Destruction and Removal of Toluene and MEK from Gas Streams with Silent Discharge Plasmas

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The effectiveness of applying silent discharge plasmas (SDP) for destroying and removing volatile organic compounds (VOCs) from gas streams is experimentally evaluated with a laboratory-scale reactor. The VOCs selected for study include toluene and methyl ethyl ketone (MEK). Direct collision with energetic electrons and reaction with generated gas-phase radicals are two major mechanisms responsible for destruction and removal of VOCs from gas streams. Operating parameters investigated include applied voltage, gas residence time, and temperature and composition of the gas stream. Experimental results indicate that the removal efficiency of toluene and MEK achieved with SDP can be enhanced by operating the system at a higher gas temperature and applied voltage due to the generation of more energetic electrons and radicals. O_2 *is essential for removing VOCs from gas streams with SDP. More than 80% removal efficiencies were achieved with this system for both toluene and MEK. SDP can potentially serve as an alternative control technology for removing VOCs from gas streams.*

Introduction

Destruction and removal of volatile organic compounds (VOCs) from gas streams by nonthermal plasma processing has been an active research topic in recent years. The electrons in a nonthermal plasma have a much higher energy (or temperature) than the gas molecules. As a result, reactions that do not take place under normal conditions can be driven to proceed by providing appropriate energy to the electrons in the gas stream. Since little energy is wasted in heating the gas molecules, nonthermal plasma processing can be more effective in decomposing gaseous contaminants compared to conventional control technologies. Various technologies have been demonstrated to be able to destroy VOC molecules from gas streams by generating nonthermal plasmas, such as an electron beam, corona discharge, or dielectric barrier discharge (Koch et al., 1993; Nunez et al., 1993; Chang and Lee, 1995).

In this article, an emerging control technology that destroys and removes VOCs from gas streams is described and demonstrated. This method employs silent discharges to generate nonthermal plasmas in which energetic electrons excite, dissociate, and ionize gas molecules to form free gas radicals, thereby driving the reactions of decomposition and oxidation of VOCs into end products, including H_2O, CO, and CO_2, that are less hazardous to the environment and human health. Silent discharge (also known as dielectric barrier discharge) is a gas discharge process that has been widely used for O_3 generation (Horvath et al., 1985). The presence of a dielectric material between the discharge gap and one of the two discharge electrodes is a unique characteristic of silent discharge plasma (SDP) (Eliasson et al., 1987). Existence of a dielectric material is essential for proper functioning of a silent discharge. As the potential across the gap reaches the breakdown voltage, the dielectric acts as a stabilizing material leading to the formation of a large number of microdischarges with relatively high electric fields. Existing electrons in the gas stream can then be accelerated to gain sufficient energy for inelastic collisions with gas molecules. Typically, a material with high dielectric strength (V/mm) and a high dielectric constant, such as glass, quartz, or ceramic, is used as the dielectric.

The advantages of applying SDP to generate plasmas for VOC control include: (1) use of ac power supply for easy assembly and operation, and (2) SDP can be effectively generated and sustained at atmospheric pressure, and can therefore be readily applied for abating the emission of gaseous air pollutants from typical industrial processes. SDP technology has been studied as a possible control technology for removing odor-causing substances, including NH_3 and H_2S and

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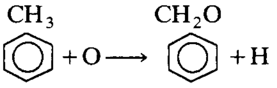
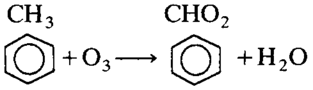
organic compounds such as benzene, toluene, trichloroethylene, and formaldehyde, from gas streams (Chang and Tseng, 1996; Nunez et al., 1993; Neely et al., 1989; Evans et al., 1993; Chang and Lee, 1995). In this study, SDP is experimentally evaluated as an alternative air-pollution-control technology for destroying and removing VOCs from gas streams. Usually, two mechanisms are involved in the destruction and removal of VOCs from gas streams by generation of SDP: (1) direct dissociation caused by the collision of energetic electrons with VOC molecules, and (2) reactions between VOCs and generated gas-phase radicals. Gas-phase radicals may consist of OH (hydroxyl), HO_2 (hydroperoxyl), and O (oxygen atom), which are highly reactive and can react with VOC molecules to form stable final products with less environmental impact.

