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APPLICATIONS OF SUPERCRITICAL FLUID TECHNOLOGY TO POLLUTION PREVENTION AND WASTE MINIMIZATION

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INTRODUCTION

Many commonly used solvents and extractants are hazardous materials. In the past, careless disposal of these materials resulted in widespread contamination of groundwaters as proven by the large number of Superfund sites having this kind of contamination. Lack of adequate worker protection also resulted in a significant health risk in the workplace from contact with the liquid and vapor forms of the solvents.

One approach to the prevention of pollution and the reduction of worker exposure from conventional solvents is the use of less hazardous substitutes. One of the more novel substitutes is carbon dioxide. Although carbon dioxide is a gas at ordinary conditions, it can be liquified by application of pressure. In its supercritical state, it exhibits good solvent properties. Separation of the carbon dioxide from the extracted materials can be accomplished by pressure reduction, adsorption onto activated carbon, or with a membrane process, e.g., decaffeination of coffee.

Supercritical fluid extraction has been studied extensively on a laboratory scale to remove organic compounds from hazardous mixtures and contaminated waters. Few such systems have been employed commercially. One used liquified propane/butane to demonstrate extraction of organics from sediment at New Bedford Harbor, Massachusetts, under the EPA's Superfund Innovative Technology Evaluation program. However, supercritical carbon dioxide (SCCO2) may be the preferred choice for industrial extractions where relatively low temperatures are required.

Carbon dioxide is a non-polar solvent which is relatively non-toxic, non-flammable, with a critical temperature of only 31 degrees C and a critical pressure of 73 atmospheres. Extraction with SCCO2 offers several advantages over conventional solvent extraction, including minimization of organic liquid waste generation. Its solvent strength and low viscosity dependence on temperature and pressure makes SCCO2 attractive for replacement or recovery of organic compounds from liquid and solid materials. The use of SCCO2 in a remediation process allows rapid extraction of toxics and relatively easy solute concentration and recovery. Brady et.al.(1) successfully extracted PCBs, DDT and toxaphene from two types of contaminated soil using SCCO2. They observed that over 90 percent of the PCBs could be extracted in less than one minute. The SCCO2 extraction of naphthalene, anthracene, hexachlorobenzene and phenol from soil has also been reported.

The EPA is supporting a competitive university-based supercritical carbon dioxide research program administered by the Risk Reduction Engineering Laboratory, Cincinnati. The goal of this program is to develop and demonstrate current and new uses of SCCO2 in industrial processes as pollution prevention and waste minimization alternatives to chlorinated and other hazardous solvents. The degree to which this goal is accomplished will be determined by the acceptance of the SCCO2 processes for commercialization. A major factor limiting the commercial applications of supercritical fluid technology is the lack of reliable data for the design of the extraction or synthesis units.

This paper presents a brief overview of the university and federal laboratory collaborative efforts focusing on processes using supercritical carbon dioxide as a substitute for hazardous solvents. The SCCO2 technology applications under this program include extraction of natural pharmaceutical materials, phase-transfer catalysis, solvent replacement in chemical synthesis, temperature-solubility relationships, and separation of organic materials from soils and slurries. A paper on the extraction of heavy metals with SCCO2 was presented by Ataai et.al. at the 87th National Meeting, A&WMA (2). This work is also supported by the EPA.

OVERVIEW OF THE SUPERCRITICAL CARBON DIOXIDE RESEARCH PROGRAM

Selective Oxidation in Supercritical Fluids (Department of Energy, Los Alamos National Laboratory)

This research partnership will develop new, environmentally-friendly, selective catalytic oxidation routes to the production of oxygenated hydrocarbons, using supercritical carbon dioxide as the reaction medium in place of hazardous process solvents. This should reduce by-product wastes and improve downstream separation of products/catalysts. For example, a new class of heterogeneous oxidation catalysts, titanium silicates, catalyze a number of useful reactions including epoxidation, alcohol oxidation, aromatic hydroxylation, and ammoxidation. Titanium silicates and analogs will be examined in both supercritical carbon dioxide and water/carbon dioxide mixtures using a number of substrates (alkenes, arenes, alcohols). The reactivity of olefins with several palladium catalysts in supercritical carbon dioxide/water mixtures will also be investigated, as there is considerable industry interest in new routes to polymer intermediates or precursors.

Supercritical Fluids for Phase-Transfer Catalysis (Georgia Institute of Technology)

This research, under C.A. Eckert, will study the replacement of toxic and hazardous fluids with supercritical carbon dioxide to design "cleaner" manufacturing processes. This includes catalyst solubility studies and determinations of reaction kinetics. Phase-transfer catalysis in supercritical fluids will be demonstrated, providing opportunities for faster heterogeneous reaction rates at milder conditions, tailored to achieve a variety of process goals. In correspondence with the EPA, Dr. Eckert cited an example of a successful phase-transfer catalysis reaction in a supercritical fluid which produced benzyl bromide from a quaternary ammonium bromide salt and benzyl chloride. This reaction is representative of an industrially important class of processes. A major chemical company is collaborating with Dr. Eckert to identify specific reactions where phase-transfer catalysis can be used for pollution prevention. This partnering will improve commercialization opportunities.

