

Cleaning of Air Streams from Organic Pollutants by Plasma-Catalytic Oxidation

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Oxidative removal of a mixture of chlorinated ethylenes and aromatic compounds in air in a pulse corona discharge reactor combined with metal oxide catalyst downstream was investigated in a field experiment. Discharge was initiated by high-voltage pulses of 70–75 kV peak voltage and 200 ns risetime. A flow of 60 m³/h was treated at 11–12 Wh/m³ with catalyst held at 110°C at a space velocity of 6000 h⁻¹. Removal rates of 70–90% have been found with input concentrations in the parts per million and the subparts per million range. No partially oxidized hydrocarbons could be detected in cleaned air. A closed carbon balance was confirmed under laboratory test conditions.

KEY WORDS: Nonthermal discharge; plasma treatment; plasma-catalytic oxidation; plasma-assisted catalysis.

1. INTRODUCTION

Stripping technologies are used very often for cleaning of contaminated ground water. During this process, gaseous or volatile organic compounds (VOC) dissolved in the ground water are taken over by an air stream, which has to be cleaned thereafter. At normal pressure, an air flow of 40–50 m³/h is necessary for the stripping 1 m³/h of contaminated water. Depending on the concentration of the various contaminants, hardware components for filtration, liquid condensation, thermal, or catalytic combustion are part of the water-cleaning equipment.

There are several drawbacks in the present state of technology. In case of vinyl chloride (VC) contamination, for instance, the normally used active carbon filters are inefficient because of low absorption. In complex situations, with a variety of contaminants, catalytic combustion is the method of choice in order to achieve high purification levels, but the running costs are high because of the necessary high-process temperatures of 450–500°C.

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In recent years, different plasma systems have been reported for VOC removal from gas streams using nonthermal atmospheric pressure discharges.⁽¹⁾ Based on these and the authors results from laboratory-scale experiments, the nonthermal plasma method was studied in a field experiment within an industrial ground water treatment facility.

The ground water contamination consisted of a mixture of aromatic solvents and chlorinated alkenes. Previous studies had shown that with a nonthermal plasma alone it was not possible to reach a sufficient degree of total oxidation.⁽²⁾ Therefore, a plasma-catalytic oxidation process was applied, which consisted of a discharge treatment followed by low-temperature catalytic combustion. The experiments were performed both in a laboratory scale, using synthetic off-gas mixtures, and in a bench scale at the water treatment facility.

2. EXPERIMENTAL EQUIPMENT AND PROCEDURE

The laboratory studies were carried out in a small-pulse corona system (reactor I: 1 m tube, 100 mm diameter, 60–65 kV peak voltage, 100 ns rise time) with heated Mn–Cu oxide catalyst downstream to the reactor. From earlier investigations, mixed oxide catalysts were already known to be effective at low temperatures.⁽²⁾ A flow of 2 L/min (STP) of synthetic as well as normal laboratory air was seeded with 5–10 ppm VC, 1,2-*cis*-dichloroethylene (DCE), and benzene from lecture bottles and treated at an energy density up to about 14 Wh/m³ (STP). A high-space velocity of 30.000 h⁻¹ was chosen in this low-flow case in order to reach stationary conditions within a reasonable time. Organic compounds were monitored by a photoionization detector and a gas chromatograph (see below); inorganic products and by-products were monitored by FTIR absorption spectroscopy (20 m cell).

A larger pulse corona reactor (Fig. 1; Ref. 3) was used in the field experiment. The discharge chamber is formed by six 150-mm diameter stainless steel tubes. The corona electrodes are thread rods with an active length of about 7 m. A thyatron (EG&G, LS3229) is used together with a high-voltage pulse transformer to generate pulses of 70–75 kV peak voltage and 200 ns risetime. Corona voltage and total current are measured by means of a capacitive voltage divider, a high voltage (Tektronix P6015A), and a fast current (Pearson PEA 1010) probe. With 30–40 kV of primary voltage, a pulse energy of 3.5–7 J can be deposited into an air plasma of atmospheric pressure (Fig. 2).

