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Passage of the Clean Air Act Amendments by President Bush in 1990 is placing more stringent control on VOC emissions. These emerging regulations are forcing industries to reduce VOC emissions through new manufacturing techniques or through the use of air pollution control equipment. An emerging air pollution control technology is the use of ultraviolet (UV) photochemical and radical oxidation to destroy pollutant VOCs in process gas streams. A commercial system based in part on this technology has been developed and a pilot scale version has been installed at the Applied Research Laboratory (ARL) at The Pennsylvania State University. Research is currently being performed with the pilot scale system to determine the systems effectiveness in removing different classes of VOCs and to recommend design improvements that enhance VOC destruction throughout the system. A numerical model of the photolytic reactor in the pilot scale system has been developed in support of this research effort.

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NUMERICAL MODEL OF FORMALDEHYDE PHOTO-OXIDATION IN A TWO DIMENSIONAL FLOW FIELD OVER CYLINDRICAL UV LIGHT SOURCES

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Introduction

Passage of the Clean Air Act Amendments by President Bush in 1990 is placing more stringent control on VOC emissions. These emerging regulations are forcing industries to reduce VOC emissions through new manufacturing techniques or through the use of air pollution control equipment. An emerging air pollution control technology is the use of ultraviolet (UV) photochemical and radical oxidation to destroy pollutant VOCs in process gas streams. A commercial system based in part on this technology has been developed and a pilot scale version has been installed at the Applied Research Laboratory (ARL) at The Pennsylvania State University. Research is currently being performed with the pilot scale system to determine the system's effectiveness in removing different classes of VOCs and to recommend design improvements that enhance VOC destruction throughout the system. A numerical model of the photolytic reactor in the pilot scale system has been developed in support of this research effort.

The numerical model describes the interaction between the fluid dynamics of a flowing volatile organic compound (VOC) laden gas stream and the photochemical and chemical processes occurring within the photolytic reactor. The gas velocities and chemical species concentrations are predicted as a function of spatial location within the reactor under steady state conditions. Formaldehyde (HCHO) in moist air with trace amounts of ozone is used to evaluate the reactor performance. The effects of residence time, ozone inlet concentration and actinic flux on formaldehyde destruction in the reactor were investigated.

Model Description

Figure 1 provides the reactor configuration analyzed in this study. The reactor is a rectangular duct containing two cylindrical medium-pressure mercury arc lamps (Heraeus Amersil TQ718) which emit electromagnetic radiation over the wavelength range from 238 to 579 nm. An air stream containing formaldehyde, methanol, ozone and water vapor enters the reactor and passes perpendicular to the cylindrical lamp axes.

The mathematical model of the reactor was constructed using Harwell (CFDS)-FLOW3D, which is a Computational Fluid Dynamics (CFD) package developed by Harwell Laboratory in the United Kingdom. The photolytic reactor model combines: (1) a description of the light intensity distribution in the reactor, (2) a description of the reaction kinetics for HCHO destruction in air in the presence of UV light and (3) a description of the velocity field through the reactor. The chemical and photochemical reaction processes occurring within the photolytic reactor are modeled with the addition of a FORTRAN 77 subroutine.

The model analyzes the photolytic reactor in two dimensional space with a radiation field emitted by the TQ718 lamps that is purely radial. It is also assumed that HCHO and O_3 are the only chemical species which contribute significantly to light attenuation in the reactor. The light intensity distribution in the reactor based on these assumptions is given by the Beer-Lambert Law:

$$I_r = \frac{r_o I_{ro}}{r} e^{-(r-r_o)\sum [C]\sigma} \qquad (1)$$

Subsequently, the photolysis rate constants for formaldehyde, ozone and hydrogen peroxide are calculated with equation (2) where a summation is provided to account for the dominant wavelengths emitted by the TQ718 lamp:

$$k = \frac{r}{r_o} \sum_{\lambda_1}^{\lambda n} \sigma(\lambda, T)\phi(\lambda, T) e^{-(r-r_o)\sum [C]\sigma} J(\lambda) \qquad (2)$$