Toluene ($C_6H_5CH_3$) and methyl ethyl ketone (MEK, $CH_3COC_2H_5$) are widely used in industry for solvent degreasing, graphic arts manufacturing, and surface-coating application (USEPA, 1991). However, both chemicals are also classified as hazardous air pollutants (HAPs) due to their potential hazards to human health. Since these two compounds have quite different molecular structures and functional groups, they are chosen as target pollutants for destruction and removal in this study. Major reactions leadings to the destruction and removal of toluene in SDP along with the rate constants evaluated at 1 atm and 298 K are described in Reactions 1 through 4 (Atkinson and Lloyd, 1984; Emdee et al., 1992):

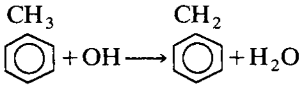
Reaction Mechanism — K_{298} (cm^3/molecule·s)



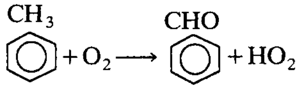
8.4×10^{-14} (1)



1.5×10^{-22} (2)



2.7×10^{-13} (3)



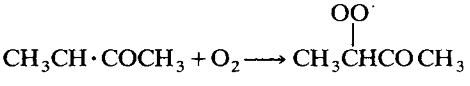
6.9×10^{-15} (4)

Reaction of toluene with OH radicals is the most important pathway leading to its destruction. Radicals generated by reactions 1 through 4 are transient in SDP and tend to react with other radicals, including OH, HO_2, and O, to form final products such as CO_2 and H_2O.

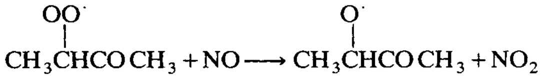
Major pathways responsible for MEK removal include its reaction with OH radicals as described in reactions 5 through 7 (Atkinson and Lloyd, 1984):

Reaction Mechanism — K_{298} (cm^3/molecule·s)

$$CH_3CH_2COCH_3 + OH \longrightarrow CH_3CH\cdot COCH_3 + H_2O \qquad 5.5\times10^{-13} \quad (5)$$



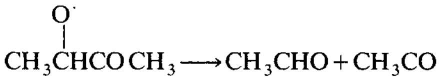
$$CH_3CH\cdot COCH_3 + O_2 \longrightarrow CH_3\overset{OO^{\cdot}}{C}HCOCH_3 \qquad * \quad (6)$$



$$CH_3\overset{OO^{\cdot}}{C}HCOCH_3 + NO \longrightarrow CH_3\overset{O^{\cdot}}{C}HCOCH_3 + NO_2 \qquad 6.4\times10^{-12} \quad (7)$$

The asterisk in Reaction 6 means the rate constant is unavailable. The $CH_3CO^{\cdot}CHCOCH_3$ radical is unstable and will decompose rapidly as described in Reaction 8.

Reaction Mechanism — K_{298} (s^{-1})



$$CH_3\overset{O^{\cdot}}{C}HCOCH_3 \longrightarrow CH_3CHO + CH_3CO^{\cdot} \qquad 1.3\times10^{5} \quad (8)$$

The CH_3CHO (acetyldehyde) and $CH_3CO^{\cdot}$ radicals can then be further oxidized to form final products, including CO, CO_2, and H_2O.

Experimental Design

An experimental system was designed and constructed to evaluate the effectiveness of applying SDP in removing toluene and MEK from simulated gas streams (Figure 1). The system comprises a continuous-flow gas-generation system, laboratory-scale SDP reactor, and gas-sampling and measurement system. Gas streams with specific mass-flow rates of O_2 and N_2 were initially generated from compressed gas cylinders and mass-flow controllers (Teledyne Hastings-Raydist HFC202). Gaseous toluene and MEK were generated by passing the gas streams through liquid of toluene or MEK that were kept in a controlled-temperature water bath. The laboratory-scale silent-discharge reactor was made of a Pyrex glass tube with an inner diameter of 3.6 cm and a wall thickness of 0.2 cm. The length of the tube was 40 cm. The inner electrode, made of a molybdenum rod with a diameter of 0.24 cm, was aligned horizontally along the center line of the reactor. The outer electrode was made of stainless-steel wire mesh and was wrapped around the outside of the Pyrex glass tube. Plasma was sustained within a control volume of 202 cm^3. The reactor was equipped with an air jacket made of glass tube with an outside diameter of 9.6 cm. Hot air was then generated and passed through the air jacket to keep the gas within the discharge volume isothermal for elevated-temperature experiments. Silent discharge was generated with a step-up transformer that was constructed with a turns ratio of 273. The applied voltage to the silent-discharge reactor was adjusted by varying the primary voltage. A 40-kV peak probe with a 1,000 times divider (Tektronix, Model P6015A) and a 150-MHz digital oscilloscope (Tektronix, Model TDS410) were connected to the transformer and reactor to check its accuracy. The power consumption of the silent-discharge system was measured with a power meter (Chun Hwa, Model 2100). Toluene and MEK concentrations ([C_7H_8] and [$CH_3COC_2H_5$]) in the resulting gas stream were determined by first sampling the gas stream into a 5-L Tedlar sampling

