A Study of Volatile Organic Compounds Decomposition with the Use of Non-Thermal Plasma

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Non-thermal plasma processing is an effective method to decompose diluted VOC contaminants in manufacturing rooms for the electronic industry. In this paper, two different discharge-type laboratory scale reactors (Double Dielectric Barrier Discharge and Packed-Bed Discharge) that generate non-thermal plasma have been developed and the decomposition tests were conducted. The tested VOC was Benzene, Toluene, Xylene, P-cumene, Diethylether and Dichlormethane. It was found from the experimental results for the present reactors that Benzene oxidization required higher energy than the other aromatic hydrocarbons with side branches. The decomposition efficiency was high for Cumene and Xylene (two methyl-side groups) and low for Toluene (one methyl group) and Diethylether. One of the frequently used solvents in semiconductor industry, Dichlormethane which can destroy atmospheric ozone layer, could be decomposed in the Double Dielectric Barrier Discharge with minimum power consumption and the DDBD reactor had a little higher decomposition efficiency than the Packed-Bed reactor.

Key Words : NTPD(Non-Thermal Plasma Discharge), DDBD(Double Dielectric Barrier Discharge), VOCs, Packed-bed, Active radicals, Microdischarges.

1. Introduction

Volatile Organic Compounds (VOC) exhausted to the atmosphere have caused environmental problems. Noxious gases, such as vapours of volatile organic compounds (VOC) are produced during printed circuit boards (PCB) painting and drying. These gases and odors can create health hazards for workers and nuisance for neighboring properties, threatening public relations (1988). To solve these problems, non-thermal plasma discharge (NTPD) have been widely studied and developed in many countries. NTPD has long been used to induce chemical reactions, creating desirable compounds. For example, the reaction of benzene in a corona discharge was reported more than a century ago

and NTPD technologies have been commonly used in the commercial ozone generators. The increased awareness of air quality over the last decade has intensified interest in developing NTPD for the destruction of various pollutants (1994).

Researchers have demonstrated NTPD for destruction of many compounds including CCl_4 (Coogan et al., 1993), DCB (Coogan et al., 1993), toluene (Coogan et al., 1993; Yamamoto et al., 1994), p-cumene (Coogan et al., 1993), TCA (Coogan et al., 1993), CFCs (Coogan et al., 1993), methylene chloride (Yamamoto et al., 1994), CFC-113 (Yamamoto et al., 1994), CH_2O (Storch et al., 1993), dioxin (Masuda, 1994), acetone (Masuda, 1994), isopropyl alcohol (Masuda, 1994), hydrogen sulfide (Abolentsev et al., 1994; Helfritch, 1994), TCE (Newhouse et al., 1996; Petreskey et al., 1995), SO_2 (Clements et al., 1989) and NO (Federle et al., 1996).

Non-thermal plasma chemical processes have been highly effective in promoting oxidation,

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enhancing molecular dissociation and producing free radicals to enhance chemical reactions. Non-thermal plasma technologies have the advantages of energy efficiency and capability for simultaneous removal of coexisting air pollutants.

Non-thermal plasma technologies have the following advantages over the conventional technologies:

1. High decomposition efficiency
2. No concentration gradient limited
3. Low temperature operation
4. Can be tuned by adjusting the power level to match the source flow, concentration and ozone/NOx generation
5. No additional disposal required

There are many types of NTPD and they are typically categorized by their electrode geometry, breakdown mechanism, and the presence (or absence) of dielectric materials between the gas flow and the electrodes. Some of the common NTPD are pulsed corona, dielectric barrier (Pietsch et al., 1994), barrier flashover, surface (Masuda, 1994; Penetrante, 1994), ferroelectric bed, and fast flow DC discharges.

