

Photocatalytic and Chemical Oxidation of Organic Compounds in Supercritical Carbon Dioxide

Project Number: 54847

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RESEARCH OBJECTIVES:

1) Determine if photocatalytic or other clean oxidation chemistry can be applied to the removal of organic or inorganic contaminants that are introduced into supercritical carbon dioxide during its use as an extraction and cleaning medium in DOE environmental and waste minimization applications. The targets are those contaminants left in solution after the bulk of the solutes have been separated from the fluid phase by changing pressure and/or temperature (but not evaporating the CO₂). This is applicable to development of efficient separations of contaminants from the fluid stream and will strengthen pollution prevention strategies that eliminate hazardous solvents and cleaning agents.

2) Explore the use of supercritical carbon dioxide as a solvent for the photocatalytic oxidation of organic compounds and compare it to other types of oxidation chemistry. This will add to the fundamental understanding of photocatalytic oxidation chemistry of particulate semiconductors and provide new knowledge about conditions that may have relevance to the chemical fixation of carbon dioxide under photocatalytic conditions.

RESEARCH PROGRESS AND IMPLICATIONS:

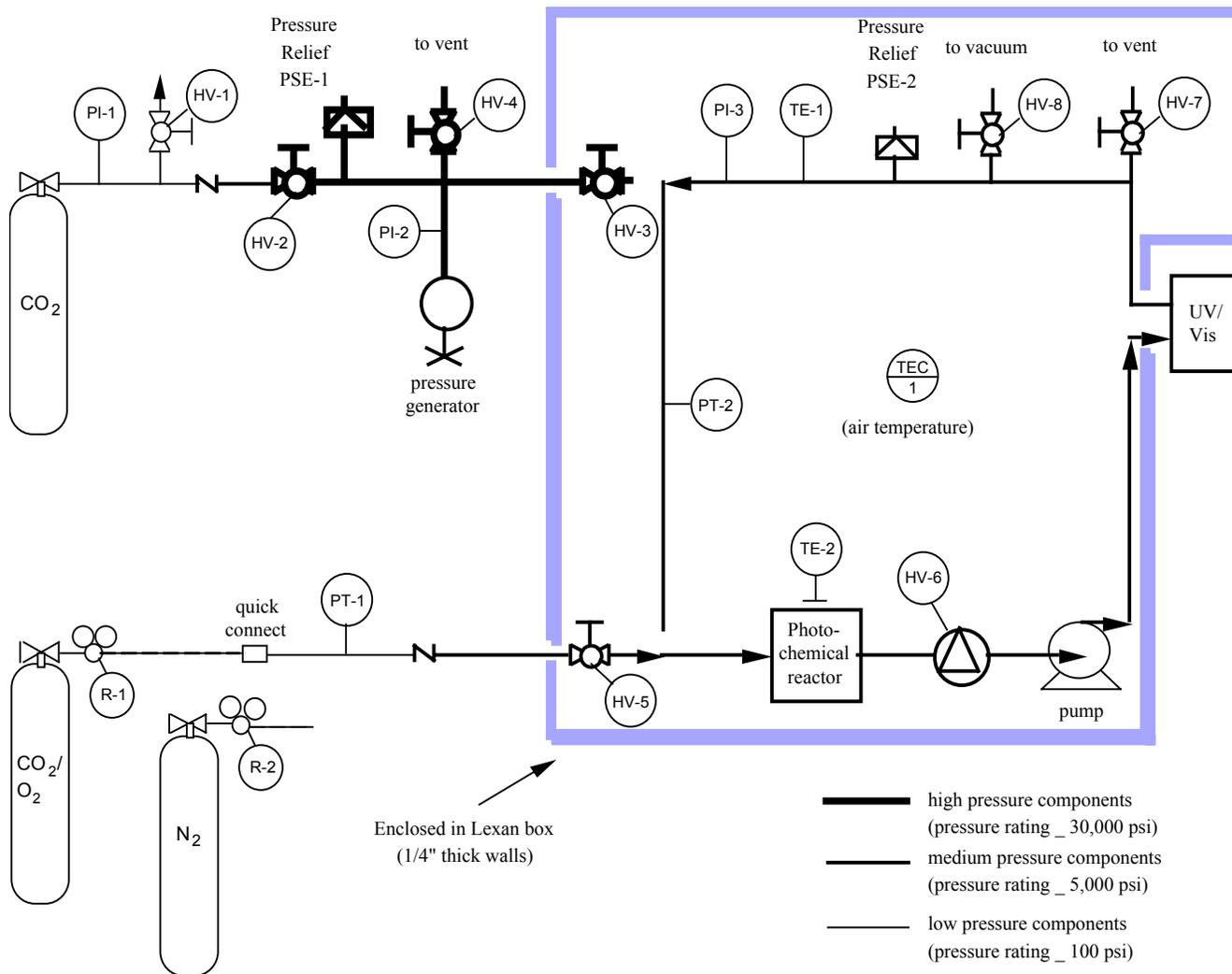
This annual report covers progress during the second year of the project, ending in May 1999. During the first year a system was designed, constructed, and modified so that the photocatalytic oxidation of organic compounds could be carried out in supercritical carbon dioxide. Prior to this work there were no reports of photocatalytic oxidation using titanium dioxide catalysts in supercritical fluids. The experimental system is now being operated at temperatures from 25-50 C, pressures from 15-5000 psi, and with gas, liquid, and supercritical fluid phases. The concentration of organic solutes can be followed using on-line gas chromatography and UV-Vis spectroscopy. Experiments during the past year measured the rates of oxidation of benzene, toluene, hexane, cyclohexane, and acetone in gas phase (80:20 N₂:O₂ or CO₂:O₂) and in supercritical CO₂ (SCCO₂). Rates are lower in supercritical CO₂ than in the gas phases. This may be due to reduced diffusion rates in the supercritical phase, competitive CO₂ adsorption, or differences in flow rates in the supercritical phase experiments.

