Photocatalytic and Chemical Oxidation of Organic Compounds in Supercritical Carbon Dioxide

Project Number 54847

National Renewable Energy Laboratory

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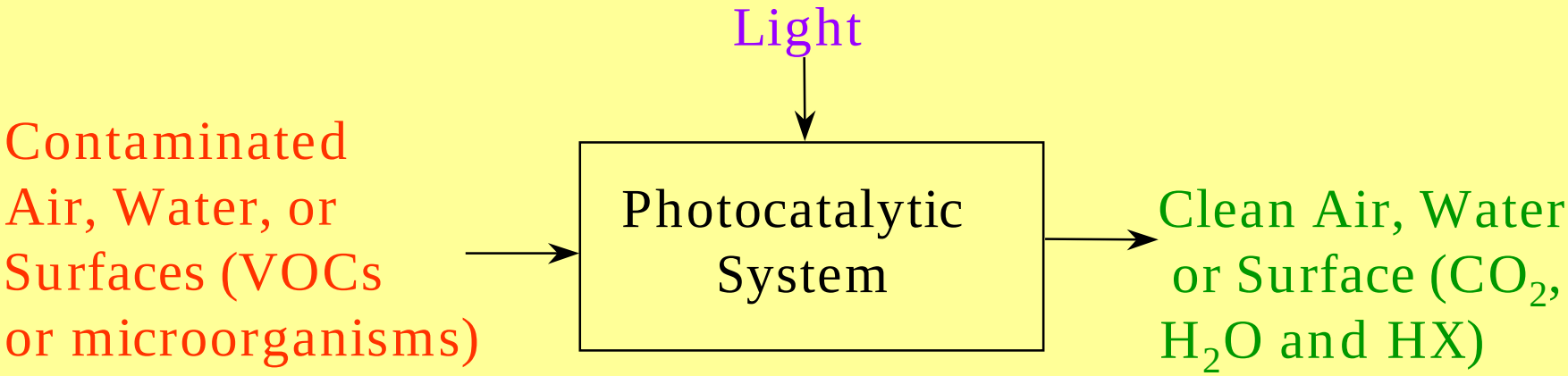
Abstract

- This poster reports progress during the first 30 months of the project. During this period 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 can operate 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 or UV-Vis spectroscopy. Experiments have measured the rates of oxidation of benzene, toluene, hexane, cyclohexane, and acetone in gas phase 80:20 N_2:O_2 and CO_2:O_2 and in supercritical CO_2 ($SCCO_2$). The concentration versus time data for the reactions can be fitted to a Langmuir-Hinschelwood model. Rates are lower in supercritical CO_2 than in the gas phase. We have also demonstrated the self cleaning function of TiO_2 coated filters covered with molecular or biological deposits.

Objective of The Project

- Demonstrate the technical feasibility of a low maintenance photocatalytic oxidation process that can be applied to the removal of organic, inorganic, or microbial contaminants that are introduced into supercritical carbon dioxide during its use as an extraction and cleaning medium in DOE environmental and waste minimization applications. 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.
- The second objective is to explore the use of supercritical carbon dioxide as a solvent for the photocatalytic oxidation of organic compounds and to compare it to other types of oxidation chemistry. This will add to the fundamental understanding of photocatalytic oxidation chemistry of particulate semiconductors.

