Performance tests of newly developed adsorption/plasma combined system for decomposition of volatile organic compounds under continuous flow condition

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Abstract

The adsorption/plasma decomposition with the combination of adsorption honeycomb-sheets and a plasma element is a new technology for small-sized apparatuses to decompose volatile organic compounds (VOCs) at concentrations lower than about 100 ppm. The feasibility of the prototype adsorption/plasma decomposition apparatus was evaluated with the simulated exhausts containing one VOC component and with real exhausts from a painting booth and an adhesion factory. The apparatus decomposed VOCs effectively at the painting booth exhaust but not always satisfactorily at the adhesion factory exhaust. The performance test results with real exhausts were discussed with respect to the concentration and discharge pattern of the exhausts and the basic properties of the system such as cooperation of adsorption and plasma reaction and the concentration dependence of the performance.

Introduction

Volatile organic compounds (VOCs) have been discharged in large quantities from many industrial processes, such as painting industry, printing industry, adhesion industry etc. (Aoki, 2006). Since VOCs are causing photochemical smog and offensive odor pollution, VOC emissions are regulated in many countries (Hoshi et al., 2008).

Two representative methods have been used for VOC treatment (Chimoto, 2007). One is a solvent recovery apparatus in which VOCs are removed from the effluent gas by an adsorbent, representatively activated carbon, and recovered by the desorption procedure. The other is a combustion apparatus. The combustion apparatus is suitable for the relatively large-scale factory where the reuse of VOCs is difficult. Especially, this system is economically favorable for the factory with a full-day operation because the catalytic system can be operated continuously without start-up and shut-down procedures. At the start-up of the combustion apparatus, the combustion temperature cannot be usually reached only by the combustion heat

of discharged VOCs and therefore combustion improvers, gas or oil fuels, and their supplying plants are necessary. This is an important reason why the installation of the combustion apparatus is difficult to minor factories with intermittent operations.

Plasma decomposition method was reported as an advanced technology of VOC treatments (Nunez et al., 1993; Vercammen and Berezin, 1997; Kim et al., 2005; Ehara et al., 2010). Recently, we have developed a new technology with the combination of adsorption and plasma decomposition of VOCs to be used for a small-sized VOC treatment apparatus (Urae et al., 2002; Inoue et al., 2007). The adsorption/plasma combined system could effectively decompose VOCs at very low concentration of 100 ppm or less (Okano and Inoue, 2005, 2006). It should be noted that the efficient and economical treatment of such dilute VOCs is difficult with the existing technologies like combustion apparatus. Since it is driven only by electricity, the adsorption/plasma combined system is suitable for the intermittent operation (Okano and Inoue, 2005, 2006). These features suggest the feasibility of the adsorption/plasma combined system as a small-sized VOC treatment apparatus for minor factories. From
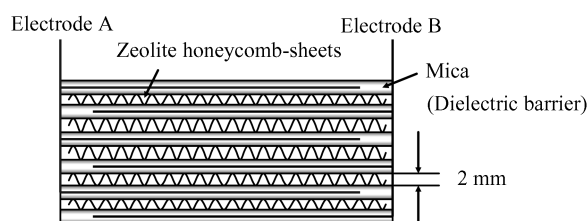
the viewpoint of environmental protection, the developed system seems to be of significance, because the removal of pollutants is indispensable not only from large-scale sources but also dispersed and small-scale sources.

A newly developed technology becomes a real technology when its feasibility is proved by performance tests under practical and real conditions. In the present study, the prototype apparatuses based on the adsorption/plasma combined technology were fabricated, and they were subjected to the performance tests in simulated VOC exhausts as well as real VOC exhausts from characteristic small-scale sources.
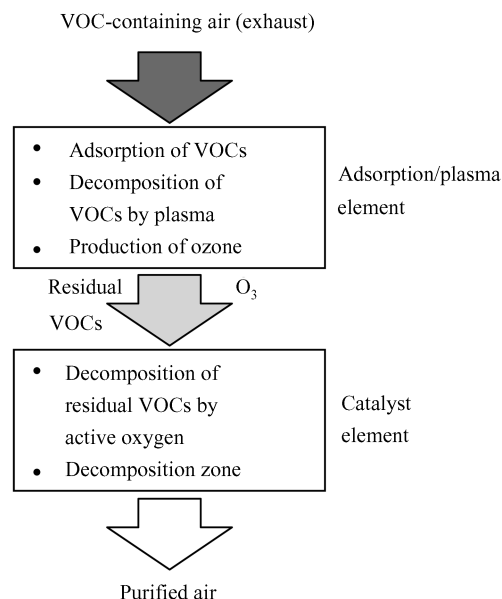
1 Experimental

