Photocatalytic and Chemical Oxidation of Organic Compounds in Supercritical Carbon Dioxide - TTP No. AL7-7-SP-22

Progress Report for FY97

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Abstract

The background for the project is briefly reviewed and the work done during the nine months since funding was received is documented. Work began in January, 1997. A post doctoral fellow joined the team in April. The major activities completed this fiscal year were: staffing the project, design of the experimental system, procurement of components, assembly of the system. preparation of the Safe Operating Procedure and ES&H compliance, pressure testing, establishing data collection and storage methodology, and catalyst preparation.

Objective

The objective of the project is to develop new chemistry for the removal of organic contaminants from supercritical carbon dioxide. This has application in processes used for continuous cleaning and extraction of parts and waste materials. A secondary objective is to increase the fundamental understanding of photocatalytic chemistry. Cleaning and extraction using supercritical carbon dioxide (scCO_2) can be applied to the solution of a wide range of environmental and pollution prevention problems in the DOE complex. Work is being done that explores scCO_2 in applications ranging from cleaning contaminated soil to cleaning components constructed from plutonium. The rationale for use of scCO_2 are based on the benign nature, availability and low cost, attractive solvent properties, and energy efficient separation of the extracted solute from the solvent by moderate temperature or pressure changes. To date, R&D has focussed on the methods and applications of the extraction steps of the process. Little has been done that addresses methods to “polish” the scCO_2 for recycle in the cleaning or extraction operations. In many applications it will be desirable to reduce the level of contamination from that which would occur at steady state operation of a process. This proposal addresses chemistry to achieve that. This would be an alternative to removing a fraction of the contaminated scCO_2 for disposal and using makeup scCO_2. A chemical polishing operation can reduce the release of CO, from the process. It can also reduce the consumption of reagents that may be used in the process to enhance extraction and cleaning. A polishing operation will also reduce or avoid formation of an additional waste stream. Photocatalytic and other photochemical oxidation chemistry have not been investigated in scCO2. The large base of information for these reactions in water, organic solvents, or air suggest that the chemistry will work in carbon dioxide. There are compelling reasons to believe that the properties of scCO_2 should increase the performance of photocatalytic chemistry over that found in more conventional fluid phases.

The objectives for this project are:

1) 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. The target will be contaminants left in solution after the bulk of solutes have been separated from the fluid phase by changing pressure and/or temperature (but not evaporating the CO,). This is applicable to development of efficient separations and will strengthen pollution prevention strategies that eliminate hazardous solvents

and cleaning agents.

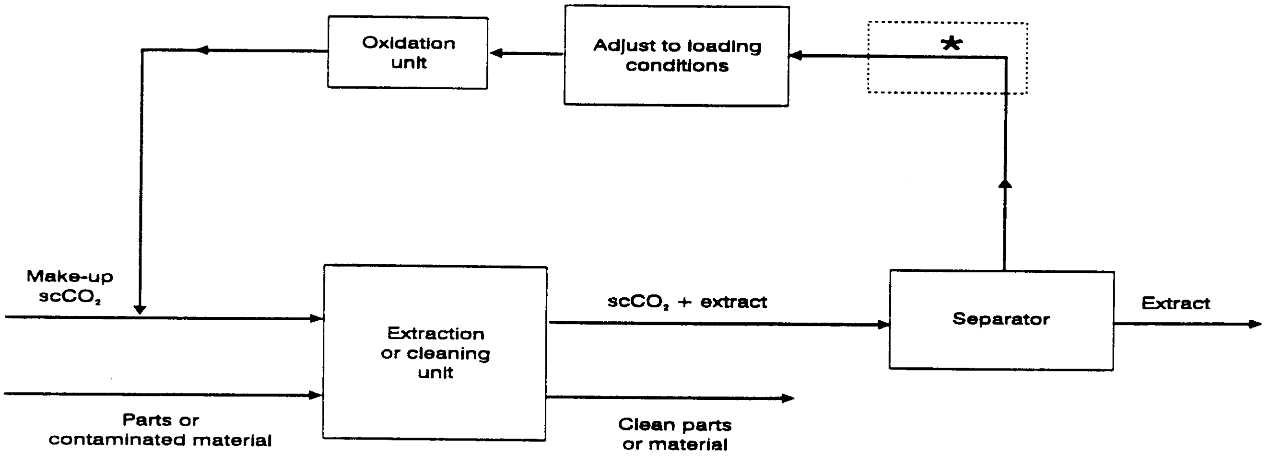
2) to explore the use of supercritical carbon dioxide as a solvent for the photocatalytic oxidation of organic compounds and to compare it to other types of oxidation chemistry. This will add to the fundamental understanding of photocatalytic oxidation chemistry of particulate semiconductors and provide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

Narrative

Background and Significance

Supercritical carbon dioxide, $scCO_2$, is being considered for a wide range of applications. It is attractive because the solvent properties allow it to replace organic solvents that are hazardous, flammable, and/or are ozone depleting substances. Carbon dioxide, as the liquid or solid form, is in the top 25 commodity chemicals and the price is below that of common solvents. The critical temperature is 31 °C (304 K) and the critical pressure is relatively low, 78 atm (1073 psi = 7.3 mPa). Applications of interest within the DOE complex’ that are being explored include: cleaning precision parts,[2,3] cleaning plutonium parts,[4,5] separation of mixed wastes and cleaning laboratory wastes,[6] extraction of hazardous organic compounds from contaminated soil,[7,8] extraction of radionuclides from contaminated water,[9,10] in coal desulfurization,[11] and separation of organic and inorganic wastes. The R&D based on $scCO_2$ are in support of the crosscutting technologies that will have impact on a range of DOE requirements for improved methods to solve pollution problems.” Outside of DOE environmental requirements, work is underway on the use of $scCO_2$ as a solvent in a wide range of chemical, enzymatic, photochemical, analytical, and separation processes. The focus of this proposal will be on chemistry that will improve the performance and economics of extraction and cleaning processes using $scCO_2$. The results will also have impact on the understanding of chemical fixation of CO, for chemical production and will provide fundamental new insight to the mechanism of photocatalytic oxidation. The need for this kind of information was highlighted in a DOE report from a workshop held in Estes Park, CO in February 1996.[13]

A schematic of the general layout of an $scCO_2$ cleaning or extraction process is shown in Figure 1. This shows the main steps that are involved in a process that recirculates the CO, and the



(*Optional location for oxidation unit)

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Figure 1. Schematic of a supercritical carbon dioxide process for cleaning parts or extracting hazardous components from waste material.

proposed oxidation step. The main operations are: extraction or cleaning, separation of the extracted substances from the CO, by reduction in temperature and/or pressure, and readjustment of pressure to the extraction conditions to repeat the cycle. In a process of this type the main bulk of material that is extracted from the material being cleaned, be it soil or sensitive components that are being processed, will be deposited in the separator where a change in temperature or pressure or both, results in phase separation. The contaminant phase is removed and the CO, is recirculated. Ideally this step is accomplished without vaporization of the CO, so that recompression to the liquid or supercritical state is not required. In steady state operation, the CO, stream will retain a level of contaminants that will be determined by the solubilities under the conditions at which the separator operates. If, 1) that level of contamination does not compromise the performance required for the cleaning or extraction step to meet specifications; or 2) it does not result in a trace substance carried into the process with the raffinate building up to unacceptable levels; then the process can operate as shown. However, if at steady state the contaminant concentration that remains in the recirculated CO, causes the performance to fall below requirements, then the concentration of contaminant must be reduced to an acceptable level. This could be accomplished by removing a “bleed stream” to be disposed of and adding an equal amount of make-up CO,. However, this would add a cost to the process and create a new waste stream.

The objective of this proposal is to explore photocatalytic chemistry or other clean oxidation methods that can accomplish the control of steady state contaminant level with no or, more likely, reduced requirement for make-up CO,. The oxidation unit could be inserted to operate after the fluid was returned to the extraction conditions or prior to adjustment of conditions. Both options are shown in Figure 1. A third possibility would be to use the oxidation operation to treat a bleed stream so that the $scCO_2$ could be returned to the process rather than discarded. In that configuration a smaller volume of fluid would be treated by the oxidation unit. The oxidation step will produce CO_2, H_2O, and an acid, if the compound that is oxidized contains a heteroatom such as sulfur or chlorine. The acid and water could be removed at the separator.

Photocatalytic chemistry can be used for oxidation of organic compounds and, under some circumstances, for reduction of metal containing contaminants. Other oxidation processes will be tested to provide a baseline of understanding of oxidation in $scCO_2$. These will include homogeneous photooxidation with oxygen or hydrogen peroxide. This project will provide fundamental work exploring a new fluid phase for photocatalytic chemistry and will provide new operations that can be used to improve the performance of supercritical cleaning and extraction processes for use in the solution of environmental problems at DOE sites and for new processes that will not contaminate the environment in the future.

