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The Effect of Red Mud on the Liquefaction of Waste Plastics in Heavy Vacuum Gas Oil

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The main aim of this study was to investigate the effect of red mud on the decomposition and dechlorination of waste plastics. Thermal and catalytic degradation of a mixture of municipal waste plastics (MWP) and heavy vacuum gas oil (HVGO) into fuel oil was carried out by a one-step and a two-step process. One-step processing was performed at 430 °C by stepwise pyrolysis. Red mud (RM) was used as a dechlorination catalyst. In two-step processing, degradation in the presence and absence of solid acid catalyst (silica–alumina, SA1) was carried out at 430 °C followed by dechlorination in a flow-type fixed-bed reactor at 350 °C over RM. Copyrolysis of MWP with HVGO led to a synergic effect, increasing the liquid yield. TR99300 had a good dechlorination effect in two-step processing, however it was not effective for MWP/HVGO mixture. In both processes, RM was very effective in the sorption of both inorganic and organic chlorine compounds. Hydrogen chloride (HCl) formation from the degradation of poly(vinyl chloride) (PVC) in MWP was depressed by RM. In one-step processing, the yield of liquid products from the degradation of MWP in HVGO was about 70 wt %. The chlorine content of the liquid product was 1127 ppm in the absence of RM, whereas it decreased to the very low level of 90 ppm in the presence of RM. We obtained oil having a negligible amount of chlorine using TR99300 and RM in the two-step process. The carbon number distribution of liquid products was similar in both processes. The liquid hydrocarbons derived from the degradation of MWP/HVGO were distributed in a wide range of carbon number (C_5–C_{25}) with a big peak at C_9.

Introduction

The amount of waste plastics increases annually worldwide. Each year, Europe generates about 15 million tons of post-consumer plastic waste,[1] the United States generates approximately 20 million tons,[2] and Japan about 15 million tons.[3] Disposal of waste plastics causes serious environmental problems. At present, both landfilling and incineration are widely practiced. Landfilling is not a solution because landfill space is limited and plastic wastes are resistant to environmental degradation. Incineration to produce heat is a possibility, but it may lead to the formation of highly toxic pollutants such as dioxins and furans. As an alternative feedstock recycling methods are currently being developed, and pyrolysis is one of the most promising of them. However, during thermal pyrolysis, the PVC in waste plastics generates HCl, causing a contamination of all product streams with chlorinated organics as well as corrosion problems. When the PVC mixed plastic derived oil is used as fuel, the chlorine compounds in the oil cause the corrosion of instruments and produce harmful substances.

Therefore the dechlorination of waste plastics is necessary. Much attention has been paid to the dechlorination of MWP- or PVC-containing polymer mixtures. Dechlorination attempts can be categorized into two groups, namely stepwise pyrolysis and catalytic. In stepwise pyrolysis, the degradation of PVC takes place at a lower temperature (around 300 °C) than that of other polymers, and HCl is evolved from PVC prior to the degradation of other polymers in the second step (>400 °C).

Bockhorn et al. [4] studied the stepwise pyrolysis of a mixture PVC/PS/PE/PA 6 polymers in a cascade of well-stirred reactors. In the first step (at 330 °C), a 99.6% dechlorination was achieved. Hydrochloride separation from household waste plastics by PVC decomposition has been attempted using extruders in several oil reclamation plants.[5–7] In extruders the waste plastics are pressurized by kneading and HCl gas is generated. However, at high pressure HCl gas can easily react with

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(1) Williams, P. T.; Williams, E. A. *J. Anal. Appl. Pyrolysis* **1999,** *51,* 107–126.
(2) Ramdoss, P. K.; Tarrer, A. R. *Fuel* **1998,** *77* (4)*,* 293–299.
(3) Saito, K.; Narita, H. Studies on the dechlorination and oil-production technology of waste plastics with high efficiency. *ISFR'99 The 1st International Symposium on Feedstock Recycling of Plastics,* Sendai, Japan, Oct. 31–Nov. 3, **1999,** pp 5–8.