Twenty-three chemical reactions involving 14 chemical species are analyzed in the model. This is a simplified kinetic model developed based on over 56 chemical reactions for 21 chemical species that were compiled from the literature to describe gas phase oxidation of HCHO in the presence of UV light (Schmelzle, 1994 and Albano, 1994). The kinetic mechanisms were incorporated into the flow field model by introducing the species mass conservation equation for each of the following chemical species: HCHO, CH_3OH, $OH^{\bullet}$, $H^{\bullet}$, $HO_2^{\bullet}$, $O(^3P)$, $O(^1D)$, H_2O_2, O_3, HCHO and CO. The kinetic mechanisms which lead to generation or removal of a given species were incorporated as source/sink terms, symbolized by S, in the species mass conservation equation given below:

$$\nabla \cdot (\rho UC) - \nabla \cdot ((\frac{\mu_T}{\sigma_s} + \rho D)\nabla C) = S \qquad (3)$$

The flow field in the reactor was modeled with the Navier-Stokes and mass conservation equations by assuming that a turbulent air stream entering the reactor was a Newtonian incompressible fluid with constant properties. The turbulence was analyzed using the k-ε turbulence model. The final model includes the numerical solution of 16 equations for 16 unknowns.

Results

The goal of the current modeling effort was to describe the physical and chemical processes occurring in a photolytic reactor and determine courses of action to increase the efficiency of the reactor. HCHO is destroyed in the reactor by two routes: direct photolysis and radical oxidation by $OH^{\bullet}$. It was found that destruction by photolysis is an order of magnitude slower than by $OH^{\bullet}$ radical attack. For this reason methods were researched to increase the $OH^{\bullet}$ concentration in the reactor. It was found that photolysis of O_3 leads to the production of $OH^{\bullet}$ radicals in the presence of water vapor. Parametric studies were therefore performed with varying ozone concentrations from 75 ppm to 300 ppm. It was found, as was expected, that the destruction of HCHO increased with increasing O_3 inlet concentrations. However, 90% of the ozone input into the reactor was discharged out the reactor outlet. This implies that an ozone scrubber would be required with a photolytic reactor design employing ozone to enhance VOC oxidation rates.

The effect of light intensity on HCHO destruction was also studied. Increasing the light intensity not only increases the HCHO photolysis rate but also the photolysis of O_3. A 10 fold increase in light intensity significantly increased HCHO oxidation. However, Figure 2 shows that the light intensity emitted by the lamps drops off with distance from the bulbs. Therefore proper arrangement of bulbs in the reactor to optimize the light intensity distribution would be beneficial. Several smaller wattage bulbs would be more efficient than one high intensity bulb in the middle of the reactor.

Next the interaction between gas stream advection (hence residence time) and the chemical reaction rates were investigated. It was found that when the chemical reaction rates are much faster than the gas stream advection, the species concentration distributions are unaffected by the flow field. An example is the $OH^{\bullet}$ concentration distribution in the reactor shown in Figure 3. The distribution mimics the light intensity profile emitted by the TQ718 lamps shown in Figure 2. HCHO (shown in Figure 4) and O_3 concentration distributions in the reactor, on the other hand, are influenced strongly by the reactor flow field. Figure 4 shows an overlay of the reactor velocity field on the HCHO concentrations contours. The concentration contours follow the velocity vectors which are overlaid on top. The acceleration of flow over the top surfaces of the bulbs result in lower destruction of HCHO whereas the recirculating regions behind the bulb surfaces lead to high HCHO oxidation rates. The rates of advection were varied in the reactor by varying the reactor inlet velocities from 0.5 m/s to 3.5 m/s. The

highest HCHO removal occurred for the lowest inlet velocity case with negligible destruction occurring for an inlet velocity of 3.5 m/s. An improvement in the reactor design would therefore be to increase the gas stream residence time in the reactor. This can be accomplished by increasing recirculation in the reactor.

Based on the results of this study, a photolytic reactor design should have close placement and arrangement of UV bulbs to optimize light intensity distribution. The UV lamps should also be chosen to maximize power output in the wavelength ranges that produce photolysis of the target VOC and ozone. If the bulbs are placed too far apart, part of the gas stream will remain essentially untreated due to the decrease of light intensity (hence $OH^{\bullet}$ radical concentration) with distance from the bulb. A photolytic reactor design should also optimize recirculation of the process gas stream within the reactor to increase gas stream residence time.

References

Albano, M., 1994. *Computer Simulation of a Photolytic Reactor to Study the Effects of a Variety of Wavelengths.* A Thesis in Environmental Pollution Control, The Pennsylvania State University, State College, Pa.

Schmelzle, J. P. 1994. *Ultraviolet Photochemical and Radical Oxidation of Airborne Volatile Organic Compounds.* A Thesis in Environmental Pollution Control, The Pennsylvania State University, State College, Pa.