The Photocatalytic Fluid Purification - Process Concept

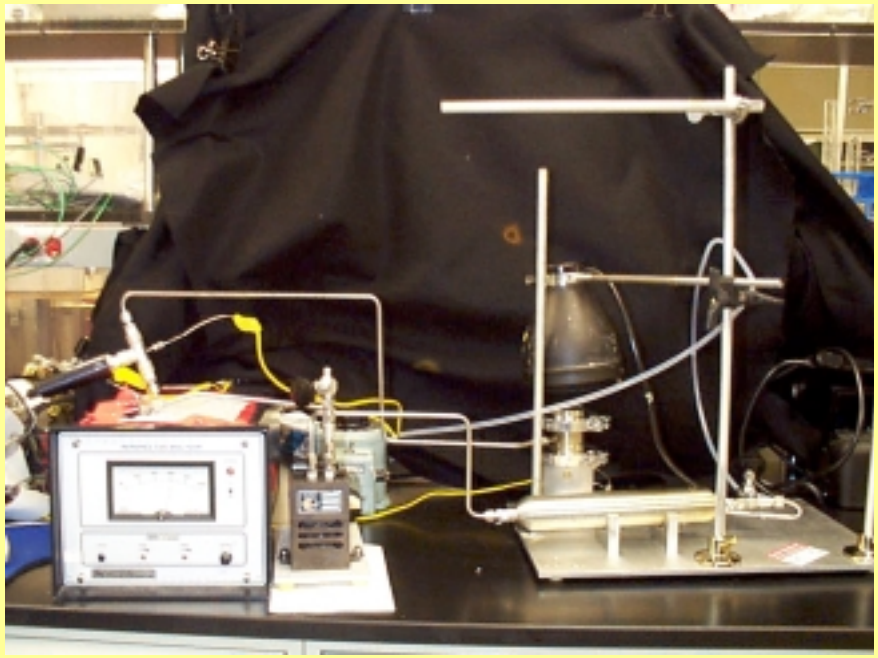


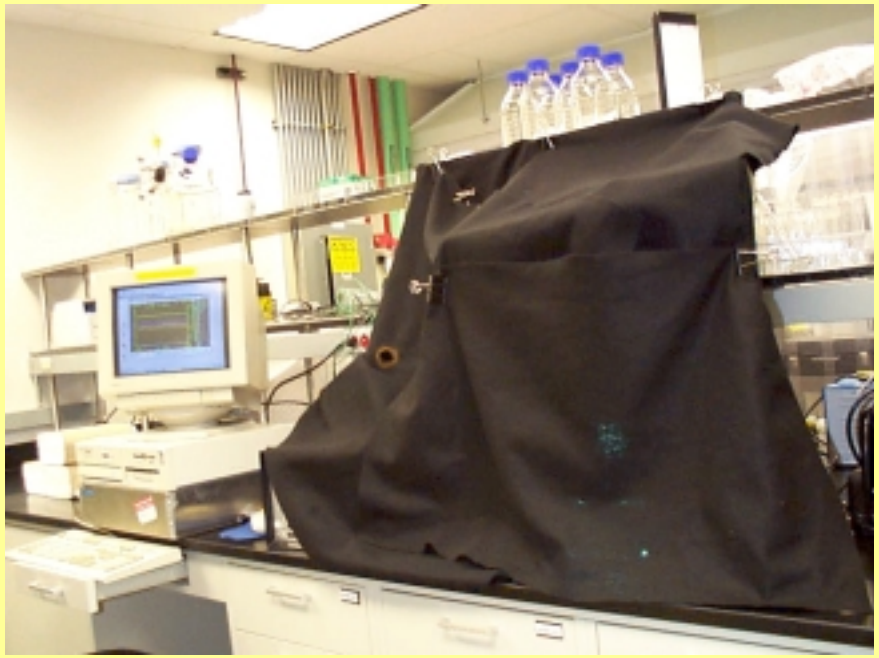
Light = $\lambda < 385$ nm
Photocatalyst = Titanium dioxide - immobilized particles or thin films
Reaction regimes: Photocatalytic < ~100 C
Photo- and thermal catalytic ~100-200 C
Thermal catalytic > 200 C

Photocatalysis on TiO_2: Background

- Most activity currently focussed on self-cleaning surfaces, IAQ, and disinfection of air, water, and surfaces
- Over 4000 published documents in the literature of photocatalytic oxidation for environmental applications
  - Blake, Daniel M. "Bibliography of Work on the Photocatalytic Removal of Hazardous Compounds From Water and Air Update Number 3 to January, 1999." 162 pp., Golden, CO: National Renewable Energy Laboratory, 1999. A bibliography with 1517 new references to work on photocatalytic chemistry for purification of air and water.
- Mechanism usually involves oxidative attack on molecules or microbes - In aqueous systems hydroxyl radical, superoxide, and hydrogen peroxide are invoked. In other fluid phases this is not so clear.
- Killing of bacteria involves major disruption of cell walls as the initial step
  - Blake, D. M., P.-C. Maness, Z. Huang, E. J. Wolfrum, J, Huang, and W. A. Jacoby. "Application of the Photocatalytic Chemistry of Titanium Dioxide to Disinfection and the Killing of Cancer Cells." *Separation and Purification Methods*, 28, no. 1 (1999): 1-50.

Demonstration of the Self-Cleaning Property of Illuminated TiO_2 Surfaces



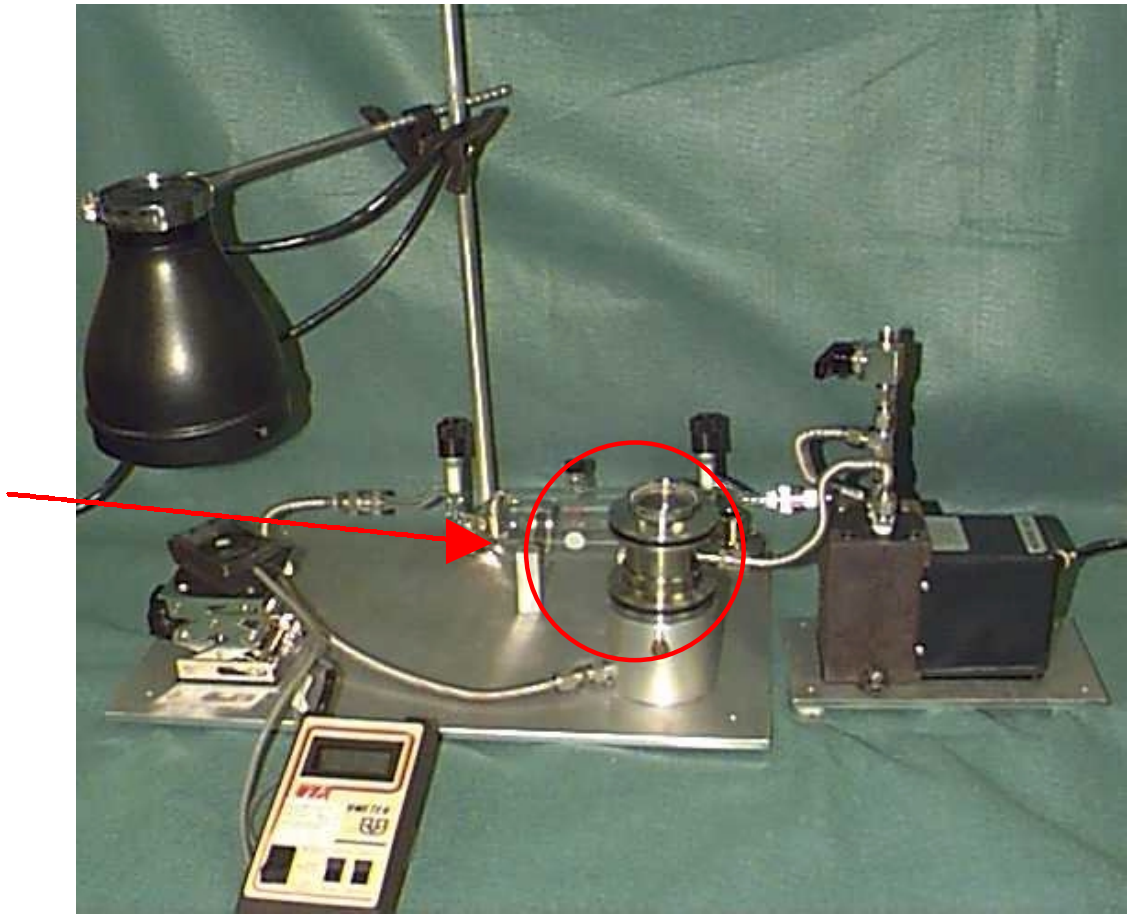


Batch reactor measurements of carbon dioxide evolution during total oxidation of organic and biological films on titanium dioxide surfaces