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(5) Kajiyama, R. Waste Plastics Liquefaction Technology of Niigata Plastic-to-oil Conversion Center. *ISFR'99 The 1st International Symposium on Feedstock Recycling of Plastics,* Sendai, Japan, Oct. 31–Nov. 3, **1999,** pp 9–12.
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CaCO$_3$, metals, and organic matter which are included in the waste plastics. Kosugi[7] has reported that the residual chlorine concentration after the first step was decreased by the depressurization. They suggested that the dechlorination step should be conducted under low pressure in order to decrease the chlorine concentration. Recently, catalytic dechlorination is of increasing interest. The literature related to sorption of HCl from PVC degradation on metal oxides shows that HCl reacts with some metal oxides to form metal chlorides. Blazso et al [8] suggested that HCl formation can be depressed by using iron, zinc, Ca/Zn carboxylate, cupric oxides, and titanium dioxide. Kaminsky [9] employed lime for HCl fixation in the pyrolysis of MWP in a fluidized reactor. Pyrolysis gases were free from chlorine compounds and the oil had a chloro organic content of 15 ppm. However, he pointed out [10] that the excessive amount of CaCl$_2$, formed by the reaction between HCl from PVC and calcium carbonate, led to a blockage problem. So the PVC content of MWP must be limited. Horikawa et al[11] studied the fixation of HCl evolved from PVC by metal oxides,such as CaO, TiO$_2$, Fe$_2$O$_3$, MgO, etc. Sakata et al[12,13] studied the removal of organic and inorganic chlorine compounds from degradation products of PVC/PP mixed plastics by metal oxides sorbents, such as iron oxides (FeOOH, Fe$_2$O$_3$, Fe$_3$O$_4$, Fe$_3$O$_4$−carbon composite), ZnO, MgO, TiO$_2$, CaO, and CuO. They suggested that iron oxides, in particular FeOOH, Fe$_3$O$_4$, Fe$_3$O$_4$−carbon composite, were very effective for the removal of organic and inorganic chlorine compounds. In another work,[14] they studied the fixation of chlorine in oil derived from waste plastics with iron oxide−carbon composite sorbents. They suggested that Fe$_3$O$_4$ acts as both a chlorine sorbent and dechlorination catalyst.

In this study the thermal and catalytic degradation of MWP or MWP/HVGO mixture was carried out by both one-step processing and two-step processing. HVGO was used as a solvent to ensure homogeneity. The main purpose of this work is to investigate the effect of an industrial waste (red mud: RM) as a dechlorination catalyst.

Experimental Section

Materials. The municipal waste plastics (MWP) were obtained from Niigata City, Japan, in the form of fluff. MWP

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(8) Blazso, M.; Jakab, E. *J. Anal. Appl. Pyrolysis* **1999,** *49,* 125−143.

(9) Kaminsky, W.; Kim, Joo-Sik *J. Anal. Appl. Pyrolysis* **1999,** *51,* 127−134.

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(11) Horikawa, S.; Takai, Y.; Ukei, H.; Azuma, N.; Ueno, A. *J. Anal. Appl. Pyrolysis* **1999,** *51,* 167−179.

(12) Sakata, Y.; Uddin, Md. A.; Muto, A.; Shiraga, Y.; Murata, K. Removal of inorganic and organic chlorine compounds from the degradation products of PVC/PP mixed plastics by metal oxide sorbents. *Asia-Pacific Chemical Engineering Symposium, APCRE 99,* June 13−16, **1999,** pp 473−477.

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(14) Uddin, Md. A.; Shiraga, Y.; Muto, A.; Sakata, Y.; Murata, K. Liquefaction of Waste plastics by catalytic degradation and fixation of chlorine in waste plastics derived oil with iron oxide sorbents. *5th ARAB INTERN. CONFER. POLY. SCI., TECHNOL.* September **1999,** 18−22, Aswan-Egypt.

Table 1. Composition of Municipal Waste Plastic (MWP) from Niigata City, Japan (wt %)

| PE	PP	PS	PVC	PVDC	PET	ABS
30	18	26	5	6	13	2

also contain small amounts (5−6 wt %) of inorganic substances aluminum foil, iron foil, dirt (sand). They were cut into pieces of 2−5 mm. Their composition is shown in Table 1. Heavy vacuum gas oil (HVGO) (boiling point range of 242−578 °C, S = 2.55%) was supplied by TUPRAS−Izmir Refinery, Turkey. Red mud (RM) (specific surface area = 16 m^2 g^{-1}) was supplied by Seydisehir Alumina Plant, Turkey. It contains mainly Fe$_2$O$_3$ (37.72%), Al$_2$O$_3$ (17.27%), SiO$_2$ (17.10%), TiO$_2$ (4.81%), Na$_2$O (7.13%), and CaO (4.54%). The solid acid catalyst (SA-1) used is a commercial silica−alumina (SiO$_2$/Al$_2$O$_3$ = 8/2(molar ratio), specific surface area = 420 m^2 g^{-1}). TR97300(iron oxide−carbon composite) was developed by Okayam University and Toda Industries Co. Ltd., Japan, jointly: A mixture of 90 wt % FeOOH and 10 wt % phenol resin was compressed into pellets, then heat treated at 530 °C in nitrogen flow. After carbonization, the crystalline phase of the composite was Fe$_3$O$_4$. The resultant iron oxide−carbon composite contained 0.6.7 wt % amorphous carbon and had a surface area of 70. m^2 g^{-1}.