In the operation of a generic NTPD, the required energy was provided by a high-voltage power supply. This high voltage and the corresponding high electric field is applied to the electrodes. As the working gas flows between the electrodes, the applied field breaks down the gas, creating a partially ionized plasma. At atmospheric pressure, this breakdown results in a multitude of current filaments or breakdown channels, called microdischarges. Within the microdischarges, the input power is efficiently transferred to the electrons. The diameter of each of these discharge channels has been found to be on the order of 100 μm and the lifetime ranges between 1~100 ns (Eliasson and Kogelschatz, 1991). Because of the short time duration of the discharges, the electrons and, heavy particles do not thermally equilibrate and while the temperature of the electrons is on the order of 3~8 eV (40,000~100,000 K), the bulk gas (heavy particles) temperature remains approximately constant. The relatively large collisional cross-sec-

tion between 3~8 eV electrons and most molecules leads to collisions between them (Hollahan and Bell, 1974), resulting the formation of excited atomic/molecular states and other highly reactive species. It is important to note that the reactive species are the result of energetic electron/molecule collisions and hence, they are formed only within the microdischarges. After a discharge extinguishes, the created reactive species collide with other molecules, causing the chemical reactions that alter hazardous compounds into benign, more controllable or simpler compounds.

The present study selected a double dielectric barrier discharge reactor and a packed bed reactor for simple design and high efficiency. The potential air cleaning system could be installed to treat air in the PCB manufacturing room at the outlet of air ventilation system.

2. Volatile Organic Compounds Decomposition with the Use of Double Dielectric Barrier Discharge (DDBD) Reactor

In a DDBD reactor both electrodes are separated from the working gas by a dielectric. Because it does not emit or absorb a significant amount of free electrons, the charge transfer across the gap through the microdischarges eventually reduces the "net" electric field at the location of each discharge, causing them to extinguish. Consequently, the device does not rely on the imposed voltage pulse-width to limit the duration of the
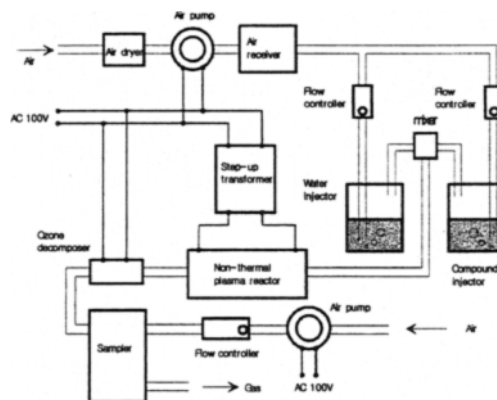

Fig. 1 Experimental setup.

microdischarges and is usually driven by a simple high voltage AC power supply. A side effect of the dielectric is that the discharge operation is relatively quiet and hence, dielectric barrier discharges are sometimes called Silent Electric Discharges (SED).

Various stages of experimental testing were conducted toward optimization of the barrier discharge for destruction of VOC. Tests relevant to optimize the chemical efficiency of the system were primarily performed with a bench scale, radial DDBD device. The experimental apparatus used in each stage of testing are described below.

The radial, bench scale DDBD device consists of two coaxial tubes arranged so that the gas flow is directed between the two tubes as shown in Fig. 2. The inner tube has an outside diameter of 10 mm while the outer tube has an inside diameter of 14 mm and a length of 620 mm. The 2 mm coaxial gap created by the tubes has a total active volume of 46.8 ml. A copper tape running the length of the inner tube serves as the inner conductor. The outer tube is wound with 56 gauge of copper tape to form the outer grounded conductor. In this experiment, glass tube is used for inner electrode
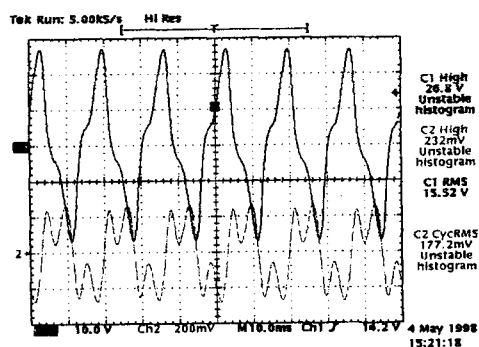
isolation and quartz pipe for outer electrode isolation. Typical voltage and current waveforms are shown in Fig. 3. X axis is time (ms) and Y axis is voltage ($\times 1000$)

The power consumption characteristic of the DDBD reactor is shown in Fig. 4.

In a silent discharge, the discharge-generated ions traverse in space in a pulse and are stored in the surface of the dielectric materials. Since these accumulated space charges generate a reverse electric field, the corona discharge will be terminated. Therefore it produces sparkless high electron temperature / low gas temperature reactive plasma to enhance the chemical reactions. Generally, ozone generation in a corona discharge is a two step process as follows:

A. Generation of oxygen free radicals by ionic process

1. $O_2 + e \rightarrow O_2^+ + 2e$ — direct ionization
2. $O_2 + e \rightarrow O^+ + O + 2e$ — dissociative ionization
3. $O_2 + e \rightarrow O + O + e$ — dissociation
4. $O_2 + e \rightarrow O^- + O$ — dissociative attachment.