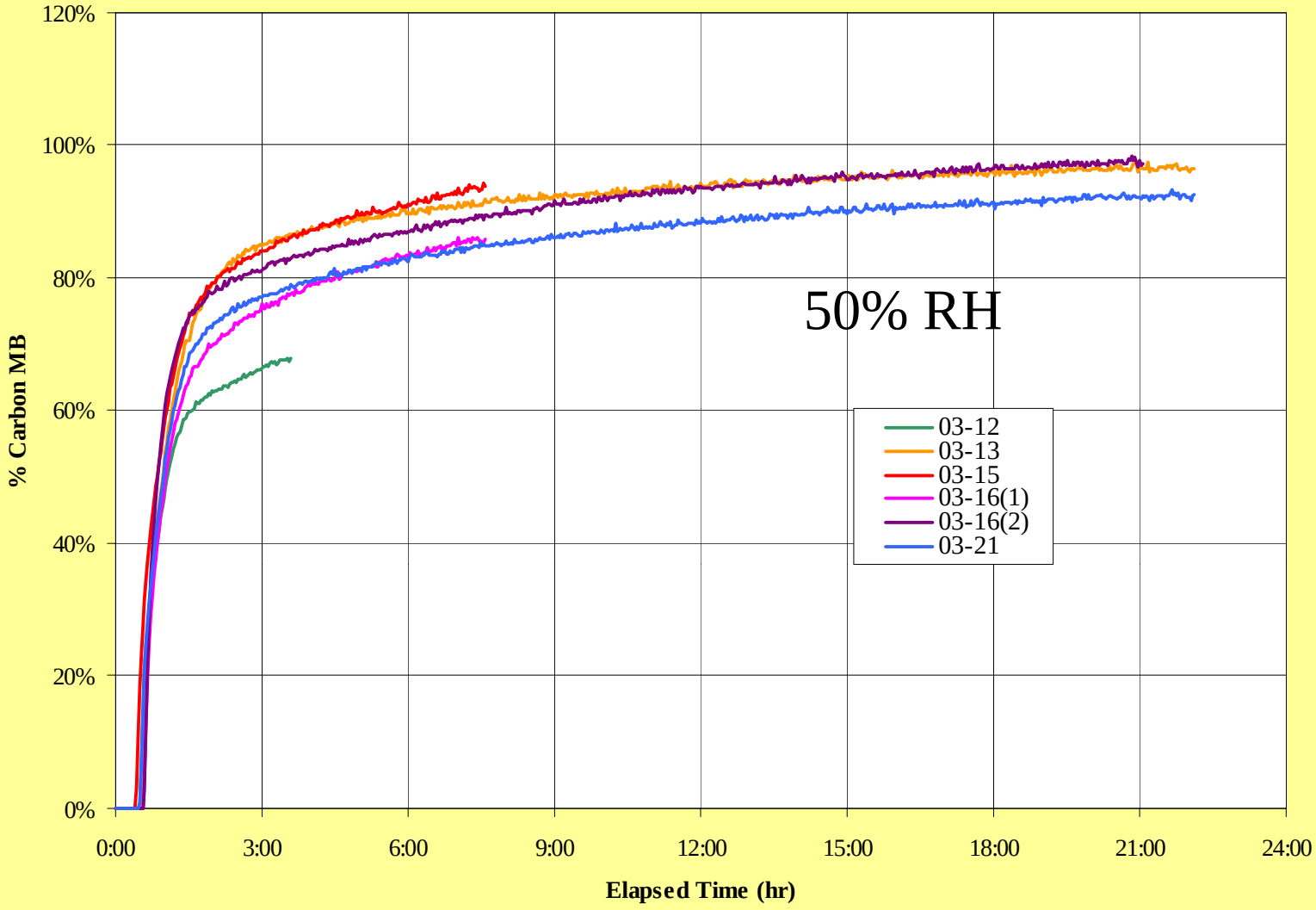
Photograph of Photocatalytic Reactor Assembly

