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Processing of C_3H_7OH , C_2HCl_3 and CCl_4 in Flue
Gases Using Silent Discharge Plasmas,
Enhanced by $D(UV)$ at 172 nm and 253.7 nm

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Report for CRADA Activities LA94-C10164

Processing of C_3H_7OH , C_2HCl_3 and CCl_4 in Flue Gases using Silent Discharge Plasmas, enhanced by (V)UV at 172 nm and 253.7 nm

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Abstract:

We present experimental results on (V)UV enhanced, barrier discharge processing of trichloroethylene (C_2HCl_3) and carbon tetrachloride (CCl_4) in dry and humid air. The contaminated air streams are treated by using a combination of barrier discharges, UV (253.7nm) from a commercial low pressure mercury lamp and VUV from an in-house Xe-excimer source (172nm) driven by a dielectric barrier discharge. Removal efficiencies for both excitation of the contaminated air by the barrier discharge and VUV at 172 nm will be compared with a combined treatment of discharge and irradiation at 253.7 nm and 172 nm. Significant photo-chemical effects include improved generation of both atomic and molecular singlet oxygen from the absorption of ozone in the Hartley band and VUV-regions, and for (V)UV irradiation, direct photolysis of molecular oxygen, water and the pollutant itself. The application of (V)UV irradiation has a substantial effect on final concentrations of the long lived byproducts phosgene and DCAC.

Introduction:

The silent discharge is well established for ozone production [1], the removal of volatile organics in flue gases and for generating excited dimers in light sources. The electrical energy coupled into the gas is mainly used to produce energetic electrons. Through electron impact, excited species, dissociation products and ionized species of the background gas molecules are formed while the gas remains at ambient temperatures. The non-thermal behavior of the silent discharge is due to the presence of at least one dielectric barrier between the electrodes. As the charge-transfer of a micro discharge proceeds, a small area at the dielectric surface, facing the anode, will be depleted by electrons, whereas a small area at the dielectric surface, facing the cathode, will accumulate electrons. In both cases, radial fields at the dielectric will arise, which causes surface discharges, called "Lichtenberg-figures". The internal, electrical field, caused by accumulation and depletion of electrons on the dielectric surface, will reduce the local field strength and the microdischarge will choke itself when the extinction field strength is reached. The whole process occurs within a few 10's of ns in air, depending on the gas composition.

Discharging pure rare gases (rare gas-halogens, rare gas-metals) in silent discharges, excited dimers (and trimers) will be formed through plasma chemical reactions, which will i.e. "funnel-down" to lower excited states (in the case of pure rare gases it is the lowest excited state). The molecule will decay from the less excited state in a thermal unstable or repulsive ground state, emitting light. In ozonizers, atomic oxygen is formed in the discharge by electron impact dissociation of oxygen and, in air, additionally by penning dissociation by electronically excited nitrogen. Mainly atomic oxygen and other oxygen states will form ozone. In (humid) flue gases highly reactive radicals will be formed (including OH), which will initiate radical chain reactions with volatile organic compounds, oxidizing and decomposing them. However, complete mineralization of the organics is hardly achieved as stable, often toxic, byproducts are produced.

Photo-chemical decomposition of organic pollutants in both water and flue gas is another well established advanced oxidation process. Radicals with high oxidizing potential, the same as in the silent discharge, are formed by UV-dissociation of oxidative additives, e.g. ozone or hydrogen peroxide, or by chemical reactions. For example, OH radicals are formed by ozone photolysis in water by the reaction of $O(^1D)$ with water.

In the present work a combined treatment by the silent discharge and UV-oxidation was used to increase the efficiency of the degradation of TCE and CCl_4 in wet and dry flue gases. The main purpose of (V)UV at 253.7 nm and 172 nm was to increase the concentration of atomic singlet oxygen and, in humid gas streams the concentration of hydroxyl radicals, by UV absorption of excess ozone in the Hartley-band or VUV region, respectively. An addendum for VUV at 172 nm is, that it is energetically capable to dissociate water and molecular oxygen. Additionally, UV at 172 nm efficiently excites and dissociates both the TCE and carbon tetrachloride. Furthermore, the most significant byproducts of oxidation, phosgene and dichloroacetyl chloride [2], are reduced by UV-oxidation. This is equivalent to a more complete mineralization of the organic compound to water, carbondioxide and hydrochloric acid.

The addition to the chemical effects desired of ultraviolet radiation also influences the fundamental physical properties determining the plasma parameters within the system. For example, the Joshi effect [4,5]. In some gases, UV-illumination of the dielectrics changes the charge transferred in a micro discharge, but not the amount of totally transferred charge per half cycle. Therefore, more microdischarges must occur, making the overall discharge "more homogeneous". The Joshi effect is due to UV illumination of the gas layer which is always present on the dielectric surface. Electronegative species will be formed by photodissociation on the dielectric surface, which will attach slow electrons before they will cause an avalanche in the field. By attachment of a few, slow electrons by electronegative species on the dielectric the transferred charge per micro discharge will be reduced remarkably. [Reference publication being prepared].