B. Generation of ozone by free radical reactions:
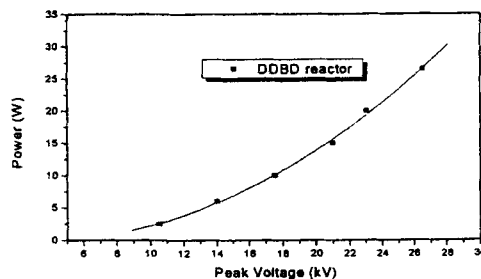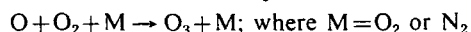$O + O_2 + M \rightarrow O_3 + M$; where $M = O_2$ or N_2

Fig. 2 Radial DDBD device.
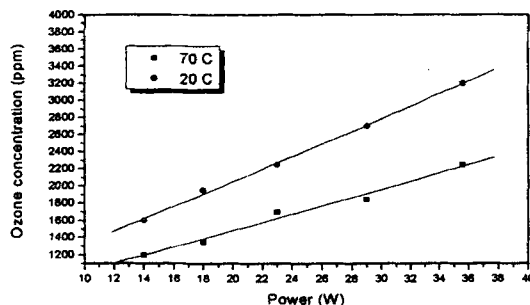

Fig. 4 Power consumption rate.
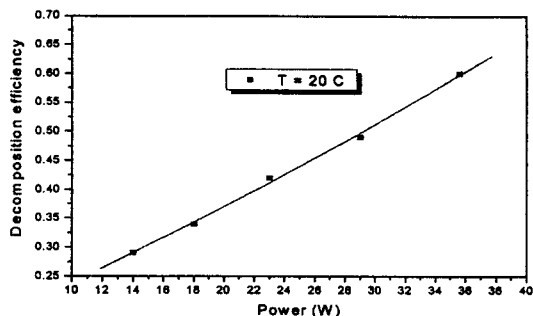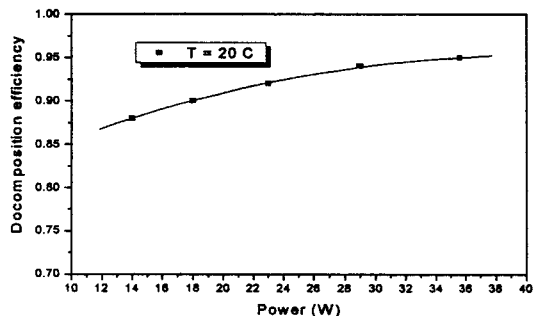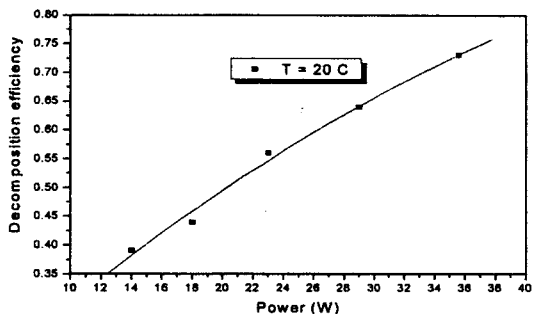

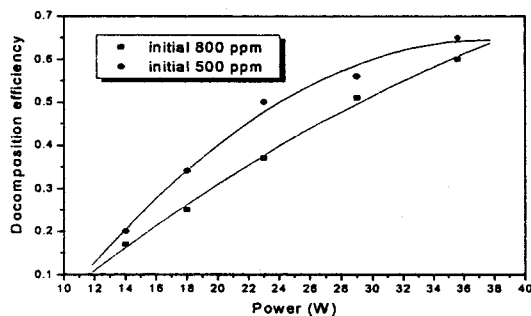Fig. 3 Current and voltage waveforms.

Fig. 5 Ozone generation rates.