Liquefaction Procedure. Thermal and catalytic degradation of MWP or MWP/HVGO mixture was carried out by two different processes, namely one-step processing and two-step processing. The one-step process was performed in a glass reactor (35 mm i.d. and 350 mm length) with nitrogen flow at 430 °C, mainly by batch operation. MWP (10 g) or MWP (8 g)/HVGO (14 g) was loaded into reactor. The ratio of catalyst was 20 wt %. The reactor contents were heated to 120 °C and held at this temperature for 60 min to remove the physically absorbed water. Then it was heated to 300 °C at a rate of 3 °C min^{-1} and held at this temperature for an hour to evolve the HCl from the degradation of PVC. After dechlorination, temperature was increased to 430 °C at a rate of 3 °C min^{-1}. The outlet of the reactor was connected to a water-cooled condenser in order to condense the liquid products. The liquid products were collected in a graduated cylinder. Gaseous products passed through a flask with sodium hydroxide solution to trap hydrogen chloride and were finally collected in a Teflon bag.

A schematic diagram of the experimental set up has been given previously.[15] In the two-step process, the first step (degradation of MWP/HVGO mixture) was the as same as the one-step process. In the catalytic experiments, the catalyst was used at a ratio of 10 wt %. Following degradation, fixation of chlorine compounds in the oil derived from the degradation of MWP/HVGO was carried out in a fixed-bed flow-type reactor at 350 °C. An amount of 4 g of TR99300 or RM was packed in the reactor as a dechlorination catalyst or an equivalent volume of glass beads was used for the noncatalytic run.. The temperature of the second reactor was set at 350 °C. The products (both gaseous and liquid) evolved from the degradation in the first reactor were passed over a chlorine sorbent bed in the flow-type reactor (Figure 1). A detail of two-step processing has been given previously.[14] The liquid products were collected in a graduated cylinder. The evolved hydrogen chloride was trapped in a flask containing an aqueous solution of NaOH. In this work it was assumed that the degradation was completed when no more accumulation of liquid products was observed in the graduated cyclinder over a 30 min period. The lapsed time was counted from when the sample reached 120 °C to the end of degradation.

Analysis Methods. The quantitative analysis of the degradation compounds in oils was performed with a gas chromatograph equipped with a FID detector (YANACA:G 6800;

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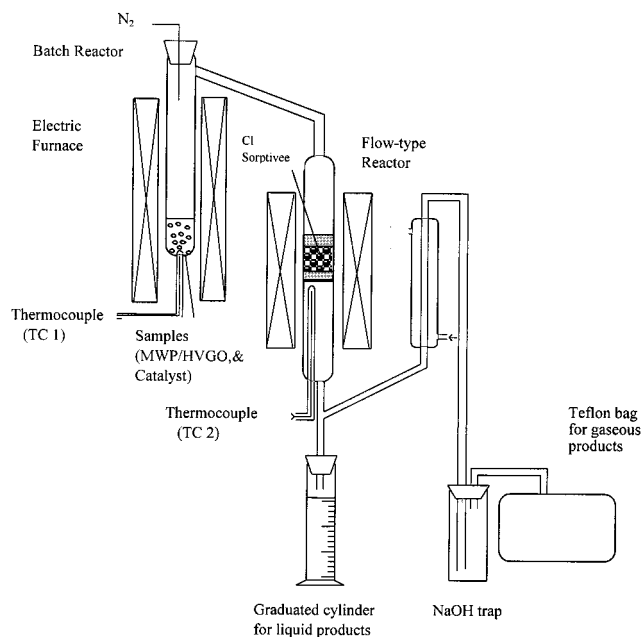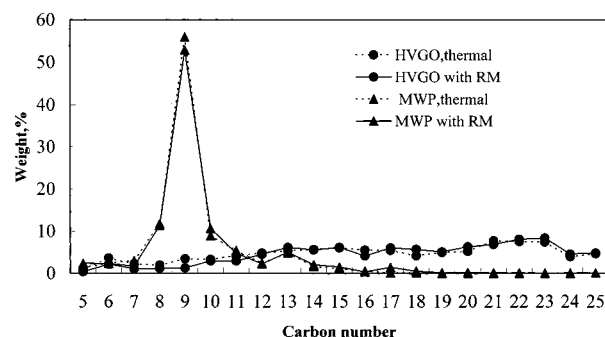
Figure 1. Experimental setup for thermal degradation of waste plastics and dechlorination of plastics-derived oil with solid sorptive catalyst in a two-step process.

Figure 2. Distribution of carbon number (NP-gram) in liquid products from degradation of MWP and HVGO in absence and presence of red mud.