Properties of $scCO_2$ that make it attractive for use in chemical and photochemical processes The properties of $scCO_2$ provide unique advantages in extraction/cleaning applications and the potential for manipulation of chemical reactions by variation of conditions of pressure, temperature, and concentration. Key factors include: the effect of pressure on the rates of reaction which is manifested through the volume of activation and solvent density effects;

miscibility of reactant gases such as O_2, H_2, and others; low viscosity and improved mass transfer: ability to control solute solubility by varying pressure and temperature near the critical point; and the low viscosity allows good penetration into pores in catalytsts or into fine structure in parts to be cleaned.[14,15,16,17,18,19,20] Co-solvents, also termed entrainers, can be used to modify the solvent properties of $scCO_2$ to enhance solubility of more polar compounds. Examples of entrainers include acetonitrile or methanol.[21] Solute. co-solvent, and solvent clustering effects have been utilized to advantage for controlling chemistry and photochemistry in supercritical solvents when the kinetics are on the time scale of solvent rearrangement. For the case of photocatalytic chemistry, the further advantages of oxidative stability and the modification of adsorption equilibria for solutes will also be important.

<u>Photocatalytic Chemistry</u> Heterogeneous photocatalytic chemistry of systems based on semiconductors as photocatalysts has been studied for nearly 25 years, since the report of photocatalytic water splitting by Fujishima and Honda.[22] During this period the photocatalytic reactions of more than 300 organic and inorganic compounds have been studied under a wide range of conditions. The organic compounds provide a cross-section of structure types and functional groups. The compounds that have been tested include surfactants, oils, fuel components, herbicides, PCBs, and chlorinated, oxygenated, and hydrocarbon solvents. Carbon tetrachloride and chlorofluorocarbons resist oxidation but most organic compounds can be oxidized to carbon dioxide. Hundreds of variations of titanium dioxide and other semiconductors have been tested for activity. The principal investigator maintains a data base covering the literature in this field (currently over 2000 references) and has prepared three reports which provide a bibliography for work on environmental and synthetic applications.[23,24,25] The fundamental aspects of photoelectrochemistry of single crystal and particulate electrode systems that are the foundation for this area of work has been reviewed in a number of books and journals.[26,27,28,29,30,31] Photocatalytic reactions based on the use of particulate semiconductors have been extensively studied for application to environmental remediation, organic synthesis, and water splitting for hydrogen production.[32,33,34,35,36,37,38,39,40,41]

The focus of this proposal is photocatalytic oxidation reactions of organic compounds. Oxidation reactions have been most studied but examples of the reduction of olefins and acetylenes,[42,43] reduction of aqueous and gaseous carbon dioxide,[44,45,46,47,48,49,50,51,52,53,54,55,56,57,58,59,60] and noble metal deposition[61,62,63] have been reported. Recently there have been reports of reduction of nitro groups in aromatic compounds.[64,65] There have been many reports of the semiconductor catalysed photoreduction of molecular nitrogen but a recent review has concluded that there is no solid evidence that the reaction has been achieved? A number of workers have investigated the species formed by the interaction of CO, with semiconductor. This work has been included in a review by Cunningham.[67] No evidence was found for chemisorption of CO, from the gas phase onto zinc oxide.[68] Formation of carbonate and bicarbonate species was observed on titanium dioxide when oxidized surfaces were exposed to CO_2.[56]

Aqueous systems have been the most studied because of the interest in developing methods to remediate contaminated ground and process water.[33,35,36,69,70,71] Significant effort has also been devoted to systems in which the organic compound is carried in a gas stream, usually air. Early work on gas phase photocatalytic chemistry was motivated by the search for solar photochemical processes that could be used to produce useful chemicals from commodity hydrocarbon feedstocks.[72,73,74] More recently the work has been directed toward removal of hazardous organic compounds from contaminated air streams which can be found in environmental,[75] industrial process,[76] or indoor air quality applications.[77,78] Finally there is a body of work that explores the use of photocatalytic chemistry for organic synthesis. These reactions are usually carried out in an organic solvent or in neat organic phase, where the target compound is the fluid medium. The work has been reviewed.[37,40] The extensive work in a wide range of liquid solvents and in air strongly suggest that the chemistry will also work in $scCO_2$.

There are a few key characteristics of photocatalytic chemistry, independent of the fluid phase, that define the process.[29-40] First, a photon with energy exceeding the band gap of the semiconductor must be absorbed to produce the excited state, a valence band hole and a conduction band electron. Further, the organic reactant and oxidant or reductant must be at the surface of the semiconductor, although not necessarily in contact with each other, in order for reaction to occur. The nature of reactions on the surface is of fundamental interest. The efficiency of the process, which can be discussed in terms of effective quantum number (molecules reacted/photon absorbed),[79,80,81] depends on the rate at which the chemical reactions consume electrons and holes compared to the rate of their recombination and return to the group state. For this reason the efficiency of chemical reaction is very sensitive to diffusion and adsorption effects.[82,83] For most compounds it is not known how many photons are required for complete oxidation.

A very wide range of semiconductors have been investigated but the anatase form of titanium dioxide has been found to be most effective under a wide range of conditions (see prior references to review articles). Modifications of anatase achieved by different preparation methods, heat treating, substitution with other metal ions, and deposition of noble metals have been investigated.[34-39] Immobilization by coating on glass,[84,85] metals,[86,87] ceramics,[88,89] carbon,[90] and organic polymers[91] have been demonstrated.[23,24,25] Immobilization of photocatalysts on surfaces by coating using slurries of titanium dioxide powders[92], vapor deposition,[93] sol gel methods, and spray pyrolysis have been used.[23,24,25,35,36,94,95] Reactor design and engineering issues have been explored and reviewed?” Innovative designs for photoreactors, many of which could be adapted to use at elevated pressure, including the use of fiber optics to carry light have been developed.[98,99] There is not space to document all the pertinent references but they are covered bibliographies prepared by the PI and other reviews that have been cited previously.

Activity During FY97

Work was started in January, 1997, when funds became available at NREL. The. major activities completed this fiscal year were: staffing the project, design of the experimental system, procurement of components, assembly of the system, preparation of the Safe Operating Procedure (Appendix 1) and ES&H compliance, pressure testing, establishing data collection and storage methodology, and catalyst preparation.

Construction of the Experimental System

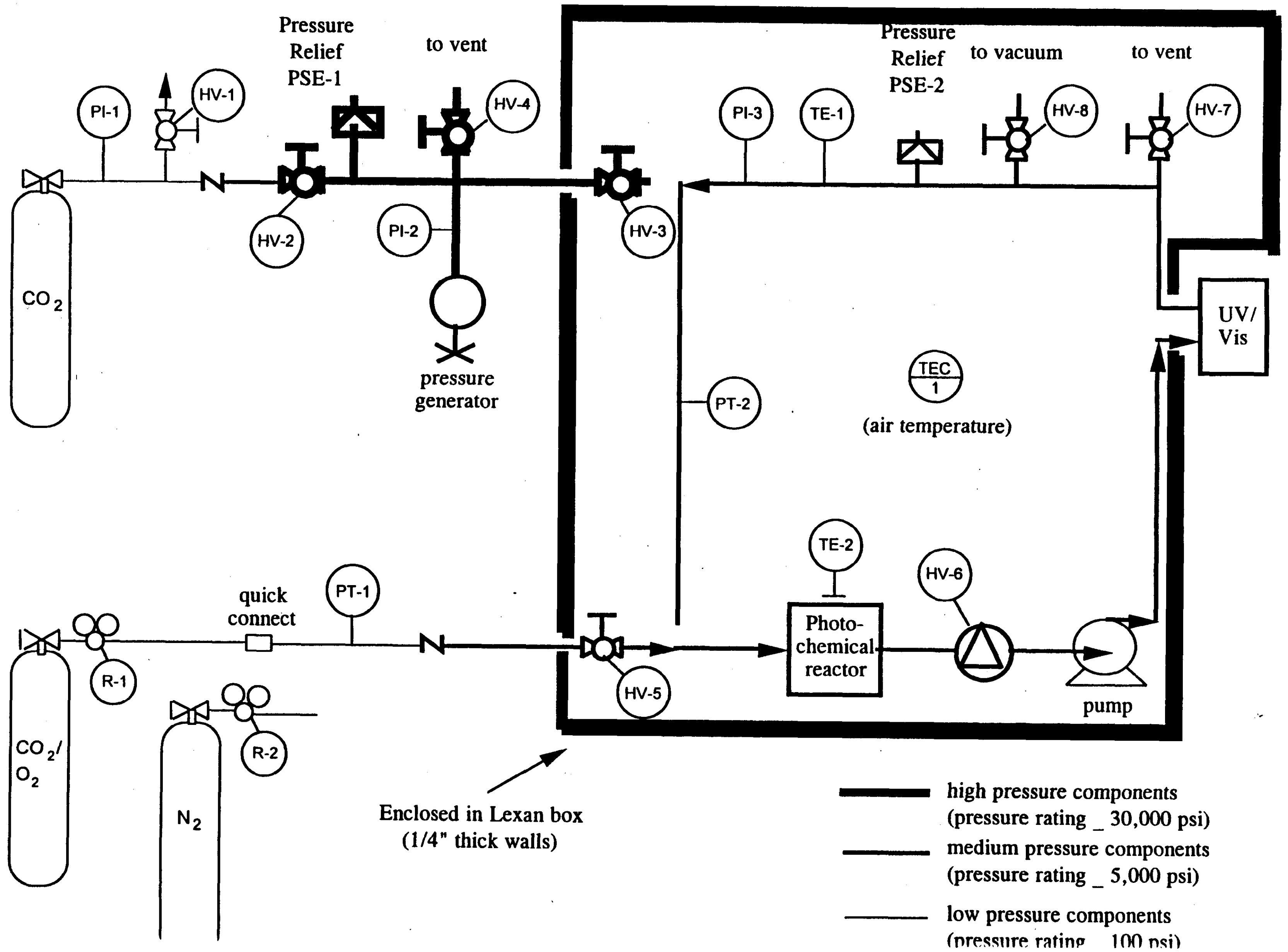
The as constructed layout for the system is shown in Figure 2 and the list of components is given in Table 1. Photographs of the system are shown in Figure 3. The system will be operated in a recirculating mode and has been pressure tested to 5000 psig. Variable amounts of oxidant, water, and target organic compound can be added via the gas inlet valve and multiport sample valve. Analysis will be done using on line UV-Visible spectroscopy. The on line UV cell, with sapphire windows was the last major component to be received (9-30-97). Irradiation for the photochemical experiments will be done using low pressure mercury or fluorescent black lights.

