Photocatalytic and Chemical Oxidation of Organic Compounds in Supercritical Carbon Dioxide

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Abstract

This poster reports progress during the first 18 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 and UV-Vis spectroscopy. Initial 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. This may be due to the reduced diffusion rates, CO_2 adsorption, or differences in flow rate in the supercritical phase experiments.

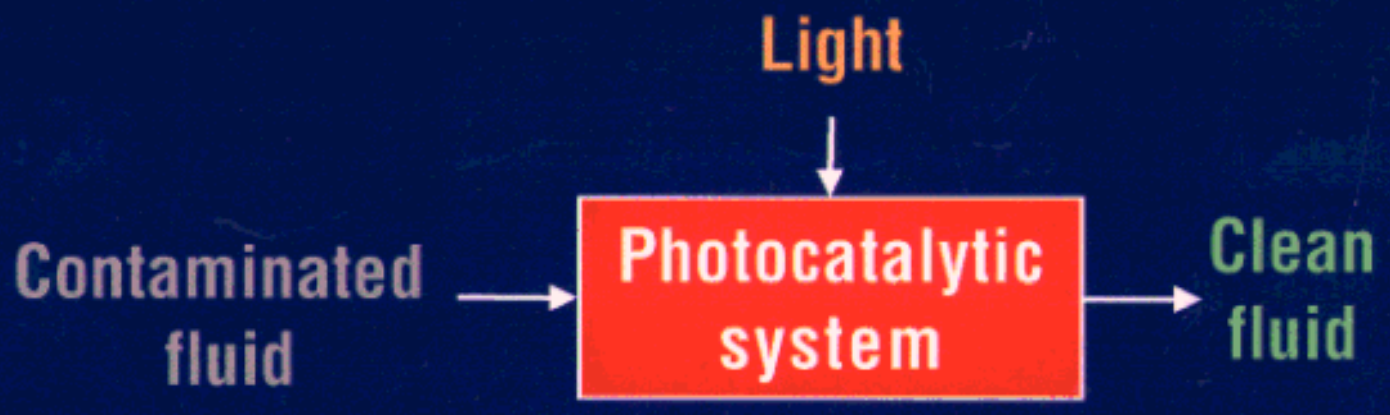
Objectives of the Project

- The first objective is to 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. 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.

Background

- Supercritical or liquid carbon dioxide is a safe and benign solvent that has the benefit of being inert to oxidation
- No reports to date on photocatalytic chemistry of semiconductor photocatalysts in supercritical fluids
- More than 2500 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