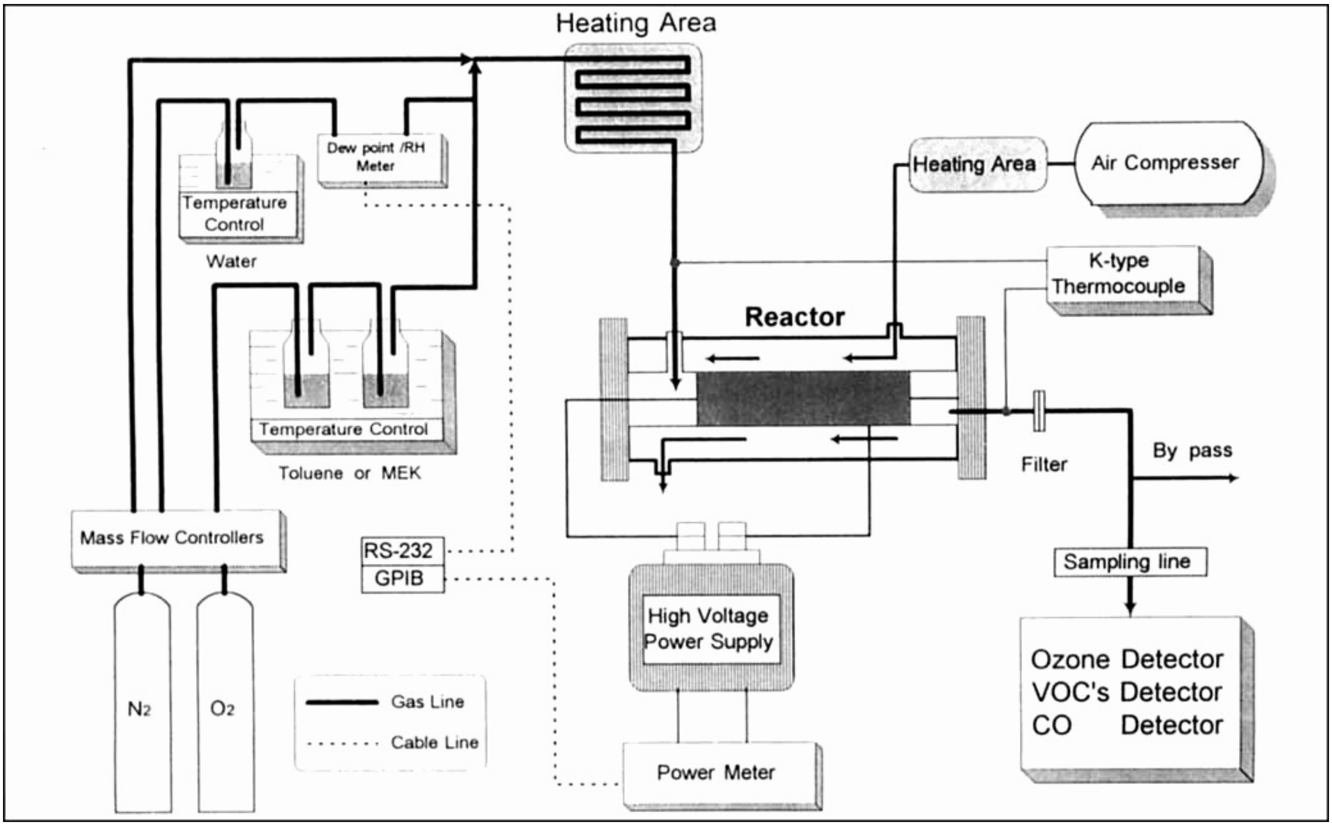


Figure 1. Experimental setup.

bag. [$C_6H_5CH_3$] and [$CH_3COC_2H_5$] of the resulting gas stream were then measured by a gas chromatograph (HP, Model 5890 II). In addition, an ozone analyzer (Sorbios, Model OMH 100.2/EG-2001) was used to measure the [O_3] of the gas stream leaving the reactor.