Table 2. Product Yields for Thermal and Catalytic Degradation of MWP, HVGO, and MWP/HVGO Mixture at 430 °C by One-Step Processing, (wt %)

	catalyst	oil	gas	residue	liquid density, g cm^{-3}
MWP		39.7	21.2	39.1	0.814
MWP	red mud	46.8	8.5	44.8	0.810
HVGO		76.3	6.2	17.6	0.832
HVGO	red mud	68.6	13.9	17.6	0.824
MWP/HVGO		77.9	7.8	14.7	0.834
MWP/HVGO	red mud	70.2	12.0	17.8	0.835
MWP/HVGO	TR 99300	68.3	12.6	19.2	0.830

column, 100% methyl silicone; 50 m × 0.25 mm × 0.25 μm; temperature program, 40 °C(hold 15 min) → 280 °C(rate 5 °C/ min; hold 37 min). Total chlorine and total sulfur amount in liquid products were determined with a gas chromatograph–atomic emission detector instrument (AED;HP 62350A; column, HP-1;cross-linked methyl siloxane; 25 m × 0.32 mm × 0.17 μm; temperature program, 40 °C (hold 10 min) → 300 °C (rate 5 °C/min) hold 5.0 min). 1,2,4-Trichlorobenzene and dimethyl sulfur were used as the internal standard for the quantitative determination of chlorine and sulfur, respectively, in the GC-AED analysis. The composition of the oil was characterized using C-NP grams[16](C stands for carbon and NP from normal paraffin) and Cl-NP[13] grams (Cl stands for chlorine). These curves were obtained by plotting the weight percent of the products and the Cl amount, respectively, in the oil versus the carbon number of the normal paraffin having equivalent boiling points. Hydrogen chloride trapped in a flask containing an aqueous solution of NaOH was analyzed by ion chromatograph (IC).

Results

The Degradation and Dechlorination of MWP and MWP/HVGO by One-Step Processing. MWP and MWP/HVGO mixture were degraded at 430 °C with and without catalyst. The catalysts RM and TR99300 (iron oxide–carbon composite) were used to fix the chlorine compounds derived from the degradation of PVC in MWP. Iron oxide–carbon composites have shown a good effect on the fixation of chlorine.[14] In our unpublished study, we mentioned that RM is effective for the fixation of chlorine. Table 2 shows the yield of products obtained from the degradation of MWP and MWP/HVGO mixture with and without catalyst.

Although RM is a chlorine sorbent, it increased the oil yield and decreased the gas and residue amount in the degradation of MWP. With regard to the inorganic content (5–6 wt %) in MPW, we can suggest two ideas. First; the inorganic materials in MWP had an effect on

the cracking of small fragments of polymeric structure, leading to an increase in the amount of gas. Second, if the inorganic materials in MWP have no effect on the cracking, RM should lead to an increase in the amount of residue amount and a decrease in gas amount. But in our previously study (unpublished), we observed that RM had no considerable effect on the product yields from the degradation of both PVC-containing polymer mixtures (PVC/PE, PVC/PP, PVC/PS) and single polymers. The first idea seems to be more reasonable. Inorganic materials in MWP might have an effect either in their initial form or in the form of metal chlorides which formed from the reaction between the metals and HCl gas from degradation of PVC in MWP. In a previous study,[17] we investigated the spontaneous degradation of model mixed plastics having a composition similar to the MWP, in the presence of Al foil, and we mentioned that the coexistence of hydrogen chloride and Al foil led to the occurrence of an unusual reaction. In the present study, a drastic frothing occurred at the dechlorination step in the absence of RM. A mixture of carbonaceous particles and the melted plastics was blown out of the reactor. But in the presence of RM, there was no drastic reaction.

Composition of the liquid products from the degradation of MWP is shown in Figure 2. For both thermal and catalytic degradation, the main liquid products were from the degradation of PP and PS. In our unpublished study, we observed that PP and PS could be very easily cracked at 430 °C, and that the liquid hydrocarbons were distributed sharply in the range of C_8–C_{10} in the case of PS. The liquid hydrocarbons from PE degradation were distributed in a wide range of carbon numbers (C_5–C_{25}). The liquid products from PP also had a carbon number distribution of C_5–C_{25} with peaks at C_6, C_9, C_{11},
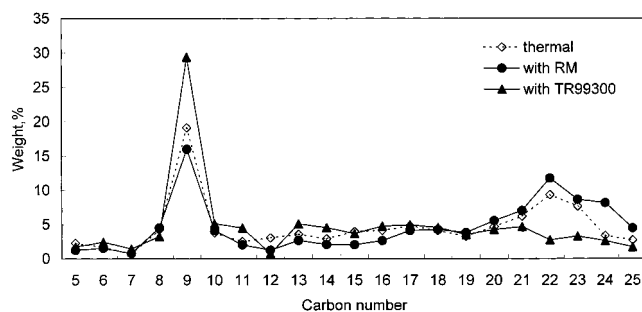
(16) Murata, K.; Makino, M. *Nippon Kagaku Kaishi* **1975**, *1*, 192–200.