Coating of TiO_2 onto Al_2O_3 supports

Al_2O_3 supports were acquired in dimensions which will fit into the reaction cavity of the Jergusen Gage. Porosities of the supports are 10, 20, and 30 pores per inch. Two procedures of placing TiO_2 onto the supports were used. One procedure involved air brushing a TiO_2 solution onto the 10 pores per inch support while the second procedure involved soaking the 30 pores per inch support in a TiO_2 solution with sonication. In both cases: 1) a dry weight for the support was obtained prior to placement of TiO_2 onto the support and 2) application of a 10 wt% solution of TiO_2 in deionized water was repeated three times with drying between each application. Initial drying was accomplished with a heat gun followed by placement of the coated support in an approximately 120 °C oven overnight. The airbrush procedure resulted in 2.2 wt% TiO_2 being placed on the support after three applications while the procedure of soaking the support in the TiO_2 solution resulted in 1.7 wt%.

Irradiance through Jergusen Gage Glass

A UV-vis spectrum through the glass window from the Jergusen Gage photoreactor shows a minimum of 90% transmittance of light in the range of approximately 340 nm to 800 nm. Spectroradiometric analysis of the blacklight source through the glass of the Jergusen Gage showed no diminishment of light with the glass present. Indeed, some focusing effect appears to occur, resulting in the detection at 365 nm of a higher light flux, approximately 5.7 Wm^{-2}, at the midpoint of the glass vs light flux from that distance without the glass present, approximately 2.8 Wm^{-2}. Irradiance was also measured as a function of distance from the Jergusen Gage glass. The variation of ix-radiance with distance will be used in experiments that will assess the dependence of reaction rates on light flux.


Pressure Relief PSE-1
to vent
Pressure Relief PSE-2
to vacuum
to vent
PI-1
HV-1
HV-2
HV-4
PI-2
HV-3
PI-3
TE-1
HV-8
HV-7
CO2
pressure generator
PT-2
TEC 1
(air temperature)
UV/ Vis
quick connect
PT-1
TE-2
HV-6
R-1
R-2
HV-5
Photo-chemical reactor
pump
CO2/ O2
N2
Enclosed in Lexan box (1/4" thick walls)
high pressure components (pressure rating _ 30,000 psi)
medium pressure components (pressure rating _ 5,000 psi)
low pressure components (pressure rating 100 psi)

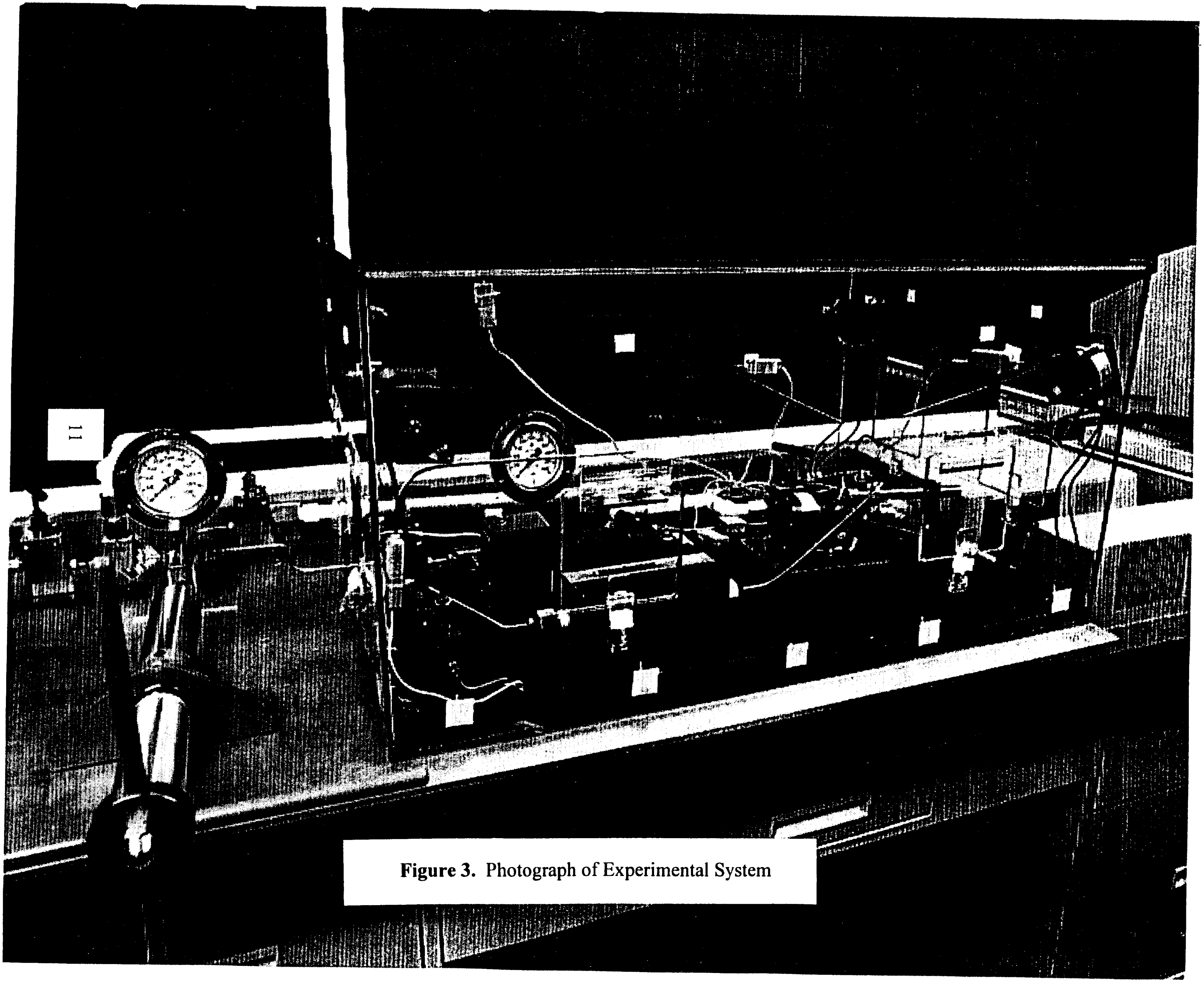


Figure 3. Photograph of Experimental System

Table. Parts List for Supercritical CO_2 Photocatalytic Oxidation System
(All wetted parts are composed of 316 stainless steel, unless otherwise noted).