1.1 Adsorption/plasma element

Figure 1 shows the structure of the adsorption/plasma element which is the core of the adsorption/plasma combined technology. Electrodes A and B were covered with a specially designed sheet of mica dielectrics. Corrugated honeycomb sheets containing a hydrophobic zeolite were inserted between the electrodes. Requirements for the zeolite adsorbent are high adsorption capacity, large pore size to adsorb VOCs with larger molecular size, and hydrophobicity to suppress the adsorption of water vapor which retards the efficiency of plasma generation. In order to meet the requirements, a dealuminated Y-type zeolite was used. The adsorption honeycomb was proved to be effective in promoting decomposition performance of VOCs, preventing contamination of the electrode plates and suppressing the performance degradation of the element (Yamagata et al., 2006).

Fig. 1 Illustration of the adsorption/plasma combined element with insertion of corrugated honeycomb sheets between discharge electrodes.

1.2 Outline of adsorption/plasma decomposition technology

The adsorption/plasma decomposition apparatus is composed of two elements; an adsorption/plasma element at the upstream and a catalyst element at the downstream (Fig. 2). High voltage of 9 kV (AC 60 Hz) is applied between the electrodes, and plasma is generated in the discharge space in which honeycomb sheets are inserted. VOCs are decomposed by the action of plasma during passing through the discharge space either on the adsorbent surface or in gas phase. Residual VOCs and ozone produced by the discharge enter the catalyst element, where the decomposition of VOCs by the active oxygen generated from ozone takes place (Okano and Inoue, 2005, 2006).

Fig. 2 Working principle of the adsorption/plasma treatment for dilute VOC decomposition.

The catalyst element works also to prevent the discharge of ozone from the apparatus. A manganese dioxide-based catalyst commercially available as an ozone decomposition catalyst (Süd-Chemie Catalysts Japan, Inc) was used.

1.3 Prototype apparatuses and performance tests

Two prototype apparatuses were fabricated (Table 1). The difference was the type of transformers for power supply and the size of casing. The core specifications of the apparatus, that is, adsorption/plasma and catalysts elements, and gas flow rate were common, and therefore the performance of two prototype apparatuses were basically the same.

The conversion (R) of a VOC was calculated by Eq. (1).

$$R = 100 \times (C_{\mathrm{VOC_{in}}} - C_{\mathrm{VOC_{out}}})/C_{\mathrm{VOC_{in}}} \tag{1}$$

where, $C_{\mathrm{VOC_{in}}}$ and $C_{\mathrm{VOC_{out}}}$ mean the concentrations at inlet and outlet of the apparatus, respectively.
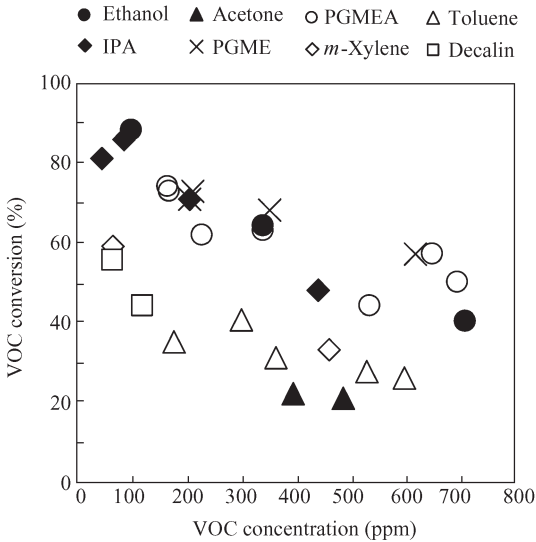
2 Results and discussion

2.1 One-component tests

The purpose of the one-component test was to understand the effect of VOC species on the performance of the prototype apparatus under the condition close to a real exhaust. Information about the performance for each VOC is indispensable to understand the performance with a real exhaust which usually contains various kinds of VOCs.