Catalyst Support

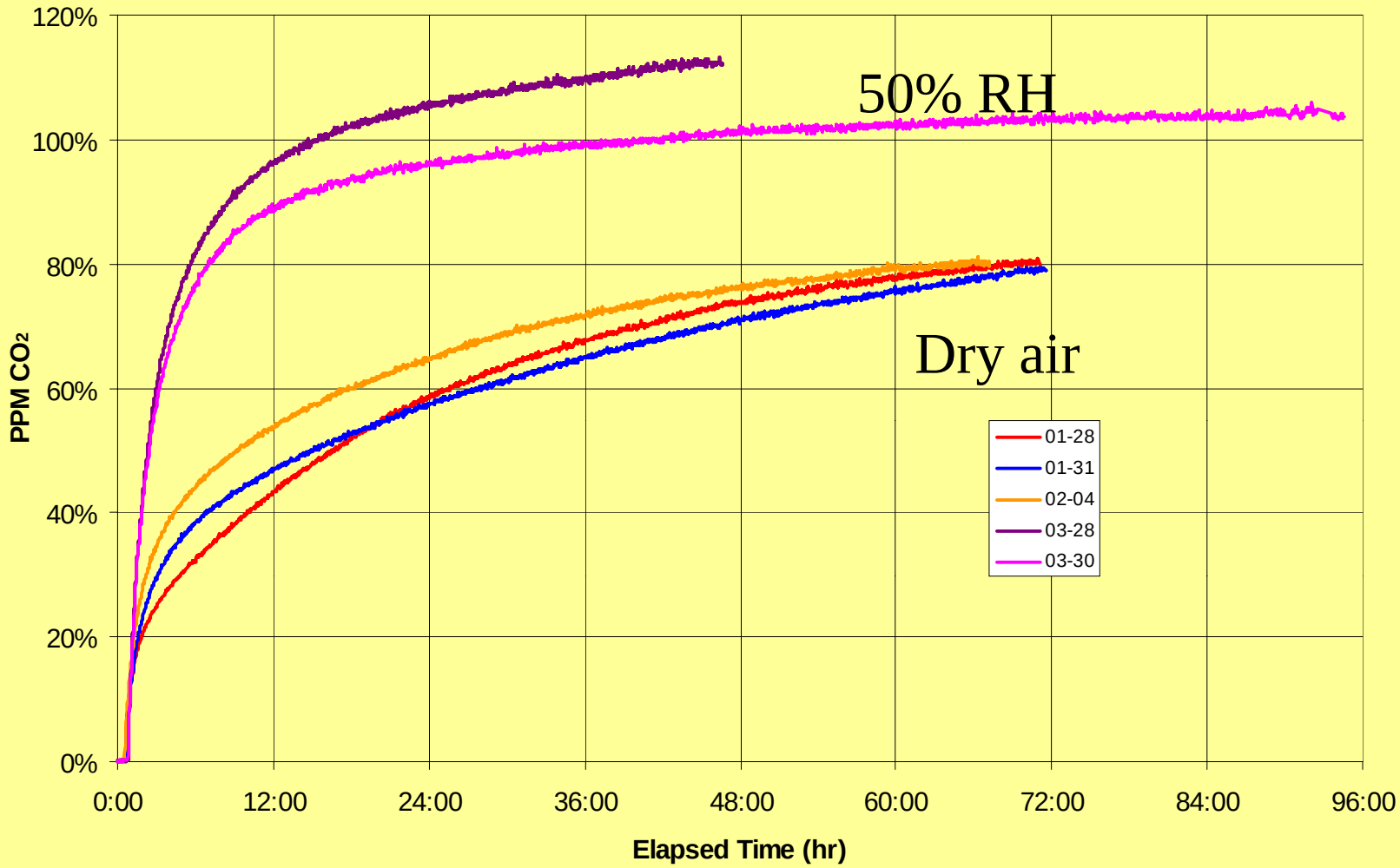
Quartz disk coated with TiO_2



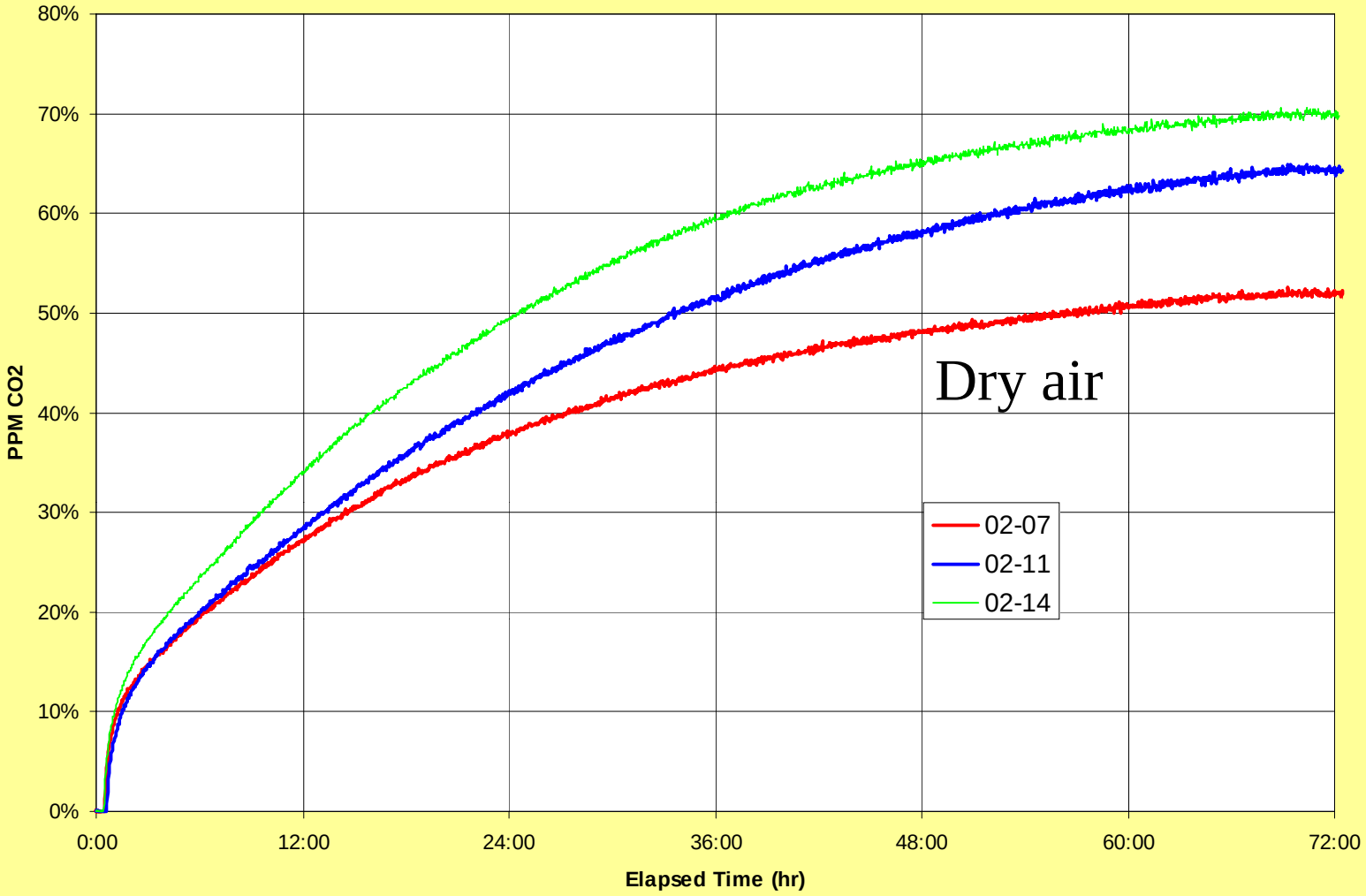
CO_2 yield from glucose deposited on a TiO_2 surface - Removal of molecular contamination