Fig. 6 Benzene decomposition efficiency.
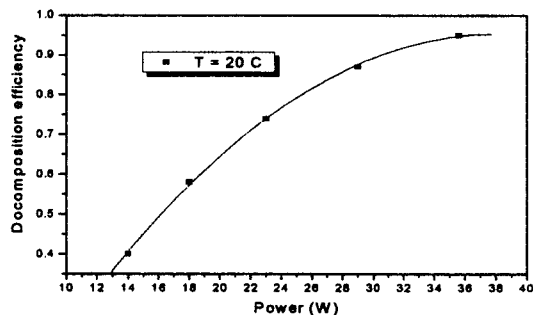(initial concentration 500 ppm, temperature 20℃,
gas flow rate 1 l/min)

Fig. 9 P-Cumene decomposition efficiency.
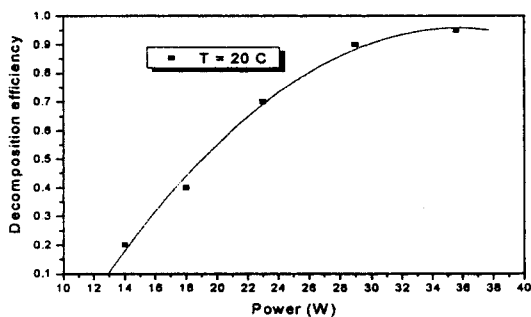(initial concentration 450 ppm, temperature 20℃,
gas flow rate 1 l/min)

Fig. 7 Toluene decomposition efficiency.
(initial concentration 480 ppm, temperature 20 ℃,
gas flow rate 1 l/min)

Fig. 10 Diethylether decomposition efficiency.
(initial concentration 500 and 800 ppm,
temperature 20℃, gas flow rate 1 l/min)

Fig. 8 Xylene decomposition efficiency.
(initial concentration 480 ppm, temperature 20 ℃,
gas flow rate 1 l/min)

Fig. 11 Dichlormethane decomposition.
(initial concentration 460 ppm, temperature 20℃,
gas flow rate 1 l/min)

Ozone generation as a function of applied
voltage was investigated. Ozone concentration
was measured by *Gastec* tubes No. 18M with the
use of constant volume sampler to match the
output concentration with tube measurement
range. The outlet ozone concentration is shown in
Fig. 5.

Increasing gas temperature substantially
reduces the ozone generation process, while
increasing gas temperature significantly enhances
the ozone loss processes.

For VOC decomposition, the following sub-
stances were selected;

1. Benzene — C_6H_6

2. Toluene — $C_6H_5CH_3$
3. Xylene — $C_6H_4(CH_3)_2$
4. P-Cumene — $C_6H_5CH(CH_3)_2$
5. Diethylether — $(C_2H_5)_2O$
6. Dichlormethane — CH_2Cl_2

Figures 6~11 show the variations of experimental decomposition efficiencies with respect to input power for the above VOC, respectively.

Figures 12 and 13 show the variations of experimental decomposition efficiencies with respect to the gas velocity for Toluene and P-cumene, respectively.

Gas velocity was changed in the range of 0.5 ~2.5 liters per minute. Power level was maintained at the maximum of 35. 6 W.

Temperature is varied in the range of 20~50°C, because these values correspond to the real temperature conditions in the manufacturing room.

Also the initial gas was dried by silicagel package and its humidity was about 10%. The initial concentration of toluene was 500 ppm and
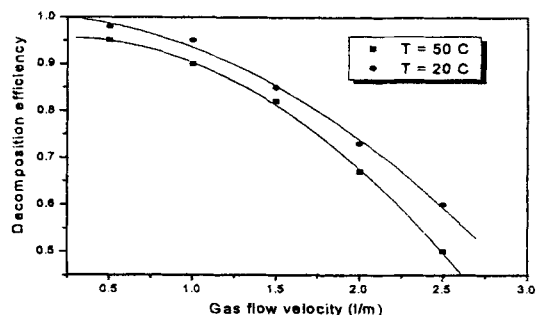
Fig. 12 Toluene decomposition efficiency. (maximum power 35. 6 W, initial concentration 500 ppm)
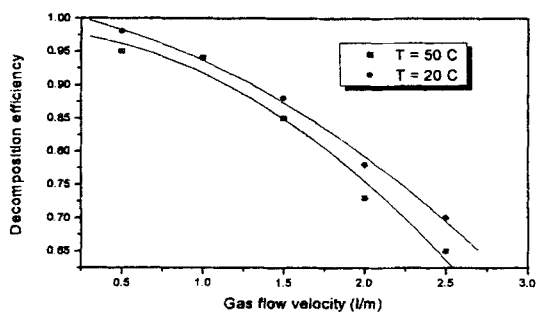
Fig. 13 P-cumene decomposition efficiency. (maximum power 35. 6 W, initial concentration 600 ppm)

that of cumene was 600 ppm.