The reactor was combined with a commercial catalytic combustion unit for volume flows of 60 m³/h maximum. Blower, gas heater with temperature controller, heat exchanger, and catalyst chamber with 10 L of $\frac{1}{4} \times \frac{1}{4}$ -inch Mn–Fe oxide pellets were installed in a separate container and connected with

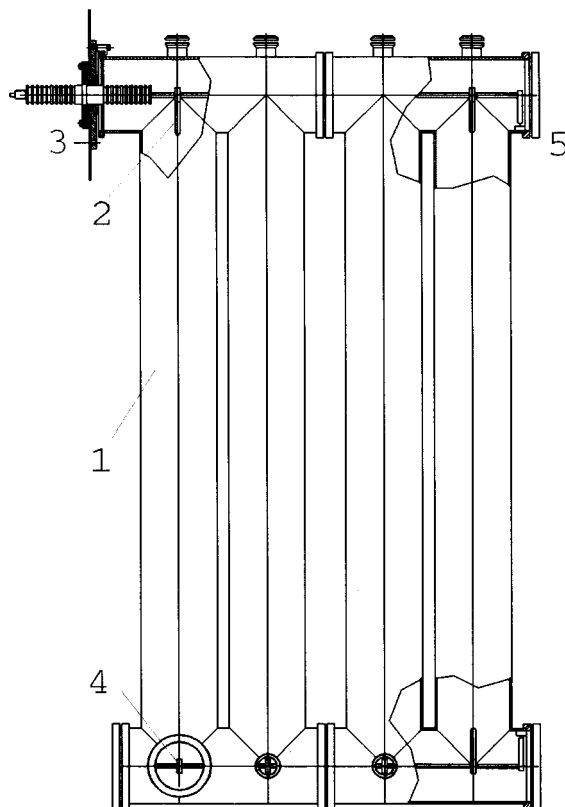


Fig. 1. Discharge chamber of pulse corona reactor II; (1) stainless steel tubes; (2) $h\nu$ electrode; (3) $h\nu$ feed-through; (4) gas outlet flange; (5) gas inlet flange.

the plasma reactor via a gas pipe of approximately 10 m length composed of high-density polyethylene. The reactor was fed with a partial off-air flow from the stripper of the ground water treatment facility. Then, at the entrance of the catalytic combustion unit, the gas stream was heated to 120°C, resulting in a constant catalyst temperature of 110°C. In this way, a flow of 60 m³/h was treated plasma-catalytically over a longer period (from December 98 until June 99). Over the 65 test hours, input concentrations changed considerably. The plasma reactor worked without damage or breakdown.

On-line gas analysis was based on a photoionization detector (PID, 10.6 eV) for monitoring the total concentration of organic compounds at the entrance of the plasma reactor versus time. Furthermore, a small, portable gas chromatograph (GC-PID) was used to measure the concentration

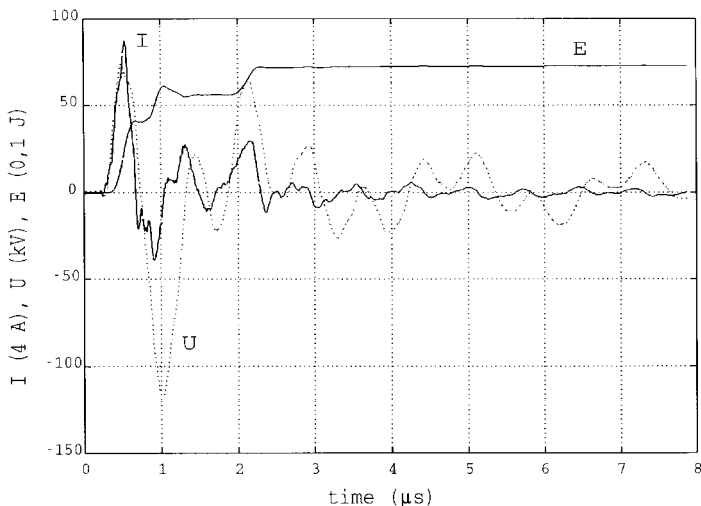


Fig. 2. Discharge current, gap voltage, and plasma energy versus time for reactor II.

