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Decomposition of Odorous Gases in a Pilot-scale Nonthermal Plasma Reactor

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Abstract

An experimental study was performed on the decomposition of gaseous ammonia and two selected volatile organic compounds (VOCs: toluene and acetone) in a combined nonthermal plasma reactor with corona and glow discharges. A lab pilot scale reactor (206 liter) equipped with a high electric power pack was used to determine the decomposition efficiency in relation with the inlet concentration and applied voltage. Three different types of discharging electrode such as wired rack, wire strings for corona discharge, and thin plate for glow discharge were put in order in the reactor. While decomposition of ammonia decreased with an increase in the initial concentration, acetone showed an opposite result. In the case of toluene however no explicit tendency was found in toluene and aceton. Negative discharge resulted in high decomposition efficiency than the positive one for all gases. A better removal of gas phase element could be achieved when fume dust were present simultaneously.

Key words : Nonthermal plasma, Corona discharge, Odorous materials, Ozone

1. INTRODUCTION

Removal process of odorous materials including volatile organic compounds (VOCs) with nonthermal plasma is of interest not only in scientific fields but also in the industrial fields in which applications of conventional techniques for gaseous pollutants removal process have been limited. Many researchers have studied the decomposition of hazardous air pollutants such as SO_2, NO_x, H_2S, styrene, toluene, ammonia and other VOCs in various types of nonthermal plasma reactors (Rudolph *et al.*, 2002; Mok *et al.*, 2002; Ogata *et al.*, 2002; Song *et al.*, 2002; Tonkin *et al.*, 1996). The electronic device such as nonthermal plasma system generates very oxidative ozone of three oxygen atoms which is beneficial for the control of gaseous pollutants. Ozone production by high voltage plasma can be achieved through silent discharge, dielectric barrier discharge, glow discharge, microwave discharge and corona discharge. As dry air or oxygen molecules entering this electric discharge field, some of oxygen molecules are ionized and form ozone.

Meanwhile, glow discharge occurs in between flat plates when high electrical field is formed with low pressure gases. In here, the ionized high energy electrons excite the neutral atoms and molecules, leading to low temperature plasma formation. Typical glow discharge is usually maintained under

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a low voltage and current.

Amongst various methods for harmful gas treatment, the plasma process can supply a suitable amount of oxides required for the reaction when it needs. Its strong oxidation activity also can oxidize other pollutants. Unreacted ozone is in part naturally deoxidized in air.

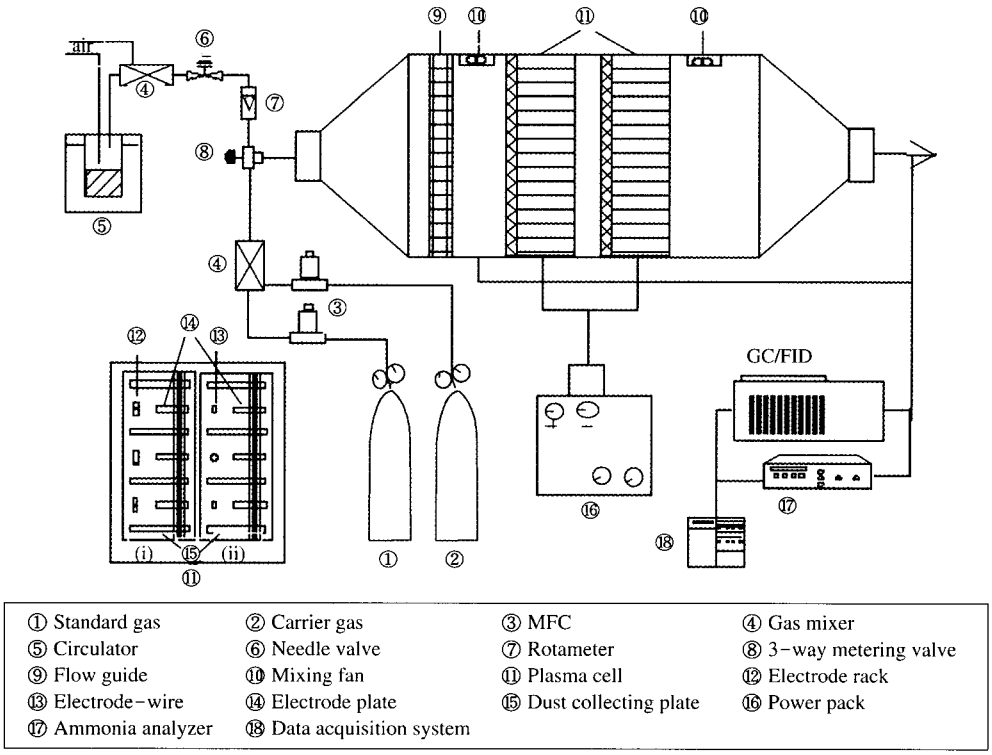
In this study, decomposition of ammonia, toluene and acetone in a high voltage plasma reactor was investigated for batch and continuous processes. Variables such as initial gas concentration, applied voltage and presence of fume dust were studied with a relatively large lab scale.

