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Decomposition of PVC and Ion Exchange Resin in Supercritical Water

Jung-Sung Kim, Sang-Hwan Lee*, Yoon-Yul Park, Hoshikawa Yasuyo* and Tomiyasu Hiroshi***

Department of Chemistry Education, Daegu University, Daegu 712-714, Korea
**Department of Chemistry and Material Engineering, Shinsu University, Nagano 390-8621, Japan*
***Life Science Institute, Busan College of Information Technology, Busan 617-737, Korea*
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This study introduces the development of new supercritical water oxidation(SCW)(multiple step oxidation) to destruct recalcitrant organic substances totally and safely by using sodium nitrate as an oxidant. This method has solved the problems of conventional SCW, such as precipitation of salt due to lowered permittivity, pressure increase following rapid rise of reaction temperature, and corrosion of reactor due to the generation of strong acid.

Destruction condition and rate in the supercritical water were examined using Polyvinyl Chloride(PVC) and ion exchange resins as organic substances. The experiment was carried out at 450℃ for 30 min, which is relatively lower than the temperature for supercritical water oxidation (600-650℃). The decomposition rates of various incombustible organic substances were very high [PVC(87.5%), Anion exchange resin(98.6%), Cationexchange resin(98.0%)]. It was observed that hetero atoms existed in organic compounds and chlorine was neutralized by sodium (salt formation).

However, relatively large amount of sodium nitrate (4 equivalent) was required to raise the decomposition ratio. For complete oxidation of PCB was intended, the amount of oxidizer was an important parameter.

Key Words : Polyvinyl Chloride(PVC), Ion exchange resin, Supercritical water, Oxidation, Nitrate, Nitrite

1. Introduction

In general, chlorinated organic substances including PCB and dioxins which are stable against heat and hard to decompose. Polyvinyl chloride (PVC), a chlorinated organic substance, is not harmful in itself but it produces highly toxic material like dioxin during decomposition[1].

Disposal of PVC is more difficult than other plastics. As 57wt% of its molecules weight is chlorine, it produces large amount of hydrogen chloride during incineration, and in the result, the incinerator can be easily damaged. And the chlorine reacts with the additionally produced organic ring compounds and produces dioxins[2~5].

In addition, disposables, paper, masks, and rubber gloves used in nuclear facilities are contaminated with low level radioactivity and cannot be simply discarded. Plastics used in nuclear power generation facilities contain a lot of incombustible material such as PVC. This makes very difficult to incinerate and to reduce low level radioactive wastes.

Like polyethylene (PE), PVC [$(CH_2CHCl)n$] is difficult to decompose with supercritical water. PVC is more dangerous than PE because it produces hydrogen chloride at temperatures above 190℃[6]. If strong acid such as hydrochloride is generated in supercritical water, the reactor becomes to be corroded.

The reaction mechanism shown in Fig. 1, occurs in common combustion reaction[7]. The aromatic compounds can be produced by byproducts of diene and dienophile, and the reaction is proceeded according to Diels-Alder reaction. Because large amount of chlorine exists at this time. dioxins could be produced by additional reaction.

Some problems are occurred, while PVC is treated

Corresponding Author : Jung-Sung Kim, Department of Chemistry Education, Daegu University, Daegu 712-714, Korea
Phone: +82-53-850-6984
E-mail: jskim2@daegu.ac.kr

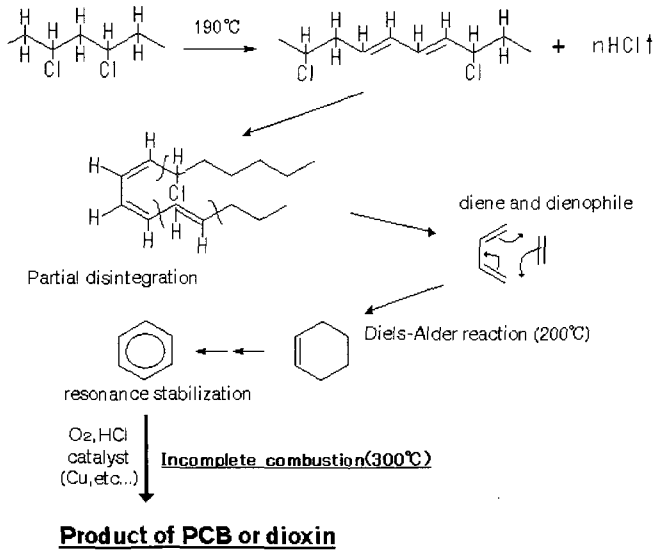

Fig. 1. Generating process of PCB or Dioxin for by- product of PVC combustion.