Valves:

HV-1: Needle valve with 1/4" swagelok nut-type connectors. MAWP is 5,000 psi.
HV-2: Needle valve with 1/4" high pressure connections. Maximum Allowable Working Pressure (MAWP) = 30,000 psi. High Pressure Equipment Part # 30-11HF4.
HV-3 : Needle valve with 1/4" high pressure connections. Maximum Allowable Working Pressure (MAWP) = 30,000 psi. High Pressure Equipment Part # 30-11HF4-REG.
HV-4: Needle valve with 1/4" high pressure connections. Maximum Allowable Working Pressure (MAWP) = 30,000 psi. High Pressure Equipment Part # 30-11HF4-REG.
HV-4: Needle valve with 1/8" medium pressure ("taper seal" type) connections. Maximum Allowable Working Pressure (MAWP) = 15,000 psi. High Pressure Equipment Part # 15-11AF2.
HV-5: Needle valve with 1/8" medium pressure ("taper seal" type) connections. Maximum Allowable Working Pressure (MAWP) = 15,000 psi. High Pressure Equipment Part # 15-11AF2.
HV-6: Valco 10-port valve (Ed or Lee must supply details)?
HV-7: Needle valve with 1/8" medium pressure ("taper seal" type) adapter connections. Maximum Allowable Working Pressure (MAWP) = 30,000 psi for the valve body itself, and MAWP of the adapter connections is 15,000. High Pressure Equipment Part # 30-11HF4-REG.
HV-8: Needle valve with 1/8" medium pressure ("taper seal" type) connections. Maximum Allowable Working Pressure (MAWP) = 15,000 psi. High Pressure Equipment Part # 15-11AF2.

Pressure relief components:

PSE-1: Tee-type safety head with 3,500 psi rupture disk (+5%, -3% of specification pressure). Has 1/4" high pressure connections and MAWP of 60,000 psi. High Pressure Equipment Part #60-63HF4.
PSE-2: Tee-type safety head with 3,500 psi rupture disk (+5%, -3% of specification pressure). Has 1/8" medium pressure ("taper-seal" type) connections and MAWP of 15,000 psi. High Pressure Equipment Part #15-63AF2.

Pressure gauges:

PI-1 : 0-2,000 psi gauge with 1/4" NPT connection and MAWP of 2,000 psi.
PI-2: 0-5,000 psi gauge with 1/4" high pressure connection and MAWP of 5,000 psi. High Pressure Equipment Part #6PG30.
PI-3: 0-5,000 psi gauge with 1/4" high pressure connection and MAWP of 5,000 psi. High Pressure Equipment Part #6PG30.

Table Continued.

Pressure transducer:
PT-1: 1- 100 psig pressure transducer with current output (4/2OmA), Heise HPO series.
PT-2: 0-3, 000 psig pressure transducer with current output (4/2OmA) - Validyne P-2 **series.**

Pressure generator:
Hand pressure generator (pump) with capacity of 60cc/stroke and vernier indicator handle. MAWP is 5,000 psi. High Pressure Equipment Part #87-6-5.

Pump:
Recirculation pump manufactured by Micropump. Model Number 1805C, with Model 415 motor. MAWP is 5,000 psig and maximum operating temperature is 250 °C. Wetted parts are graphite and seals are Viton®. Typical pump conditions allow for a 10 to 20 psi pressure rise through the pump inlet to outlet. Flow rate range according to manufacturer's specifications is 50 to 1000 ml/min for $SCCO_2$.

Photochemical Reactor:
Jerguson gage. MAWP=5,000 psi. Borosilicate or quartz windows. Fluorescent or low pressure mercury lamps with output in 254-400 nm range depending on requirement. Catalyst supports - porous alumina frit from HiTech Ceramics or stainless steel screen.

UV/Vis
2 cm path length cell. Saphire windows. MAWP=5,000 psi. HP-8452A diode array spectrometer.

Regulators:
R- 1: Two-stage regulator with CGA-320 connector.
R-2: Two-stage regulator with CGA-580 connector.

Tubing and miscellaneous fittings:
Tubing and fittings connecting high pressure components have an MAWP of at least 30,000 psig.
Tubing and fittings connecting medium pressure components have an MAWP of at least 10,000 psig.
Tubing and fittings connecting low pressure components have an MAWP of at least 3,000 psig. However, the low pressure portion of the system is limited to a working pressure of 100 psi when pressure transmitter PT- 1 is connected.

Table Continued.

Heater:
Omega, OTF Series finned strip heaters, 300 and 600 W

Fans
Muffin fans for air circulation and thermal equilibration in the system enclosure.

Thermocouples:
TE-1 is a type-K chromel-alumel thermocouple located in the fluid stream in a tee-type adapter fitting. TE-2 is a type K chromel-alumel thermocouple (surface mounting) located on the outside of the photochemical reactor. TEC-1 is a type-K chromel-alumel thermocouple measuring the temperature of the air in the enclosed, temperature-controlled area. It is the thermocouple providing input to the temperature controller for the heater.

Instrumentation:

Temperature Controller: Omega CN7600 1/16 DIN autotune temperature controller connected to external solid-state relay for heater control. Output passes through High-limit switch described below.
High-Limit Temperature Switch: Omega CN375 High Limit temperature switch with manual reset. Output passes through mechanical (magnetic) contactor and controls power (on/off) to heater.
Thermocouple Panel Meter: Omega DP462 High Accuracy temperature indicator with six-channel input.
Pressure Transducer Panel Meters: Omega DP25 Panel Meter with built-in sensor excitation and scaleable analog output.

Data collection and storage: LabView, Version 4.1.

References

1. Roach. J. A. "Mixed waste focus area. Department of Energy complex needs report." U. S. Department of Energy, INEL-95/0555 (16 Nov. 1995): 33pp. plus addenda.

2. Spall, W. D. ; Williams, S. B. ; Laintz, K. E. "Precision cleaning with supercritical carbon dioxide for the elimination of organic solvents and the reduction of hazardous wastes." Los Alamos National Lab., NM. (1994): 16pp.

3. Williams, J. M. ; Bongianni, W. L. "Supercritical CO, cleaning for waste minimization." Los Alamos National Lab., NM. CONF-920623l-2 (1992): 4pp.

4. Hale, S. J. ; Haschke. J. M. ; Cox, L. E. "Supercritical fluid carbon dioxide cleaning of plutonium parts." Los Alamos National Lab., NM., CONF-9308150-2 (1993): 21pp.

5. Motyl, KM.: Thomas, R.L. (ed.); Morales, L.M. "Cleaning metal substrates using liquid/supercritical fluid carbon dioxide." Rockwell International Corp., Golden, CO (USA). Rocky Flats Plant, (25 Jan 1988): 33pp.

6. Adkins. C. Sandia National Laboratory, December 6, 1994, Presentation to International Fabricare Institute Representatives.

7. Brady, Basil O., Kao, Chien-Ping C., Dooley, Kerry M., Knopf, F. Carl, and Gambrell, Robert P. "Supercritical extraction of toxic organics from soils." *Ind. Eng. Chem. Res. 26* (1987): 261-268.

8. Hunter. G. B. "Extraction of pesticides from contaminated soil using supercritical carbon dioxide." National Fertilizer and Environmental Research Center, Muscle Shoals. AL. CONF-9102188-3 (1991): 14pp.

9. Lin, Y.; Wai, C.M.; Jean. F.M.; Brauer, R.D. "Supercritical fluid extraction of thorium and uranium ions from solid and liquid materials with fluorinated [beta]-diketones and tributyl phosphate." *Environ. Sci. Technol. 28* (1994): 1190-3.

10. Brauer, R.D., Carleson, T.E., Harrington, J.D., Jean, F., Jiang, H., Lin, Y., and Wai, C.M. "Selective chelation and extraction of lanthanides and actinides with supercritical fluids." EG and G Idaho. Inc., Idaho Falls. ID (Jan 1994): 28pp.

11. Kocher, B. S., Azza., F. O., and Lee. S. "Removal of residual chlorine from Indiana 5 coal by supercritical carbon dioxide extraction." *Fuel Science & Technology International.* 12 (1994): 303-313.

12. Anon. "Decontamination and decommissioning focus area. Technology summary." U. S. Department of Energy (June 1995): 63 pp.

13. Nozik, A. J. and Ronco, S. (Compilers). "Research opportunities in photochemical science Work shop proceedings." U. S. Department of Energy (5-8 Feb. 1996): 252 pp.

14. Savage, P. E., Gopalan, S., Mizan, T. I., Martino, C. J., and Brock, E. E. "Reactions at supercritical conditions: Applications and fundamentals." *AIChE J.* 41, (1995) 1723-78

15. Subramaniam, B. And McHugh. " Reactions in supercritical fluids - a review." *Ind. Eng. Chem. Process Des. Dev. 25 (1986):* 1-12.

16. Paulaitis, M. E., Krukonis, V. J., Kumik, R. T., and Reid, R. C. "Supercritical fluid extraction." *Rev. Chem. Eng.* 1 (1983): 179-250.

17. Hoyer, G. G. "Extraction with supercritical fluids: Why, how, and so what," *Chemtech.* (1985): 440-8.

18. Black, H. "Supercritical carbon dioxide: The greener solvent." *Environ. Sci. Technol.* (1996): 124A-127A.

19. Kiran, E. and Levelt Sangers, J. M. H. (Eds.). *Supercritical Fluids - Fundamentals for Application.* Dordrecht: Kluwer Academic Publishers, 1991,789 pp.