of each of the main VOCs. It consists of a short multicapillary column (30 cm), a PID, and a molecular sieve in a closed gas loop. No carrier gas is necessary to operate this device. Sample gas is continuously pumped through the probe loop (300 ml/min). It takes about 2 min to monitor a complete spectrum. By means of valves, samples could be taken from the plasma reactor entrance (raw air), after plasma treatment, and downstream to the catalytic combustion unit (cleaned air). The sensitivity of the GC-PID is about 3.7, 5.6, 7.4, and 10–11 mV per ppm VC, acetone, 1,2-*cis*-DCE, and benzene/styrene, respectively. Both PID and GC-PID were combined with gas cooling units (0°C) in order to minimize water vapor influence.

The discontinuously operating stripping process (with periods from 10 min up to 1 h) delivered contaminated air with a dew point of 12–14°C. In winter, together with the gas flow, water droplets entered the corona reactor because of water vapor condensation in the nonisolated gas pipes. Figure 3 shows the GC-PID spectrum at a time when total VOC concentration is at its maximum. VC, DCE, toluene, ethylbenzene, and xylene could be identified as the main contaminants. Small amounts of heavy organic compounds are also seen. Peak 3 is believed to result from traces of trichloroethylene (TCE).

3. RESULTS AND DISCUSSION

The results of the laboratory studies are shown in Fig. 4. The relative concentrations of VC, DCE, and benzene are displayed, the resulting

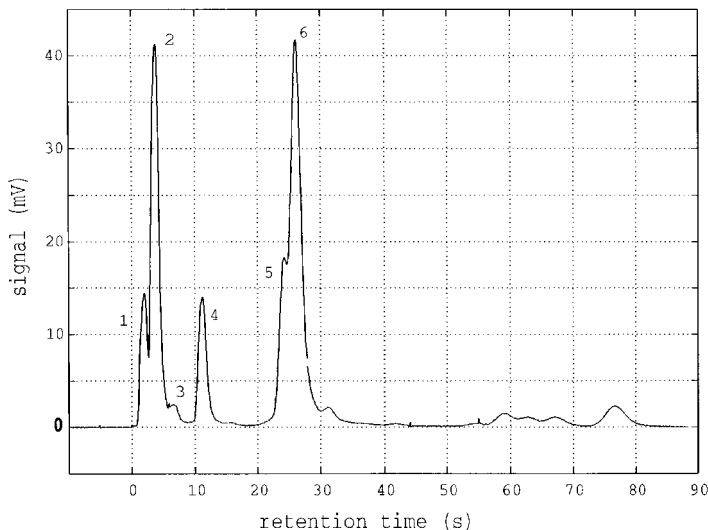


Fig. 3. GC spectrum of raw air with VC (1), *cis*-DCE (2), TCE (3), toluene (4), ethylbenzene (5), and xylene (6).

concentrations depend on energy density deposited into reactor I at catalyst temperatures of 50 and 120°C. A zero energy density corresponds to the pure catalytic reaction.

Without plasma, the catalyst has no effect at 50°C. After discharge treatment, the removal rates are 75–99% for VC, 44–69% for DCE, and 17–34% for benzene. At the combined action of plasma and catalyst, removal efficiency decidedly increases.

At 120°C, catalyst alone removes 17% of VC and 6% of both DCE and benzene. The synergy is even more pronounced at this temperature. At 10 Wh/m³ (STP), all organic compounds can be reduced by at least one order of magnitude. Downstream to the catalyst, the GC spectra do not show organic by-products in the parts per million range (Fig. 5).