with supercritical water. One problem is the generation of chlorine, second is low decomposion ratio, and the third is value of materials produced by decomposition. The problem of chlorine generated could be solved by using an appropriate additive to neutralize chlorine[8,9]. Another problems could be solved by using catalyst, ruthenium (Ⅳ) dioxide. This catalyst is reduced to Ru(0) by the energy obtained from the oxidation of hydrocarbon, which reacts with water and produces ruthenium (Ⅳ) dioxide and hydrogen. However, Tomiyasu et al[10]. found that the catalytic effect of ruthenium (Ⅳ) dioxide in organic compounds containing chlorine was very low. The catalyst was interfered by chlorine ligand because ruthenium was converted to ruthenium tetrachloride.

Supercritical water oxidation (SCWO) is the widest method of the oxidization of chlorinated organic substance[11,12]. It was very difficult to treat PVC for reusing as a resource because the incinerator is corroded by harmful dioxins and chlorine which were produced during the incineration of PVC. So it was necessary to devise a new incineration process.

In this study, we described the usefulness of the supercritical water oxidation reaction of polyvinyl chloride (PVC), ion exchange resin needed oxidant of sodium nitrate ($NaNO_3$) and sodium nitrite ($NaNO_2$). The reaction pathways including side reaction were also discussed.

<Principles of multi-step SCW oxidation>

The multi-step oxidation supplements the drawbacks of conventional SC for the destruction of chlorinated organic substances, This method involves multiple step oxidation using sodium nitrate as an oxidant. The multi-step oxidation consists of oxidation in multiple steps starting from $NaNO_3$ to the final product of N_2 via $NaNO_2$ and NO_X as intermediates. The reaction occurs as follows.

$$NaNO_3(\text{V}) \rightarrow NaNO_2(+\text{III}) + \frac{1}{2}O_2 + 2e^- \quad (1)$$

$$NaNO_2(+\text{III}) + \frac{1}{2}H_2O \rightarrow NaOH + NO(\text{II}) + \frac{1}{4}O_2 + e^- \quad (2)$$

$$NO(\text{II}) \rightarrow \frac{1}{2}N_2(0) + \frac{1}{2}O_2 + 2e^- \quad (3)$$

These are reaction equations when oxygen molecules are generated from sodium nitrate. However, oxygen molecules were not generated, as sodium nitrate is stabilized

$$NaNO_3 + Org \rightarrow NaNO_2 + CO_2 \quad (4)$$

Direct reaction like (4) or reaction equation like (5) instead of (2) and (3) can be conjectured,

$$NaNO_2 + Org \rightarrow Na+ + \frac{1}{2}N_2 + nCO_2 + nH_2O + 4e^- \quad (5)$$

In this reaction, it is thought that hydrogen is supplied by organic substance.

As the oxidizers react in several steps, this method was named Super Critical Water Multiple-step Oxidation (SCWMO), It is to differentiate from SCWO. This reaction is caused by the special structure of nitric acid molecule, but multi step oxidation is not limited to sodium nitrate salt used in this experiment.

In addition to above reaction, sodium nitrate has a big advantage as an oxidizer because it contains Na+.

When PVC is applied, NaOH produced in equation (2) works as a neutralizer and the following reaction can be conjectured,

$$HCl + NaCl \rightarrow NaCl + H_2O \quad (6)$$

As this can incapacitate the corrosion capability of acid during reaction, it is very important.

After Cl^- is all used up, the following reaction can be conjectured,

$$NaOH + CO_2 \rightarrow NaHCO_3 \quad (7)$$

This seems to apply to organic substance without hetero atoms like the chlorine in PVC. Similarly, in organic substances containing sulphur, like cation resin and inflammable rubber glove, the following salt formation reaction can be conjectured.

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O \quad (8)$$

Above are the results of the experiment that applied SCWMO using sodium nitrate to various organic substances.