2. EXPERIMENTALS

2. 1 Materials and analysis

Two typical VOCs: toluene and acetone, which are released from various industrial processes, and an odorous gas: ammonia, were attempted to decompose by plasma reactions. Gas flows to the reactor were adjusted by means of mass flow controllers. In order to prepare the odorous gases, 28%-liquid ammonia (JUNSEI), 99.5%-toluene and 99.5%-acetone solutions were evaporated by a temperature controllable circulator (JEIO Tech., RW-025G), then diluted with bottled air (21% O_2 + 79% N_2) respectively. Feed concentration was adjusted through the bath temperature control depending on the vapor pressure of each solution.

Ammonia was measured using an ammonia analyzer (TG-2400, USA) under the low relative humidity (RH) less than 25%, which can minimize the analysis error due to moisture. A humidity meter (HI 8564, HANNA Ins.) indicated RH during ammonia test. Toluene and acetone were analyzed by a gas chromatograph (SHIMADZU, 2010 AF) equipped with a hydrogen flame ionization detector (FID) at the inlet and outlet of the reactor. It was



① Standard gas	② Carrier gas	③ MFC	④ Gas mixer
⑤ Circulator	⑥ Needle valve	⑦ Rotameter	⑧ 3-way metering valve
⑨ Flow guide	⑩ Mixing fan	⑪ Plasma cell	⑫ Electrode rack
⑬ Electrode-wire	⑭ Electrode plate	⑮ Dust collecting plate	⑯ Power pack
⑰ Ammonia analyzer	⑱ Data acquisition system		

Fig. 1. Schematic diagram of experimental apparatus.

calibrated by standard gases of toluene; 50 ppm, and of acetone; 484 ppm (Daeduk Gas Co.). Ozone was measured immediately downstream of the plasma cell using detector tubes (GASTEC, 18 L/18 M, JAPAN). In order to enhance the experimental reliability, measurement was repeated more than five times at a same condition. Particulate materials for plasma reaction was prepared by burning a mosquito coil. Its median size was 1.07 μm. A mass basis particle analyzer (SIBATA, GT-331) measured particle size distribution of the fume dust.

2. 2 Experimental apparatus

As can be seen in Fig. 1, the experimental apparatus consists of gas supplying region (1 ~ 8), plasma reactor (9 ~ 15), power control package (16) and gas analysis system (17 ~ 18). In order to visually observe the plasma generation and dust flow, the reactor was made of transparent acryl, and its length was 75 cm with 55 cm in height and 50 cm in width. Power Pack (UiF, KOREA) (16) converted and amplified AC power (220 V) up to DC (15 kV). A set of the aluminum plasma cell (11) was arranged in series: wired racks (12), thin wires (13) and flat plates (14). Wired rack type electrodes in the front cell (i) generated a large volume of high energy electrons; whilst, it was predicted electrode wires (0.2 mm in diameter) in the rear cell (ii) did comparatively small quantity of electrons. Since it was designed to supply the electric power separately, a few relative tests should be possible for each condition. This paper deals with the case that three electrodes always are ON. Two small electric ceiling fans (10) assisted gas dispersion in the reactor.