20. Williams, D. F. "Extraction with supercritical gases." *Chem. Eng. Sci.* 34 (1981): 1769-8

21. Levy, J. M. Storozynsky, E. and Ashraf-Khorassani, M. "Use of modifiers in supercritical fluid extraction." *Supercritical Fluid Technology - Theoretical and Applied Approaches to Analytical Chemistry,* eds. Bright, F. V. And McNally, M. E. 336-61, American Chemical Society, Washington, DC, 1992.

22. A. Fujishima and K. Honda, Nature, 37 (1972) 238.

23. Blake, Daniel M. *Bibliography of Work on the Photocatalytic Removal of Hazardous Compounds From Water and Air,* NREL/TP-430-6084. NREL, Golden, CO, 1994. DE94006906 (663 refs.).

24. Blake, Daniel M. *Bibliography of Work on the Photocatalytic Removal of Hazardous Compounds from Water and Air Update Number I, to June, 1995,* NREL/TP-473-20300 NREL, Golden, CO, 1995. UC1404 (574 refs.).

25. Blake, Daniel M. *Bibliography of Work on the Photocatalytic Removal of Hazardous Compounds from Water and Air Update Number 2, to October, 1996,* NREL/TP-430-22197. NREL, Golden, CO, 1995. (518 refs.).

26. Nozik, A. J. "Photoelectrochemistry: Applications to solar energy conversion." *Ann. Rev. Phys. Chem. 29, Annual* Reviews, Inc. (1978): 189-222.

27. Henglein, Arnim. “Small-Particle Research: Physicochemical Properties of Extremely Small Colloidal Metal and Semiconductor Particles. ” *Chem. Rev. 89,* no. 8 (1989): 1861-73.

28. Lewis, Nathan S. “Mechanistic Studies of Light-Induced Charge Separation At Semiconductor/Liquid Interfaces. ” *Acc. Chem. Res. 23 (1990): 176-83.*

29. Kamat, Prashant V. “Interfacial Charge Transfer Processes in Colloidal Semiconductor Systems.” *Prog. Reaction Kinetics* 19 (1994): 277-316.

30. Augustynski, Jan. “Aspects of Photo-Electrochemical and Surface Behavior of Titanium(IV) Oxide.” 61 pp. Structure and Bonding, 69. Berlin, Germany: Springer Verlag, 1988.

31. Bard, Allen J. “Photoelectrochemistry and Heterogeneous Photocatalysis At Semiconductors.” *J. Photochem.* 10 (1979): 59-75.

32. Mills, Andrew and Stephen Le Hunte, “An Overview of Semiconductor Photocatalysis.” J. *Photochem. and Photobiol. A: Chem.,* 108 (1997): l-35.

33. Ollis, David F., Ezio Pelizzetti, and Nick Serpone. “Photocatalyzed Destruction of Water Contaminants.” *Environ. Sci. Technol. 25,* no. 9 (1991): 1522-29.

34. Kalyanasundaram, K. “ Semiconductor Particulate Systems for Photocatalysis and Photosynthesis: an Overview. ” *Energy Resources Through Photochemistry and Catalysis,* ed. Michael Gratzel, 217-60. New York: Academic Press, 1983.

35. Hoffmann, Michael R., Scot T. Martin, Wonyong Choi, and Detlef W. Bahnemann. “Environmental Applications of Semiconductor Photocatalysis.” *Chem. Rev. 95,* no. 1 (1995): 69-96.

36. Matthews, R. W. “Environment: Photochemical and Photocatalytic Processes. Degradation of Organic Compounds. ” *Photochemical Conversion and Storage of Solar Energy, Proceedings of the 8th International Conference on Photochemical Conversion and Storage of Solar Energy,* eds. E. Pelizzetti, and M. Schiavello, 427-3, Dordrecht: Kluwer Academic Publishers. 1991.

37. Fox. M. A.. and Dulay, M. T. “Heterogeneous photocatalysis.” *Chem. Rev. 93* (1993): 341-57.

38. Kamat. P. V. “Photochemistry on nonreactive and reactive (semiconductor) surfaces.” *Chem. Rev. 93* (1993): 267-300.

39. Linsebigler. Amy L., Guangquan Lu. and John T. Yates, Jr. “Photocatalysis on TiO_2 Surfaces: Principles. Mechanisms. and Selected Results.” *Chem. Rev. 95,* no. 3 (1995):

735-58.

40. L. Wang and Y. Li, “Semiconductor Particles Mediated Photocatalysis for Organic Synthesis% *Nanocrystalline Semiconductor Materials,* P. Kamat and D. Meisel, eds., Elsevier, 1996: in press.

41. Hagfeldt, A. and Gratzel, M. “Light-induced redox reactions in nanocrystalline systems.” *Chem. Rev. 95 (1995): 49-68.*

42. Anpo, M., Aikawa, N., and Kubokawa, Y. “Photocatalytic hydrogenation of alkynes and alkenes with water over TiO_2. Pt-loading effect on the primary process.” *J. Phys. Chem.* 88 (1984): 3998-4000.

43. Lin, Lufei, and Robert R. Kuntz. “Competative Photocatalytic Reduction of H+ and C_2H_2 b $Mo_2S_4(S_2C_2H_4)_2(2-)$ on Colloidal TiO_2." *J Photochem. Photobiol. A: Chem.* 66 (1992): 245-51.

44. Liu, Bi-Jin, Tsukasa Torimoto, Hajime Matsumoto, and Hiroshi Yoneyama. “Effect of Solvents on Photocatalytic Reduction of Carbon Dioxide Using TiO_2 Nanocrystal Photocatalyst Imbedded in SiO_2 Matrices.” *J. Photochem. and Photobiol. A: Chem.* 10: (1997): 187-192.

45. Anpo, M., and Chiba, K. “Photocatalytic reduction of carbon dioxide on anchored titanium oxide catalysts.” *.J Mol. Catal. 74*, no. l-3 (1992): 207-12.

46. Hirano, Katsuhiko, Kohei Inoue, and Tomomi Yatsu. “Photocatalyzed Reduction of CO, in Aqueous TiO_2 Suspension Mixed With Copper Powder.” *J. Photochem. and Photobiol. A: Chem. 64* (1992): 255-8.

47. Inoue, Hiroshi, Takehiko Matsuyama, Bi Jin Liu, Takao Sakata, Hirotaro Mori, and Hiroshi Yoneyama. “Photocatalytic Activities of TiO_2 Microcrystals Prepared in SiO2 Matrixes Using a Sol-Gel Method for Carbon Dioxide Reduction.” *Chem. Lett.,* no. 3 (1994): 653-6.

48. Ishitani, Osamu, Chieko Inoue, Yuji Suzuki, and Takashi Ibusuki. “Photocatalytic Reduction of Carbon Dioxide to Methane and Acetic Acid by an Aqueous Suspension of Metal-Deposited Titania.” J. *Photochem. Photobiol., A 72,* no. 3 (1993): 269-71.

49. Matsumoto, Yasumichi, Michio Obata, and Jukishi Hombo. “Photocatalytic Reduction of Carbon Dioxide on p-Type $CaFe_2O_4$ Powder.” *J. Phys. Chem. 98,* no. 11 (1994): 2950-51.

50. Solymosi, Frigyes, and Imre Tombacz. “Photocatalytic Reaction of $H_2O + CO_2$ Over Pure and Doped Rh/TiO_2." *Catal. Lett. 27,* no. l-2 (1994): 61-5.

51. Taqui Khan, M. M., D. Chatterjee, A. Hussain, and M. A. Moiz. “Synthesis and Characteristics of Mixed Ligand Ru(III) Complexes With EDTA-Polypyridyl, and $Pt/TiO_2/RuO_2$ Semiconductor Particulate System Modified by the Complexes.” *J. Photochem. Photobiol., A 76,* no. l-2 (1993): 97-101.

52. Anpo, M., and Chiba, K. “Photocatalytic reduction of carbon dioxide on anchored titanium oxide catalysts.” *J Mol. Catal.* 74, no. l-3 (1992): 207-12.

53. Inoue, T., Fujishima, A., Konishi, S., and Honda, K. “Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders.” *Nature 277* no. 5698, (1979): 637-8.

54. Hirano, K., Inoue, K., and Yatsu, T. “Photocatalyzed reduction of carbon dioxide in aqueous titania suspension mixed with copper powder.” *J Photochem. Photobiol., A 64,* no. 2 (1992): 255-8.

55. Ibusuki. T., Kutsuna, S., Takeuchi, K., and Ishitani, O. “Chemical conversion of solar photoenergy - photoassisted catalysis for carbon dioxide fixation and pollutants treatment.” IEA Conf. on Tech. Responses to Global Env. Challenges. Kyoto, Japan, 6 November 1991.

56. Ishitani, O., Inoue, C., Suzuki, Y., and Ibusuki, T. “Photocatalytic reduction of carbon dioxide to methane and acetic acid by an aqueous suspension of metal-deposited TiO_2." *J. Photochem. Photobiol. A: Chem. 72* (1993): 269-71.