2. Experimental

An experiment of destructing recalcitrant organic substances was carried out using multi-step SCW oxidation and sodium nitrate as an oxidant. PVC, anion exchange resin and cation exchange resin were used as chlorinated organic substances.

PVC is manufactured by addition polymerization of vinyl chloride monomer, which is made by adding silver chloride, a catalyst, and chlorine to ethylene. Ion exchange resin is used for the treatment of organic substances in the filtration and dechlorination processes of liquid radioactive waste. After the treatment, the ion exchange resin becomes radioactive waste. SCW oxidation was carried out for the ion exchange resin.

The used batch reactor was made of corrosion resistant INCONEL 625 (Ni 60%, Cr 20%, Mo 10%, Fe, Ni, Ta) alloy and its volume was 10.8 mL. 150 mg of each organic substance was treated in supercritical water and its decomposition rate was measured. Sodium nitrate as an oxidizer was used by various equivalent of organic substance. the sample and water (3 mL) was injected into the reactor. Then, a rod heater was connected to the reactor to raise the temperature. The reaction temperature was at 450℃ for all samples. After the temperature reached to 450 ℃, it was maintained for 30 minutes. Then, the heater was turned off and the reactor was cooled at room temperature for 3 hours. The cross sectional view of the reactor is described in Fig. 2.

To measure the reaction product, the following method was used. ① After thr reaction mixtyre was cooled, pH was measured of it. ② Then the mixture was extracted with organic solvent, the organic and aqueous layer was dried by an evaporator. Using phase separation, the reaction product was separated into organic liquid phase and water phase.

③ The diffraction pattern of aqueous layer residue was analyzed by a powder X-ray diffractometer (RINT2200V/PC-SV, RIGAKU). Then the JADE standard diffraction pattern data was referenced for the identification of the salt formed.

④ The gas generated was analyzed. After putting the sample in the reactor, a valve was connected and reactor was charged with Ar or He. For the analysis of gas components, Gas chromatography mass spectrometry (GC-MS) (GCMS-QP5000, SIMMATSU) was used, and for the analysis of the amount of gas generated, TCP (GC8APT, SIMMATSU), and FID (GC8APF,

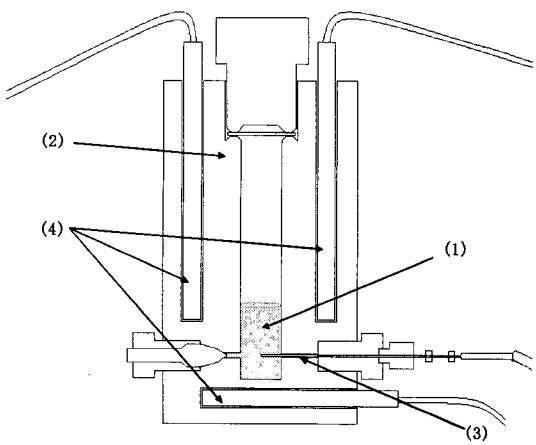

Fig. 2. Schematic diagram of batch reactor system: (1) reaction mixture; (2) reactor; (3) thermocouple; (4) rod-like heater.

SIMMATSU) were used. This pressure was not measured of the inside of the reactor.

3. Results and discussion

3.1. Time to reach to the reaction temperature and exothermic reaction

Fig. 3 illustrates the temperature variation of reaction vessel and heater according to heating time when PVC was treated in supercritical water. As shown in Fig. 3, the supercritical temperature (374℃) of water was reached after heating for 17 min and the reaction vessel temperature exceeded the heater temperature after about 9 minutes. This result indicated that supercritical water oxidation was an exothermic reaction alike a combustion reaction of organic material.

In supercritical water oxidation, generally organic material is used as 1～10 wt% of solvent. if the organic substance is very concentrated, the reaction device is radiated much heat[13]. So external cooling facility is necessary even if cost is increased. The concentration of organic substance used in this study was 20 wt%, but the experiment was carried out 450℃ of lower temperatures than the supercritical water oxidation temperature (600～650℃). The real reaction time was around 30 minutes reaching the supercritical temperature.