Inorganic products are mainly CO₂, CO, ozone, and small amounts of nitrogen oxides (Fig. 6). Table I provides a summary of the reaction products. The second column shows the products of the input flow behind a furnace at 1000°C (total oxidation). As can be seen, carbon balance is closed at 120°C, i.e., a real plasma-assisted catalysis takes place. At 50°C, however, adsorption effects probably cannot be avoided. As a consequence, a catalyst temperature above 100°C was chosen in the field experiment.

Results of the field experiment are presented in Figs. 7–9. Data points for pure discharge treatment as well as pure catalytic reaction are especially marked, in addition to the traces of raw and cleaned air. While input

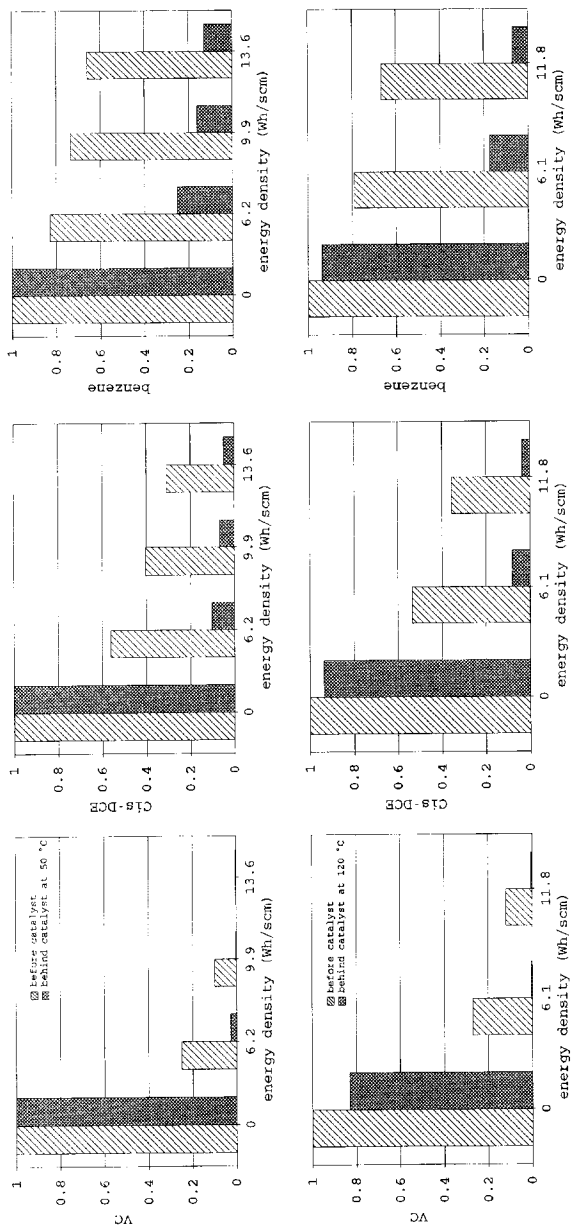


Fig. 4. Treatment of synthetic off-air in reactor I [2 L/min (STP), 30,000 h⁻¹].

