

## Thermal Degradation of the Mixture of Spent Anion Exchange Resin and Polystyrene into Fuel Oil

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The used ion exchange resins (IERS) granule ( $\text{OH}^-$  and  $\text{Cl}^-$  types) and plastics (PE, PP, PS) were degraded thermally at 360-430 °C by batch operation into fuel oil. The  $\text{OH}^-$  and  $\text{Cl}^-$  type resins gave liquid yields of 28 wt% and 23 wt% at 360 °C, respectively. For the mixture of 50 wt% IER- $\text{OH}^-$  and 50 wt% polystyrene, the total liquid yield was 64 wt%. As the liquid yield of PS for thermal degradation at 360 °C was 74 wt%, an estimated recovery yield from the mixture (IER- $\text{OH}^-$  50 wt% and polystyrene 50 wt%) should be 54 wt% based on simple addition. Since the yield for the mixture was (64 wt%) greater than the estimated yield (54 wt%), it is suggested that the co-degradation of IER with PS promotes the conversion into fuel oil effectively. Thermal degradation of chlorine ( $\text{Cl}^-$ ) exchanged resin (IER- $\text{Cl}^-$ ) produced a very small amount of organic chlorine compounds in the product oil. However, the mixture of IER- $\text{Cl}^-$  and PS generated a significant amount (10600 ppm) of organic chlorine compounds mainly chloromethane. The iron oxide carbon composite catalyst reduced the organic chlorine content to 680 ppm.

### Introduction

A large quantity of used ion exchange resins (IER) are discarded every year in Japan, most of which are incinerated and landfilled without any proper treatment. As the IER are synthesized mainly from hydrocarbon resources, the energy contents in them can be re-utilized by appropriate recycling methods. Pyrolysis or thermal degradation of waste plastics and resins into fuel oil and gases is receiving much attention as a chemical or energy recycling method [1]. Our preliminary study on the thermal degradation of various types of IER such as anion, cation and chelate type resins showed that anion type resin has an advantage over cation and chelate type resins for the recovery yields of liquid products [2]. The chelate and cation type resins are favorable for obtaining carbonaceous products [3].

In this work we report the thermal degradation of a mixture of IER and plastics (PE, PP, PS) into fuel oil. In particular, the effect of the co-degradation of IER in the presence of polystyrene, polypropylene and polyethylene melts on the product yield and product compositions are investigated. Thermal degradation of Chloride ( $\text{Cl}^-$ ) type resins was studied to examine the route of formation of the organic chlorine compounds in product oil. Iron oxide carbon composite was used as a catalyst to remove the organic chlorine compounds.

### Materials and Methods

The IERs employed in this study, (cation type PK, chelate type CR11, anion type PA) were supplied by Mitsubishi Chemical Industries. Polystyrene (PS) was obtained from Asahi Kasei Industries Co., Ltd., Japan, polypropylene (PP) from Ube chemical Co., Ltd., Japan, and high-density polyethylene (HDPE) from Mitsui Petrochemical Co., Ltd., Japan. The chlorine sorbent  $\text{Fe}_3\text{O}_4$  [TR99300] were supplied by Toda Industries Co., Ltd., Japan.

The IERs were ion exchanged to  $\text{OH}^-$  type,  $\text{Cl}^-$  type and  $\text{H}^+$  type by conventional method and dried naturally. Thermal and catalytic degradation of IER and plastic was carried out in a glass reactor under atmosphere pressure by batch operation. Figure 1a shows the experimental setup. In brief, 40 g of sample mixed IER and Plastic [weight ratio: IER (PK, CR11, PA) : Plastic (PS, PP or PE) = 1:1] was loaded into the reactor, for thermal degradation. In the case of

degradation using catalyst, 4 g of catalyst was added to 40 g of sample. For catalytic degradation in vapor phase contact, catalyst was placed on a stainless steel net located 15 cm from the bottom of the reactor as shown in Figure 1b. In a typical run, after the reactor was set, air remaining in the reactor was purged with nitrogen gas. The reactor was then heated with an electric furnace from room temperature to 120 °C at 3 °C/min and held at 120 °C for 60 min to remove the physically absorbed water from the samples and catalyst. The nitrogen gas flow was then cut off, and the reactor temperature was increased to the degradation temperature at a heating rate of 3 °C/min. The hydrogen chloride evolved from the degradation of IER- $\text{Cl}^-$  was trapped in a flask containing an aqueous solution of NaOH and analyzed for  $\text{Cl}^-$  by an ionchromatograph (DIONEX DX-120). The liquid and gaseous products were analyzed by two gas chromatographs with a conductivity detector (Shimadzu: GC-8A-TCD) and a flame ionization detector (Yanako: G-6800-FID), respectively. Organic chlorine compounds in the liquid product were analyzed by gas chromatographs with either an atomic emission detector (HP: G2350A-AED) or a mass selective detector (HP: 5973-MSD).