3.2. The decomposition rate of PVC

Complete oxidation of PVC can be expressed in the following equation.

$$-(CH_2CHCl)_n- + 11/2n(O) \rightarrow n(2CO_2 + 3/2H_2O + Cl^-) \quad (9)$$

When the sample (150 mg) is converted to viny chloride (2.4 mmol), the oxygen atoms (13.2 mmol) are needed for complete oxidizing from above equation. The numbers of moles of oxygen atom in 374 mg of sodium nitrate are equal to moles of the oxygen atom for complete oxidizing. The data of decomposition ratio is illustrated in Table 1 and Fig. 4. The decomposition ratio was about 70% at the 3 equivalent of $NaNO_3$, but on the other hand the decomposition rate was increased over 10% at the 4 equivalent of $NaNO_3$.

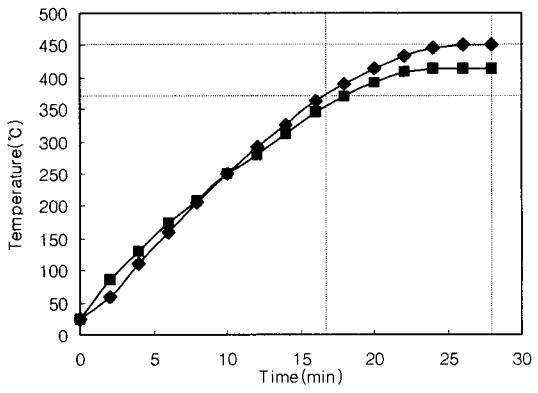

Fig. 3. The plot of temperature in the reactor system against heating time when PVC was treated in supercritical water. ◆:Temperature in reaction vessel, ■:Heater temperature. Reaction temperature was 450℃.

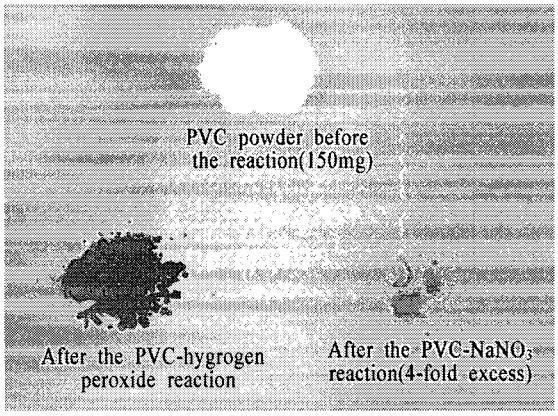

Fig. 4. Comparison of solid residues after the multi-step SCW oxidation using sodium nitrate as the oxidant and conventional SCW oxidation.

Table 1. Result of decomposition rate after supercritical water at 450℃ for 30 min versus equivalents of $NaNO_3$

PVC (g)	$NaNO_3$ (g)	$NaNO_3$/Org	Water phase residue(g)	Organic liquid phase residue(g)	Residue total	Decomposition rate(%)
0.150	-	-	0.046	0.014	0.060	60.0
0.150	0.150	**1.0**	0.050	0.007	0.057	62.1
0.150	0.300	**2.0**	0.047	0.002	0.049	67.7
0.150	0.450	**3.0**	0.037	0.001	0.038	74.7
0.150	0.600	**4.0**	0.018	0.001	0.019	87.3
0.150	0.750	**5.0**	0.017	0.001	0.018	88.0