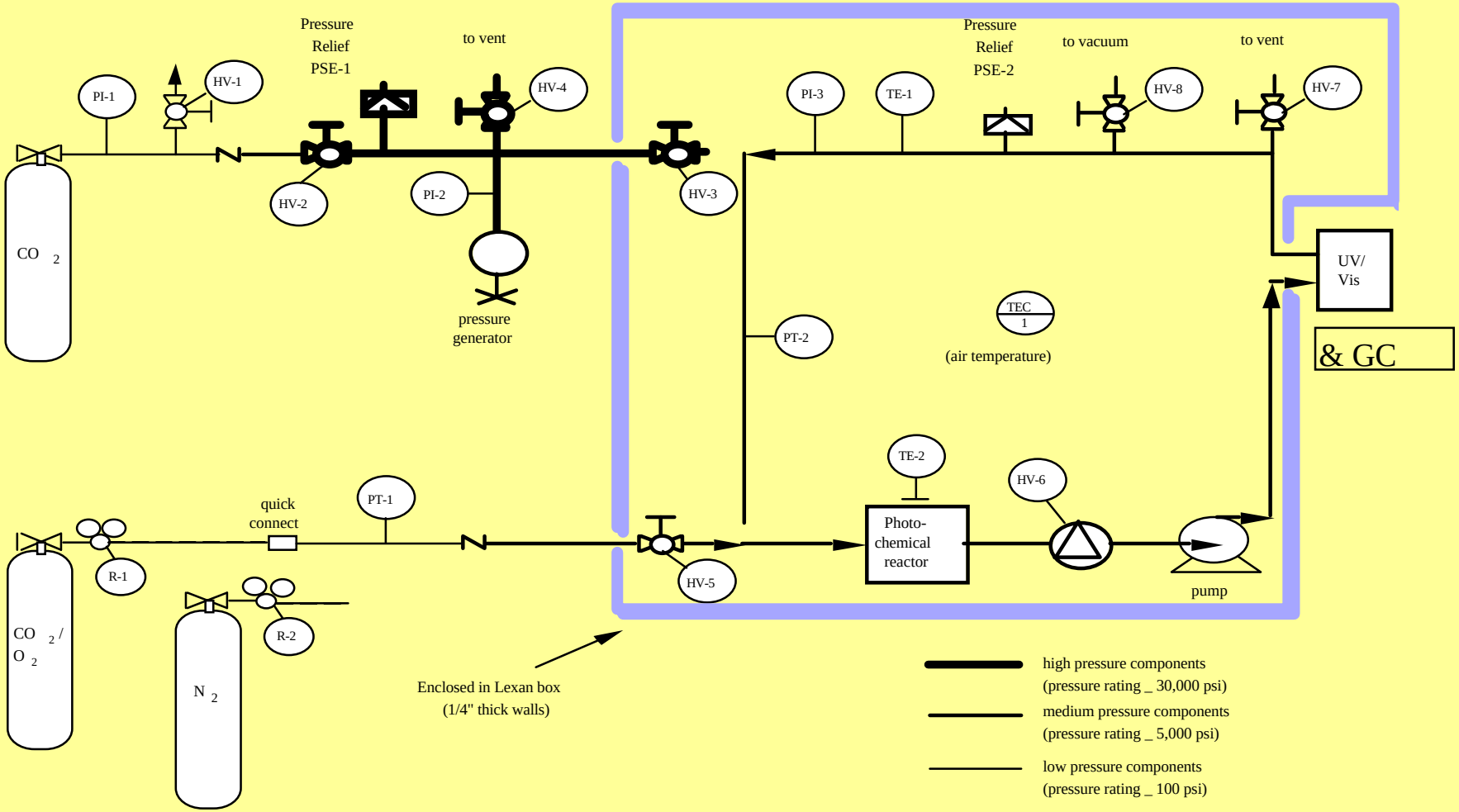
CO_2 yield from *Bacillus* spores deposited on a TiO_2 surface - Removal of microbial contamination



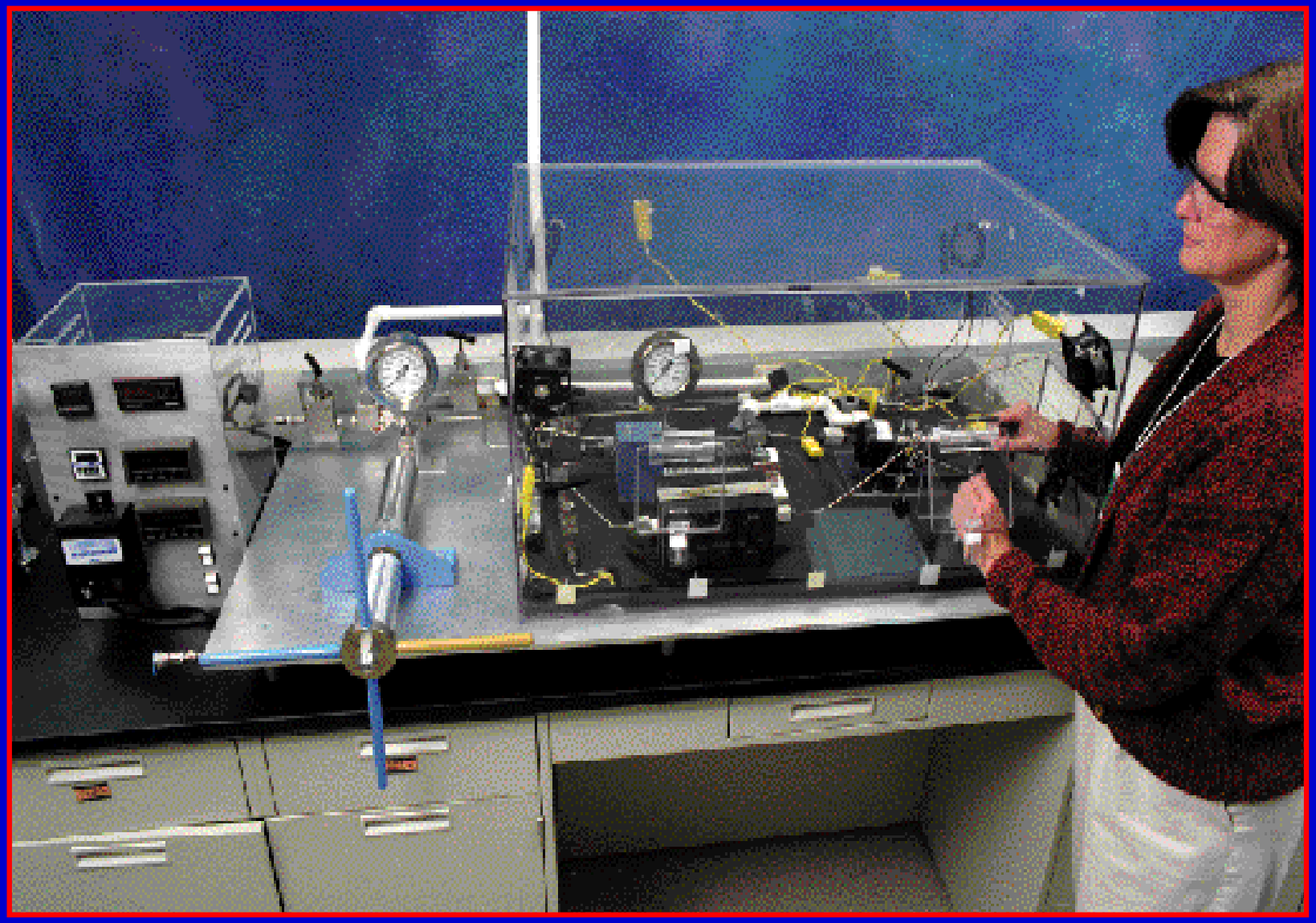
CO_2 yield from *Bacillus* cells deposited on a TiO_2 surface - Removal of microbial contamination