3. Volatile Organic Compounds Decomposition with the Use of Packed-Bed Reactor

The dielectric packed-bed reactor, shown schematically in Fig. 14, employs a reactor packed with dielectric pellets. The inner reactor diameter was 120 mm and gap distance 30 mm where 5 mm diameter $BaTiO_3$ pellets (relative dielectric constant = 4500 at 200°C) were packed. The gas stream flowed through the 3 mm entry tube and dispersed into the plasma zone. When an external high voltage is applied, the pellets are polarized and an intense electric field is formed around each pellet contact point.

Many pulsed discharges take place around each contact point of the dielectric pellets. Because pellets are packed closely together, there is a possibility that the electric field in the microdischarges is significantly enhanced, thus potentially increasing the radical production efficiency.

Observation of the AC current waveforms by *Tektronix 744* oscilloscope showed that the current was non-sinusoidal with numerous pulses (microdischarges). Microdischarges started to occur at about 15 kV as an onset voltage and increased with increasing voltage.

An increasing plasma activity becomes visible across the transparent envelope. These microdischarges, where the free electron energy (electron temperature) is extremely high, generate radicals,
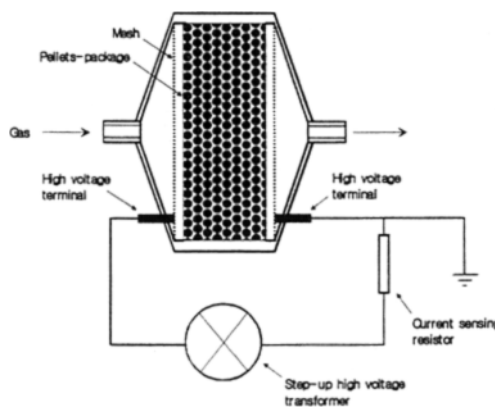
Fig. 14 Packed-bed non-thermal plasma reactor.
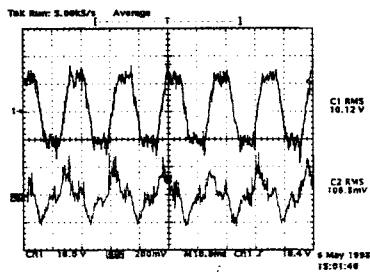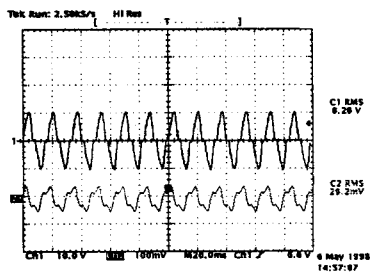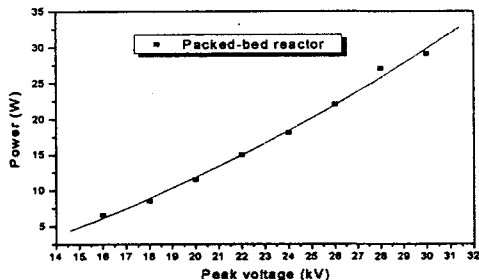
Fig. 15   Current and voltage waveforms.

Fig. 16   Power consumption rate.

excited atomic and molecular species that initiate plasma chemical reaction, whichs in turn, decomposes the targeted air toxics. In a study of decomposition of the ppm-level VOC using a packed-bed reactor, Yamamoto et al. (1992) found that the use of small pellets (1 mm in diameter) caused a high breakdown voltage (18 kV) and a low current resulting in high destruction efficiencies. The trends showed that with smaller pellet size and lower concentrations of gases in the air, the decomposition efficiency was higher. Residence time is also a significant effect on the destruction efficiency. For a specified design volume of the reactor, different residence times can be achieved by changing the flow rate of passing air or gases.