2. 3 Method

This study used a combined system of corona discharge from wired rack, thin wire strings, and glow discharge from rectangular aluminum plates. It could be visually observed through minute luminescence along the electrodes which proves the plasma discharge. Decomposition performance was investigated for batch and continuous processes. Feeding concentrations of the test gases were 100, 50 and 10 ppm, and applied electric power varied 7 kV to 13 kV with the additional condition of negative discharge at −13 kV and −10 kV. For 30 minutes' reaction of ammonia, the concentration variation in the reactor was recorded every 5 minutes. Toluene and acetone have been analyzed every 10 minutes for one hour. Dust collection efficiency based on the principle of the electrostatic precipitation was evaluated at each voltage. The performance of simultaneous removal with ammonia also was assessed at a constant gas concentration (100 ppm) with variable voltage.

The reactant gas mixture was fed into the continuous reactor at a flow rate of 200 liter per minute, which allowed the mean residence time (approximately 62 seconds). Outflow gas was detected at the discharging line (ID 10 cm) apart 1 m from the reactor exit.

3. RESULTS AND DISCUSSION

3. 1 Examination of reactor

In order to find an appropriate mixing condition depending on the inlet structure of the reactor, the computer simulation work by using a commercial fluid dynamics package (CFX-4.4, UK) was conducted for three arbitrary configurations (Type-I, II, III). Fig. 2 shows simulated flow patterns for each reactor. Gas and dilution air are entering through the same inlet in type-I. Since the gas flow would follow the streamlines, it does not afford well mixing in the reactor. Type-II was designed with a perpendicular inlet of the gas to the air injection, which presented quite vigorous mixing. As shown in type-III, simultaneous feeding of the gas from two tangential inlets did not provide sufficient mixing of air and gases.

Corona discharge occurs when the voltage applied to the metallic electrodes is high enough to ionize the gaseous species surrounding the electrodes. The number of electrons produced by corona discharge decreases with increasing distance from the electrode surface (Chen and Davis, 2002). In accordance, vigorous flow pattern may give more chances to travel through the vicinity of the electrodes, poten-

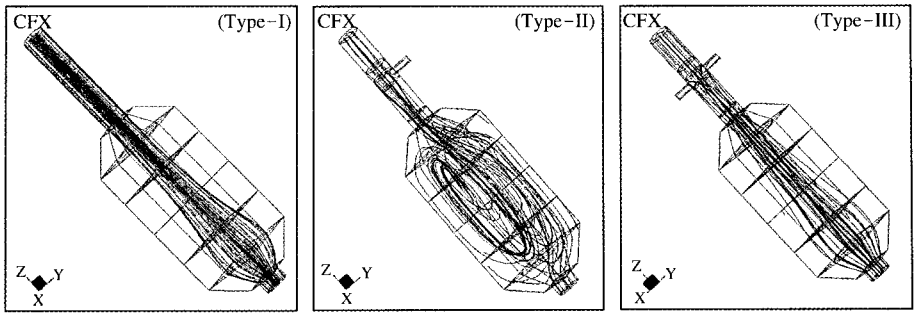


Fig. 2. Flow pattern in the reactor simulated by CFD.

tially forming a number of electrons and excited molecules. Thus, the inlet configuration defined in type-II was chosen in this work. The reactor of type-II could lead to frequent collisions and contact between excited molecules of oxygen or nitrogen and ozone or free electrons. Relative retention time of the gas molecules might be certainly prolonged in type-II. In practice, type-II produced more ozone at all flow rates than the other types.

Table 1 gives the ozone concentration for the three types of gas inlet at different flow rate and more ozone was produced at low flow rates. In other words, flow velocity rather than absolute flow quantity greatly affects ozone formation due to a relatively long residence time. Although the effect of gas velocity has been in part uncertain (Boelter and Davidson, 1997), Chen and Davidson (2002) presented a potential possibility that low velocity could produce a large number of ozone molecules widely distributed in the reactor. Generation of ozone in ambient air is more complicated than in pure oxygen due to the presence of nitrogen and water vapor. It has been known that the factors to effect on the ozone generation are electric voltage, current level, electrode size, temperature, relative humidity and air velocity (retention time). According to an open literature, as increasing the gas temperature, the ozone production rate gradually decreased for both negative and positive coronas (Peyrous *et al.*, 1998). The wire radius is monotonically proportional to the ozone generation for both polarities (Chen and Davidson, 2002). In this paper, the electric

Table 1. Ozone generation depending on inlet structure and air flow rate (ppm).