Before applying power to the reactor, the gas stream with specific composition and mass-flow rate was generated and passed through the reactor for 5 min to allow the system to reach steady-state conditions. Flow rates, temperature, and [$C_6H_5CH_3$] of the gas stream were then monitored, and the power was applied to generate plasmas. Depending on the gas composition and temperature, the electrical discharge glow could be generally seen in the dark when the applied voltage was greater than 15 kV (rms value). The discharging process was maintained for 5 min to make sure that new steady-state conditions had been achieved before the gas stream was sampled for analysis. Power supply was then turned off and the system was monitored to make sure the system returned to its initial conditions. All experimental tests were conducted at atmospheric pressure. Destruction efficiency of $C_6H_5CH_3$ ($\eta_{C_7H_8}$) was determined by measuring the SDP reactor's inlet and outlet concentrations of $C_6H_5CH_3$ in the gas stream.

Results and Discussion

Experimental tests were first performed to determine the dependence of $\eta_{C_7H_8}$ on the applied voltage at four different temperature levels ranging from 300 to 373 K (Figure 2). Experiments were carried out with dry gas streams containing 200 ppmv C_7H_8, 21% by volume O_2, and N_2 as the carrier gas. The flow rate of the gas stream was controlled at 3 standard liters per minute (SLPM) resulting in typical gas residence times in the plasma of 4 s. When the applied voltages were less than 16 kV (rms value), $\eta_{C_7H_8}$ values were relatively low (less than 20%). Given a constant gas temperature, $\eta_{C_7H_8}$ achieved with SDP increases with increasing applied voltage. This is attributed to the higher electric-field strength and more power deposited into the gas stream when it is op-

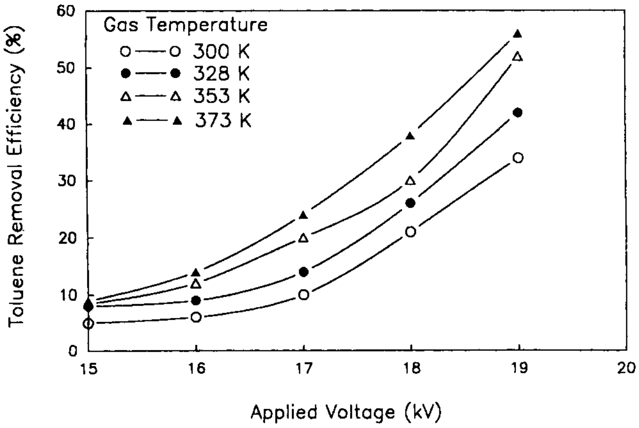


Figure 2. Dependence of $\eta_{C_7H_8}$ on applied voltage for select gas temperatures.

The gas streams contain 200 ppmv C_7H_8, 21% by volume O_2, and N_2 as the carrier gas. The gas flow rates are 3 SLPM.

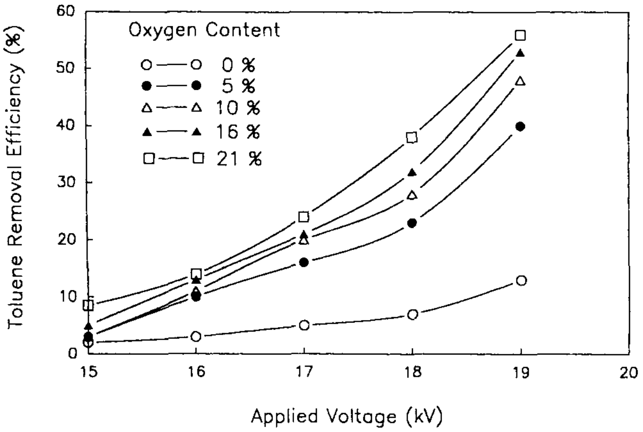


Figure 3. Dependence of $\eta_{C_7H_8}$ on applied voltage for select inlet $[O_2]$.