Figure 3 shows the concentration dependence of the conversion of VOCs. The conversion of each VOC decreased with increasing its concentration. VOCs are seemingly classified into two groups with higher conversions (ethanol, IPA, PGME, PGMEA) and lower conversions (acetone, toluene, m-xylene, decalin). It is noted that VOCs in higher-conversion group contain the C—O bond
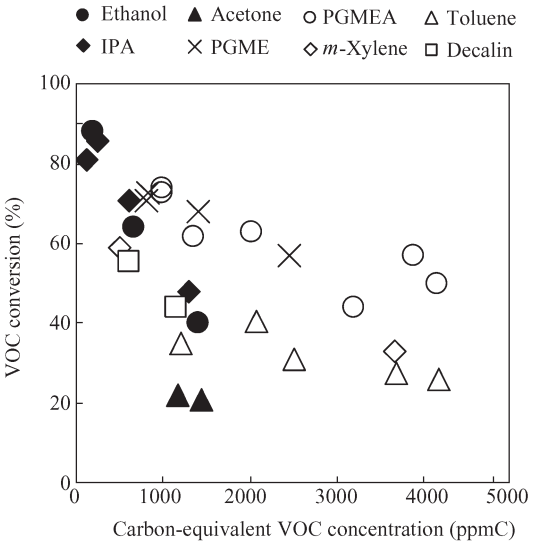
Table 1　Specifications of prototype apparatuses

Size of casing	Prototype apparatus No. 1: 1381 mm × 600 mm × 1010 mm
	Prototype apparatus No. 2: 1100 mm × 650 mm × 1150 mm
Gas flow rate	60 m^3/hr (1.3 m/sec)
Weight	200 kg
Power consumption	2 kW
Power supply	Prototype apparatus No. 1: neon transformer (200 V–12 kV, AC 60 Hz),
	Prototype apparatus No. 2: leakage transformer (200 V–12 kV, AC 60 Hz)
Adsorption/plasma element	Size: 200 mm × 340 mm × 300 mm
	Electrode: stainless-steel sheet, effective area 100 mm × 200 mm
	Dielectric: specially designed mica sheet, 140 mm × 300 mm (Okabe Mica Co., Ltd., Japan)
	Gap of two electrodes: 2 mm
	Pair of electrodes: 16 steps × 4
	Honeycomb sheet
	Zeolite-honeycomb sheet: 100 mm × 300 mm × 2 mm
	Honeycomb matrix: glass fiber paper
	Channel size: 1.6 mm × 3.0 mm
	Content of zeolite: 50%
	SV (gas flow rate/total volume of adsorption/plasma element): 2940 hr^{-1}
Catalyst element	Manganese dioxide-honeycomb block: 260 mm × 130 mm × 250 mm
	Honeycomb matrix: ceramic fiber paper
	Channel size: 1.8 mm × 3.4 mm
	Content of manganese dioxide-based catalyst: 50%
	SV (gas flow rate/volume of honeycomb): 7100 hr^{-1}

Fig. 3　Concentration dependence of VOC conversion in the one-component performance test.

Fig. 4　Conversion of various VOCs as a function of carbon-equivalent VOC concentration.

in molecules. Since the number of carbon atoms in one molecule (N_C) is different for different VOCs, the carbon-equivalent VOC concentration (C_{CE}), which is a product of the concentration and N_C, is often used to collectively discuss the VOC removal efficiency. In addition, C_{CE} is of practical importance because the VOC emission is usually regulated on the basis of C_{CE}. In Fig. 4, conversions of VOCs are plotted as a function of C_{CE}. Although the trend that the conversion decreased with increasing the concentration was common in both Figs. 3 and 4, more
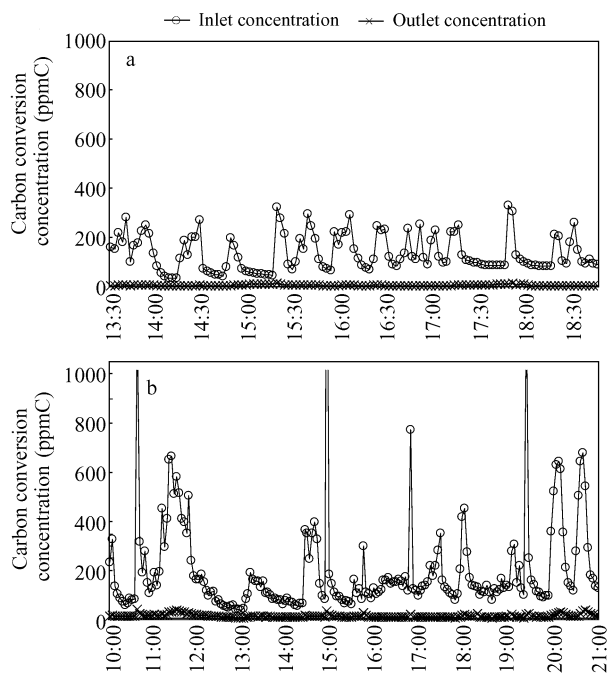
detailed classification of the reactivity of VOCs in the adsorption/plasma combined system was possible from the results in Fig. 4. The classification was based on the magnitude and concentration dependence of the conversion (Table 2). Conversions of ethanol and IPA at around 200 ppmC of C_{CE} were high (80%–90%), and the conversions decreased steeply with increasing C_{CE}. Therefore, the high conversion at low concentration and large concentration dependence are the reactivity characteristics of ethanol and IPA, both of which are alcohols, in the adsorption/plasma