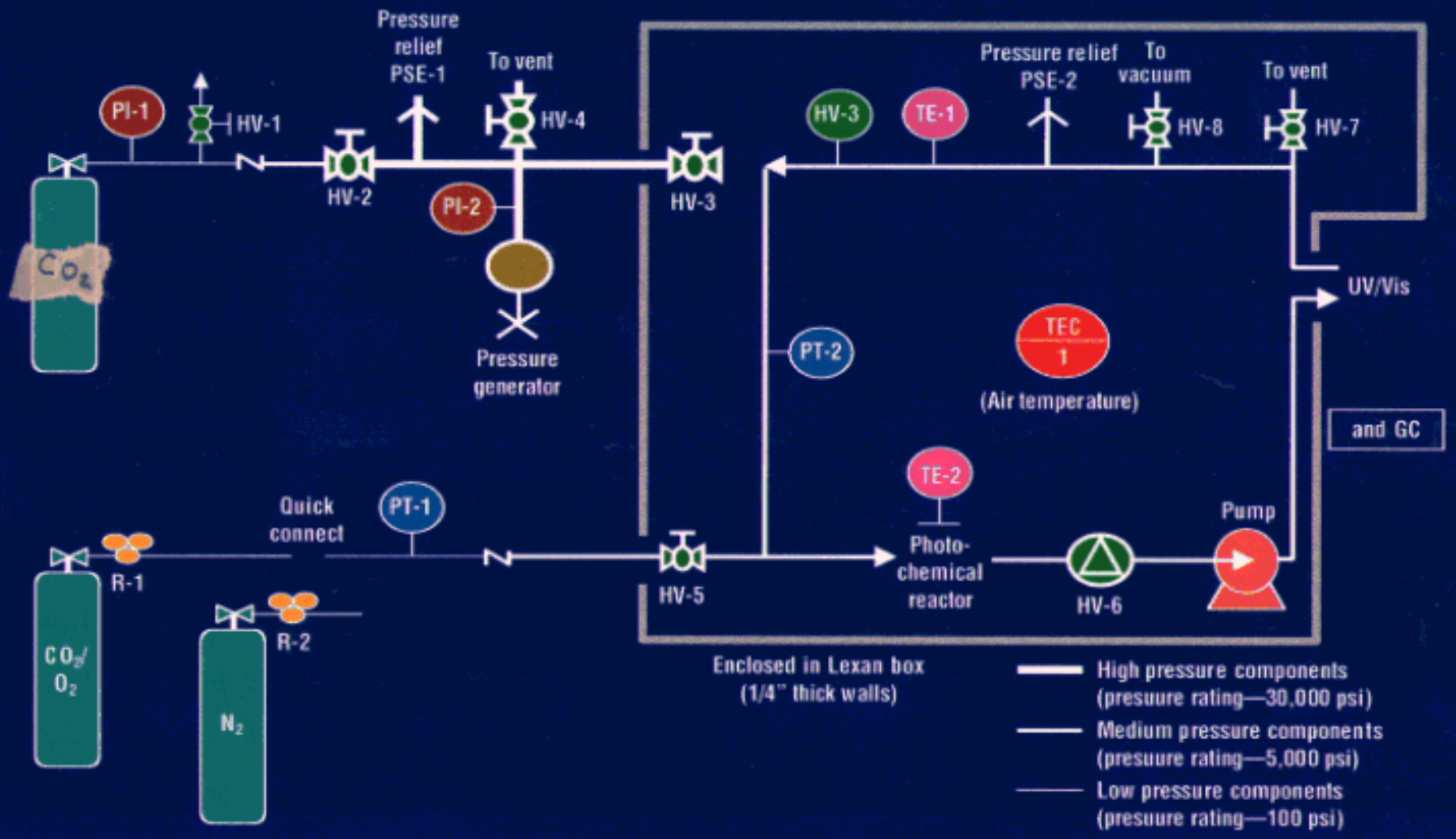
Process Concept



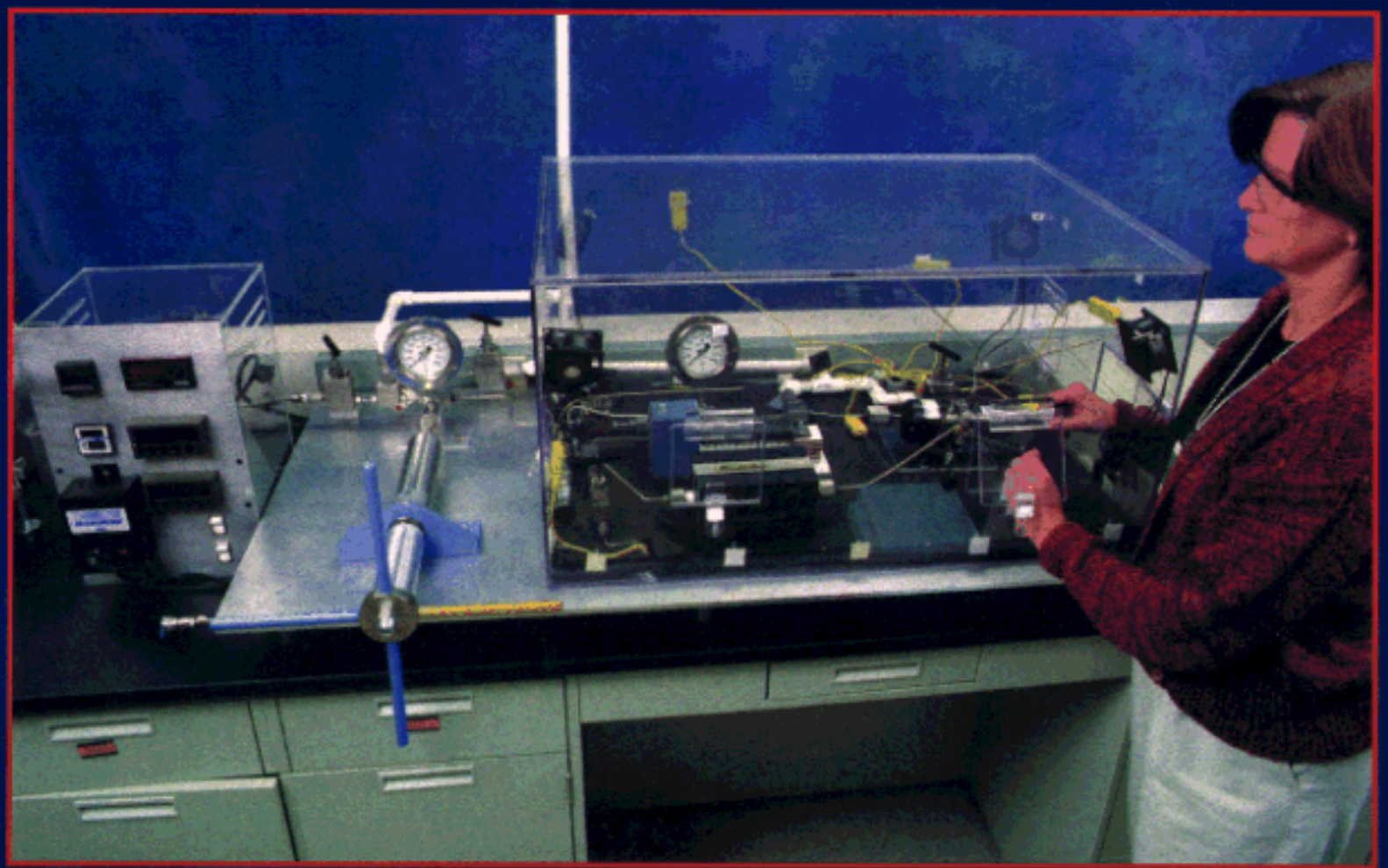
Light = UV below 380 nm

Photocatalyst = Titanium dioxide or modified form