Gas streams are dry, and contain 200 ppmv C_7H_8, and N_2 as the carrier gas. The gas flow rates and temperatures are kept at 3 SLPM and 373 K, respectively.

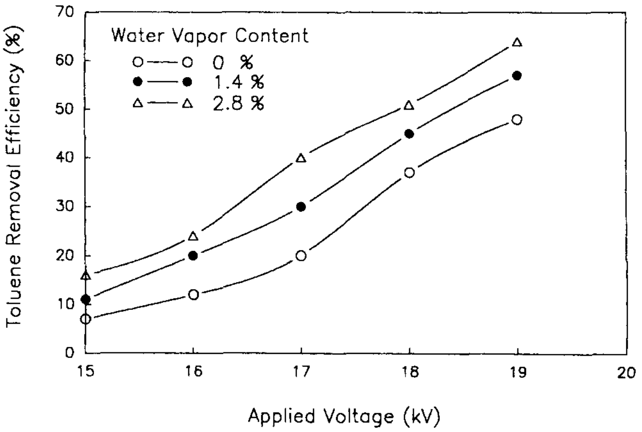


Figure 4. Dependence of $\eta_{C_7H_8}$ on applied voltage for select inlet $[H_2O_{(g)}]$.

Gas streams contain 120 ppmv C_7H_8, 21% by volume O_2, and N_2 as the carrier gas. The gas temperature and flow rate are 300 K and 3 SLPM, respectively.

erated at a higher applied voltage. $\eta_{C_7H_8}$ achieved with SDP is also found to increase with increasing temperature at a given applied voltage. Since the gas density (N) decreases as the gas temperature increases, SDP tends to operate at a higher reduced electric field (E/N), resulting in a higher $\eta_{C_7H_8}$ at a higher gas temperature due to the generation of more energetic electrons. In addition, the power consumption was also found to increase as the gas temperature increases.

To determine how the O_2 content of the gas stream would affect $\eta_{C_7H_8}$ at different applied voltages, a set of tests was carried out, with $[O_2]$ in the N_2 of the gas stream varying from 0 to 21% by volume (Figure 3). The gas stream was dry and the temperature was kept at 373 K. The gas flow rate was 3 SLPM and the inlet $[C_7H_8]$ was controlled at 200 ppmv. The carrier gas was N_2. Apparently, higher O_2 content favors C_7H_8 removal with SDP. Since the gas stream was dry, SDP would generate significant amounts of O_3, and O, which can oxidize C_7H_8 resulting in a higher $\eta_{C_7H_8}$ as O_2 content of the gas stream increases (as described in Reactions 1 and 2). Without oxygen in the gas stream, $\eta_{C_7H_8}$ achieved with SDP are relatively low (less than 15%). As a result, the existence of O_2 in the gas stream is essential for effective destruction and removal of C_7H_8 with SDP.

The effects of adding moisture to the gas stream on $\eta_{C_7H_8}$ achieved with various applied voltages were also experimentally determined (Figure 4). The gas stream contained 120 ppmv C_7H_8 21% by volume oxygen, and the carrier gas was N_2. The temperature of the gas stream was controlled at 300 K. $\eta_{C_7H_8}$ achieved with SDP is effectively enhanced as $[H_2O_{(g)}]$ of the gas stream is increased from 0% to 2.8% by volume despite decreasing $[O_3]$ with increasing $[H_2O_{(g)}]$. As a result, other destruction mechanisms that are more effective in removing C_7H_8 compared to O_3 reaction must exist to account for the higher $\eta_{C_7H_8}$. As described previously, reaction of toluene with OH (Reaction 3) most likely resulted in its destruction. Therefore, adding moisture to the gas stream would increase the generation of OH and enhance $\eta_{C_7H_8}$ (Chang et al., 1991). After a few hours' operation, a thin layer of particulate matter was observed on the inner wall of the reactor. Further study is needed to identify the composition of these particles.