57. Khalil. L. B., Youssef, N. S., Rophael, M. W., and Moawad. M. M. “Reduction of aqueous carbonate photocatalyzed by treated semiconductors.” *J Chem. Technol. Biotechnol. 55,* no. 4 (1992): 391-6.

58. Rophael, M. W., Khalil. L. B., and Moawad, M. M. “The reduction of aqueous carbonate to methanol, photocatalyzed by titanium dioxide phthalocyanine.” *Vacuum* 41, no. l-3 (1990): 143-6.

59. Tanaka. K., and White, J. M. “Characterization of species adsorbed on oxidized and reduced anatase.” *J. Phys. Chem.* 86 (1982): 4708-14.

60. Kuwabata, S., Uchida, H., Ogawa, A., Hirao, S., and Yoneyama. H. “Selective photoreduction of carbon dioxide to methanol on titanium dioxide photocatalysts in propylene carbonate solution.” *J. Chem. Soc., Chem. Commun. (* 1995) 829-30.

61. Serpone, N., Borgarello, E., Barbeni, M., Pelizzetti, E., Pichat, P., Hermann, J. M., and Fox. M. A. “Photochemical reduction of gold(III) on semiconductor dispersions of titanium dioxide in the presence of cyanide ions: disposal of cyanide by treatment with hydrogen peroxide.” *J Photochem.* 36, no. 3 (1987): 373-88.

62. Prairie, M. R., Evans, L. R., Stange, B. M., and Martinez, S. L. “An investigation of TiO_2 photocatalysis for the treatment of water contaminated with metals and organic chemicals.” *Environ. Sci. Technol. 27,* no. 9 (1993): 1776-82.

63. Foster, N. S., Brown, G. N., Noble, R. D., and Koval, C. A. “Use of Titanium Dioxide Photocatalysis in the Treatment of Spent Electroless Copper Plating Baths. ” *Photocatalytic Purification and Treatment of* Water and Air, eds. David F. Ollis, and Hussain Al-Ekabi, 365-73, Trace Metals and the Environment, ed. Jerome O. Nriagu, New York, NY: Elsevier, 1994.

64. Mahdavi, F., T. Bruton, and Y. Li, “Photoinduced Reduction of Nitro Compounds on Semiconductors,” *J. Org. Chem. 58,744* (1993).

65. Blake, D. M., Boulter, J. E., Wolfrum, E. J., Showalter, S. K., Prairie, M. R., and Hess, T. “Photocatalytic oxidation and reduction of trinitrotoluene.” Manuscript in Preparation, 1996.

66. Davies, J. A., Boucher, D. A., and Edwards, J. G. “The Question of Artificial Photosynthesis of Ammonia on Heterogeneous Catalysts,” *Adv. Photochem.* 19 (1995): 235-310.

67. Cunningham, J. “Radiation and photoeffects at gas-solid interfaces.” *Simple Processes at the the Gas-Solid Interface,* 27l-427. Comprehensive Chemical Kinetics, eds. Bamford C. H., Tipper, C. F. H., and Compton, R. G. Vol. 19, New York: Elsevier, 1984.

68. Shapira, Y., Cox, S. M., and Lichtman, D. “Chemisorption, photodesorption and conductivity measurements on ZnO surfaces.” *Surface Science, 54 (1976): 43-59.*

69. Ollis, David F., Ezio Pelizzetti, and Nick Serpone. “Heterogeneous Photocatalysis in the Environment: Application to Water Purification.” *Photocatalysis Fundamentals and Applications,* eds. Nick Serpone and Ezio Pelizzetti, 603-37. New York: John Wiley & sons, 1989.

70. Blake, D. M., H. F. Link, and K. Eber. “Solar Photocatalytic Detoxification of Water.“, 16’ 210. Advances in Solar Energy, Karl W. Boer, 7. Boulder, CO: American Solar Energy Society, Inc., 1992.

71. Parent, Yves, Daniel M. Blake, Kim Magrini-Bair, Carol Lyons, Craig Turchi, Andrew Wa, Edward Wolfrum, and Michael Prairie. “Solar Photocatalytic Processes for the Purification of Water: State of Development and Barriers to Commercialization.” *Solar Energy,* In Press (1996).

72. Bickley, R. I. “Heterogeneous Photo-Catalysis.“, *308-2. Catalysis, A Specialist Periodical Report,* eds. G. C. Bond, and G. Webb, 5. London: The Chemical Society, 1982.

73. Formenti, M., and S. J. Teichner. “Heterogeneous Photo-Catalysis.” 87-106. Catalysis, *A Specialist Periodical Report,* eds. C. Kemball and D. A. Dowden, 2. London: The Chemical Society, 1978.

74. Formenti, M., Juillet, F., and Teichner, S. J. “Photocatalytic oxidation mechanism of alkanes over titanium dioxide. I. Kinetic study.” *Bull. Soc. Chim. Fr.* 7-8, Pt. 1 (1976): 1031-6.

75. Dibble, L. A., and Raupp, G. B. “Kinetics of the gas-solid heterogeneous photocatalytic oxidation of trichloroethylene by near *W* illuminated titanium dioxide.” *Catal. Lett. 4,* no. 4-6 (1990): 345-54.

76. Rabago, R., Turchi, C. T., and Wolfrum E. J. “Photocatalytic treatment of organic emissions from semiconductor processing lines.” EPRI Conference, March, 1996, San Francisco, CA.

77. Obee, Timothy N.. and Robert T. Brown. "TiO_2 Photocatalysis for Indoor Air Applications: Effects of humidity and Trace Contaminant Levels on the Oxidation Rates of Formaldehyde, Toluene, and 1,3-Butadiene.” *Environ. Sci. Technol. 29,* no. 5 (1995): 1223-31.

78. 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 And Waste Management Assoc.,* In Press (1996).

79. Serpone, Nick, Rita Terzian, Darren Lawless, Pierre Kennepohl, and Genevieve Sauve. “On the Usage of Turnover Numbers and Quantum Yields in Heterogeneous Photocatalysis.” *J. Photochem. Photobiol., A 73,* no. 1 (1993): 11-16,

80. Palmisano, Leonardo, Vincenzo Augugliaro. Renzo Campostrini, and Mario Schiavello. “A Proposal for the Quantitative Assessment of Heterogeneous Photocatalytic Processes.” *J. Catal.* 143, no. 1 (1993): 149-54.

81. Augugliaro, V., M. Schiavello, and L. Palmisano. “Rate of Photoabsorption and Turnover Number: Two Parameters for the Comparison of Heterogeneous Photocatalytic Systems in a Quantitative Way.” *Coord. Chem. Rev.* 125, no. l-2 (1993): 173-81.

82. Gerischer, H. “Conditions for an Efficient Photocatalytic Activity of Titanium Dioxide Particles.” *Photocatalytic Purification and Treatment of Water and Air,* eds. David F. Ollis and Hussain Al-Ekabi. 1 - 17. Trace Metals and the Environment, ed. Jerome O. Nriagu. New York, NY: Elsevier, 1994.

83. Gerischer. H., and Heller, A. “The role of oxygen in the photooxidation of organic molecules on semiconductor particles.” *J Phys. Chem. 95* (1991): 5261-67.

84. Matthews, R. W. "Photooxidation of organic impurities in water using thin films of titanium dioxide." J. *Phys. Chem.* 91, no. 12 (1987): 3328-33.

85. Jackson, N. B., C. M. Wang, Z. Luo, J. Schwitzgebel, J. Norrell, J. R. Brock, and A. Heller "Attachment of TiO_2 Powders to Hollow Glass Microbeads: Activity of the TiO_2 Coated Beads to the Photoassisted Oxidation of Ethanol to Acetaldehyde." *J. Electrochem. Soc.* 138 (1991): 3660-4.

86. Sugimura, Hiroyuki, Tatsuya Uchida, Nobuo Shimo, Noboru Kitamura, and Hiroshi Masuhara. "Scanning Tunneling Microscopy, Spectroscopy of Surface Oxide on Titanium Photoexcitation Effect and Nanoanodization." *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A 252-253* (1994): 497-506.

87. Yazawa, K., Kamogawa, H., and Morisaki, H. "Semiconducting titanium dioxide films for photoelectrolysis of water." *Int. J. Hydrogen Energy 4,* no. 3 (1979): 205-9.

88. Sanchez, Beningo, Manuel Romero, Alfonso Vidal, Begona Fabrellas, Jesus Blanco, and Pedro Avila. "Destruction of Toluene and Xylene Using Concentrated Solar Photons. " *Solar Engineering* 1994, eds. David E. Klett, Roy E. Hogan, and Tadayoshi Tanaka, 123-9, 1994.

89. Aguado, M. A., M. A. Anderson, and C. G. Hill Jr. "Influence of Light Intensity and Membrane Properties on the Photocatalytic Degradation of Formic Acid Over TiO_2 Ceramic Membranes." *J. Mol. Catal. 89(* l-2) (1994): 165-78.