Table 2　Classification of VOCs according to the reactivity in the adsorption/plasma combined system

Category	VOC	Remarks
A	PGME, PGMEA	High conversion at low and small concentration dependence
B	Ethanol, IPA	High conversion at low and large concentration dependence
C	Toluene, *m*-xylene, decalin	Low conversion at low and small concentration dependence
D	Acetone	Low conversion

Fig. 5 Performance test results of VOC decomposition at a painting booth exhaust on typical two days with low (a) and high (b) exhaust concentration. VOC concentrations at the inlet and outlet of the prototype apparatus No. 2 are shown. The inlet concentration is the same as the concentration exhausted from the booth.

decomposition apparatus (category (B) in Table 2). As compared with ethanol and IPA, ether and its relatives (PGME, PGMEA) with relatively larger molecular sizes were decomposed effectively over the concentration range examined. The conversions of them at low concentration seemed to be high from the extrapolation of the conversion vs. C_{CE} relations (category (A)). The reactivity of toluene was characterized by the small concentration dependence and, by the extrapolation, low conversion at low concentration. Although the decomposition of them was evaluated only at two C_{CE} values, m-xylene and decalin could be classified in the same category (C) as toluene. VOCs in category (C) are aromatic and nonaromatic cyclic hydrocarbons. Acetone with two experimental data was tentatively categorized in (D) with low reactivity (conversion).

For decomposition of 80 ppm toluene, the energy efficiency of the present system was 11 g/(kW·hr) which was superior to that of the corona discharge reactor combined with catalysts, 2–6.4 g/(kW·hr) (Ohkubo et al., 2003).

As stated in Section 1.2, three reactions are involved in the VOC conversion in the adsorption/plasma decomposition apparatus; decomposition on the surface of the adsorbent and in the gas phase in the adsorption/plasma element, and decomposition in the catalyst element with the aid of the catalyst (MnO$_2$) and active oxygen generated from ozone. Therefore, it is not straightforward to understand the decomposition efficiency of each VOC which may relate with adsorption property on the hydrophobic zeolite and the chemical reactivity by active oxygen formed by the effect of the low-temperature plasma. Nevertheless, it is worth noting that VOCs in the same relative are classified in the same group based on

the decomposition efficiency (Table 2). The mechanism of VOC decomposition in the present system especially under the influence of the low-temperature plasma should be evaluated in future basic studies. The present results, however, are very significant to understand the performance of the apparatus under the real exhaust conditions and to evaluate its feasibility.

2.2 Performance tests at painting booth exhaust

The discharged VOCs from the painting booth were a mixture of toluene, xylene, ethyl acetate, butyl acetate, butyl cellosolve (butoxyethanol), and butanol. They are categorized in aromatic hydrocarbons (toluene and xylene, category (C) in Table 2), alcohol ((B), butanol), and esters (others). Although the reactivity of esters was not measured in the one-component test, they are supposed to be easily decomposed because the C–O bond is included in molecules.