Experimental System



System as Built

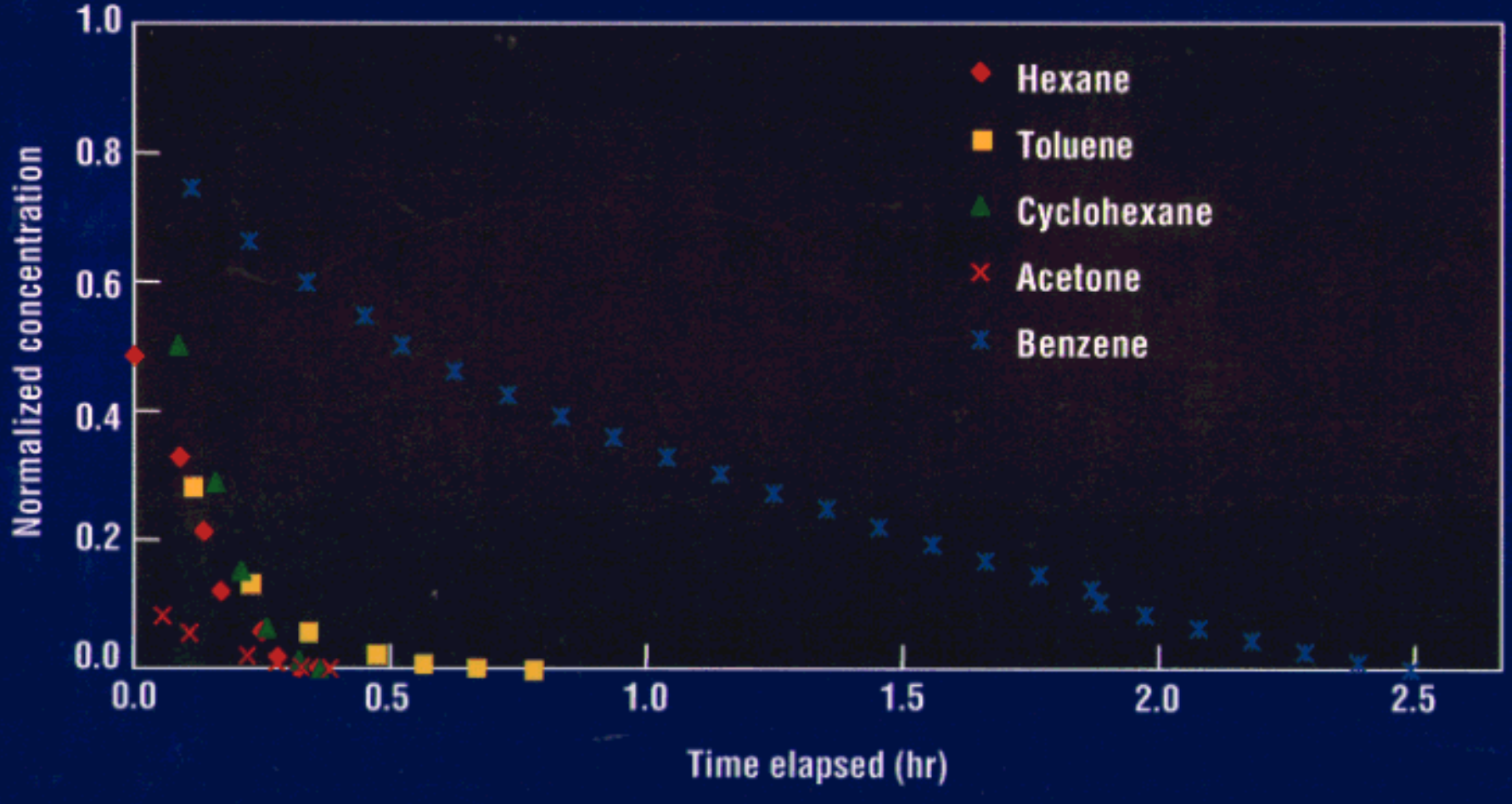


High Pressure Photo Reactor

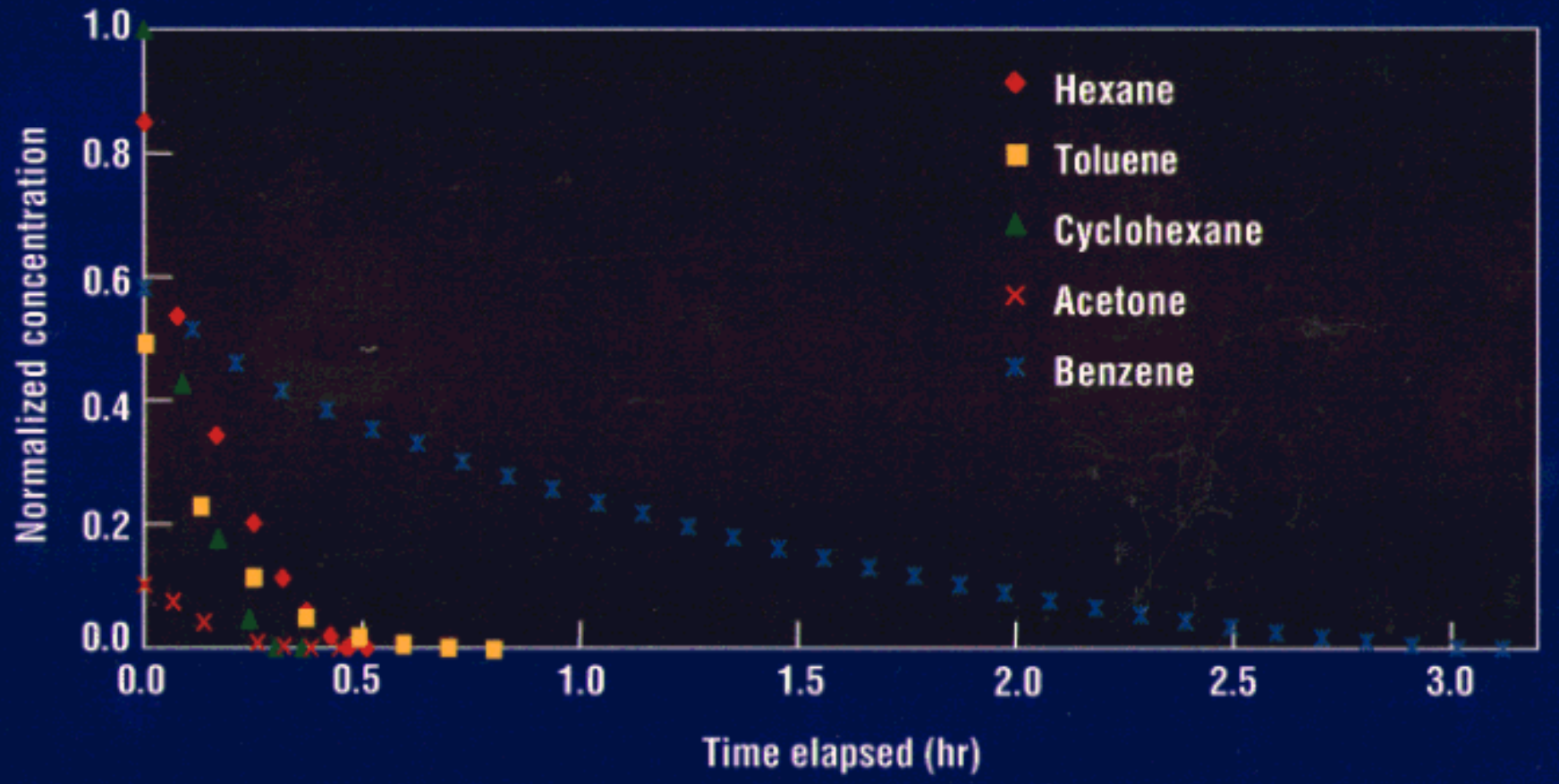
Experimental Conditions