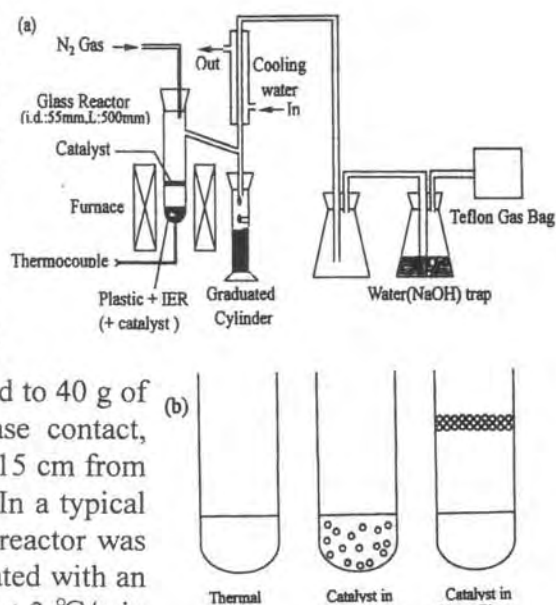


Figure 1. Schematic diagram of (a) experimental set up and (b) catalyst contact mode

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## Result and Discussion

### Thermal Degradation of IERs into Fuel Oil.

The degradation of IERs (PK, CR11, PA) (20 g) was carried out at 360 °C by batch operation. Table 1 shows the yield of products such as Gas, Liquid and Residue. At the initial stage of the reaction PK( $\text{H}^+$ ) and CR11( $\text{H}^+$ ) produced a significant amount of water, so the yield was calculated after subtracting the amount of water from the total amount of liquid collected. The residue yield was highest (73 wt%) for PK( $\text{H}^+$ ) and lowest (35 wt%) for PA( $\text{OH}^-$ ) degradation. This implies that the PK and CR11 are favorable for preparing carbonaceous products and anion type IER (PA) is favorable for the production of fuel oil efficiently.

### Thermal Degradation of PA( $\text{OH}^-$ ) Mixed Plastics into Fuel Oil.

The degradation of PS (20 g)/PA( $\text{OH}^-$ ) (20 g) was carried out at 360 °C. Table 2 shows the yield of products. The thermal degradation of PA( $\text{OH}^-$ ) gave a liquid yields of 28 wt% and the mixture of PS/

Table 1 Product yields for thermal degradation of IERs [PK( $\text{H}^+$ ), CR11( $\text{H}^+$ ) and PA( $\text{OH}^-$ )] at 360°C

Sample <sup>a)</sup>	Water evolved [ml]	Degradation yields <sup>b)</sup> [wt%]			Liquid Density $\bar{C}_{sp}$ <sup>c)</sup>	
		Liquid(L)	Gas(G)	Residue(R)	[g/ml]	[-]
PK( $\text{H}^+$ )	7.7	2.5	24.5	73.0	0.73	9.1
CR11( $\text{H}^+$ )	4.0	31.6	24.5	43.9	0.90	10.7
PA( $\text{OH}^-$ )	1.1	27.7	36.9	35.4	0.75	11.0

a) Sample feed = 20 g

b)  $G = 100 - (L + R)$

c) Average carbon number of liquid product obtained from C-NP gram

Table 2 Product yields for thermal degradation of PA(OH) (20g) and PS or PP or HDPE (20g)

Run No.	Sample	Temperature [°C]	Water evolved [ml]	Degradation yields <sup>a)</sup> [wt%]			Liquid <sup>b)</sup>	
				Liquid(L)	Gas(G)	Residue(R)	[g/ml]	$\bar{C}_{50}$ [-]
1	PA(OH)	360	1.1	27.7	36.9	35.4	0.75	11.3
2	PA(OH)	380	5.5	29.0	34.4	36.6	0.83	11.2
3	PA(OH)	430	5.4	39.5	27.7	32.8	0.85	11.1
4	PS / PA(OH)	360	3.0	63.9 (1.18) <sup>c)</sup>	10.7 (0.62)	25.4 (0.89)	0.89	11.3
5	PP / PA(OH)	380	5.3	58.6 (0.89)	19.2 (1.15)	22.2 (1.30)	0.75	10.1
6	PE / PA(OH)	430	5.0	66.9 (1.07)	20.2 (0.97)	12.9 (0.77)	0.77	13.1
7	PS	360	-	73.9	2.6	23.5	0.90	9.3
8	PP	380	-	93.1	3.9	3.0	0.78	12.6
9	PE	430	-	79.3	15.7	5.0	0.73	11.1