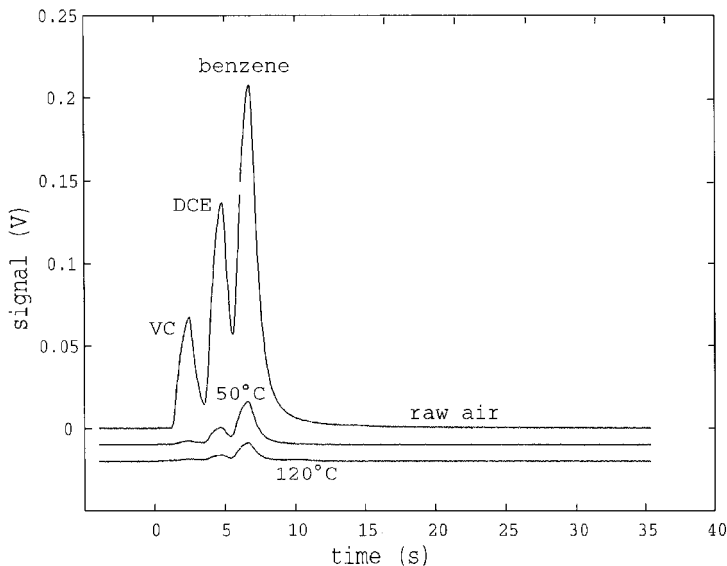


Fig. 5. GC spectra of plasma-catalytic oxidation of treated synthetic air with 10 ppm of VC, *cis*-DCE, and benzene [2 L/min, 10 Wh/m³ (STP), 30,000 h⁻¹].

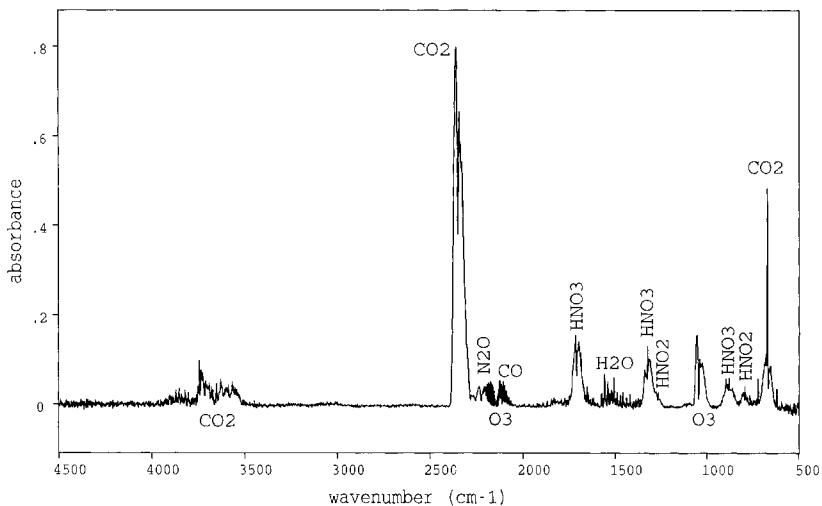


Fig. 6. IR spectrum of inorganic products [2 L/min, 10 Wh/m³ (STP), 120°C, 30,000 h⁻¹].

Table I. Reaction Products

Compound	Input	Total oxidation	10 Wh/m ³ (STP)	
			50°C	120°C
VC (ppm)	6	—	4%	2%
<i>cis</i> -DCE (ppm)	7	—	8%	3%
Benzene (ppm)	9	—	12.5%	5%
CO ₂ (ppm)	—	68.5	40	65
CO (ppm)	—	14.1	16.2	15.3
CO ₂ + CO (ppm)	—	82.6	56.2	80.3
Organic C (ppm)	80	—	8.35	3.36
CO ₂ + CO + organic C (ppm)	80	<u>82.6</u>	<u>64.6</u>	<u>83.7</u>
HCl (ppm)	—	20	?	?
O ₃ (ppm)	—	—	21	75
H _x N _y O _z (ppm)	—	—	5–10	5–10

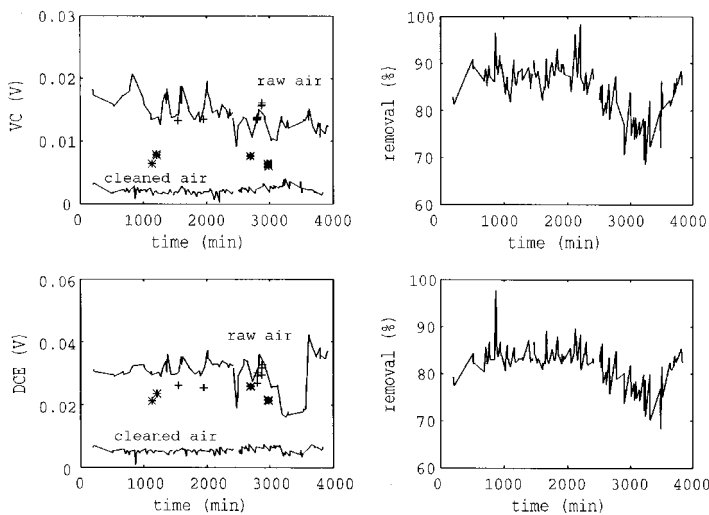


Fig. 7. GC-PID response of plasma oxidation of VC and *cis*-DCE (60 m³/h, 11–12 Wh/m³, 110°C, 6000 h⁻¹); (*), discharge treatment; (+), pure catalytic reaction.