- Initial concentration of organics approximately 2000 ppm
- Initial concentration of O_2 >50 times stoichiometric amount
- Catalyst Degussa P25 TiO_2 on glass beads
- Gas phase experiments were performed at ~10 psig; T ambient
- Supercritical phase experiments were performed at ~1200 psig; T~37°C

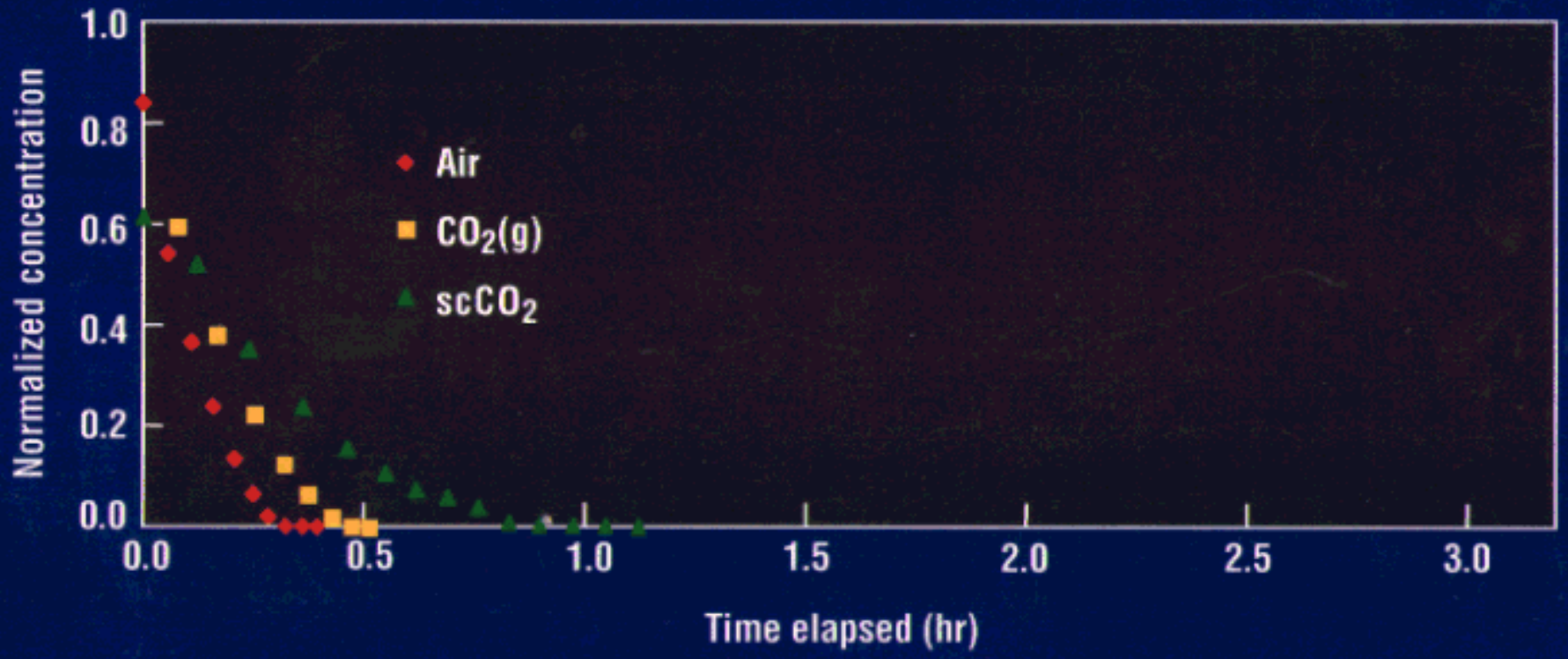
Oxidation of Organics in N_2/O_2 (80:20)