(17) Sakata, Y.; Uddin, Md. A.; Muto, A.; Narazaki, M.; Koizumi, K.; Murata, K.; Kaji, M. *Ind. Eng. Chem. Res.* **1998**, *37* (7), 2889–2892.
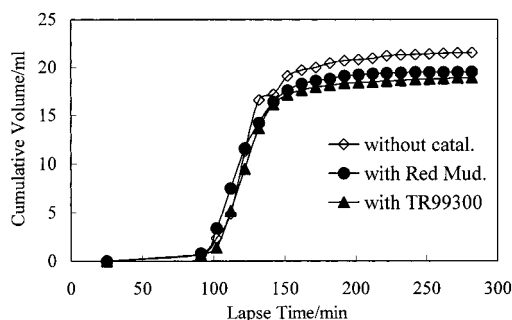
**Figure 3.** Cumulative volume of liquid products from thermal and catalytic degradation of MWP/HVGO mixture.

Figure 4. Distribution of carbon number (NP-gram) in liquid products from thermal and catalytic degradation of MWP/HVGO mixture.

C_{14}, C_{16}. Plastic waste composition had an effect on the liquid hydrocarbon's relative distribution.

The degradation of MWP in the presence of heavy petroleum products was also carried out. In this experiment, a mixture of MWP (8 g) and HVGO (14 g) was loaded in the reactor. In catalytic experiments RM and TR99300 were used as dechlorination catalyst. HVGO was used as a solvent to prevent blockage of the gas line and to obtain a homogeneous surrounding. To observe the effect of RM on the degradation of HVGO, HVGO (14 g) was pyrolyzed alone at 430 °C with and without RM. Red mud led to the degradation of liquid products to gas in the HVGO pyrolysis. When MWP and HVGO were pyrolyzed together, we observed a synergic effect. Considering the individual liquid yield of HVGO and RM, the theoritical liquid yield from the degradation of MWP/HVGO mixture is 63.5%. However the actual liquid yield was 23% higher than expected. This synergic effect may be explained thus: HVGO acted as a solvent, provided homogeneous conditions, and prevented the repolymerization and formation of gaseous product in the degradation of MWP. The inorganic materials in MWP acted as a catalyst for the degradation of HVGO.

The addition of RM or TR99300 led to a decrease in the liquid yield and increase in gas and residue yield, but had no considerable effect on the degradation rate (Figure 3). Figure 4 shows the composition of liquids from the degradation of MWP/HVGO with/without catalyst. In the presence of TR99300, the amount of C-9 hydrocarbons increased and the heavier hydrocarbons (>C_{20}) decreased dramatically.

Distributions of organic chlorine compounds derived from the degradation of MWP and MWP/HVGO mixtures with/without RM are shown in Figure 5 and 6 as Cl-NP gram as proposed by Md. A. Uddin et al[13] (The curve was obtained by plotting the Cl amount in oil
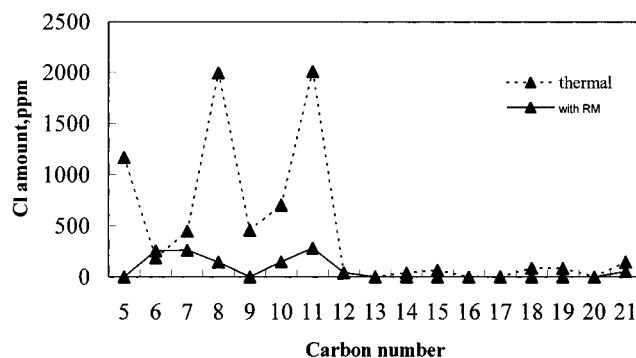
Figure 5. Cl-NP gram of liquid products from degradation of MWP at 430 °C.

**Table 3. Cl and S Content in Oil and in Traps for Catalytic and Thermal Degradation of MWP, HVGO, and MWP/HVGO, (ppm)**

| | | in oil | | in trap |
	catalyst	Cl	S	Cl⁻
MWP		7435		668
MWP	red mud	1185		53
HVGO			4030	
HVGO	red mud		3634	
MWP/HVGO		1127	1978	1803
MWP/HVGO	red mud	90	1888	13
MWP/HVGO	TR 99300	1283	2019	1489

versus the carbon number of the normal paraffin having equivalent boiling points). These compounds were mainly distributed in the range of n-C_5 to n-C_{11}.

RM had a big effect on the chlorine amount (both in liquid and gas products). The use of RM decreased the chlorine amount dramatically in both liquid and gaseous products (Table 3). The chlorine amount in liquid product was 1185 ppm in the presence of RM, and 7435 ppm in the absence of RM. However in the degradation of PVC-containing pure polymer mixtures (PVC/PE, PVC/PP, PVC/PS) with a dechlorination step, we obtained oil containing a lower amount of chlorine in the absence of RM than in the presence of RM. We mentioned that the inorganic materials in MWP catalyze the formation of organic chlorine compounds by the reaction between HCl and decomposition products. The HCl amounts in traps were 668 and 53 ppm in the absence and in the presence of RM, respectively. These results show that the RM is very effective for the adsorption of HCl.

