethylene, J. Polym. Sci. 54 (1961) 253–260.

[2] H. Bockhorn, A. Hornung, U. Hornung, Stepwise pyrolysis for raw material recovery from plastic waste, J. Anal. Appl. Pyrol. 46 (1998) 1–13.

[3] H. Bockhorn, J. Hentschel, A. Hornung, U. Hornung, Environmental engineering: stepwise pyrolysis of plastic waste, Chem. Eng. Sci. 54 (1999) 3043–3051.

[4] T. Kuroki, T. Sawaguchi, N. Ikebayashi, T. Ikemura, N. Sakikawa, Pyrolysis of polystyrene — prediction of product yield, Bull. Chem. Soc. Jpn. 11 (1976) 1766–1772.

[5] C.H. Wu, C.Y. Chang, J.L. Hor, S.M. Shih, L.W. Chen, Pyrolysis kinetics of waste PVC at high conversion, Chem. Eng. J. 55 (1994) 87–92.

[6] M. Bisi, C. Nicolella, E. Palazzi, M. Rovatti, G. Ferraiolo, HCl formation via pyrolytic degradation of polyvinyl chloride (PVC): an empirical approach to kinetic modeling, Chem. Eng. Technol. 17 (1994) 67–72.

[7] N. Lingaiah, M.A. Uddin, A. Muto, Y. Sakata, Hydrochlorination of chlorinated hydrocarbons over metal-carbon composit catalysts prepared by modified carbothermal reduction method, J. Soc. Chem., Chem. Commun. 8 (1999) 1657–1658.

[8] Y. Sakata, Y. Shiraga, M.A. Uddin, A. Muto, K. Murata, in: Proceedings of the Gorden Research Conference on Dechlorination of Waste Plastic Derived Oil Using a Carbon and Iron Oxide Composite, January 1999.

[9] T. Yoshioka, K. Furukawa, A. Okuwaki, Chemical recycling of rigid-PVC by oxygen oxidation in NaOH solution at elevated temperature, Polym. Degrad. Stab. 67 (1999) 285–290.

[10] T. Masuda, Y. Niwa, A. Tamagawa, S.R. Mukai, K. Hashimoto, Y. Ikeda, Degradation of waste poly(ethylene terephthalate) in a steam atmosphere to recover terephthalic acid and to minimize carbonaceous residue, Polym. Degrad. Stab. 58 (1997a) 315–320.

[11] T. Masuda, Y. Niwa, K. Hashimoto, Y. Ikeda, Recovery of oil from waste poly(ethylene terephthalate) without producing any sublimate materials, Polym. Degrad. Stab. 61 (1998) 217–224.

[12] S.H. Ng, H. Hesham, M. Stanciulescu, Y. Sugimoto, Conversion of polyethylene to transportation fuels through pyrolysis and catalytic cracking, Energy Fuels 9 (1995) 735–742.

[13] K. Murata, T. Makino, Thermal degradation of high density polyethylene, Bull. Chem. Soc. Jpn. 46 (1973) 2414–2420.

[14] T. Moriya, H. Enomoto, Characteristics of polyethylene cracking in supercritical water compared to thermal cracking, Polym. Degrad. Stab. 65 (1999) 373–386.

[15] A.R. Songip, T. Masuda, H. Kuwahara, K. Hashimoto, Test to screen catalysts for reforming heavy oil from waste plastics, Appl. Catal. B2 (1993) 153–164.

[16] A.R. Songip, T. Masuda, H. Kuwahara, K. Hashimoto, Kinetic studies for catalytic cracking of heavy oil from waste plastics over REY zeolite, Energy Fuels 8 (1994a) 131–135.

[17] A.R. Songip, T. Masuda, H. Kuwahara, K. Hashimoto, Production of high quality gasoline by catalytic cracking over REY zeolites of heavy oil from waste plastics, Energy Fuels 8 (1994b) 136–140.

[18] T. Masuda, H. Kuwahara, S.R. Mukai, K. Hashimoto, Production of high quality gasoline from waste polyethylene derived heavy oil over Ni-REY catalyst in steam atmosphere, Chem. Eng. Sci. 54 (1999) 2773–2779.

[19] W. Kaminsly, B. Schlesselmann, C.M. Simon, Thermal degradation of mixed plastic waste to aromatics and gas, Polym. Degrad. Stab. 53 (1996) 189–197.

[20] W. Kaminsly, J.S. Kim, Pyrolysis of mixed plastics into aromatics, J. Anal. Appl. Pyrol. 51 (1999) 127–134.

[21] T. Masuda, Y. Fujikata, S.R. Mukai, K. Hashimoto, A method of calculating adsorption enthalpy distribution using ammonia TPD spectrum under adsorption equilibrium conditions, Appl. Catal. 165 (1997b) 57–72.

[22] H.L. Friedman, J. Polym. Sci. C6 (1964) 183.