Experimental System for Supercritical CO_2 Experiments



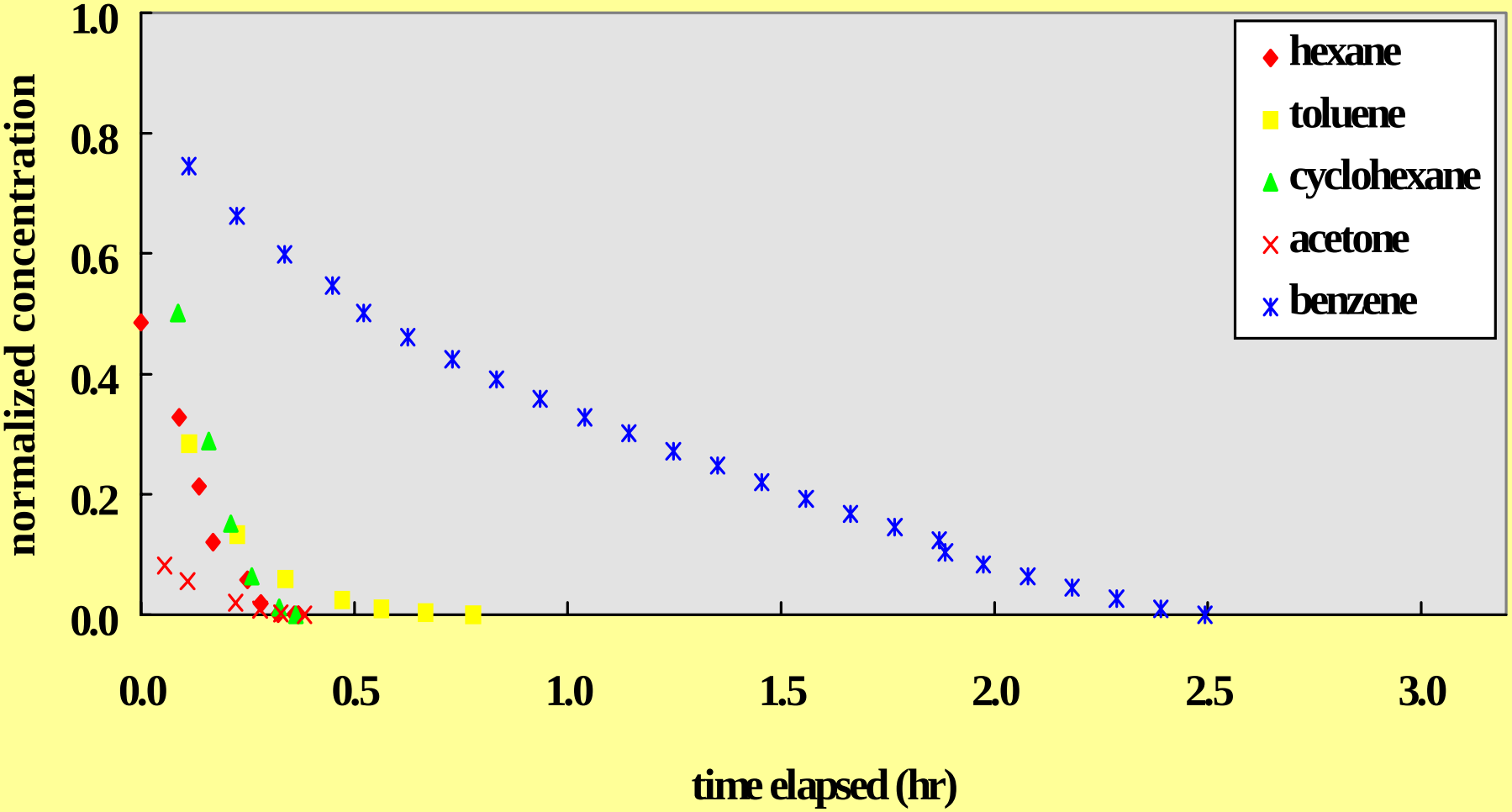
System as Built



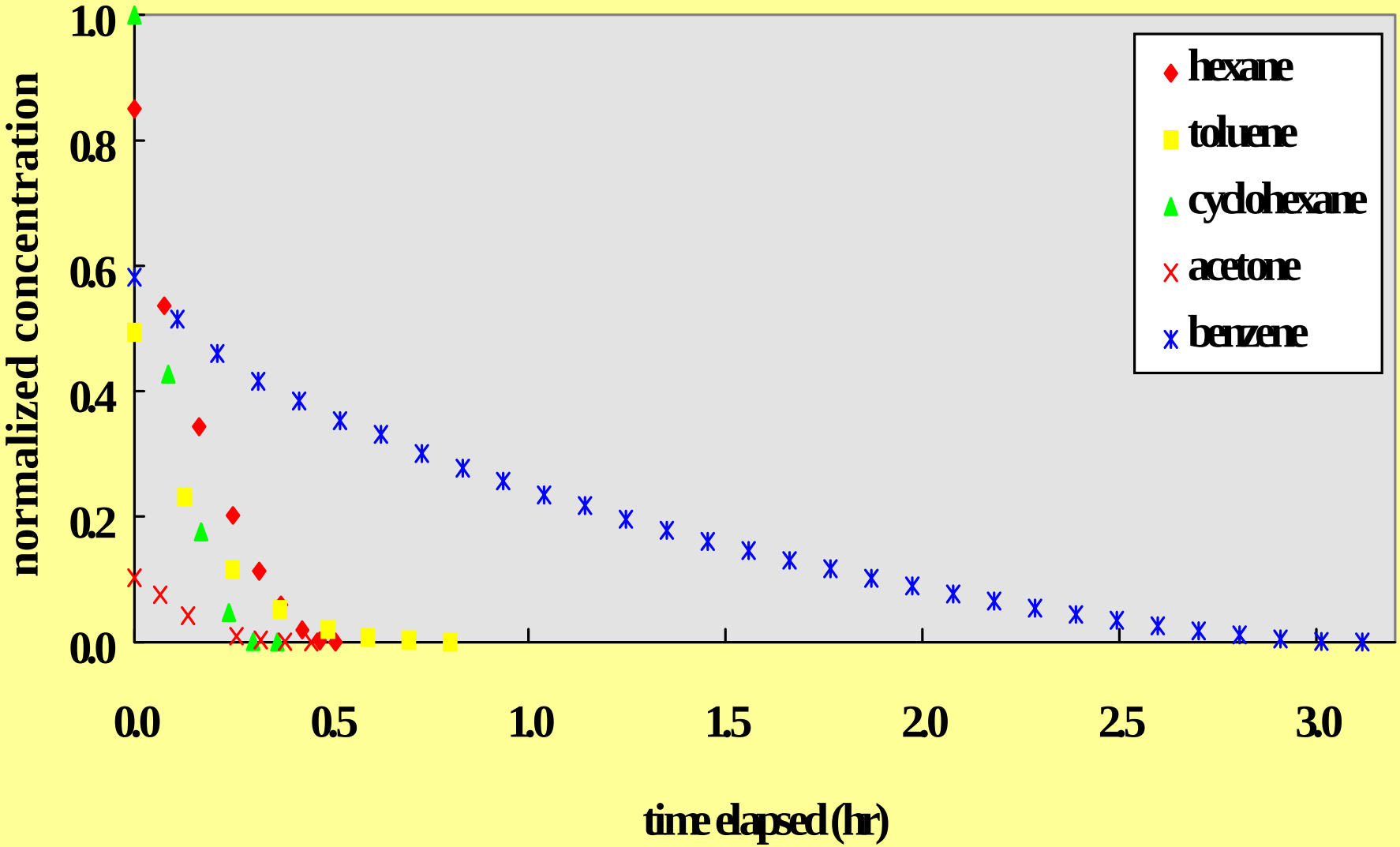
Experimental Conditions

- initial concentration of organics 50-2000 ppm
- initial concentration of O_2 > 50 times stoichiometric amount