Total VOC concentration (C_{CE}) was continuously monitored during operation hours at the outlet of the booth (the inlet of the prototype adsorption/plasma decomposition apparatus) and the outlet of the apparatus. Results of two typical cases are shown in Fig. 5. When one worker painted a small object, the maximum concentration of VOCs exhausted from the booth did not exceed 350 ppmC (Fig. 5a). The fluctuation of the exhausted concentration of course reflected painting activity. The outlet VOC concentration from the prototype adsorption/plasma decomposition apparatus were practically zero during the operation even at the peak inlet concentration. In case of the painting of a relatively larger object by a few workers, on the other hand, the peak concentration sometimes exceeded 1000 ppmC (Fig. 5b); the highest peak concentration of about 2000 ppmC was observed at 15:00 pm. The leakage of VOCs from the apparatus was observed when the inlet concentration was high, but on the whole, VOCs were effectively removed by the adsorption/plasma decomposition apparatus. As reported previously, the adsorption/plasma combined system worked effectively when the VOCs at concentrations less than 100 ppm were continuously introduced to the apparatus (Okano and Inoue, 2005, 2006): taking account of the VOC molecules used, the critical concentration (C_{CRT}) was around 300 ppmC. As seen from Fig. 5, the apparatus could effectively decompose VOCs under the critical concentration when they were introduced continuously to the apparatus. At the sudden increase in the VOC discharge, especially in Fig. 5b, the VOC concentration temporarily exceeded the critical concentration. It is inferred that over-charged VOCs are adsorbed or trapped on the zeolite adsorbent and they desorb and are decomposed when the inlet VOC concentration becomes low. The leakage of a little amount of VOCs was observed due to the balance of adsorption capacity and decomposition ability when the inlet concentration instantaneously increased or higher inlet concentrations continued, for example, from 11:00 to 12:00 in Fig. 5b.

These results clearly indicate the potentiality of the developed adsorption/plasma decomposition apparatus for the VOC discharging sites where the base VOC concentra-

tion is lower than C_{CRT} and that the apparatus can respond to the temporary over-discharged VOCs by the cooperative action of adsorption and decomposition.

2.3 Performance tests at adhesion factory exhaust

The prototype apparatus No. 1 was installed at a branched exhaust pipe from an adhesion factory. Figure 6 shows a variation of the VOC concentration discharged from the factory during working hours in a day. In this particular case, toluene and methyl ethyl ketone (MEK) were discharged, and the former was the discharged VOC major in the amount. The concentration of VOC fluctuated depending on the operation condition of the factory, but the total discharged concentration was always higher than 3000 ppmC. The performance tests were carried out four days per month and continued for fourteen months. VOC concentration averaged between 14:00 pm and 17:00 pm in each day is shown in Fig. 7. In some days, acetone was discharged in addition to toluene and MEK. The total concentration and the composition of VOC varied from one day to another. The annually averaged composition of discharged VOCs was about 70% (toluene), 25% (MEK) and 5% (acetone). The characteristic of the adhesion factory exhaust was the continuous discharge of VOCs in concentration higher than C_{CRT} of the adsorption/plasma decomposition apparatus (300 ppmC).

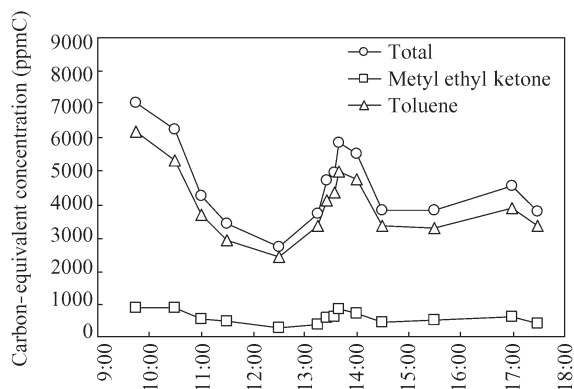The performance test results of the adsorption/plasma decomposition apparatus at the adhesion factory exhaust are shown in Fig. 8a, in which the conversion of total VOCs is plotted against the inlet carbon-equivalent concentration of total VOCs. The on-site test results clearly show the tendency that the VOC conversion decreased with increasing the inlet VOC concentration, which agrees with the one-component experiment described in Section 2.1. The concentration of each VOC discharged from the adhesion