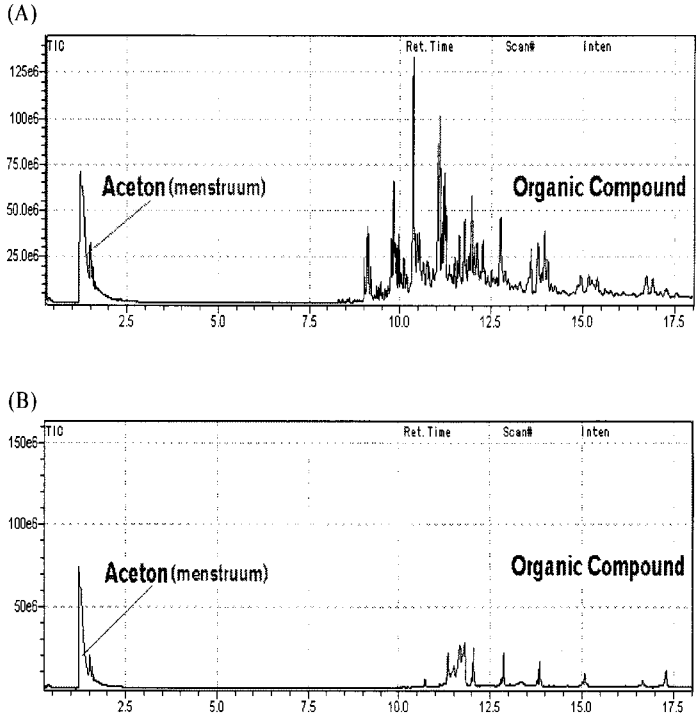

Fig. 5. GC spectra of treatment (A) without oxidizer and (B) with oxidizer (4 equivalent of NaNO3) after supercritical water treatment for PVC.

However, the decomposition ratio at the 5 equivalent of $NaNO_3$ was similar to that of the 4 equivalent of $NaNO_3$. Thus, the decomposition ratio of 4 equivalent of $NaNO_3$ was more efficient. The gas chromatography spectra of organic layer residue is shown in Fig. 5. Acetone was used as solvent. From the analysis of MS spectrum, the peaks of only unsaturated ring materials were detected in the reaction with supercritical water.

The peaks detected in Fig. 5 (B) are hydrocarbon chains (number of carbon atoms : 10-50). The structure of byproducts are drawn in Fig. 6.

The PVC existed in supercritical water is converted to various compounds through the conversion reaction as shown in Fig. 1. However, when 4 equivalent of sodium nitrate was added to the reaction, the unsaturated adduct was almost decomposed as shown in Fig. 5 (B). The oil residue was produced about 14 mg without treatment by sodium nitrate, while it was produced about 1 mg by adding 4 equivalent of sodium nitrate as shown in Table 1.

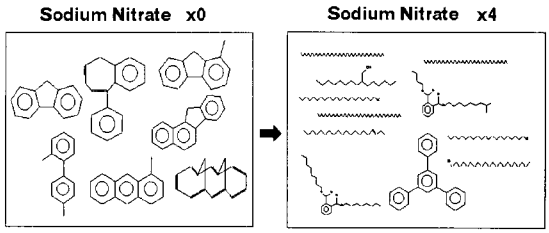

Fig. 6. Organic by product.

Also, the chlorinated material like dioxins and PCB were not observed. The materials included a basic structure like biphenyl were found in the supercritical water reaction without oxidizer, but such chlorinated materials as PCB were not observed.

The pH of the reaction mixture was measured for recognizing the amount of hydro chloride in the reaction mixture treated with sodium nitrate. Fig. 7 shows the colors of pH paper for each amount of sodium nitrate in PVC.

As shown in Fig. 7, when above 300 mg of sodium nitrate was added, PH of the reaction mixture

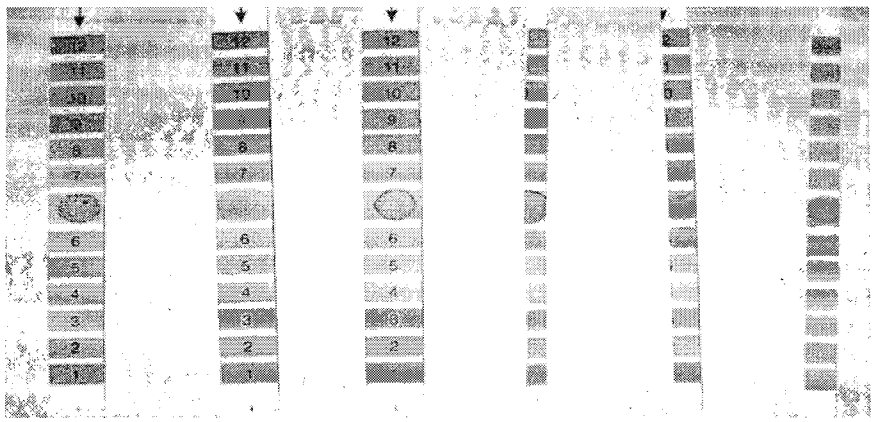

Fig. 7. The colors of pH paper for each amount of sodium nitrate in PVC (150 mg) at 450℃ for 30 min.

indicated alkaline. so the mixture to be neutralized was contained less than 300 mg of sodium nitrate.