Environmentally Benign Pharmaceutical Processing (Georgia Institute of Technology)

This study will employ supercritical carbon dioxide in a separation process, replacing alcohols and chlorinated solvents to extract compounds of therapeutic value from natural organic materials. This activity is being conducted under Dr. A.S. Teja, and includes study of solubility, extraction, and analytical characteristics of taxol and taxol-related compounds. The present separation method uses exhaustive ethanol extraction, partitioning between water and chloroform, followed by successive chromatographic separations and crystallization from aqueous methanol. Dr. Teja proposes to combine supercritical extraction with high pressure adsorption and other techniques to yield a novel hybrid separation process. His initial studies indicate that the hybrid process will eliminate the use of chlorinated solvents and reduce the use of alcoholic solvents by 85%. This process could potentially be used for the production of a large class of taxol-like pharmaceuticals.

Supercritical Carbon Dioxide Extraction at Elevated Temperatures (University of North Dakota)

The goal of this study is to provide fundamental solubility data for a variety of semivolatile organic compounds, including polycyclic aromatics, and to determine the effect of temperature on CO2 extraction efficiencies of both polar and non-polar organic compounds. Solubility is expected to increase dramatically with elevated temperatures (i.e., above typical 50 to 100 degrees C) for many components thought to be insoluble, extending the usefulness of SCCO2 for industrial processing and extractive clean-up. The results of the investigations by Dr. Steven Hawthorne should apply to the supercritical carbon dioxide extraction of organic contaminants from soils, sediments, spent sorbents, contaminated catalysts, and industrial waste sludges. The data generated in this study will also be used to predict solubility of organics in SCCO2, and will support the development of processes to replace hazardous organic solvents with SCCO2.

The Use of Supercritical Fluids for Waste Minimization (Louisiana State University)

This research will evaluate the practicality of SCCO2 to reclaim industrial organic materials by a non-destructive extraction process. Drs. K.M. Dooley and F.C. Knopf will utilize LSU's bench-and pilot-scale units to find the best conditions for specific extractions, and to implement new operating strategies for supercritical fluid extractions applicable to process streams. A countercurrent bubble column mode which can be directly scaled up to industrial practice will be operated on difficult-to-extract materials. The types of compounds to be tested include aqueous streams of alcohols, nitriles, and nitroaromatics; soils contaminated with polynuclear aromatics; and slurries of soils containing the above classes of compounds.

COMMERCIALIZATION OF SUPERCRITICAL CARBON DIOXIDE

Industrial chemists and engineers should begin to consider the potential uses of supercritical fluids as less hazardous solvents in chemical separation/synthesis applications. The successful commercial application of supercritical carbon dioxide technology for pollution prevention and waste minimization in organic solvent-using operations will help U.S. companies become more competitive by improving their manufacturing process efficiencies, reducing waste and associated disposal costs, and enhancing environmental compliance.

The EPA will assist its partners in this program with technical transfer of reports, presentations, and publications. Formation of partnerships between the technology developers and industry will also aid commercialization. Another possibility under consideration is a future EPA workshop to highlight the results of the supercritical fluid research under the EPA program with the inclusion of similar efforts conducted under private or other public sponsorship.

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DEVELOPMENT OF HIGH-RATE TRICKLE BED BIOFILTER

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INTRODUCTION

Since enactment of the 1990 amendments to the Clean Air Act, the control and removal of volatile organic compounds (VOCs) from contaminated air streams have become a major public concern (1). Consequently, considerable interest has evolved in developing more economical technologies for cleaning contaminated air streams, especially dilute air streams. Biofiltration has emerged as a practical air pollution control (APC) technology for VOC removal. In fact, biofiltration can be a cost-effective alternative to the more traditional technologies, such as carbon adsorption and incineration, for removal of low levels of VOCs in large air streams (2). Such cost effectiveness is the consequence of a combination of low energy requirements and microbial oxidation of the VOCs at ambient conditions.

Preliminary investigations (3) were performed on three media: a proprietary compost mixture; a synthetic, monolithic, straight-channeled (channelized) medium; and a synthetic, randomly packed, pelletized medium. These media were selected to offer a wide range of microbial environments and attachment surfaces and different air/water contacting geometries. The results of this preliminary work demonstrated that 95+% VOC removal efficiency could be sustained by all three media at a toluene loading of 0.725 kg COD/m^3-d, but at different empty bed contact times (EBCTs). For the pelletized medium, this performance could be achieved at an EBCT of 1 min, for the channelized medium at 4 min, and for the compost medium at 8 min. Both synthetic media developed headloss over time, with the pelletized medium showing a pressure drop in excess of several feet of water after sustained, continuous operation. These results left open the question of which medium could provide the optimum combination of high VOC elimination efficiency at high loading with minimum pressure drop.

This paper discusses the continuing research being performed for development of biofiltration as an efficient, reliable, and cost-effective VOC APC technology. The objectives of the recent research were to conclude the evaluation of the three media and to develop workable strategies for the removal and control of excess biomass from the (ultimately) selected pelletized attachment medium.

METHODOLOGY

The biofilter apparatus used in this study consisted of three, independent, parallel biofilter trains, each containing 4 ft of attachment medium: biofilters "A", "B", and "C". A detailed schematic and equipment description is given elsewhere (4). Biofilter "A" was filled with a proprietary compost mixture, "B" with a Corning Celcor® channelized medium, and "C" with a Manville Celite® pelletized medium. Biofilters "A" and "B" were square and had an inner side length of 5.75 in., and biofilter "C" was round with an inside diameter of 5.75 in. The air supplied to each biofilter was highly purified for complete removal of oil, water, CO_2, VOCs, and particulates. After purification, the air flow for each