This report summarizes work done during the first two years of the project. There have been more than 3000 publications on photocatalytic chemistry of titanium dioxide for removal of organic and inorganic compounds from water and air or partial oxidation of organic compounds in air or organic solvents but no work has been reported in supercritical fluids.¹ The work reported here has demonstrated for the first time that photocatalytic chemistry can also be carried out in supercritical carbon dioxide. We have also compared the reaction in air and gas phase carbon dioxide with that in supercritical CO₂. The results we have obtained on the photocatalytic oxidation of selected organic compounds in gas and supercritical phases must be considered preliminary since we are still working on achieving well-defined flow and light exposure conditions in the experimental system. Never the less, the results establish that representative

classes of organic compounds can be reduced from about 2000 ppmv to below detection in supercritical carbon dioxide by photocatalytic oxidation. A preliminary communication is being prepared.²

A schematic diagram of the experimental system for carrying out the experiments is shown in Figure 1. During an experiment the fluid phase is recirculated within the part of the system closed in the Lexan box and through the view cell and the sampling valve of the gas chromatograph, co-located with the UV-Visible spectrometer.

Figure 1. Schematic diagram of the experimental system.



Representative reaction conditions are: initial concentration of the organic compound is approximately 2000 ppm; initial concentration of O₂ > 50 times stoichiometric amount; the photocatalyst is Degussa P25 TiO₂ on 5mm glass beads; gas phase experiments were performed at ~10 psig and 25 C; supercritical phase experiments were performed at ~1200 psig; T~37 C; and the reaction vessel was illuminated with a 100 watt spot lamp with output centered at 360 nm.

Results are shown in Figures 2 through 5. The results for hexane, toluene, cyclohexane, acetone and benzene oxidation in synthetic air are shown in Figure 2. The rate of oxidation of benzene is typically lower than other hydrocarbons. There is evidence that intermediate oxidation products (e.g. phenol,

catechols, and quinones) are strongly adsorbed on titanium dioxide and the rate is determined by the time required to oxidize these intermediate products and create free sites for benzene.³ Comparison of the oxidation of the same compounds in a carbon dioxide/oxygen mixture yielded similar results as is shown in Figure 3. Carbon dioxide had little effect on the rates in the gas phase reaction.