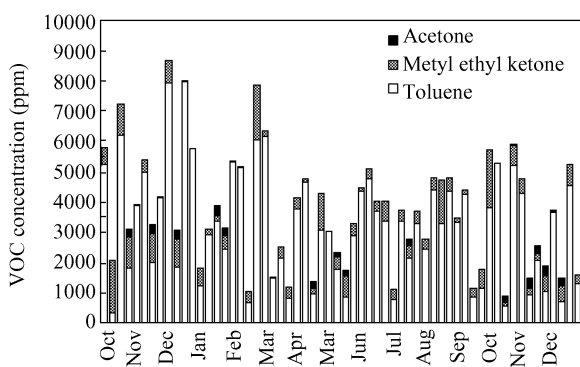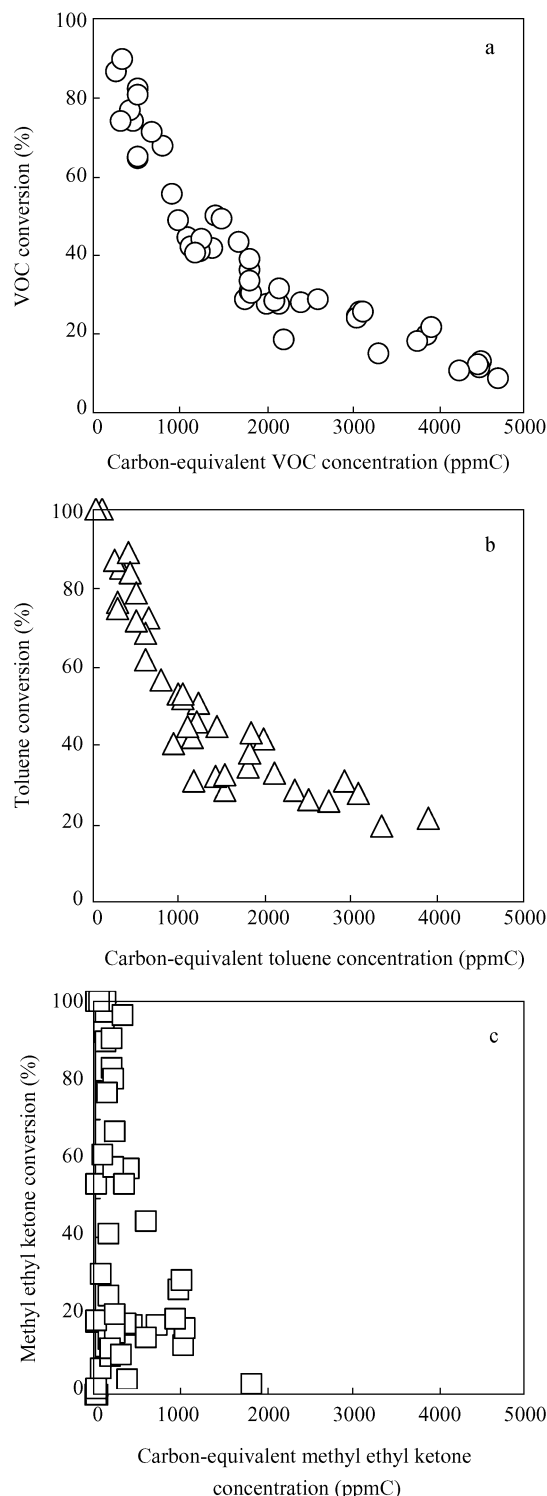**Fig. 6**   Daily variation of VOC concentration discharged from an adhesion factory.

Fig. 7   VOC concentration at the adhesion factory exhaust. On-site measurements; 14 months with 4 days per month.

Fig. 8   Decomposition of VOC (a), toluene (b), and methyl ethyl ketone (c) at the adhesion factory exhausts by the adsorption/plasma decomposition apparatus No.1.

factory was separately analyzed by the gas chromatograph, and the results of toluene and MEK were shown in Fig. 8b, c, respectively. The decomposition behavior of toluene was similar to that of total VOC (Fig. 8a). This is acceptable because toluene is the major VOC discharged from the factory. Although the data of MEK were dispersed, the conversion seemed to decrease remarkably with increasing the concentration. As described in Section 2.1 for the one-component test, the decomposition efficiency of acetone by the adsorption/plasma combined system was lower than the other kinds of VOC molecules. Therefore, the conversion of MEK which is a ketone as acetone may drop quickly with increasing concentration. In separate experiments using the adsorption/plasma decomposition element which was about half of the present prototype element, it was confirmed that the decomposition efficiency of MEK was lower than that of toluene and comparable to that of acetone. In addition, the decomposition of MEK may be suppressed when it coexists with toluene which is more easily decomposable than MEK.