a) G = 100-(L+R) b)  $\bar{C}_{50}$  Average carbon number of liquid product obtained from C-NP gram

c) Ratio of yields based on addition of individual polymer degradation yield

PA(OH) produced 64 wt% liquid products. As the liquid yield of PS for thermal degradation at 360 °C was 74 wt%, an estimated recovery yield of liquid from the PS/PA(OH) mixture should be 54 wt% based on the simple addition. Since the experimental liquid yield (64 wt%) was greater than the estimated yield (54 wt%), it can be suggested that the co-degradation of PA(OH) and PS promotes conversion of PA(OH) into fuel oil effectively. Figure 2 shows the composition of the liquid products (C-NP gram). The carbon number distribution of liquid products for the co-degradation was the same as the liquid products from the degradation of PS only. The liquid products have a carbon number distribution of C<sub>9</sub> and C<sub>17-18</sub>. The degradation of PP (20 g) /PA (OH) (20 g) was carried out at 380 °C and PE (20 g)/PA(OH) (20 g) at 430 °C. The degradation yields of liquid products were 59 wt% and 67 wt% (Table 2) respectively. The degrees of promotion in the liquid yield due to co-degradation of PA with PP or PE were smaller than with PS. The compositions of the liquid products from PP or PE/PA mixtures were similar to the composition of liquid products from the corresponding plastics (PP or PE).

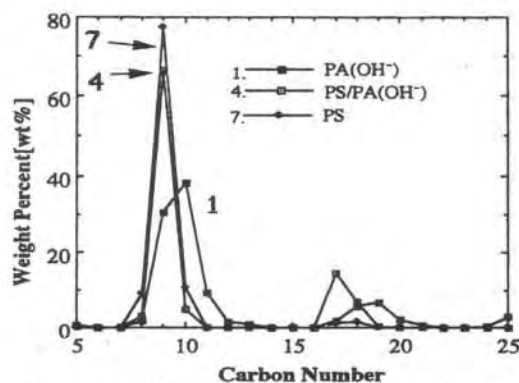


Figure 2 C-NP-gram of liquid products from thermal degradation of PS(20 g) and PA(OH)(20 g) at 360°C

Thermal Degradation of PA(Cl) Mixed Plastic into Fuel Oil. The degradation of chlorine exchanged PA (PA(Cl)) was carried out at 360~430°C in order to examine the possibility of generation of organic chlorine compounds in the liquid products. The liquid yield was increased from 23 wt% to 37 wt% (Table 3) with the increase of degradation temperature from 360 °C to 430 °C. However, no change in the composition of the liquid products were observed. Figure 3 shows the carbon number distribution of organic chlorine compounds (Cl-NP gram). Although PA(Cl) contains a significant amount of chlorine in it's framework, after thermal degradation only a little amount of organic chlorine compounds were observed in liquid products. Thermal degradation of the mixture of plastics (PP or PE or PS)/PA(Cl) were carried out at various temperatures and results are summarized in Table 3. The composition of organic chlorine compounds in the liquid products is shown in Figure 3 as the carbon number distribution curve (Cl-NP gram). Irrespective of the degradation temperature, in all cases the carbon number distribution of the organic chlorine compounds were very similar. For PP/PA(Cl) and PE/PA(Cl), the amount of chlorine in the liquid products was negligible. For PS/PA(Cl), the amount Cl in oil decreased with the increase of degradation temperature. It is suggested that at higher temperatures the degradation of PS occurs first and then the degradation of PA proceeds separately, which reduce the possibility of formation of organic chlorine compounds. It is noteworthy that the PA(Cl) alone produced only a small amount of organic chlorine compounds. The chlorine compounds produced from the degradation of PS/PA(Cl) was predicted by GC-MS as chloromethane.