Figure 2. Oxidation of Organics in N₂/O₂ (80:20)

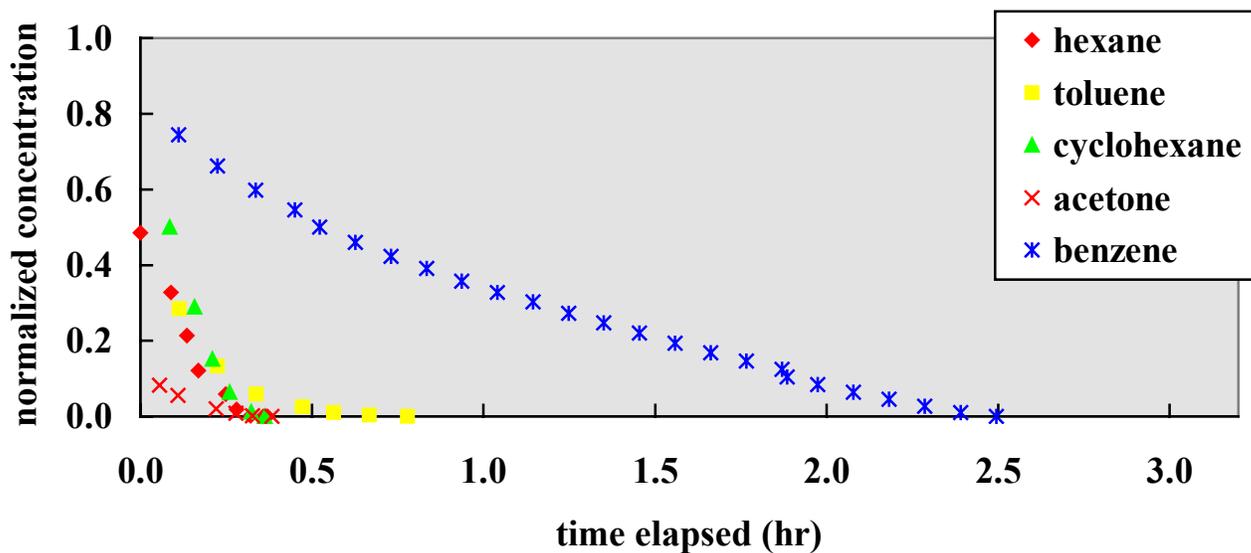


Figure 3. Oxidation of Organics in Gas Phase CO₂/O₂ (80:20).