Since the gas residence time is a very important parameter in choosing and designing an air-pollution-control device, the effect of gas residence time on $\eta_{C_7H_8}$ achieved with SDP was experimentally evaluated, and the results are presented in Figure 5. Since the discharge volume and gas temperature were constant, the gas residence time could be varied by changing the gas-flow rate. The gas stream was dry, with 21% by volume O_2, and N_2 as the carrier gas. The inlet $[C_7H_8]$ and temperature of the gas stream were controlled at 320 ppmv and 373 K, respectively. Given a constant applied voltage, $\eta_{C_7H_8}$ increases monotonously as the gas residence time increases from 3 s to 12 s. This is attributed to more energy deposited into the gas stream (in terms of mJ/cm^3) as the gas residence time increases. With the applied voltage of 19 kV (rms value), $\eta_{C_7H_8}$ reaches 80% when the gas residence time is controlled at 12 s. Dependence of the toluene removal rate on the gas residence time is also plotted at the same figure

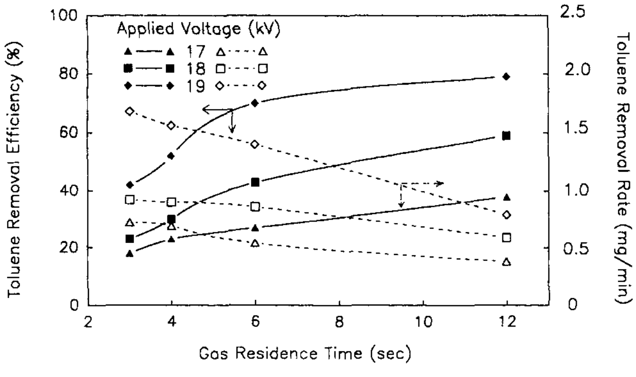


Figure 5. Dependence of $\eta_{C_7H_8}$ (solid lines) and mass removal rate (dashed lines) on gas residence time for select applied voltages.

Gas streams are dry and contain 320 ppmv C_7H_8, 21% by volume O_2, and N_2 as the carrier gas. The gas temperatures are controlled at 373 K.

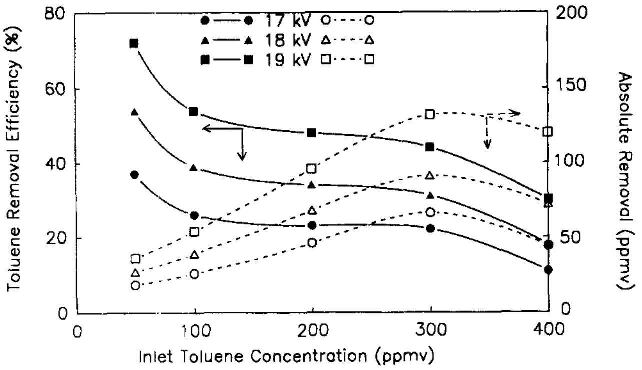


Figure 6. Dependence of $\eta_{C_7H_8}$ on inlet toluene concentration for select applied voltages.

The gas streams are dry and contain 21% by volume O_2, with N_2 as the carrier gas. The gas temperature and flow rate are controlled at 373 K and 3 SLPM, respectively (solid lines stand for percent removal, while dashed lines stand for absolute removal).

(dashed lines). Given a constant inlet $[C_7H_8]$, toluene mass removal rate is a function of removal efficiency and gas-flow rate. Experimental results indicate that operating at a smaller gas residence time actually results in a higher mass removal rate. With a gas residence time of 3 s and an applied voltage of 19 kV, the toluene removal rate is 1.7 mg/min. Since the power consumption of 20 W was measured at this operating condition, energy efficiency for removing toluene from gas stream is calculated as 5.1 g/kWH.

Dependence of $\eta_{C_7H_8}$ on inlet $[C_7H_8]$ varying from 50 to 400 ppmv at three applied voltages was determined and presented in Figure 6. The gas stream was dry and contained 21% by volume O_2, with N_2 as the carrier gas. The temperature of the gas stream was 373 K. As inlet $[C_7H_8]$ increases from 50 ppmv to 400 ppmv, $\eta_{C_7H_8}$ decreases. Nevertheless, the absolute toluene removal, which equals the product of inlet $[C_7H_8]$ and $\eta_{C_7H_8}$, actually increases as inlet $[C_7H_8]$ increases from 50 to 300 ppmv, and then decreases as $[C_7H_8]$ increases further to 400 ppmv. With a constant applied voltage, the maximum absolute removal occurs at the inlet $[C_7H_8]$ of 300 ppmv. The results indicate that SDP is suitable for controlling VOCs with relatively low concentration (up to a few hundred ppmv).