	100 LPM	200 LPM	300 LPM
Type-I	140	100	60
Type-II	190	120	80
Type-III	150	110	60

current was set to max. 10 A with 0.2 mm-discharge wire, and 0.5 mm thick wired rack at the ambient temperature.

3. 2 Generation and dissociation of ozone

In order to confirm the dependency of applied power electricity on ozone presence, a batch reactor was closed up tight under the state of full of air, and high voltage was applied for 5 minutes. After off the power, natural dissociation of ozone was observed. While maximum ozone concentration up to 200 ppm occurred at −13 kV plasma, a low voltage, 7 kV, produced only 0.4 ppm ozone for initial 5 minutes. The increase of applied voltage could generate more ozone, and the ozone concentration under the negative corona atmosphere of the reactor was risen up to 200 ppm. It matches well with other works (Bolter, 1997), and in particular Chen and Davidson (2003) developed a numerical model and proved that the negative corona discharge produced a large number of electrons more than 50 times that produced in the positive discharge. Their experimental work indicated that the ozone production in the negative corona was about one order of magni-

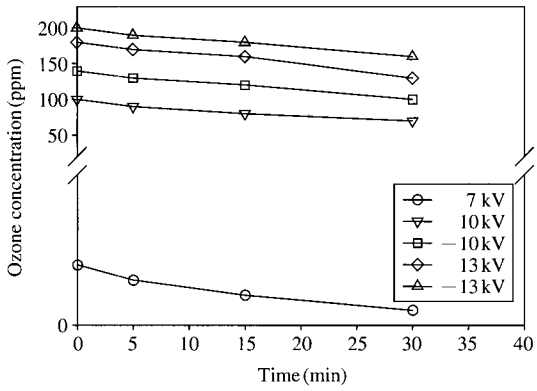


Fig. 3. Variation of ozone concentration in a batch reactor.

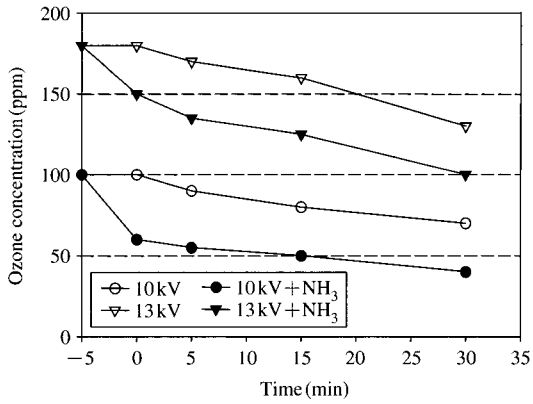


Fig. 4. Dissipation of ozone with ammonia.

tude higher than in the positive corona. As can be seen in Fig. 3, the ozone destruction in ambient air was found monotonically consistent as elapsing the time.

A large number of the produced ozone can lead to vigorous reactions with excited molecules, and in the long run facilitates decomposition of the non-degradable volatile organic matters. In air, the molecules of N_2 and O_2 excited by high energy plasma play an important role in ozone chemistry. Although nitrogen atom and its excited molecular state present oxygen atoms as seen from reactions (3) and (4) are active, the reactions (2) and (3) contribute to 80% of the ozone production in positive corona and 90% of that produced in negative corona (Chen and Davidson, 2003). In fact, it has been known that the lifetime of atomic ozone produced in reaction (1^{-1}) is only in the order of $10 \sim 20\ \mu s$ (Kransnoperov *et al.*, 1997). Thus, not only ozone formation, but also gas decomposition by atomic oxygen should not be predominant relative to the serial reactions including ozone or other excited species.

$$e + O_2 \rightarrow e + O + O \quad (1)$$

$$O + O_2 + M \rightarrow O_3^* + M \rightarrow O_3 + M(O_2, O_3, N_2) \quad (1-1)$$