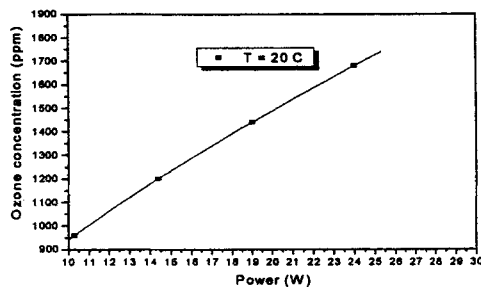Two different plasma chemical reactions may occur, depending on location of the gas injections

Fig. 17   Ozone generation rate.
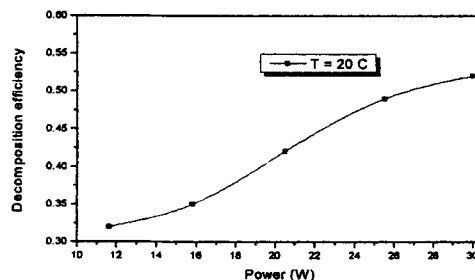(air temperature 20℃, gas flow rate 1 l/min)

Fig. 18   Benzene decomposition efficiency.
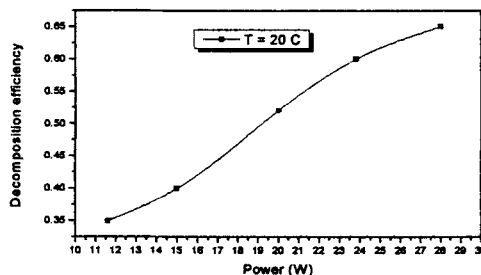(initial concentration 500 ppm, gas flow rate 1 l/min)

Fig. 19   Toluene decomposition efficiency.
(initial concentration 480 ppm, gas flow rate 1 l/min)

(Yamamoto et al., 1993). If the gas is injected upstream of the reactor, it will be subjected to a high electric field, high energy electron bombardment and excited species such as O, N, and N_2. If the gas is injected immediately downstream of the reactor, it is subjected to only long-lived excited species and ozone produced by the plasma reactor.

Figure 16 shows that packed-bed reactor had lower power consumption rate in comparison with DDBD reactor.

Figure 17 shows that ozone formation in the packed bed reactor was 60% lower than in the

DDBD reactor with the same input power. Obviously, the packed bed reactor had lower ozone output per one watt of applied power than in the
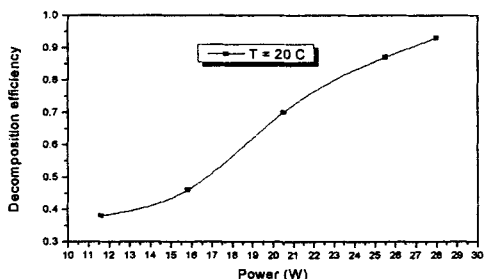

Fig. 20 Xylene decomposition efficiency.
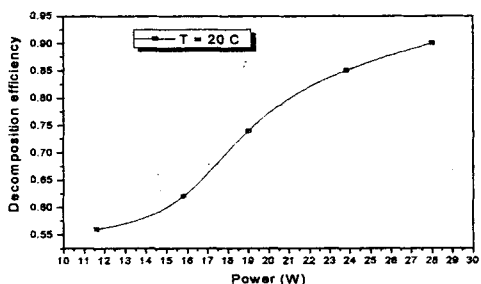(initial concentration 490 ppm, gas flow rate 1 l/min)

Fig. 21 P-Cumene decomposition efficiency.
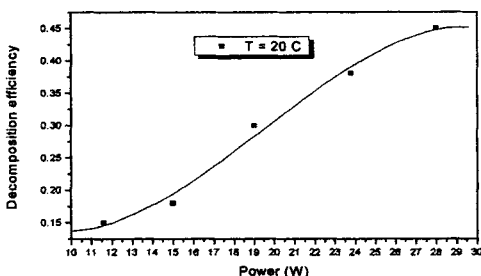(initial concentration 450 ppm, gas flow rate 1 l/min)

Fig. 22 Diethylether decomposition efficiency.
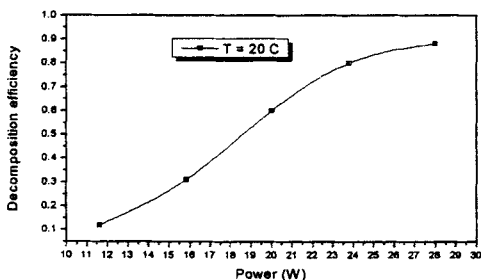(initial concentration 500 ppm, gas flow rate 1 l/min)

Fig. 23 Dichlormethane decomposition.
(initial concentration 460 ppm, gas flow rate 1 l/min)

case of double dielectric barrier reactor, because of higher dielectric losses.