- Degussa P25 TiO_2 on glass beads or glass "brushes"
- gas phase experiments were performed at ~10 psig; T ambient
- supercritical phase experiments were performed at ~1200 psig; T~37° C

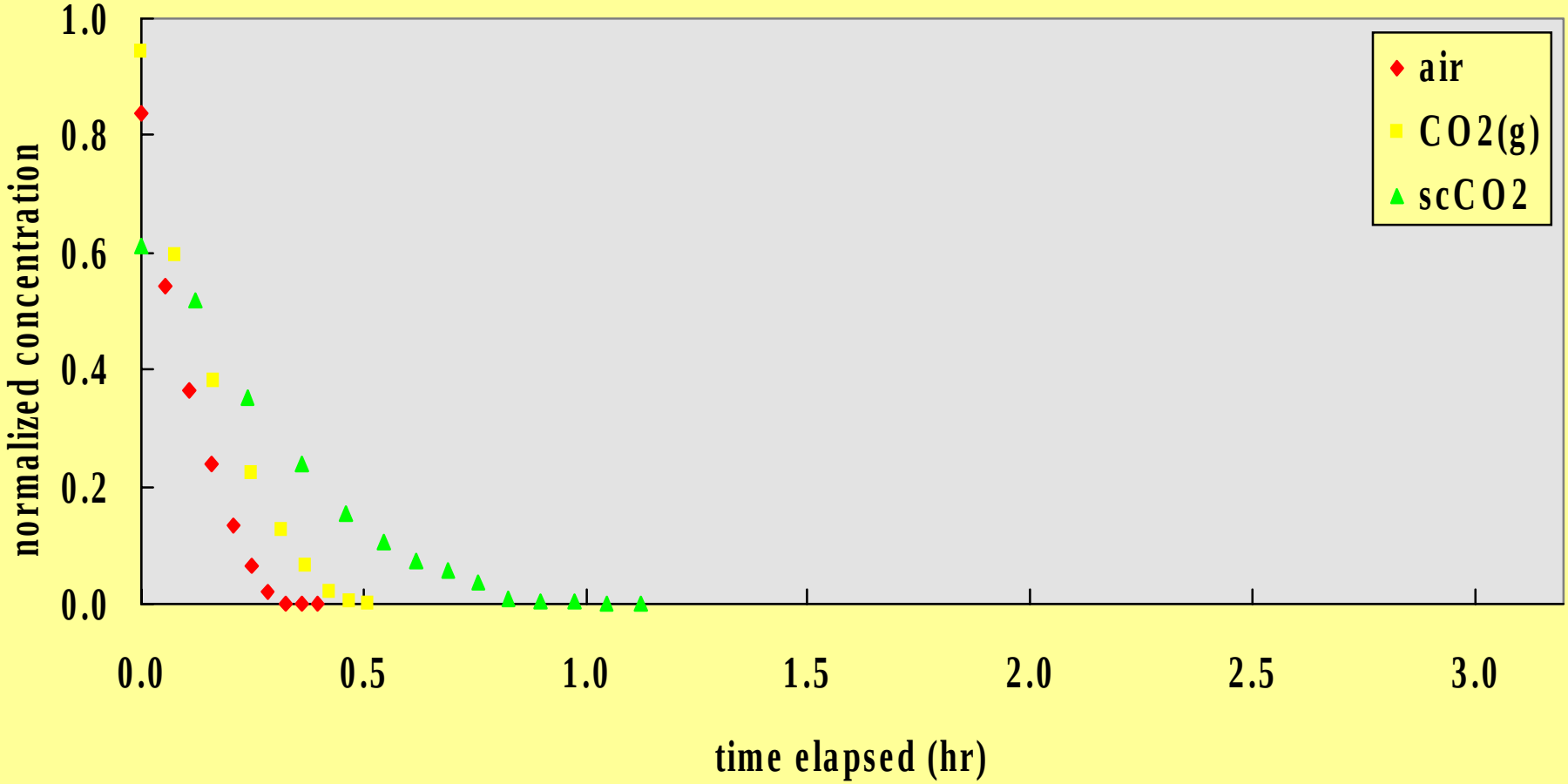
Oxidation of Organics in N_2/O_2 (80:20)