$$e + O_2 \rightarrow O_2^* + e \quad (2)$$

$$O_2^* + O_2 \rightarrow O_3 + O \quad (2-1)$$

$$e + N_2 \rightarrow N_2^* + e \quad (3)$$

$$N_2^* + O_2 \rightarrow N_2O + O \quad (3-1)$$

$$N_2^* + O_2 \rightarrow N_2 + 2O \quad (3-2)$$

$$O + O_2 \rightarrow O_3 \quad (3-3)$$

$$e + N_2 \rightarrow N + N \quad (4)$$

$$N + O_2 \rightarrow NO + O \quad (4-1)$$

$$N + NO \rightarrow N_2 + O \quad (4-2)$$

$$O_3 + O \rightarrow O_2 + O_2,\ O_3 + N \rightarrow NO + O_2 \quad (5)$$

$$O_3 + e \rightarrow O_2 + O + e \quad (6)$$

Ozone is then removed through natural dissociation reactions such as (5) and (6). Free oxygen and nitrogen as well as excited electrons attack ozone, finally being decomposed into oxygen molecules or atoms. Of course, besides a few examples as above, ozone is involved in more complicated reactions to be formed or dissipated.

In order to confirm the relative dissipation of ozone in a batch reactor, the variation of ozone concentration was examined under coexistence of 100 ppm ammonia. Injection of ammonia led to a steep decrease of ozone level at the very initial step (see Fig. 4). Ammonia was reduced to 69 ppm at 13 kV and 79 ppm at 10 kV. While ozone exists with ammonia, ozone is decomposed through the reac-

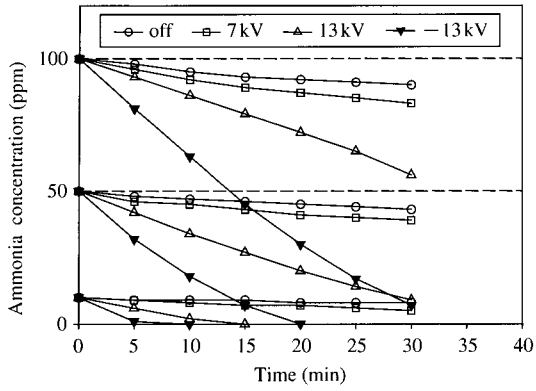


Fig. 5. Removal of ammonia in a batch reactor.

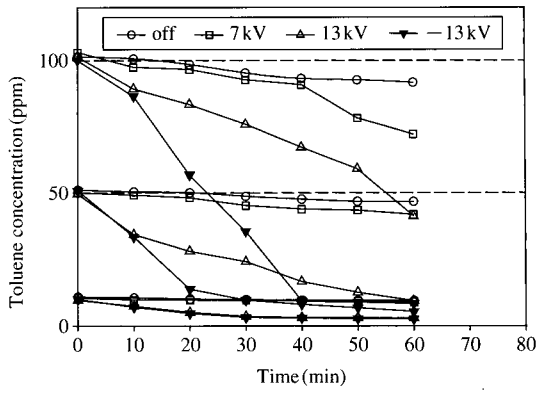


Fig. 6. Removal of toluene in a batch reactor.

tion with ammonia rather than dissipation by itself. Coincidently the decreasing rate was similar to the natural dissipation.

3. 3 Effect of initial concentration in a batch reactor

Gas decomposition was investigated while maintaining the effective corona discharge at 7 kV, 13 kV and −13 kV respectively. The ozone level of the reactor declined with reaction time in a similar fashion for three gases. In a plasma state of ammonia mixture, ammonia could be decomposed to dihydro nitrogen (NH_2) or monohydro nitrogen (NH) by attacking of electrons. Also, ozone in the reactor oxidizes ammonia, finally resulting in crystal salts such as NH_4NO_3 (Ma *et al.*, 2001). Fig. 5 shows ammonia decay at each applied voltage. The effect of initial concentration showed a similar tendency with the work of Lee (2001). The decomposition rate was high at low initial concentration; for example, at 13 kV plasma, 44% decomposition for 100 ppm and 82% for 50 ppm in 30 minutes, and 100% for 10 ppm in 15 minutes' reaction. This might be attributed to the decreased energy depleted to unit gas under the constant discharge condition. Such behavior was particularly apparent in the batch reactor, which could provide sufficient mixing and reaction time. Ammonia decay was the most rapid at −13 kV. As formerly examined, since the power of −13 kV generated a large volume of ozone, it directly influenced ammonia decomposition.