Figures 18~23 show the variations of experimental decomposition efficiencies with respect to input power for the above VOC, respectively.

4. A Comparison of the DDBD and Packed-Bed Reactors

As it is shown in the figures, DDBD reactor had a little higher decomposition efficiency than the packed bed reactor. This seems to be attributed to the lower ozone generation in the packed bed reactor than in the DDBD reactor with the same applied power. Also the humidity influence to the decomposition efficiency was investigated.

Figure 24 shows the dependence of decomposition efficiency from flue gas humidity.

Since pellets is packed very closely and a gap between pellets is short, some part of the applied energy is used for the generation of reactive OH^- radicals. As it is seen, OH^- radicals have low decomposition efficiency and dried air is more preferable to humid one.

5. The Decomposition of Residual Ozone

In the present experiments, very high residue ozone concentration was obtained. Ozone is also hazardous component and should be eliminated. So catalytic ozone decomposer was made (see Fig. 25). Ozone decomposer is ceramic tube which is wound nicrom wire as a heater.
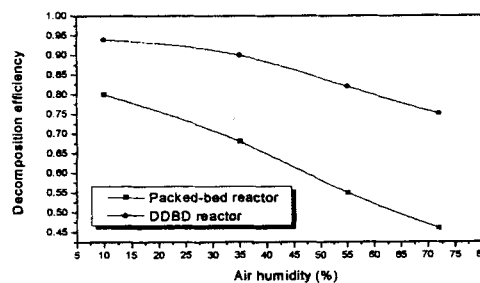
The inner volume of ceramic tube was filled

Fig. 24 Decomposition efficiency.
(p-cumene, initial concentration 420 ppm, gas flow rate 1 l/min, temperature 24°C, power 35.6 W)
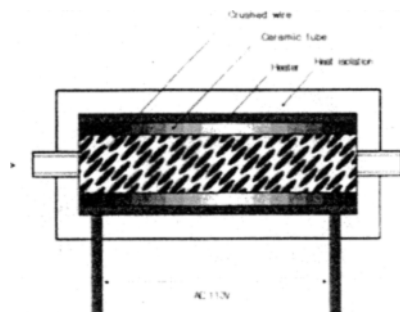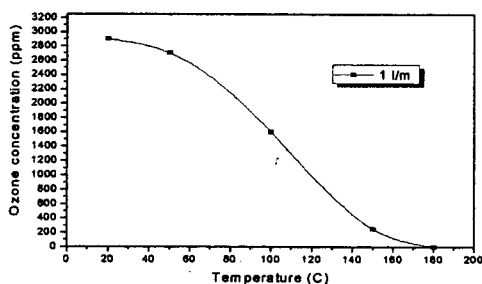
Fig. 25 The ozone decomposer.

**Fig. 26** Ozone decomposition.
(gas flow rate 1 l/min)

with crushed 0.2 mm copper wire. The operation temperature was maintained 180℃ to reach maximal ozone decomposition efficiency.

Under the influence of high temperature and high ozone concentration, copper was covered very quickly by copper oxide layer, which works as a catalyzer.

6. Conclusion

We conducted experiments with using two different types of electrical discharge reactors. It was found that VOC decomposition efficiency depended on the molecular structure. Higher energy was required for Benzene oxidization than that for other aromatic hydrocarbons with side branches. The decomposition efficiency was high for Cumene and Xylene (two methyl-side groups) and low for Toluene (one methyl group) and Diethylether. One of the frequently used solvents in the semiconductor industry, Dichlormethane which can destroy atmospheric ozone layer, could be decomposed in the Double Dielectric Barrier Discharge with minimum

power consumption. The by-product of Dichlormethane was hydrochloric acid:

$$2CH_2Cl_2 + 5/3O_3 \rightarrow 2CO_2 + H_2O + 2HCl + Cl_2$$
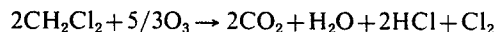
Hydrochloric acid could be removed by means of wet scrubber. The ozone was successfully removed by a heated catalytic decomposer with the efficiency of about 100% at 180℃.

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