Fig. 8 shows the peaks obtained by XRD of water residue after supercritical treatment with 5 times the equivalent weight of sodium nitrate and equivalent weight of sodium nitrate. The one treated with 5 equivalent of $NaNO_3$ shows the peaks of $NaNO_3$, $NaNO_2$, NaCl, and $NaHCO_3$. Accordingly, the product having alkalinity is thought to be due to sodium nitrite or sodium hydrogen carbonate. In the treatment with equivalent weight of sodium nitrate, sodium nitrate was all consumed and only NaCl peak remained.

3.3. Decomposition rate of other organic substances

Fig. 9 shows the structures of major organic substances contained in anion resin, cation resin, and inflammable rubber gloves.

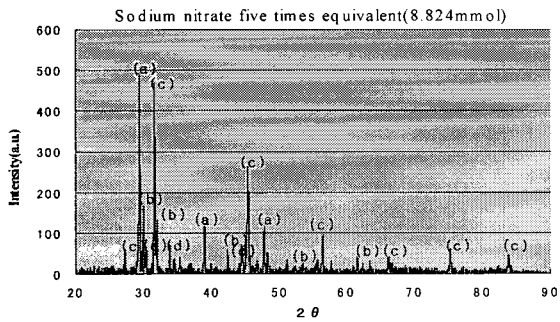

Fig. 8. Peaks obtained by XRD of water residue after supercritical treatment with 5 equivalent of sodium nitrate, (a) $NaNO_3$, (b) $NaNO_2$, (c) NaCl, (d) $NaHCO_3$.

The basic structure of ion exchange resin is a copolymer of styrene and p-divinyl benzene. An inflammable rubber glove consists of 60 wt% of natural rubber, 40wt% of sulphur and zinc. The results of the experiment are shown in Table 2.

As for ion exchange resin, the decomposition rates of trimethylamine group and sulfonic group were not different much. The decomposition rate was approached to 100% by using over 3 equivalent of sodium nitrate.

Fig. 10 shows GC-MS results after supercritical water treatment of anion resin. As shown in Fig. 10 (B), the anion exchange resin was decomposed to hydrocarbon chain when sodium nitrate was excessive.

The left peak in Fig. 10 represents acetone that is solvent, and the right peak represents the organic

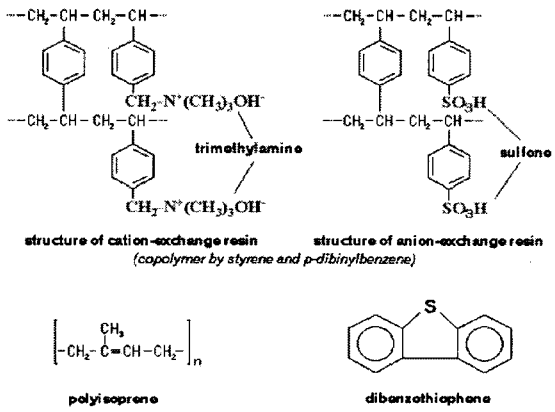

Fig. 9. Structure of each organic compound.

Table 2. Decomposition ratio for Anion exchange resin and Cation exchange resin

Organic matter	Oxident ($NaNO_3$ (g))	$NaNO_3$/Org	Water phase residue(g)	Organic liquid phase residue(g)	Residue total	Decomposition rate(%)
Anion exchange resin (0.150 g)	0.300	**2.0**	0.002	0.010	0.012	92.9
	0.450	**3.0**	0.001	0.004	0.005	98.2
	0.600	**4.0**	0.001	0.002	0.003	98.6
	0.750	**5.0**	0.002	0.003	0.002	98.5
Cation exchange resin (0.150 g)	0.450	**3.0**	0.002	0.001	0.003	98.4
	0.600	**4.0**	0.002	0.001	0.003	98.0
	0.750	**5.0**	0.002	0.000	0.002	98.2