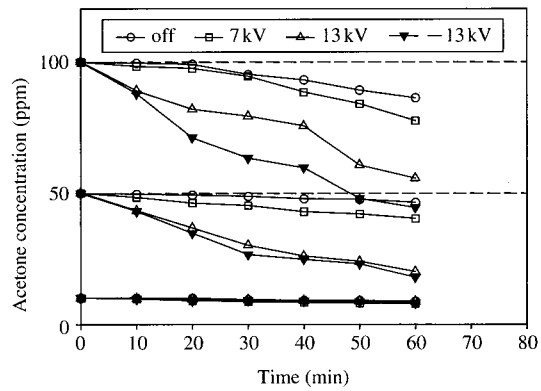


Fig. 7. Removal of acetone in a batch reactor.

Toluene is one of ubiquitous VOCs discovered in industry and house. Since toluene consists of the stable benzene ring of resonance structure, it is not easy to break the bonds between carbon and carbon. In the plasma state reactor, it can be dissociated by excited high energy oxygen atoms or OH radicals in few milli-seconds to several hundreds micron seconds (Rudolph *et al.*, 2002). Fig. 6 is the result of analysis every ten minutes. The effect by initial concentration was not as significant as ammonia. Evident decomposition occurred in 10 minutes reaction. In particular, negative corona greatly affected the decomposition.

As for acetone, the effect of applied voltage was

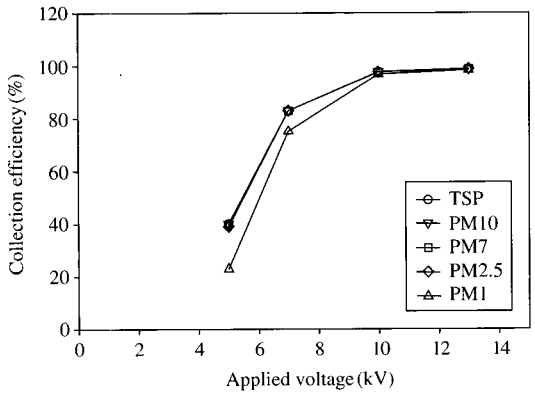


Fig. 8. Collection of fume particles with applied voltage.

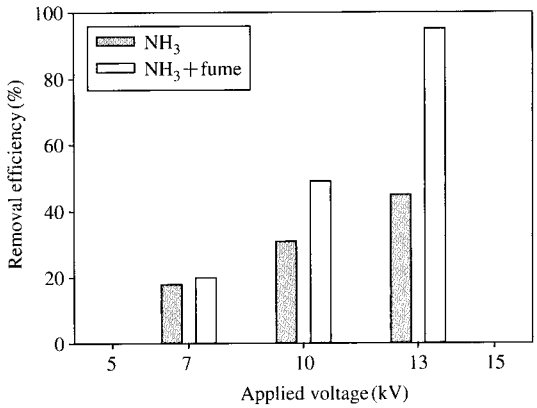


Fig. 9. Removal of ammonia with and without fume particles.

similar to the above gases, but initial concentration tended different from ammonia. The reaction for 60 minutes at 13 kV showed about 45% decomposition rate for 100 ppm, 60% for 50 ppm and 15% for 10 ppm. In particular, as can be seen in Fig. 7, the rate for 10 ppm-feeding was very low despite of negative plasma. For the operating conditions provided in this work, the removal of odorous gases by ozone did not depend explicitly on initial concentration. In other words, a large number of repeated tests did not present any identical tendency associated with gas concentration in our pilot scale reactor.

3. 4 Simultaneous treatment with fume dust

Plasma process has a high potential to take a significant charge of indoor air control, which may enable to treat various materials simultaneously. This work attempted to remove ammonia with fume dust in a batch reactor. Fig. 8 shows the removal rate of dust with applied voltage in air environment. When strong electricity is applied to the reactor, the fume dust is precipitated on the dust collecting plates ((15) in Fig. 1). Dust particles are removed from the reactor space by the same principle as an electrostatic precipitator (EP). The efficiency depends closely on the applied voltage at all particle sizes. Almost all the dust particles were collected from 10 kV charge, but the lower voltage, 5 kV, could only remove less than 40% of particles including 24% of PM 1. Alike to the conventional EP, the higher collection efficiency could be achieved in the larger particles.