The effectiveness of applying SDP for destroying and removing MEK (C_4H_8O) from gas streams was also experimentally evaluated. The dependence of $\eta_{C_4H_8O}$ on $[H_2O_{(g)}]$, ranging from 0 to 1.6 vol. % was determined at five different levels of applied voltage (Figure 7). The gas stream contained 125 ppmv C_4H_8O, 21 vol. % O_2, with N_2 as the carrier gas. The gas flow rate was controlled at 1.5 SLPM, while the temperature of the gas stream was kept at 373 K. At a given applied voltage, $\eta_{C_4H_8O}$ achieved with SDP increases with increasing $[H_2O_{(g)}]$. The trend observed here is similar to that for C_7H_8 removal (as described in Figure 4). This is probably attributed to the generation of more OH radicals at a higher $[H_2O_{(g)}]$, mainly via $H_2O_{(g)} + O(^1D) \rightarrow 2OH$ (Chang et al., 1991). Generated OH radicals can then oxidize MEK to form other products. With an applied voltage of 19 kV, $\eta_{C_4H_8O}$ achieved with SDP reaches 80% when the $[H_2O_{(g)}]$ is kept at 1.6 vol. %. Power consumption was measured to be 18 W at this operating condition, resulting in the energy efficiency of 1.6 g/kWh for removing MEK.

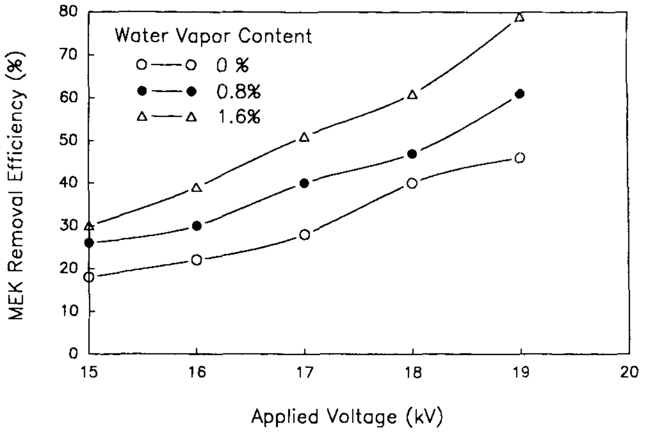


Figure 7. Dependence of $\eta_{C_4H_8O}$ on applied voltage for select inlet $[H_2O_{(g)}]$.

The gas streams contain 125 ppmv C_4H_8O, 21% by volume O_2, and N_2 as the carrier gas. The gas flow rate and temperature are controlled at 1.5 SLPM and 373 K, respectively.

The potential of applying SDP for simultaneous destruction and removal of toluene and MEK from gas streams was also experimentally evaluated (Figure 8). The gas streams contained 120 ppmv C_7H_8, 140 ppmv C_4H_8O, 21% by volume O_2, 1% by volume $H_2O_{(g)}$, and the carrier gas was N_2. The gas-flow rate was controlled at 1.5 SLPM and the temperature of the gas stream was 373 K. With all applied voltages ranging from 15 to 19 kV, $\eta_{C_7H_8}$ achieved with SDP is always higher than $\eta_{C_4H_8O}$. This is possibly due to the lower inlet C_7H_8 concentration and higher reaction-rate constant between OH and C_7H_8 compared to MEK. In addition, the ionization potential for toluene (8.8 eV) is also lower than that of MEK (9.5 eV) (Lide, 1992). Nevertheless, simultaneous removal of toluene and MEK is experimentally achieved in this study. With the highest applied voltage (19 kV), 75% of toluene and 45% of MEK are simultaneously removed from the gas streams.