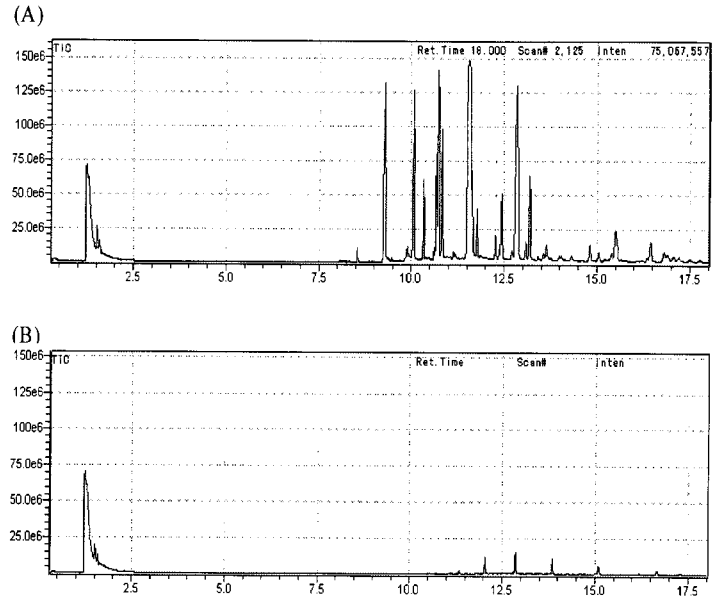

Fig. 10. Gas chromatograph peak after supercritical water treatment for anion-exchange resin. The sodium nitrite was used (A) 2 equivalent and (B) 5 equivalent.

compound.

3.4. Analysis of generated gas

In treating organic wastes, the stability of solid residue as well as the components of generated gas are important. The gases generated from PVC and cation resin was analyzed by GC-MS, and the results are shown in Fig. 11 (PVC, 5 equivalent) and Fig. 12 (cation exchange resin, 5 equivalent). As shown in Fig. 11 and 12, only CO_2 peaks for both PVC and cation resin were detected.

When a gas analysis is carried out, the nitrogen peaks are not accurately identified because nitrogen mixes with air. To prevent this, gas chromatography was carried out in a completely enclosed condition. The result was shown in Fig 13. Peak at 2.085 of retention time is nitrogen and the peak near 12.2~12.3 is CO_2. From this experiment, the absolute amount of gas generated could be measured, the reaction rate (complete decomposition rate) could be calculated from the amount of nitrogen generated.

4. Conclusion

This experiment was carried out at 450℃, a temperature relatively lower than the conventional SCW oxidation temperature of 600~650℃. The destruction rate of incombustible organic substance was very high. The decomposition rates at the 4 equivalent of $NaNO_3$ at the reactor temperature of 450℃ were as follows; PVC(87.5%), anion exchange resin(98.6%), and cation exchange resin(98.0%).

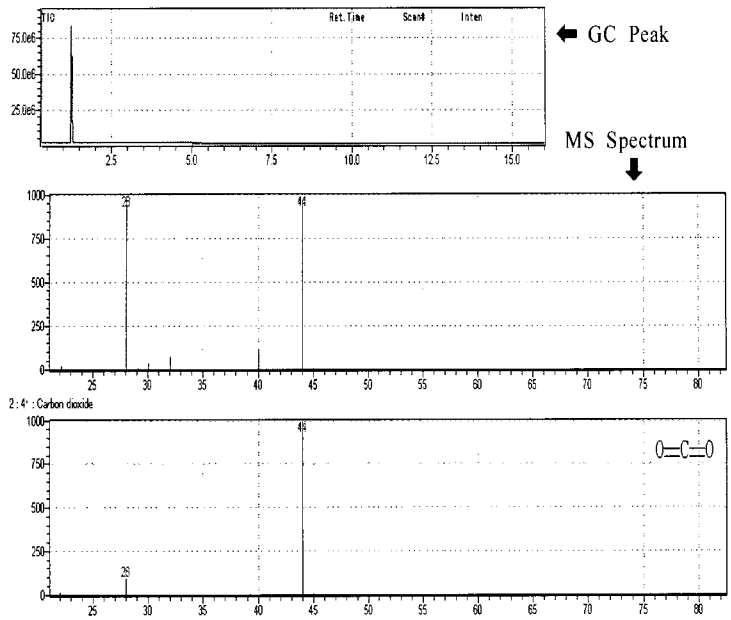

Fig. 11. GC-MS analysis of gases generated from PVC (5 equivalent). Reactions were conducted at water density 0.3 g/cm^3 on 450℃ for 30 min.