Description of the experiment:

To enable separate, as well as a combined application of the silent discharge and UV-irradiation of flue gases, a coaxial reaction vessel as shown in figure 1, has been built. The flue gas to be discharged, is fed in the spacing between two tubes, assembled with electrodes. The inner tube of the double barrier discharge vessel consists of an UV transmitting (down to 160nm at room temperature), fused quartz and is covered with a mesh electrode. The mesh has been laid on with a gold paste, using a drafting pen. After the paste has been dried and fired, a scratch resistant layer of gold remains. The method of gold mesh painting has proved to be a reliable, non-corrosive electrode arrangement at the Lighting Technology Institute of the University of Karlsruhe [6,7].

Figure 1 Sketch of the hybrid chemical reaction vessel

The (V)UV sources are placed in the inner tube of the discharge vessel, centered by two Teflon mounts. The remaining spacing of the inner tube is flushed with nitrogen to avoid absorption of VUV at (172 ± 14) nm by oxygen in the Schumann-Runge band and continuum. The irradiance of both light sources has been calibrated by photometric means. The irradiance was determined to be 5.43 W at 253.7 nm, representing 87.8 % of the total light flux of the low pressure Hg-lamp. For the nearly monochromatic Xe-excimer, an irradiance of 4.31 W was obtained. Due to the limited spectral transmittance at 172 nm of 90 % and due to the grid (50 %), this corresponds to an irradiance power of 1.94W entering the gas. The overall experimental set-up is shown in figure 2.

Figure 2 Experimental set-up

The water content of air streams, containing 190 ppm of TCE or 326 ppm of CCl_4 , respectively, has been set by flowing half of the total gas stream through a water bubbler. With room temperature of the water, this corresponds to 1.5 %abs. water content. After flowing for several minutes, a stable concentration of the organic compound is obtained. All flows were controlled by using standard flow controllers, and the total pressure in the cell was monitored. The gas mix will enter the reaction vessel, being discharged at 1 kHz. Electrical data, e.g. the voltage across the cell and the charge driven through the cell, was taken to determine the electrical power coupled in the gas via the usual "Lissajous-figure" method. The energy density has been varied by changing the flow, the power coupled in the gas was kept constant.

The composition of the gas treated by the silent discharge, VUV or a combined treatment is analyzed in a GC/MS.

Results:

Figure 3a shows a comparison of the destruction efficiencies of CCl_4 in dry air between the silent discharge, a combined treatment of silent discharge with (V)UV at 253.7 nm or 172 nm, and VUV-illumination at 172 nm only. An analogous comparison for wet air (1.5 % abs. humidity) shows figure 3b. The energy densities include the power of the (V)UV coupled in the gas (photon power, the efficiency of our Xe-excimer is 8.5 %), all removal efficiencies can be compared directly.

Figure 3a, 3b DRE and logarithmical scaling of DRE for various treatments of 326 ppm CCl_4 in dry and humid air

As shown in figure 4, phosgene was identified as the only significant long lived byproduct from CCl_4 . Figures 4a and 4b show their content in relative units.

Figure 4a, 4b Relative phosgene-contents for various treatments of 326 ppm of CCl_4 in dry and humid air

A similar set of experiments were then performed with C_2HCl_3 . The dependence of the destruction of C_2HCl_3 on the energy density is shown for dry air in figure 5a and for wet air in figure 5b. As before, the comparison refers to applying the silent discharge, only, the combined treatment of discharge and (V)UV and using VUV only.

Figure 5a, 5b DRE and logarithmical scaling of DRE for various treatments of 190 ppm TCE in dry and humid air

The main byproducts for the different treatment methods of C_2HCl_3 have found to be phosgene and dichloroacetyl chloride (DCAC). Figures 6a through 6d show their relative content. Although all byproducts are given relatively, they can be compared to each other. This includes the measurement of CCl_4 .

Figure 6a through 6d Relative phosgene- and DCAC-contents for various treatments of 190 ppm of TCE in dry and humid air

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Figure 1

Sketch of the hybrid chemical reaction vessel

Figure 2

Experimental set-up

Figure 3a, 3b DRE and logarithmical scaling of DRE for various treatments of 326 ppm CCl_4 in dry and humid air

Figure 4a, 4b Relative phosgene-contents for various treatments of 326 ppm of CCl₄ in dry and humid air

Figure 5a, 5b DRE and logarithmical scaling of DRE for various treatments of 190 ppm TCE in dry and humid air

Figure 6a through 6d Relative phosgene- and DCAC-contents for various treatments of 190 ppm of TCE in dry and humid air

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