90. Ibusuki, Takashi, and Koji Takeuchi. "Removal of Low Concentration Nitrogen Oxides Through Photoassisted Heterogeneous Catalysis." *J. Mol. Catal. 88,* no. 1 (1994): 93- 10

91: Uchida, Hiroyuki, Shinobu Katoh, and Masahiro Watanabe. "Photocatalytic Decomposition of Trichlorobenzene Using TiO_2 Supported on Nickel-Poly (Tetrafluoroethylene) Composite Plate." *Chem. Lett.,* no. 4 (1995): 261.

92. Matthews, R. W. "Kinetics of photocatalytic oxidation of organic solutes over titanium dioxide." *J. Catal.* 111 (1988): 264-2.

93. Wold, A. "Photocatalytic properties of titanium dioxide (TiO_2)." *Chem. Mater. 5,* no. 3 (1993): 280-3.

94. Bideau, M. Claudel, B., Dubien, C., Faure, L. and Kazouan, H. "On the 'immobilization' of titanium dioxide in the photocatalytic oxidation of spent waters." *J Photochem. and Photobiol. A: Chemistry, 91 (1995): 137-44.*

95. Fernandez, A., Lassaletta, G., Jimenez, V. M., Justo, A., Gonzalez-Elipe, A. R., Herrmann, J.-M., Tahiri, H., and Ait-Ichou, Y. "Preparation and characterization of TiO_2 photocatalysts supported on various rigid supports (glass, quartz, and stainless steel).

Comparative studies of photocatalytic activity in water purification." *Applied Catal. B: Environ. 7* (1995): 49-63.

96. Goswami. D. "Engineering of Solar Photocatalytic Detoxification and Disinfection Processes." *Advances in Solar Energy,* 10, ed. Boer, K. W. ASES, Boulder, CO (1995)

97. Yue, P. L., Khan. F.. and Rizzuti, L. "Photocatalytic ammonia synthesis in fluidised bed reactor." *Chem. Eng. Sci. 38,* no. 11 (1983): 1893-1900.

98. Marinangeli. R. E., and D. F. Ollis. "Photo-Assisted Heterogeneous Catalysis With Optical Fibers. Part III. Photoelectrodes." *AIChEJ. 28,* no. 6 (1982): 945-55.

99. Marinangeli, R. E.. and D. F. Ollis. "Photo-Assisted Heterogeneous Catalysis With Optical Fibers. II. Nonisothermal Single Fiber and Fiber Bundle." *AIChE J 26,* no. 6 (1980): 1000-8.

Appendix

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Safe Operating Procedure for Supercritical Fluid Photocatalytic Reactor in Laboratory 16/190

National Renewable Energy Laboratory
Golden, Colorado 80401

This report details the safe operating procedures that will be followed in conducting experiment using the supercritical fluid photocatalytic reactor (SCFPR) assembly located in Laboratory 16/190 at the National Renewable Energy Laboratory. This reactor will be used to conduct fundamental investigations of heterogeneous photocatalysis in supercritical carbon dioxide (scCO_2). Supercritical carbon dioxide is a phase of carbon dioxide which exists above 31.3 and 1055.6 psi of pressure. It is chemically inert, non-toxic, nonflammable, noncorrosive, as an inexpensive solvent currently used for continuous cleaning and extraction of waste material The photocatalytic decomposition of hazardous organic pollutants uses a non-toxic photocatalyst (TiO_2) and near-ultraviolet light to convert the reactant material to innocuous products, mainly carbon dioxide (CO,) and water.

In case of emergency, the heater and the circulation pump will be turned off, if the g cyclinders are open they will be closed, and the system will be vented.

Debra Lee Bryant 9/23/97
(1) Debra Lee Bryant, Author Date

9/23/97
(2) Dan Blake, Team Leader Date

/ /
(3) Date

Signature numbers indicate sequence of review and concurrence. After all signatures are obtained, submit a final copy of the SOP to the Safety and Security Office.

Safe Operating Procedure
Supercritical Fluid Photocatalytic Reactor Assembly
Laboratory 16/190

1.0 Introduction

Activity Location and Description The supercritical fluid photocatalytic reactor (SCFPR), located in Building 16/190, is designed to achieve high conversions of organic pollutants to CO_2 and water by photocatalytic oxidation with near-ultraviolet (near-UV) illumination in the presence of TiO_2 catalyst. The organics and a small amount of deionized water will be solvated by scCO_2 which is an attractive supercritical fluid (SCF) due to the mild conditions needed for phase transition to the supercritical state, 31.3°C and 1055.6 psi of pressure. These will be the general operating conditions for the reactor. A hand pressure generator will be used to achieve the desired pressure. Temperature and pressure will be varied during this research, with the maximum operating temperature and pressure to be approximately 50 °C and 3000 psi.

Cleaning and extraction using scCO_2 can be applied to the solution of a wide range of environmental and pollution prevention problems in the DOE complex ranging from cleaning contaminated soil to cleaning components constructed from plutonium. Research into the use of scCO_2 for waste extraction is intensive. The rationale for use of scCO_2 are based on the benign nature, availability and low cost, attractive solvent properties, and energy efficient separation of the extracted solute from the solvent by moderate temperature or pressure changes.

The laboratory experiments will normally be run using near-UV illumination, a semiconductor photocatalyst (primarily Degussa P25 TiO_2), and ppm (mg/L) levels of the organic pollutants and deionized water solvated in scCO_2 in the SCFPR. If desired, a stoichiometric amount of $O_{2(g)}$ can be added in the form of a mixture of $O_{2(g)}$ and $CO_{2(g)}$, approximately 1:9 $O_{2(g)}$:$CO_{2(g)}$, prior to pressurizing the system. A recirculating system will be used. Visual monitoring will be possible through a tempered borosilicate glass window, part of a commercially manufactured Jerguson gage. Detection of unreacted organics will be accomplished by UV-Vis spectroscopy.

Expected Results SCFs have diffusion coefficients l-2 orders of magnitude higher than liquid such that increased oxidation rates of the pollutants may occur. Catalyst deactivation, a problem in water, may potentially be avoided by adjusting the temperature and pressure of the SCFs volatilize and oxidize the absorbed compounds.

Process Onerations Information The SCFPR is designed to be operated for several hours duration. In some cases, experiments will run longer in order to establish the time of total organic oxidation.

Organization Involved The SCFPR is operated by personnel from the Center for Renewable Chemical Technologies and Materials (4300).

2.0 Description of Safety and Health Hazards and Controls

Titanium Dioxide TiO_2 is a nonhazardous, fine powder. When handling TiO_2, drafts should be avoided and gloves should be worn to prevent skin irritation. Use of a ventilation hood is not recommended because the draft will scatter the TiO_2. The TiO_2 will be placed as an aqueous suspension onto an inert alumina dioxide support and undergo solvent evaporation. The TiO_2/support will be placed within the visible portion of the Jerguson gage.

Hazardous Materials

1. Toxins/Reproductive Hazards/Tumorigens/Carcinogens Benzene is rated with IARC, NTP OSHA, and ACGIH as a known human carcinogen. It is harmful if swallowed, inhaled, or absorbed through the skin. Vapor is irritating to the eyes, mucous membranes, and upper respiratory tract. It is a skin irritant and a combustible. Gloves which have been rated to protect against benzene exposure will be used. Transfer of benzene in μL aliquots to a μ L syringe will take place in a ventilation hood. Secondary spill trays will be used. Use near flames, heat, or sparks will be avoided.

   Benzene will be introduced into the $scCO_2$ phase by sample loops in μL quantities with the resulting maximum concentration of benzene in the $scCO_2$ phase to be approximately 2C ppm. The flow of fluids through the SCFPR will be closed loop. When a run is completed benzene will ideally have been converted to CO* and water. Final concentration, if any is detectable, will be determined by UV-Vis spectroscopy. If no benzene concentration is detected, the $scCO_2$ will be vented into the ventilation hood. If benzene is detected, the length of the reaction can be increased. Condensation of the organic pollutant after temperature and pressure reduction of the $scCO_2$ can be accomplished as well, with the subsequent venting off of the CO,,,.

2. Other Potentially Hazardous Compounds Organics of interest which may be used following the same procedures sited above include ethanol, 1 -propanol, acetone, and others to be determined. These are generally combustibles and skin irritants. Transfer of the μ L quantities will take place in a ventilation hood. Exposure to flame, heat, or sparks will be avoided. Gloves rated for these materials will be worn.