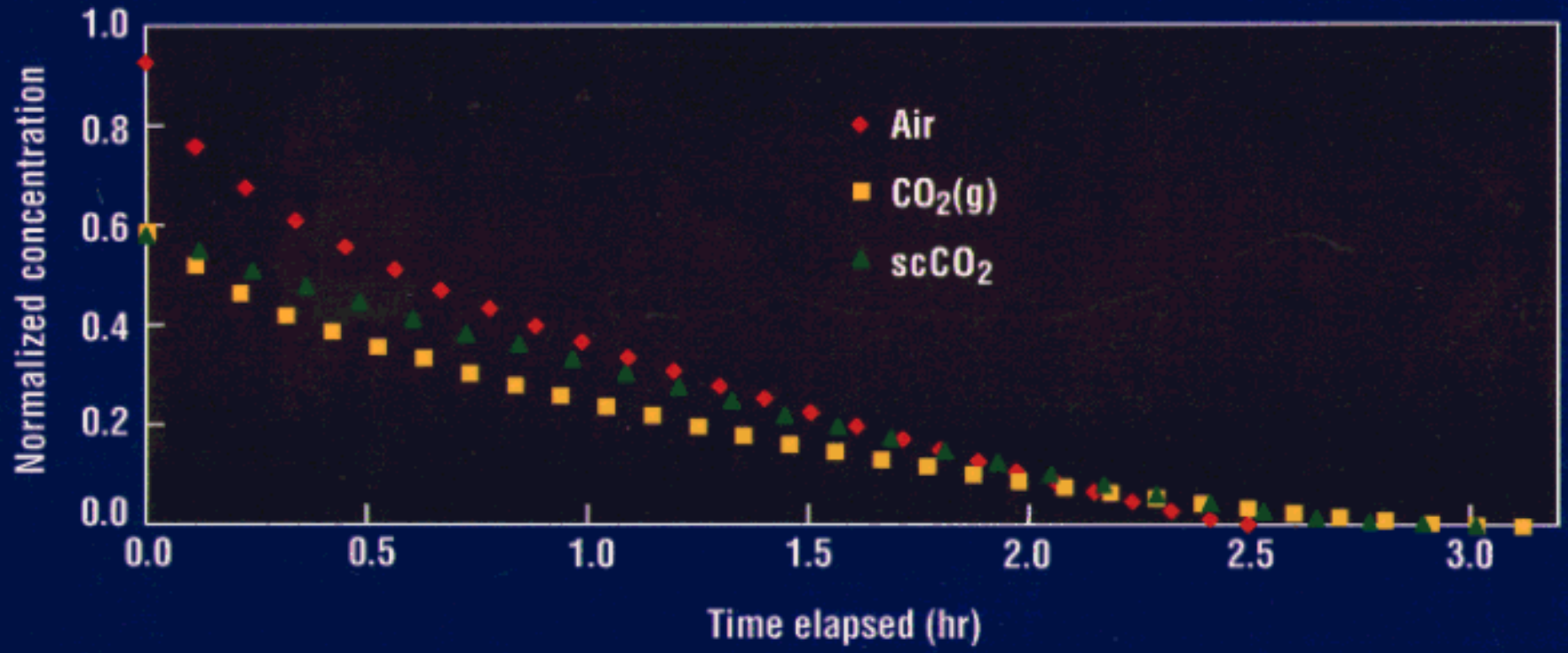
Oxidation of Organics in Gas Phase CO_2/O_2 (80:20)



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



Summary of Kinetic Data (Rate Constant, hr^{-1})

	Hexane	Acetone	Cyclohexane	Toluene	Benzene
$N_2/O_2(g)$	-5.9	-4.2	-8.2	-2.1	-1.30
$CO_2/O_2(g)$	-4.1	-5.2	-6.0	-3.7	-0.71
Supercritical	-2.4	—	—	—	-0.41

Species Identified on The Catalyst Surface after Benzene and Toluene Oxidation

Acetate	$CH_3CO_2^-$	✔
Formate	HCO_2^-	✔
Carbonate	$CO_3^=$	TBD

Conclusions

- Photocatalytic oxidation of organic compounds in super-critical 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

Future Work

- Obtain quantitative kinetic data to compare representative organic compounds in all three fluid phases
- Determine oxygen and water concentration dependence of reaction in $SCCO_2$
- Determine nature of adsorbed intermediates for each organic reactant
- Test compounds of interest in DOE applications

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