The presence of HVGO had no considerable effect on the amount of chlorine in the oil. However, it favored the evolution of HCl. The chlorine amount in traps was 668 ppm for the degradation of MWP (10 g), and 1803 ppm for the degradation of MWP (8 g)/HVGO(15 g). Because HVGO acted as a solvent, HCl from the degradation of PVC was easily released. Although TR99300 is an effective dechlorination catalyst, it was not effective in the present study. RM was very effective for fixing the chlorine. It decreased the chlorine content in the oil to a very low level (90 ppm).

But the oils derived from MWP/HVGO contained sulfur compounds in all cases, due to the sulfur content of HVGO. Neither RM nor TR99300 was effective for decreasing sulfur content in oil. The degradation of MWP in HVGO had advantages, but it also led to high sulfur content. However, the desulfurization of fuels is widly practiced.
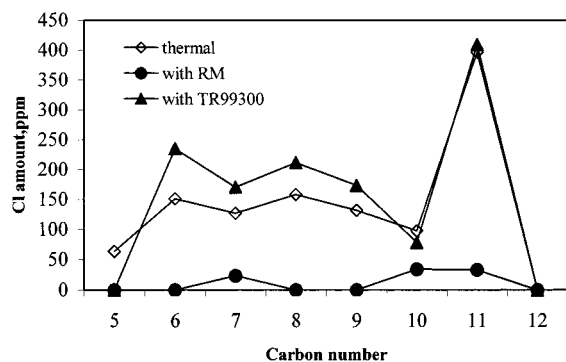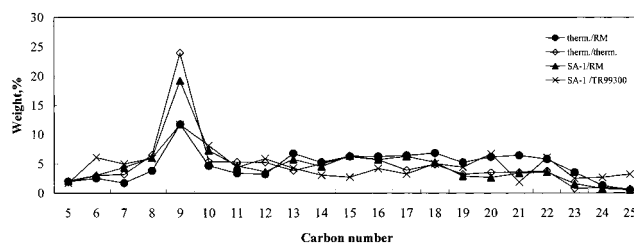
Figure 6. Cl-NP gram of liquid products from thermal and catalytic degradation of MWP/HVGO mixture.
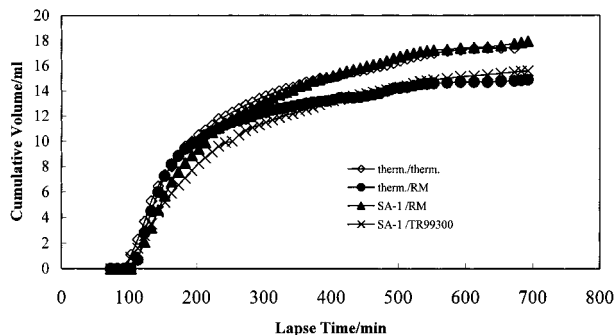
Figure 7. Cumulative volume of liquid products from degradation of MWP/HVGO mixture by two-step processing.

The Degradation and Dechlorination of MWP and MWP/HVGO by Two-Step Processing. The degradation of MWP in HVGO and the dechlorination of derived oil was carried out in two steps. First, thermal or acid catalytic (SA1) degradation in a batch reactor was carried out at 430 °C, and then the dechlorination of degradation products in a flow-type reactor over iron oxide composite catalyst (TR99300) and a waste product containing iron oxide (RM) at 350 °C was performed (Figure 1). For comparison, both the degradation and dechlorination were performed in the absence of any catalyst. In addition to MWP, dechlorinated municipal waste plastic samples also were subjected to catalytic cracking and dechlorination. Dechlorinated municipal waste plastics (abbreviated as dechlor.MWP) were collected from Kamagaya City, Japan. Their composition was very similar to that of MWP from Niigata City, Japan, but these waste plastics were subjected to dechlorination treatment at 300 °C followed by compression into small pellets of 3–5 mm size. Most of the chlorine content of the plastic samples was removed as HCl upon dechlorination, but 1.1 wt % of chlorine remained in the sample. Dechlorinated MWP (40 g) and 4 g of SA1 were loaded into the reactor. The same temperature program was applied. The cumulative volume of liquid products as a function of lapsed time for MWP/HVGO mixture degradation is shown in Figure 7. The use of SA-1 as a cracking catalyst did not have much effect on the degradation rate of MWP as in the case of PP and PE degradation.[15,18] As seen from the Figure 3 and Figure 8, the rate of degradation in one step was two times faster than that of two steps.

(18) Sakata, Y.; Uddin, Md. A.; Muto, A. *J. Anal. Appl. Pyrolysis* **1999**, *51*, 135–155.

Figure 8. Distribution of carbon number (NP-gram) in liquid products from degradation of MWP/HVGO mixture by two-step processing.