High Pressure The major components of the SCFPR are the micropump, the Valco valve, the UV cell, the Jerguson gage, and the hand pressure generator. All of the above, with the exception of the hand pressure generator, will be operated within a Lexan enclosure fastened to an aluminum 5/8" base plate. All reactor components, including fittings and valves, to be subjected to supercritical temperatures and pressures will be rated for an operating pressure of at least 5,000 psi. It should be noted that lines rated for 5,000 psi working pressure contain a safety factor of four (actual sustainable pressure is four times the rated pressure). Pressure testing will be performed at 5,000 psi. Maximum allowable pressure after pressure testing has been accomplished will be 3500 psi. The safety heads installed in the feed line will have rupture disks which rupture in the pressure range of 3500 ± 210psi for actual operation and 5000 ± 300 psi for pressure testing. A ruptured disk is completely contained in a safety head assembly and vented through a line to a ventilation hood and does not pose a safety hazard. The maximum operating pressure for the SCFPR will be 3000 psi. Safe operating procedures require that high-pressure fittings never be tightened while the system is pressurized.

Cryogenic Fluids/Apparatus Adequate ventilation will be available so that an accidental release of the entire contents of the cryogenic fluid, CO,, will not cause an oxygen deficient atmosphere. Only properly trained and authorized personnel will be allowed to handle the cryogenic fluid. When handling liquid CO_2, proper personal protective equipment (PPE) will be used, including gloves for cryogenic fluids.

UV Radiation The UV lamp for this reactor supplies a relatively low flux level of blacklight illumination (330-400 nm), equivalent to l-3 times the near-W in sunlight. The lamp is within the Lexan enclosure which absorbs light of wavelengths below 400 nm.

Exposure to any *W* radiation should be minimized since chronic *W* exposure increases the risk of skin cancer. Keratoconjunctivitis (welder’s flash) results from acute eye exposure to UV light with development of cataracts reported in animal studies using light wavelengths between 295-**320 nm.**

Ultraviolet eye protection (compliance with ANSI-287. 1-1989) will be worn at all times during *W* light exposure due to the operation of the SCFPR lamps. The lamps, however, should not be operated without the Lexan enclosure in place and closed. As with any *W* source. looking directly at the lamp output should be avoided Skin contact with the UV radiation should be avoided by the use of appropriate clothes (e. g . , long sleeves, lab coat, etc.).

3.0 Description of Environmental Hazards and Controls

Hazardous Waste Organic pollutants, as well as a small amount of deionized water, will be injected into the sample loop of the SCFPR in μL aliquots. Ideally the pollutants will be oxidized to CO, and water by the TiO_2 catalyst in the presence of UV radiation. Due to the inert character of the $scCO_2$ solvent and the low levels (approximately 200 ppm) of organic pollutants initially present, no hazardous waste from the reactor is anticipated following oxidation. If unreacted waste does occur, isolation from the $scCO_2$ is possible and will result in very minimal waste generation. Liquid products, not necessarily waste, may be used to support this research but quantities are expected to be minimal.

Waste Minimization Organic pollutants will be oxidized to CO, and water. In the case organic pollutant levels remaining above the toxic level in $scCO_2$, the system can be run longer or temperature and pressure can be reduced to allow condensation of the organics followed by venting of the $CO_{2(g)}$ into a ventilation hood. Isolation of the small quantities of unreactive organics could therefore be achieved.

Decommissioning Potential residual contamination of the SCFPR will be minimal due to the initial organic concentration (less than 200 ppm) prior to oxidation and the determination of the complete oxidation of the benzene by UV-Vis spectroscopy prior to venting. If detectable concentrations of benzene occur following reactions, further oxidation and/or isolation from $scCO_2$ will be performed. Inert gas or air flow may also be used between experiments.

4.0 Assembly/Operational Procedures

Preliminaries Engineered safety controls for the SCFPR are detailed under Section 2 of the document.

Assembly The major safety concerns during assembly of the SCFPR focus on the high pressure fittings and equipment. All parts and high pressure equipment must be safely and securely fastened in accordance with manufacturer's instruction to avoid the occurrence of part rupture once the system is pressurized.

Startup Figure 1 (Section 8.0 following this text) shows a labeled diagram of the system Before the pressurization process is begun, all valves will be closed. A small amount of $CO_{2(g)}/O_{2(g)}$ can be introduced into the reaction loop, if desired, as a mixture of approximately 1:9 $O_{2(g)}:CO_{2(g)}$, by opening tank valve R-l and valve HV-5 to allow circulation through continuous flow system of the SCFPR. The valves HV-5 and R-l will then be closed. The hand pressure generator will be opened to the appropriate level necessary for pressurizing the system to the desired degree. The CO, tank and valve HV-2 will be opened to allow this area to fill with CO,. Valve HV-2 will then be closed. The valve between the hand pressure generator and the continuous flow system, HV-3, will be opened and the hand pressure generator will be used to achieve the desired pressure for the SCF. Valve HV-3 will then be closed.

In the case where adequate pressure is not achieved by following the above procedure, the hand pressure generator will be reopened following closure of valve HV-3. The above procedure opening valve HV-2 and allowing the area to fill with CO,,, will be repeated. Valve HV-2 will then be closed. If the pressure reading on pressure gage Pl-2 is greater than the pressure reading on gage Pl-3, valve HV-3 will be opened. If the pressure reading on pressure gage Pl-2 is less than the pressure reading on pressure gage Pi-3, the hand pressure generator will be used to achieve a higher pressure reading on Pl-2 prior to opening valve HV-3. The hand pressure generator will again be used to achieve the desired pressure for the SCF. Valve HV-3 will then be closed.

Operation Safe operating procedures require that high-pressure fittings never be tightened while the system is pressurized. On-line measurement by UV-Vis spectroscopy will be used determine the extent of the oxidation of the pollutants. Pressure and temperature will be monitored by digital readouts and in-line transducers.

Sample injection will be accomplished by injecting the organics and water through sample loops into the continuous flow system via a manufactured Valco valve (HV-6). Flow can be rerouted during the placement of the sample in the valve.

Shutdown On-line measurement by UV-Vis spectroscopy will confirm reaction completion. Pressure will be relieved by slowly venting all lines into the ventilation hood.

5.0 Personnel Training

All authorized personnel will read and sign this safe operating procedure and will be instructed in the operation of the test apparatus and laboratory safety features. In particular training must include the special safety requirements of high pressure work. Persons wishing to be authorized for SCFPR operation must obtain this training from the existing operators. All safety-related NREL training shall be completed and current. Copies of the NREL Chemical Hygiene Plan are located in the laboratory.

6.0 Emergency Information

Chemical Contact

1. Eye Contact Flush eyes immediately with running water for 15 minutes. Immediate flushing after exposure is necessary to avoid permanent injury. After flushing seek medical help. An emergency eyewash station is located in 190 by the sink on the right as you enter the nearest door to the SCFPR. All personnel will be familiar with the use of this equipment.

2. Skin Contact Flush exposed areas immediately with running water. Remove contaminated clothing while flushing. In serious exposures, prolong washing until medical help arrives. An emergency shower is located at both ends of the hall as you exit 190 by the door nearest to the SCFPR.

3. Ingestion Call ext. 1234 immediately. Do not give anything by mouth or induce vomiting unless instructed by medical personnel. A telephone is located in 190 by the nearest exit to the SCFPR.

4. Inhalation Remove victim to fresh air. Administer artificial respiration if victim is not breathing. Call ext. 1234 immediately.

Injuries If a serious injury has occurred, another operator should immediately begin the appropriate first aid, including CPR if necessary. If a third person is present, that individual should immediately call ext. 1234 to report the emergency (otherwise, the first individual should call as soon as he/she is able). Be sure to stay on the phone until all questions are answered.

A first aid kit is located in the hall as you exit to the right out of 190 from the nearest door in the SCFPR. Any person sustaining an injury should administer the appropriate first aid immediately to avoid worsening the injury by contamination or other means.

Proper reporting of injuries must be followed as specified by Policy 4-11 of the NRP Environment, Safety, and Health Policies and Procedures Manual.

Evacuation The nearest fire alarm should be activated. Evacuation of Building 16 will proceed following the established evacuation procedure. All personnel are to report to the designated meeting areas outside the building. From a safe location, ext. 1234 must be called to report details of the emergency and initiate proper response procedures.

Fire In the case of fire, the nearest fire alarm which is removed from the fire should be activated. From a safe location dial ext. 1234 to report details of the emergency. A fire extinguisher is located in 190 by the nearest exit to the SCFPR. No one is required to attempt to put out a fire. Attempts to put out small fires can be undertaken if you are comfortable with your capabilities and feel you are not in danger. Another person should be present to “spot” the person using the extinguisher and the attempt to extinguish the fire should not jeopardize one's ability to safely escape. A fire blanket is located in the hall as you exit 190 to the right from the door nearest the SCFPR.

7.0 Authorized Personnel

The following personnel are authorized operators and have read the SOP and understand the hazards, precautions, and safety procedures associated with this apparatus. In addition, the following personnel have completed the training courses stated in Section 5.0 of this SOP

Name (Print)	Signature	Date

8.0 Figures (attachment)

9.0 MSDS Safety Sheets (attachment)

Benzene
Titanium dioxide

9.0 MSDS Safety Sheets (attachment)

Benzene
Titanium Dioxide

8.0 Figures

Figure 1