Table 3 Product yields for thermal degradation of PA(Cl) with PS, PP, HDPE and catalytic degradation of PA(Cl) mixture

Run No.	Sample	Mass of Sample (g-plastic/g-IER (g-catalyst))	Temperature [°C]	Water evolved [ml]	Degradation yields <sup>a)</sup> [wt%]			Density [g/ml]	C <sub>av</sub> <sup>b)</sup> [°C]
					Liquid(L)	Gas(G)	Residue(R)		
1	PA(Cl)	20	360	3.6	22.5	28.7	48.8	0.84	10.2
2	PA(Cl)	20	380	4.2	26.1	30.9	43.0	0.86	10.7
3	PA(Cl)	20	430	5.4	37.3	26.0	36.7	0.86	10.5
4	PS / PA(Cl)	20 / 20	360	3.3	59.8 (1.18) <sup>c)</sup>	12.4 (0.86)	27.8 (0.80)	0.89	8.2
5	PS / PA(Cl)	20 / 20	380	4.1	64.0 (1.14)	13.4 (0.92)	22.6 (0.76)	0.89	11.3
6	PS / PA(Cl)	20 / 20	430	4.3	66.7 (0.95)	14.0 (1.16)	19.3 (1.10)	0.89	11.0
7	PP / PA(Cl)	20 / 20	380	4.2	63.8 (1.00)	12.3 (0.78)	23.9 (1.15)	0.76	10.7
8	PE / PA(Cl)	20 / 20	430	5.0	62.6 (1.03)	22.1 (1.09)	15.3 (0.81)	0.77	12.3
9	PS / PA(Cl)+Cata(LP) <sup>d)</sup>	20 / 20 (4)	360	5.0	62.4 (1.23)	11.0 (0.76)	26.6 (0.76)	0.88	11.2
10	PS / PA(Cl)+Cata(VP) <sup>e)</sup>	20 / 20 (4)	360	3.7	61.8 (1.22)	10.9 (0.76)	27.3 (0.78)	0.91	11.2

a) G = 100-(L+R)      b) C<sub>av</sub>: Average carbon number of liquid product obtained from C-NP gram

c) Ratio of yields based on addition of individual polymer degradation yield      d,e) Catalyst: TR99300

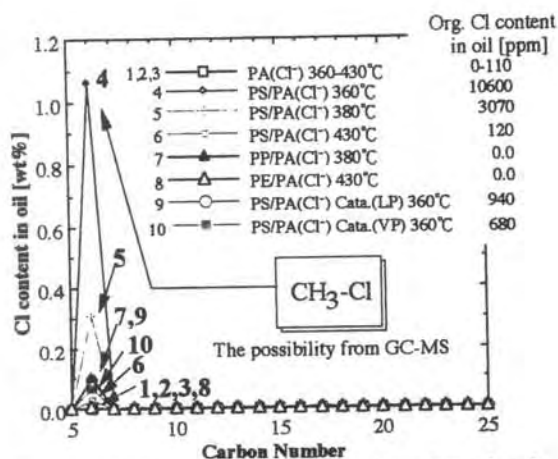


Figure 3 Cl-NP-gram of liquid products from thermal and catalytic degradation of Plastics (20 g) and PA(Cl) (20 g)

In contrast, the degradation of PS/PVC produced 1-chloroethylbenzene and 2-chloro-2-phenylpropane as the main chlorinated hydrocarbons in the liquid products[4].

The degradation of PS/PA(Cl) was also carried in presence of iron oxide (Fe<sub>3</sub>O<sub>4</sub>) carbon composite catalyst both in liquid phase (LP) and vapor phase (VP) contact at 360 °C. The modes of contact of catalyst with PS/PA(Cl) samples are illustrated in Figure 1b. The product yields and compositions for catalytic degradation did not differ significantly from that of non-catalytic thermal degradation. However, the Cl content in the oil decreased to 980 ppm for liquid phase contact (LP) and 680 ppm for vapor phase contact (VP) compared to 10600 ppm for non-catalytic thermal degradation. This catalyst was very effective for the dechlorination of plastic derived oil [5].

## Conclusions

The thermal degradation of various type of ion exchange resins, (IERS) such as anion type (PA), cation type (PK) and chelate type (CR11) and the mixture of IER with plastics (PE, PP, PS) was carried out at 360~430 °C to obtain fuel oil. The cation (PK) and chelate (CR11) type resins were favorable for preparing carbonaceous products, whereas anion type resin produced liquid efficiently. The co-degradation IER with PS promoted the conversion of IER into fuel oil effectively. The chlorine containing resin, PA(Cl), produced significant amount of organic chlorine compounds (10600 ppm) in liquid products when it was co-degraded with polystyrene (PS). The iron oxide carbon composite catalyst reduced the organic chlorine content in liquid products to 680 ppm for vapor phase contact (VP).

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