Table 4 shows the yield of products obtained from the degradation of MWP/HVGO mixture and dechlorinated MWP. The liquid products and residues were weighed and the amounts of the gases were determined from the difference. Gas amounts include also losses in the form of liquids remaining in the second reactor. The yield of the liquid products was around 50–60 wt %,which is lower than the liquid from the degradation by one step. The main reason for the low yield is losses. Since the temperature was 350 °C and the catalyst used was not a cracking catalyst in the second reactor, a part of the liquid products remained on the wall and on the catalyst bed. The liquid yield from thermal degradation was 58.8% in the case of thermal dechlorination and was 51.3% in the case of catalytic dechlorination with RM. The use of a solid acid catalyst (SA1) increased the liquid yield. When RM was used as a chlorine sorbent, the liquids yields were 62.9% in the presence of SA1. In case of the TR99300, the liquid yield was lower than that of RM. Because the TR99300 has a bigger surface area than RM, it adsorbed more liquid. The liquid yield derived from dechlorinated MWP was 50 wt %,which is almost same as the liquid yield obtained from two-step processing using SA3 (acid cracking catalyst)/TR97305-(iron oxide–carbon composite catalyst).[14]

Composition of the liquid products from the degradation of MWP/HVGO is shown in the C-NP gram of Figure 8. Liquid hydrocarbons were distributed in a wide range of carbon number (C_5–C_{25}) with a big peak at C_9. The presence of a dechlorination catalyst affected the liquid composition, especially the percentage of C_9 hydrocarbons. The carbon number distribution was similar to that of liquid products derived by one-step processing. The liquid hydrocarbons derived from dechlorinated MWP had a carbon number distribution of C_5–C_{20} with a big peak at C_9 as in the previous work.[14]

The chlorine amount in traps, which shows the HCl gas, was 800 ppm for the thermal dechlorination, but was lower than 30 ppm for the catalytic dechlorination. This shows that HCl evolved from the degradation of PVC was fixed by both RM and TR99300. We have already obtained the same result from the one-step degradation using RM. It is interesting that TR99300 was not effective in the chlorine sorption in the one-step process, but was very effective in the two-step processing. The reason is the inorganic materials in MWP. In the case of thermal degradation, we have obtained an oil having 728 ppm chlorine content by thermal dechlorination and an oil having 14 ppm chlorine content by catalytic dechlorination with RM. Distribution of organic compounds is shown in Figure 9. In thermal dechlorination, these compounds were distributed in a range equivalent to carbon numbers
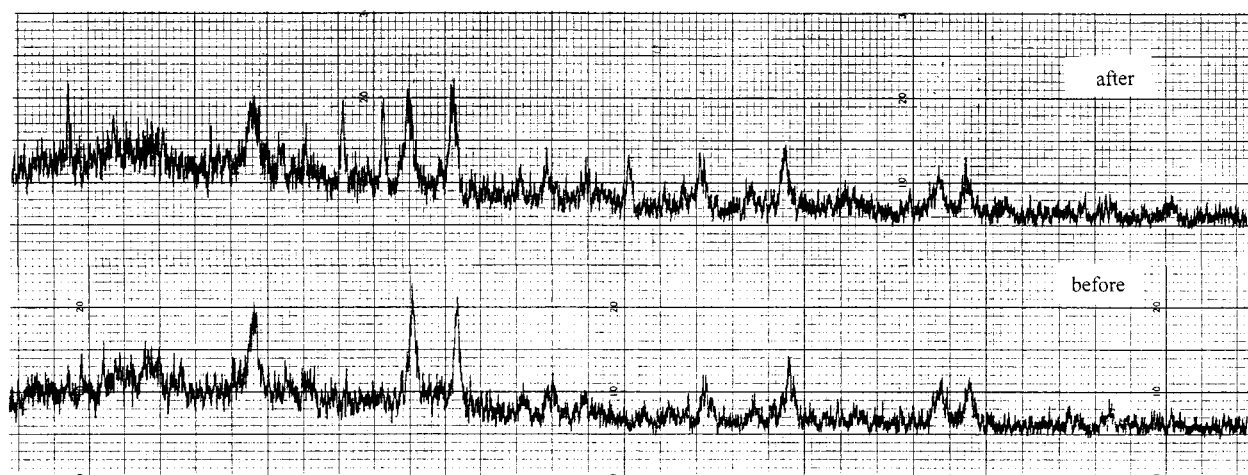
Figure 10. XRD pattern of red mud before and after use in MWP degradation.

Table 4. Product Yields for Thermal and Catalytic Degradation of MWP/HVGO Mixture and Dechlor.MWP by Two-step Processing, (wt %)