concentrations changed considerably, removal rates remain relatively stable. Average removal over the entire time of the experiment is $85 \pm 5\%$, $82 \pm 4\%$, $72 \pm 5\%$, $90 \pm 1.5\%$, $91 \pm 2\%$, and $94 \pm 2\%$ for VC, *cis*-DCE, TCE, toluene, ethylbenzene, and xylene, respectively. Compared to Fig. 4, these removal rates are partially lower, especially if the smaller space velocity is taken into account. Nevertheless, the cleaning procedure works well down to sub-parts

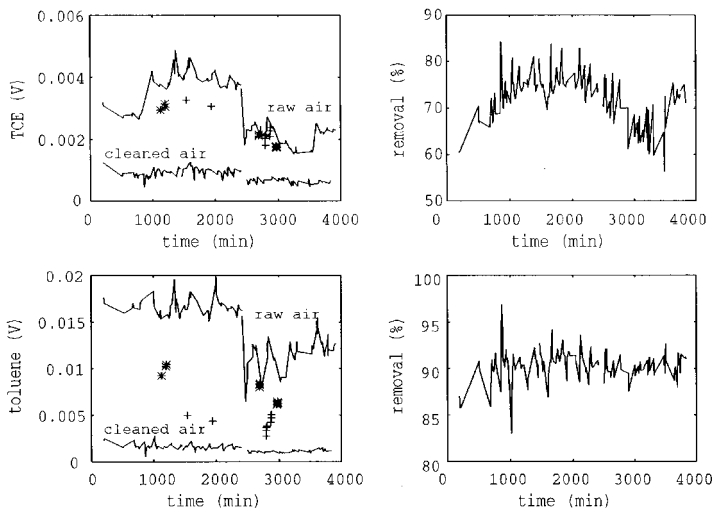


Fig. 8. GC-PID response of plasma-catalytic oxidation of TCE and toluene ($60 \text{ m}^3/\text{h}$, $11\text{--}12 \text{ Wh}/\text{m}^3$, 110°C , 6000 h^{-1}); (*), discharge treatment; (+), pure catalytic reaction.

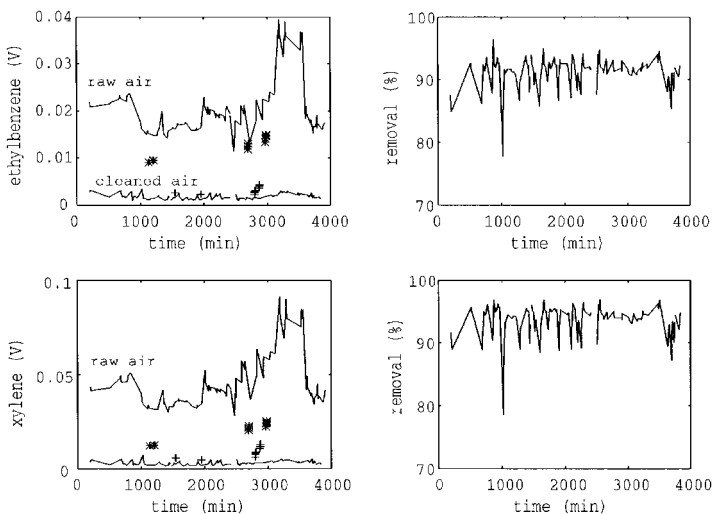


Fig. 9. GC-PID response of plasma-catalytic oxidation of ethylbenzene and xylene ($60 \text{ m}^3/\text{h}$, $11\text{--}12 \text{ Wh}/\text{m}^3$, 110°C , 6000 h^{-1}); (*) discharge treatment; (+), pure catalytic reaction.