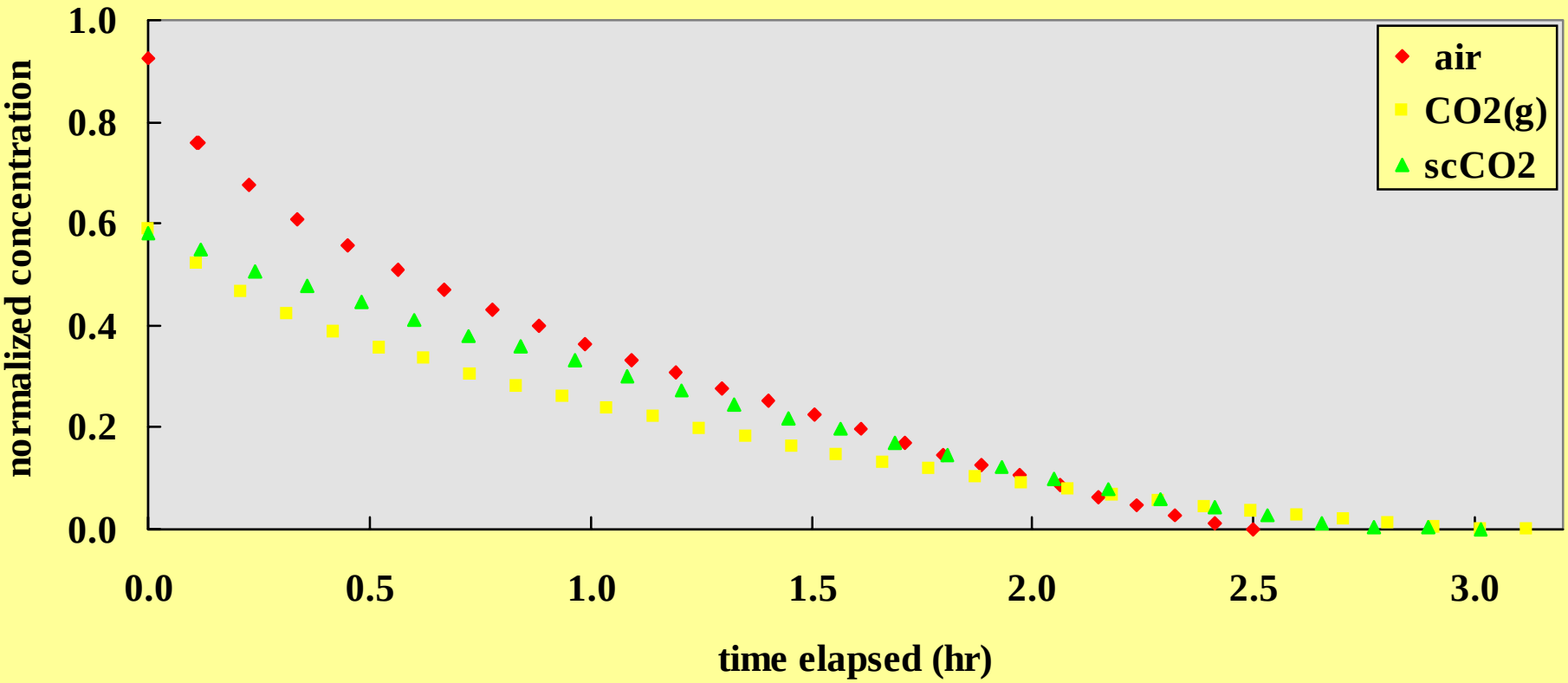
Oxidation of Organics in Gas Phase CO_2/O_2 (80:20)



Hexane Oxidation in N_2/O_2, Gas Phase CO_2/O_2 and Supercritical CO_2/O_2



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



Conclusions

- The self cleaning function of titanium dioxide surfaces under light has been demonstrated for molecular organic and biological films
- Photocatalytic oxidation of organic compounds in supercritical carbon dioxide has been demonstrated
- It is possible to reduce the level of organic compounds in $SCCO_2$ to below $1x10^{-5}$ ppm using photocatalytic oxidation
- It is possible for the first time to compare photocatalytic chemistry in gas, liquid, and supercritical phases of the same solvent

Continuing Work

- Determine oxygen and water concentration dependence of reaction in $SCCO_2$
- Test compounds of interest in DOE applications
- Determine nature of adsorbed intermediates for representative organic reactants
- Seek applications of the photocatalytic purification technology

Acknowledgement

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