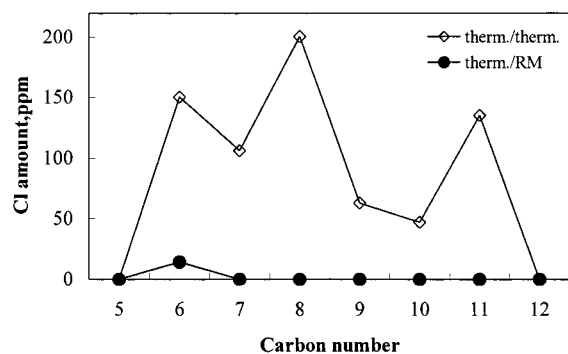|	catalyst		temperature,°C					liquid density,
	I. reac	II. reac	I. reac	II. reac	oil	residue	gas + loss	g cm^{-3}
MWP/HVGO			430	350	58.9	23.5	17.7	0.809
MWP/HVGO		RM	430	350	51.3	18.7	30.0	0.802
MWP/HVGO	SA-1	RM	430	350	62.9	19.0	18.1	0.815
MWP/HVGO	SA-1	TR99300	430	350	53.9	22.7	23.4	0.813
Dechlor.MWP			430	350	62.0	21.8	16.2	0.808
Dechlor.MWP	SA-1	RM	430	350	50.2	31.1	18.7	0.806

Figure 9. Cl-NP gram of liquid products from degradation of MWP/HVGO mixture by two-step processing.

Table 5. Cl, and S Content in Oil and in Traps for Catalytic and Thermal Degradation of MWP/HVGO and Dechl.MWP by two-step Processing, (ppm)

	catalyst		in oil		
	I. reac	II. reac	Cl	S	in trap, Cl$^-$
MWP/HVGO			728	3684	800
MWP/HVGO		RM	14	1890	nil
MWP/HVGO	SA-1	RM		2325	6
MWP/HVGO	SA-1	TR99300		2037	28
Dechlor.MWP			166		1.15
Dechlor.MWP	SA-1	RM			10

C_6-C_{11}, whereas only one single organic chlorine compound (equivalent carbon number n-C_6) was formed by catalytic dechlorination with RM. From catalytic degradation (SA1) and catalytic dechlorination (both TR99300 and RM), we have obtained chlorine-free oil from the degradation of MWP/HVGO mixture and dechlorinated MWP. These results show that both RM and TR99300 not only absorbed the HCl from PVC degradation, they also acted as a catalyst for the dechlorination of the organic chlorine compounds.

In our previous study,[14,19] we concluded that iron oxide−carbon composite catalysts acts as a sorbent as well as a dechlorination catalyst and iron oxide transformed into $FeCl_2$ finally acts as a dechlorination catalyst. RM had also showed a similar effect. We can suggest that in the dechlorination step, metal chlorides were formed by the absorption of HCl on the RM, and these metal chlorides acted as a catalyst in the dechlorination of organic chlorine compounds. Since RM is a complex mixture of inorganic materials and is not a synthesized catalyst, we do not know exactly which metal chloride compounds were formed and which of them acted as a catalyst. As in the one-step processing, in this group of experiments we obtained oils having high sulfur XRD patterns of red mud before and after use in two-step processing.

We have observed that RM had a good effect on the fixation of HCl evolved from PVC in both the degradation of MWP (in the present study) and PVC-containing pure polymer mixtures (PVC/PE, PVC/PP, and PVC/PS) (in our unpublished work). Two-step processing gave us the opportunity to analyze the XRD patterns of RM since it was not mixed with residue. Figure 10 shows the XRD pattern of RM before and after use in the two-step process. After two-step processing, only calcium chloride hydrate ($CaCl_2.2H_2O$) appeared. We expected the formation of iron chloride compounds. No crystalline phase of iron chloride was observed. The formed $FeCl_2$ may be present as a monolayer on the iron (II) oxides, no crystalline peaks of $FeCl_2$ will be observed under these conditions.[20]

(19) Lingaiah, N.; Uddin, Md. A.; Muto, A.; Sakata, Y.; Imai, T. Dechlorination of Organic Chlorine Compounds over Iron Oxide Carbon Composite Catalysts for the Refinement of Waste Plastic Derived Oil. *ISFR'99 The 1st International Symposium on Feedstock Recycling of Plastics,* Sendai, Japan, Oct. 31−Nov. 3, **1999**, pp 119−122.
(20) Xie, Y. C.; Tang, Y. Q. *Appl. Heterogen. Catal.* **1990**, *37*, 1−25.

Conclusion

The conversion of MWP in HVGO to fuel oil was carried out by two different processes in the presence and absence of a catalyst.

-Copyrolysis of MWP with HVGO led to a synergic effect. The liquid yield was 23% higher than expected.

-The use of solid acid catalyst (SA1) increased the liquid yield.

-Iron oxide−carbon composite catalyst (TR99300) was not effective in the sorption of chlorine compounds when it was in contact with MWP. However, it was very effective as a dechlorination catalyst when it was in contact with only degradation products of MWP.

-In both processes, red mud was very effective for the removal of inorganic and organic chlorine compounds from the thermal degradation of MWP. HCl formation was depressed in the presence of RM. We may conclude that metal chlorides formed by the absorption of HCl on RM acted as a dechlorination catalyst as iron oxide− carbon composite catalyst.

By using both cracking (SA1) and dechlorination catalysts (TR99300 or RM), an oil with no chlorine content was obtained in the degradation of MWP/HVGO mixture.