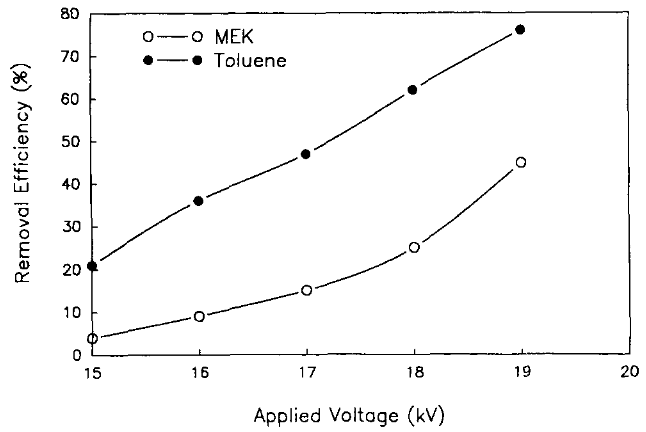


Figure 8. Simultaneous removal of C_7H_8 and C_4H_8O with SDP.

The gas streams contain 120 ppmv C_7H_8, 140 ppmv C_4H_8O, 21% by volume O_2, 1% by volume $H_2O_{(g)}$, and the carrier gas is N_2. The gas flow rate and temperature are controlled at 1.5 SLPM and 373 K, respectively.

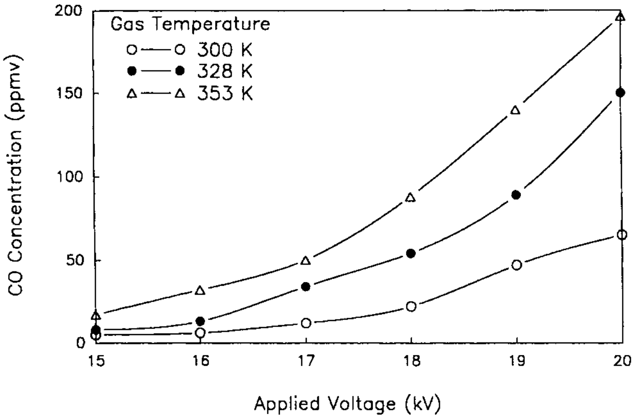


Figure 9. Dependence of CO concentration on the applied voltage for selected gas temperatures.

The gas streams are dry and contain 120 ppmv C_7H_8, 21% by volume O_2, with N_2 as the carrier gas.

Elimination of toluene and MEK from gas streams with SDP may lead to the formation of other gas species (e.g., CO, CO_2, HCHO, C, H_2, NO_x). However, all of these end products, except CO, were not extensively measured due to the lack of expensive instruments when this research was conducted. Dependence of [CO] generated on applied voltage for the dry gas stream containing 120 ppmv C_7H_8 and 21% by volume O_2 was experimentally determined (Figure 9). CO concentration increases as the applied voltage and gas temperature increase. The trend is consistent with the increase in $\eta_{C_7H_8}$ with these two parameters. About 20% of the carbon destroyed by SDP was converted to CO. More of these CO will be further oxidized to form CO_2 as $[H_2O_{(g)}]$ of the gas stream increases.

Conclusions and Recommendations

A laboratory-scale experimental apparatus was designed to evaluate the effectiveness of applying silent discharge plasmas to destroy and remove toluene and MEK from simulated gas streams. Results obtained at elevated temperature (100°C) and atmospheric pressure indicate that silent-discharge plasmas can effectively remove toluene and MEK from gas streams. Removal efficiencies achieved with SDP depend on the applied voltage, gas residence time, gas composition, and temperature of the gas stream. Water vapor and O_2 are beneficial for the effective destruction of toluene and MEK with SDP. This study demonstrates the potential of applying SDP as an alternative technology for controlling volatile organic compounds (VOCs) with relatively low concentration (down to tens of ppmv). However, further research is needed to better understand the controlling mechanisms for gas-phase removal of VOCs. Identification and accurate measurements of possible end products are also important in evaluating the suitability of applying this innovative technology for controlling VOC emissions. Gas chromatography, equipped with mass spectroscopy or Fourier transform infrared spectroscopy, is recommended for this purpose in future research. In addition, more accurate measurement of power consumption within the system should be carried out to evaluate the economic feasibility of applying this emerging technology for air-pollution control.

Acknowledgments

The authors would like to acknowledge funding provided by the National Science Council of the Republic of China under Project Numbers NSC 83-0410-E-008-024 for this study.

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Manuscript received Sept. 6, 1996, and revision received Jan. 7, 1997.