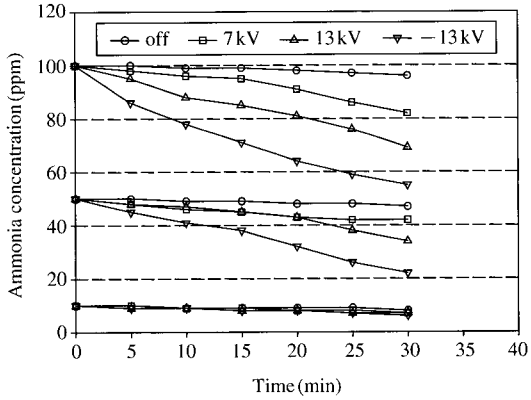


Fig. 10. Removal of ammonia in a continuous reactor.

Fig. 9 is the comparison of simultaneous removal with fume dust at several voltages. Feed gas concentration was fixed at 100 ppm. The particulate materials disappeared in a very short time as soon as fed to the reactor. Ammonia also was more rapidly decomposed than gas alone. The removal efficiency after 30 minutes has risen up to 95%, which is 40% higher than without particulate fume. A certain proportion of ammonia molecules must be adsorbed on the particulate dust, and thereby adhered on the collecting plates together. The released ammonia can be continuously decomposed in a plasma

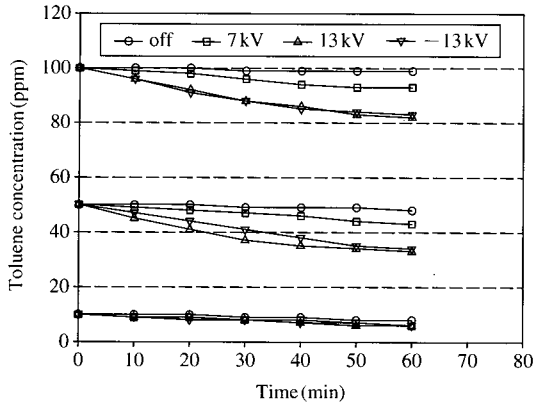


Fig. 11. Removal of toluene in a continuous reactor.

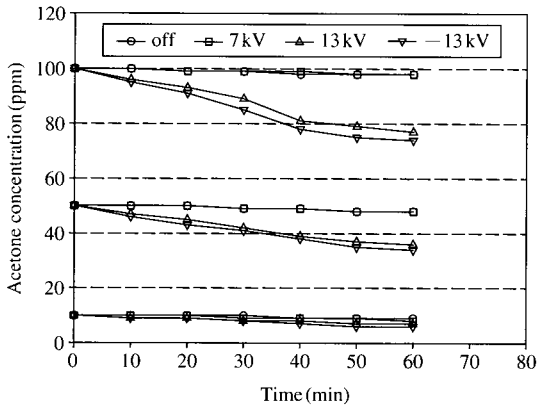


Fig. 12. Removal of acetone in a continuous reactor.

region.

3. 5 Decomposition in a continuous process

The background gas concentration was determined after stabilizing the fed mixture for about 40 minutes without plasma discharge. It could be ascertained by analyzing the local concentration within the reactor. The average residence time of gas flow in the plasma region was about 1.35 to 20 seconds. Figs. 10, 11 and 12 indicate the effect of initial concentration on the decomposition efficiency. Decomposition in a continuous process did not compete with the batch.

The maximum removal efficiency for ammonia with the initial concentration 50 ppm at −13 kV was 60%, but quite less efficiency, only 20%, in 10 ppm and 45% in 100 ppm. Toluene was much less decomposed, of which rate was about 30% even by −13 kV discharge. An apparent difference between positive and negative voltage was not seen in a continuous process as found in Fig. 11. Acetone was not much different. In the long run, contact probability between gas molecules, excited electrons and radicals seem to be much lower than the batch process.

4. CONCLUSIONS

Many studies have shown that the nonthermal plasma system is capable of cleaning dilute pollutants or odorous gases with high energy efficiency. Ozone production in laboratory air was proportional to plasma energy power, and was larger at negative electricity. It has been known that negative coronas produce a thicker plasma region and expand ionization boundary. It is difficult to make a definite statement about the dependency of the decomposition efficiency for individual gases on the initial condition. Injection of fume dust into ammonia mixture stream improved the NH_3 decomposition with its absolute precipitation. Satisfactory efficiency for the test gases so far could not be obtained in a continuous process. On the other hand, although this work did not deal with it, production of the secondary pollutants such as NOx and HNO_3 needs to be closely followed in the nonthermal plasma process.

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