Nomenclature

C	Species Concentration	U	Gas Velocity
D	Molecular Diffusion Coefficient	ϕ	Quantum Yield
I_{ro}	Light Intensity at surface of bulb	ρ	Gas Density
$J(\lambda)$	Actinic Flux	σ_s	Turbulent Prandtl Number
r	Distance from bulb	μ_T	Turbulent Viscosity
r_o	Bulb radius	σ	Absorption Cross-section

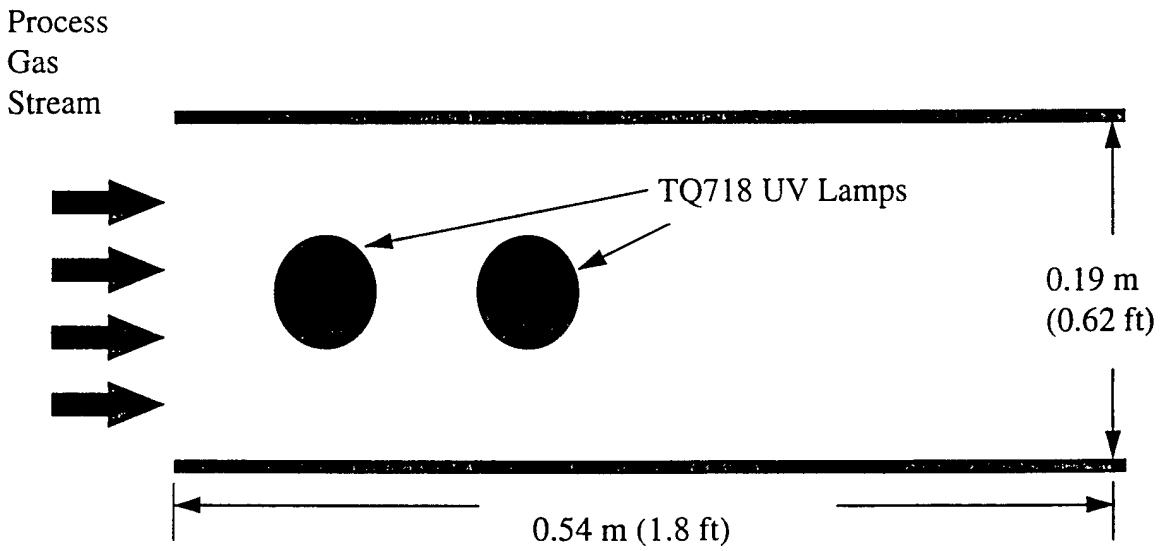

Figure 1 Photolytic Reactor Domain

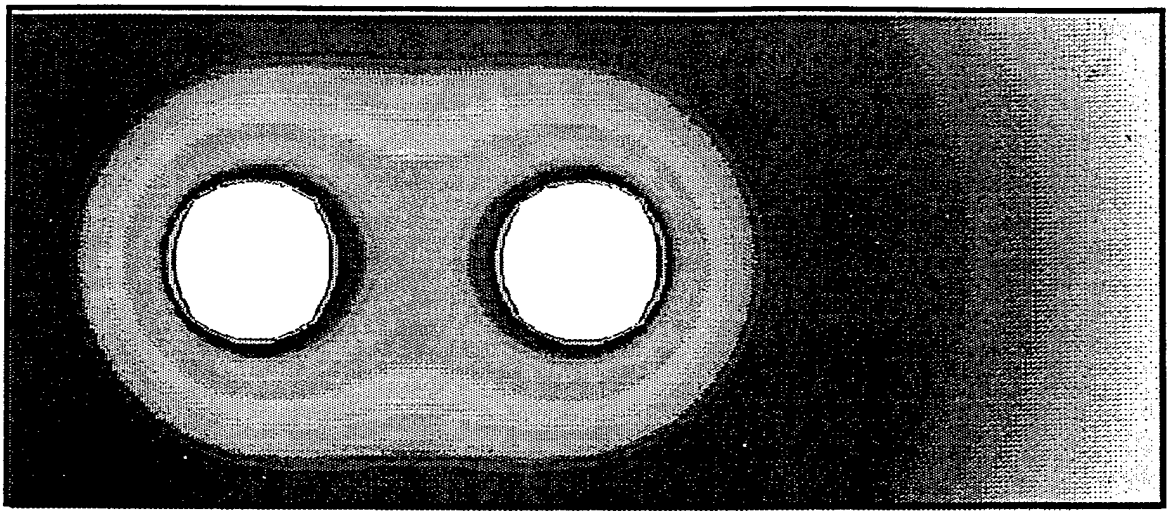

Figure 2 Light Intensity at 253 nm

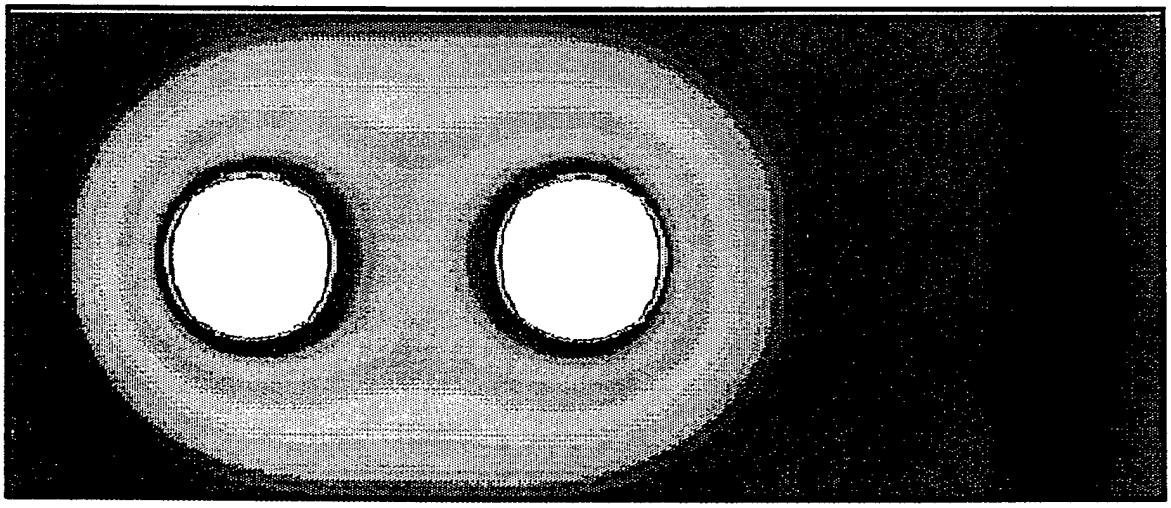

Figure 3 OH Radical Concentration

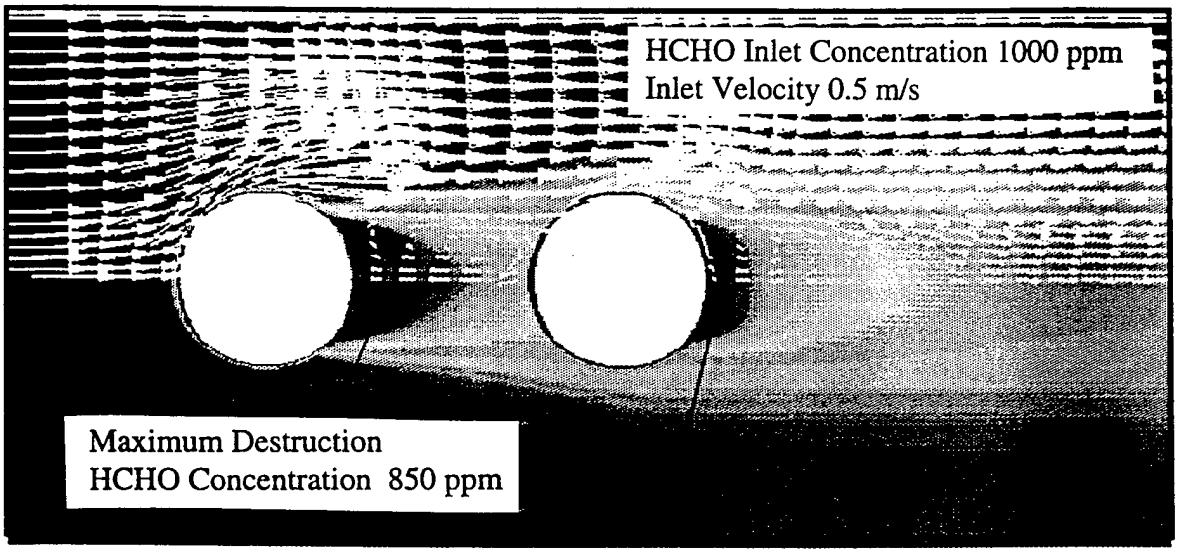

Figure 4 HCHO Concentration/Gas Velocity