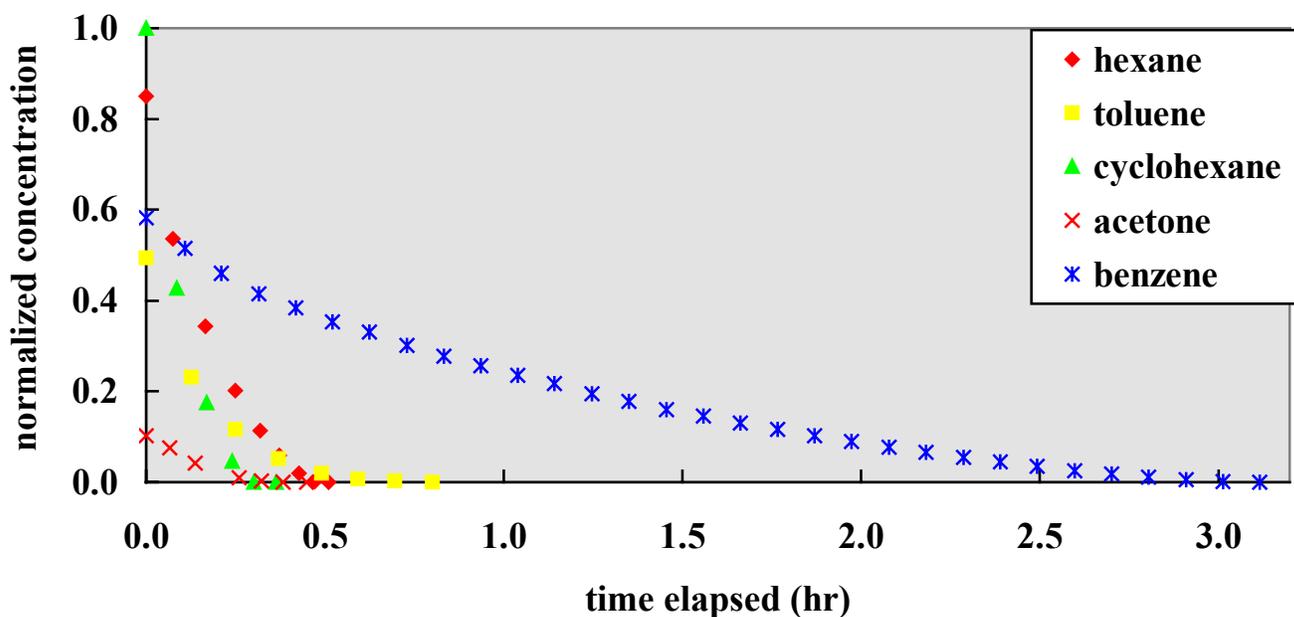


Figure 4. Hexane Oxidation in Gas Phase N_2/O_2 or CO_2/O_2 and in Supercritical CO_2/O_2

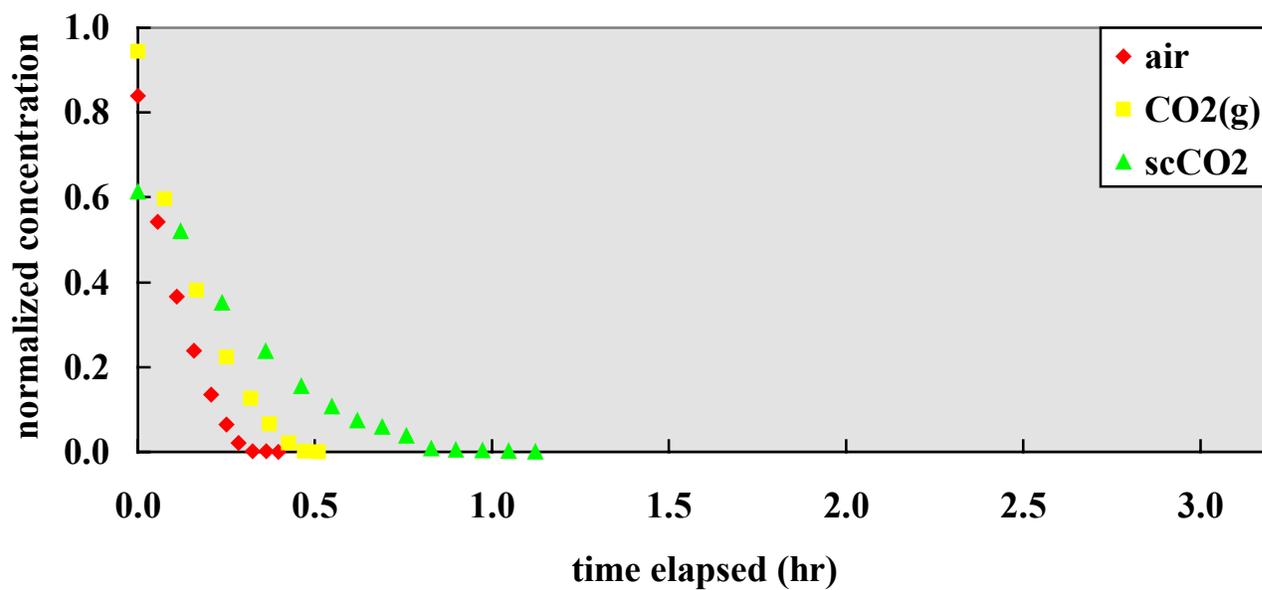


Figure 5. Benzene Oxidation in N_2/O_2 , Gas Phase CO_2/O_2 and Supercritical CO_2/O_2