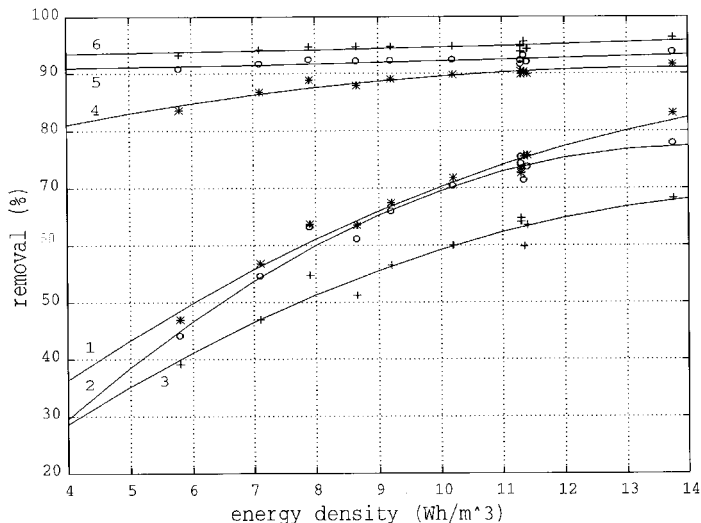


Fig. 10. Removal rates in dependence on energy density; 1, VC; 2, *cis*-DCE; 3, TCE; 4, toluene; 5, ethylbenzene; 6, xylene ($60 \text{ m}^3/\text{h}$, 110°C , 6000 h^{-1}).

per million concentrations (TCE and the heavy compounds in Fig. 3). Again, no organic by-products could be detected in cleaned air.

Decomposition of VC, DCE, and TCE seems to be different from that of aromatic compounds. Surprisingly, the latter could be removed to a large extent by catalytic combustion only. This is clearly demonstrated in Fig. 10, which shows the dependence of removal rates on energy density.

The plasma-catalytic oxidation process is rather complex and the hydrocarbons are attacked in several ways. At present, therefore, it is not possible to explain the results obtained within a mathematical model. However, a qualitative picture can be discussed. In the plasma reactor, the hydrocarbons are partly transformed into oxygenated compounds and to a lesser extent into CO and CO_2 (and HCl). This process is governed by radicals produced in the discharge, like O , O_3 , HO_2 , OH , and others. Among them, the direct reaction with ozone seems to be important. For large-volume velocities, however, the transit (reaction) time may be too low for effective decomposition of organic compounds by ozone. This is believed to be the reason why removal of VC, for instance, is considerably smaller than in low-flow experiments (Fig. 4).

Ozone as the main long-living radical is transported to the catalyst and thus can take part in heterogeneous oxidation reactions on its surface. Obviously the "ozone-activated" catalyst supports total oxidation of VOCs

as well as of oxygenated intermediates, which always rise as final products in experiments with discharge treatment only.

4. SUMMARY

1. A plasma-catalytic procedure, based on a pulse corona reactor and a catalytic combustion unit, for oxidative cleaning of air streams polluted with chlorinated ethylenes and aromates has been studied.

2. Both for laboratory studies, as well as for field experiments within a ground water treatment plant, a true plasma-assisted catalysis could be confirmed using mixed-metal oxide catalysts above 100°C.

3. Removal rates of more than 80% have been found for VC and *cis*-DCE and more than 90% for toluene, ethylbenzene, and xylene, at input concentrations in the ppm range, a plasma energy density 11–12 Wh/m³, 6.000 h⁻¹ of space velocity, and a catalyst temperature of 110°C.

4. Removal rates of chlorinated ethylenes strongly depend on plasma energy density, but reveal a surprisingly weak dependence for aromates.

ACKNOWLEDGMENTS

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