As stated above, the adhesion factory exhaust is characterized by the continuous discharge of VOCs in concentration higher than C_{CRT} in most cases. When the discharged VOC concentration was as low as C_{CRT} of 300 ppmC, the discharged VOCs were decomposed with relatively high conversion above 80% (Fig. 8a). When the discharged concentration became higher than C_{CRT}, however, the performance of the apparatus was not satisfactory. The temporarily over-discharged VOCs were effectively decomposed by the trap function of zeolite adsorbent, as described in Section 2.2. In the present case, on the other hand, such temporary trap function cannot operate because the adsorbent may be always saturated with VOCs under continuous flow of high concentration of VOCs. The dilution of exhausts to the level close to C_{CRT} should be the possible way to effectively decompose VOCs continuously discharged at high concentrations by the one-path flow system.

3 Conclusions

The feasibility of the prototype apparatus with the adsorption/plasma combined element was evaluated with the simulated exhausts containing one VOC component and with real exhausts from a painting booth and an adhesion factory. The basic performance test with simulated exhausts containing one VOC component revealed that the system could decompose effectively alcohol and ether relatives, followed by aromatic and nonaromatic cyclic hydrocarbons, and ketone. At a painting booth exhaust in which the base concentration of VOCs were lower than the critical concentration and instantaneous increases in VOC concentration occurred frequently, the system worked quite effectively by the cooperative working of plasma reaction and adsorption. On the other hand, the decomposition performance was not always satisfactory at an adhesion factory which continuously discharged VOCs in concentration higher than the critical one. The present results clearly demonstrate that the adsorption/plasma

combined system is feasible technology to remove VOCs from exhausts compatible with the capacity of the system.

References

Aoki K, 2006. The view of the VOC regulation on the air pollution control law. *Chemical Engineering of Japan*, 75(5): 235–239.

Chimoto M, 2007. VOC restriction and measures in gravure printing. *Journal of Printing Science of Technology*, 44(1): 8–14.

Ehara Y, Ito Y, Oishi Y, Yamamoto T, Oya Y, Iwata M, 2010. Fundamental characteristics of discharge using honeycomb type discharge reactor and its decomposition of toluene. *Journal of Institute of Electrostatics Japan*, 34(1): 19–24.

Hoshi J, Sasaki H, Amano S, Higuchi M, Iimura F, Ueno H, 2008. Trends of VOC composition in ambient air and contribution of ozone generation for VOC. Annual Report of the Tokyo Metropolitan Research Institute for Environmental Protection 2008, 10–17.

Inoue K, Furuki K, Okano H, Yamagata Y, Muraoka K, 2007. A new decomposition system for volatile organic compounds using combinations of dielectric barrier discharges with zeolite honeycomb sheets. *Transactions of IEE of Japan*, 127(A): 309–316.

Kim H H, Kobara H, Ogata A, Futamura S, 2005. Comparative assessment of different nonthermal plasma reactors on energy efficiency and aerosol formation from the decomposition of gas-phase benzene. *IEEE Transactions on Industry Applications*, 41: 206–214.

Nunez C M, Ramsey G H, Ponder W H, Abbott J H, Hamel L E, 1993. Corona destruction: An innovative control technology for VOCs and air toxics. *Journal of the Air and Waste Management association*, 43: 242–247.

Ohkubo T, Li D, Yakushiji D, Kanazawa S, Nomoto Y, 2003. Decomposition of VOC in air using a streamer corona discharge reactor combined with catalysts. *Journal of Advanced Oxidation Technologies*, 6: 75–79.

Okano H, Inoue K, 2005. Development of removal technology of hazardous chemical compounds which are difficult to treat by combination adsorption element with plasma. NEDO, 100004849.

Okano H, Inoue K, 2006. Development of removal technology of hazardous chemical compounds which are difficult to treat by combination adsorption element with plasma. NEDO, 100007296.

Urae H, Yamagata Y, Muraoka K, Yamada K, Yamauchi W, Okano H, 2002. Removal of volatile organic compounds at low concentration using a combination of densification by a zeolite adsorption with a barrier discharge. *Transactions of IEE of Japan*, 122(A): 965–976.

Vercammen K L L, Berezin A A, 1997. Non-thermal plasma techniques for the reduction of volatile organic compounds in air streams: A critical review. *Journal of Advanced Oxidation Technologies*, 2(2): 312–329.

Yamagata Y, Niho K, Inoue K, Okano H, Muraoka K, 2006. Decomposition of volatile organic compounds at low concentrations using combination of densification by zeolite adsorption and dielectric barrier discharge. *Japanese Journal of Applied Physics*, 45: 8251–8254.