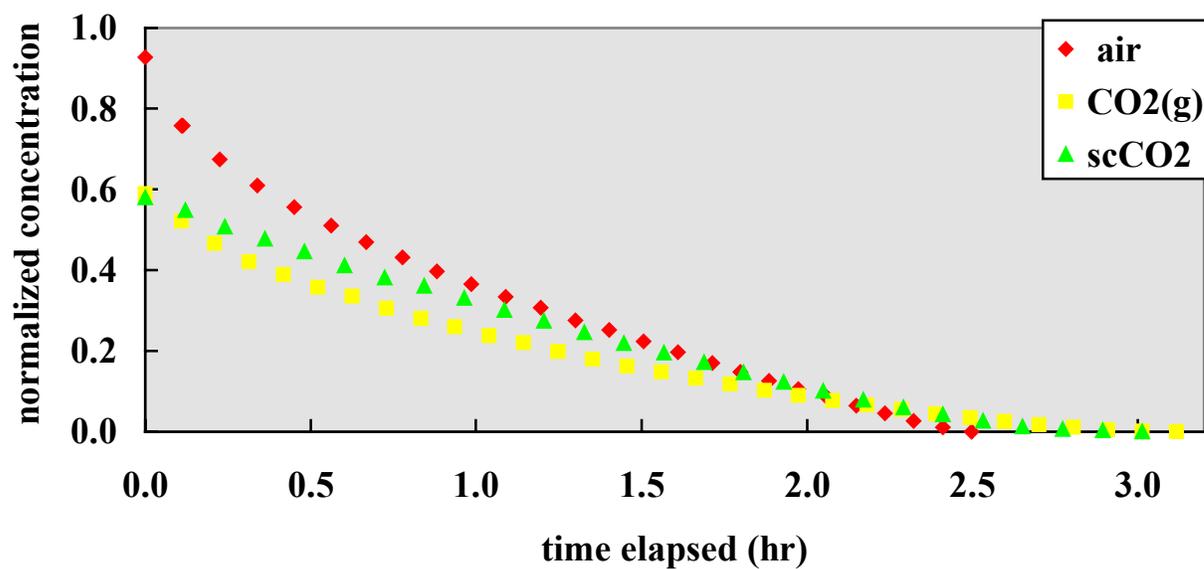


Figure 4 shows that the rate of oxidation of hexane is moderately lower in supercritical CO₂ compared to the gas phase. For benzene, Figure 5, there is little difference between the gas and supercritical phases. As mentioned above, the photocatalytic oxidation of benzene and other aromatic compounds is limited by the rate of oxidation of adsorbed, intermediate oxidation products to free surface sites. Supercritical CO₂ is apparently not sufficiently polar to dissolve the intermediate oxidation products and keep the surface open for benzene oxidation.

PLANNED ACTIVITIES:

Work to date has established that photocatalytic oxidation of organic compounds can be used to purify supercritical carbon dioxide. This establishes the technical feasibility of the proposed approach. During the final year of the project effort will be directed toward obtaining quantitative data that can be used to better define the process for representative organic compounds. Further contacts will be made with others in the DOE complex that are pursuing applications for cleaning materials or parts with supercritical carbon dioxide.

REFERENCES:

¹ (a) Blake, Daniel M. (1994). *Bibliography of Work on the Photocatalytic Removal of Hazardous Compounds from Water and Air*. NREL/TP-430-6084. Golden, CO: National Renewable Energy Laboratory. 75 pp. [DE94006906] Available from the National Technical Information Service, Springfield, VA 22161. (b) Blake, Daniel M. (1995). *Bibliography of Work on the Photocatalytic Removal of Hazardous Compounds from Water and Air. Update Number 1, to June, 1995*. NREL/TP-473-20300. Golden, CO: National Renewable Energy Laboratory. 102 pp. Available from the National Technical Information Service, Springfield, VA 22161. (c) Blake, Daniel M. (1997). *Bibliography of Work on the Photocatalytic Removal of Hazardous Compounds from Water and Air. Update Number 2, to October, 1996*. NREL/TP-430-22197. Golden, CO: National Renewable Energy Laboratory. 88 pp. Available from the National Technical Information Service, Springfield, VA 22161. (d) Blake, Daniel M. (1999). *Bibliography of Work on the Photocatalytic Removal of Hazardous Compounds from Water and Air. Update Number 3, to January, 1999*. Golden, CO: National Renewable Energy Laboratory. In Preparation.

² Debra L. Bryant, Daniel M. Blake, and Edward J. Wolfrum. Manuscript in Preparation (1999).

³ Jacoby, William A., Daniel M. Blake, John A. Fennell, James E. Boulter, LeAnn M. Vargo, Marya C. George, and Suzanne K. Dolberg. "Heterogeneous Photocatalysis for Control of Volatile Organic Compounds in Indoor Air." *J. Air Waste Manage. Assoc.*, 46, no. 9 (1996): 891-8.