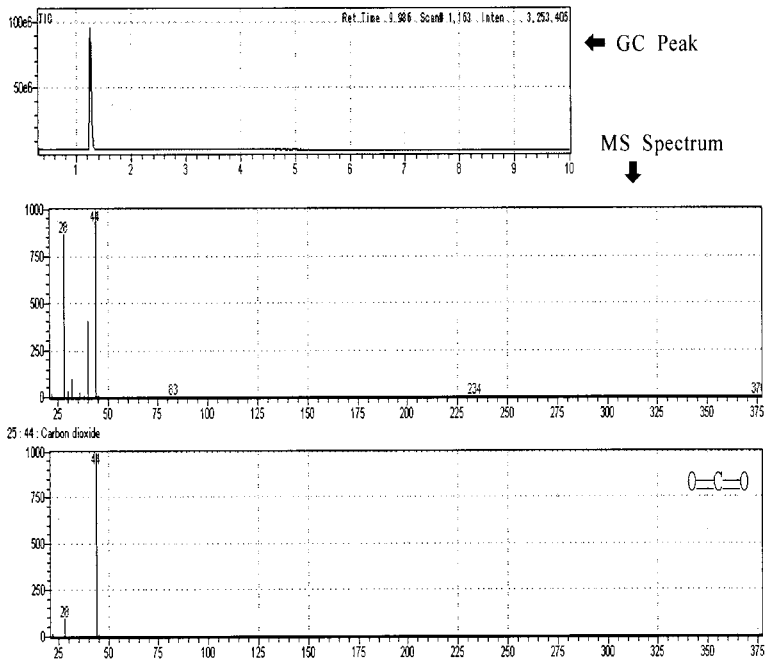

Fig. 12. GC-MS analysis of gases generated from of cation exchange resin. Reactions were conducted at water density 0.3 g/cm^3 on 450℃ for 30 min.

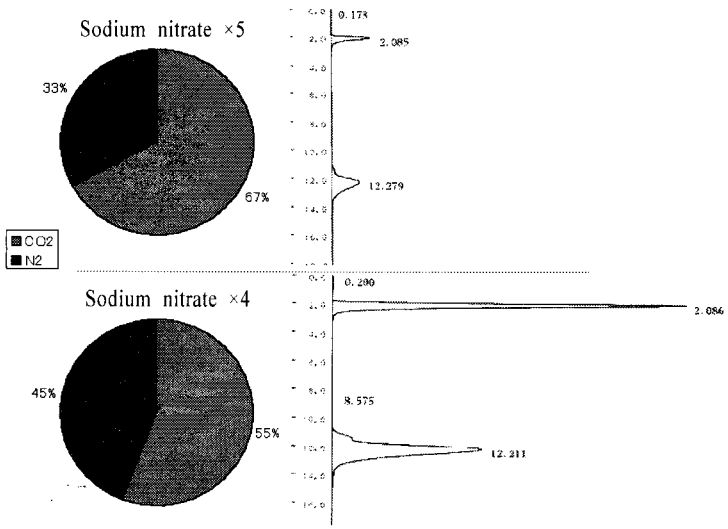

Fig. 13. The analysis results of generated gas components. After injecting the sample in the reactor, a valve was connected and the content of the reactor was substituted with Ar or He.

In the temperature ranges over 500℃, the permittivity drops rapidly and salt(NaCl) is generated in the reactor. Thus, it is difficult to treat a large amount of organic substances. However, reaction in this experiment occurs in the lower temperature range of 450℃, and such problem was avoided. In addition, hydrochloric acid generated from the destruction of chlorinated organic substance was neutralized at the same time. As a result, the solution maintained weak alkalinity(around pH 8), which prevented reactor corrosion.

It was confirmed that only the harmless CO_2 and N_2 gases were generated.

XRD measurement shows that unreacted sodium nitrate and sodium nitrite remained. This is thought that sodium nitrate, the oxidant, does not generate oxygen, instead it reacts directly with the organic substance, which releases oxygen atoms and causes oxidation. It is profoundly different from the conventional SCW oxidation, which uses oxygen to oxidize organic substances.

Acknowledgement

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