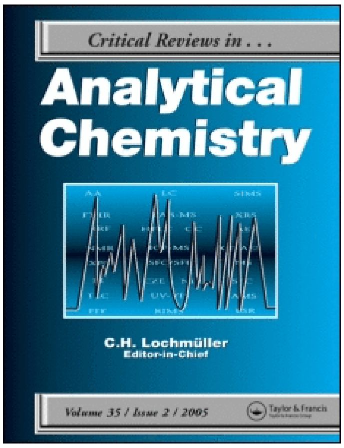

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GREEN CHEMISTRY: WASTE TREATMENT, WASTE MINIMIZATION, AND CLEAN MANUFACTURING INITIATIVES AT LOS ALAMOS NATIONAL LABORATORY

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Los Alamos National Laboratory is working with the U.S. Environmental Protection Agency (EPA) and the U.S. Department of Energy to promote fundamental breakthroughs in chemistry that accomplish pollution prevention and energy conservation through source reduction and are useful to industry. Green chemistry is defined as the use of chemical principles and methodologies for source reduction. The Los Alamos Green Chemistry Program encompasses all aspects and types of chemical processes---including synthesis, catalysis, analysis, monitoring, separations, and reaction conditions---that reduce impacts on human health, energy consumption, and the environment relative to the current state of the art.

Specifically, the talk will focus on the use of supercritical fluids to replace conventional hazardous organic solvents and also to optimize and potentially control the effect of solvent on reactions. Applications in waste treatment, cleaning, catalysis, waste minimization, and materials processing. This discussion will explore both chemical studies at Los Alamos and the development of a national and international program in dense phase fluid applications.

The use of supercritical fluids as reaction media offers the opportunity to replace conventional hazardous organic solvents and also to optimize and potentially control the effect of solvent on reactions. An advantage of supercritical fluids is that several important solvent properties can be "pressure-tuned" from gas-like to liquid-like, providing opportunities for improved chemistry. Supercritical fluids can have liquid-like densities and solvent strength which can be "tuned" by adjusting the density of the medium allowing for control of the solute solubility along with density-dependent properties such as dielectric, viscosity, and diffusivity with pressure control. Simple solubility control through pressure could also allow facile separation of products and catalysts from the solvent.

Supercritical fluids also share many of the advantages of gases including miscibility with other gases, low viscosities, and high diffusivities, thereby providing enhanced heat transfer and the potential for faster reactions, particularly for diffusion-controlled reactions involving gaseous reagents such as hydrogen or oxygen. Carbon dioxide (T_c = 31.1 °C, P_c =7.3 MPa) has the further advantages of being non-toxic, nonflammable, inexpensive and unregulated. Its electrophilic nature and the fact that it cannot be further oxidized makes CO_2 an ideal solvent for carrying out both electrophilic and oxidation catalysis. The enhanced thermal conductivity of supercritical CO_2 (SC CO_2) relative to organic solvents, coupled with its stability towards oxidation suggests that it can act as an efficient solvent for buffering heat transfer, even for highly exothermic reactions.

The focus of our research in supercritical fluids is to explore the potential for solvent replacement by understanding chemical reactivity in this medium. In addition, we are seeking enhanced selectivity and reactivity as well as new chemistry in supercritical fluids. Our approach has been to explore several fundamental and industrially important catalytic processes in supercritical fluids in order to understand their potential to benefit from the advantages of supercritical fluids as reaction media. In our view, the most promising reactions are those that: 1) work well in nonpolar solvents such as hexane or halocarbons, 2) are solvent-sensitive (and this likely to be “pressure-tunable”), 3) lead to high-value products (mitigating the capital investment barriers to implementation of new technology), or 4) utilize gaseous reagents which are not highly soluble in conventional solvents, e.g. hydrogen or oxygen.

LANL researchers are initiating chemical studies to assess the viability of supercritical media as reaction media for the replacement of hazardous solvents for industrially important chemical or catalytic transformations. Specific objectives of this research include:

- o demonstrating solvent replacement using CO_2 for electrophilic and oxidation reactions
- o understanding the extent to which one can "tune" selectivity and rate by tuning solvent density and therefore solvent properties
- o delineating the advantages of supercritical CO_2 by benchmarking results with those in conventional solvents
- o delineating effects of ligand environment, oxidant concentration, cosolvents (e.g. CH_3CO_2H in Co systems), solvent properties (temperature, pressure)
- o determining advantages of carrying out Nafion supported catalytic chemistry in SC CO_2 relative to conventional solvents and in comparison with homogeneous systems in SC CO_2
- o demonstrating enhanced separation of catalysts, reactants and products.

<u>Dense Phase Fluids National and International Program</u>

The U.S. Environmental Protection Agency (EPA) promotes fundamental breakthroughs in chemistry that accomplish pollution prevention through source reduction and are useful to industry. The U.S. Department of Energy promotes similar objectives to achieve energy conservation. Green chemistry is defined as the use of chemical principles and methodologies for source reduction. Green chemistry encompasses all aspects and types of chemical processes---including synthesis, catalysis, analysis, monitoring, separations, and reaction conditions---that reduce impacts on human health, energy consumption, and the environment relative to the current state of the art. The EPA and DOE understand that for their environmental and energy objectives to be realized new technology must be developed and applied across a range of industry sectors. The EPA approach is to establish a partnership between government agencies, national laboratories, universities, and private sector companies and to initiate pre-competitive, non-proprietary research that provides alternative chemical methods that improve environmental and energy conservation performance. The EPA refers to the overall program as the Green Chemistry Institute (GCI). The GCI will not exist as a single laboratory or building but rather as a ‘virtual” center connecting the participating organizations.

This proposal represents the first phase of this new cooperative government-industry-academia partnership. The Green Chemistry Institute is a small organizing umbrella that will oversee actual technical working programs in a number of industry areas. The development of these actual working programs is to be stepwise, beginning with a Dense Phase Fluid program, followed by a Catalysis program, an Alternative Feedstocks program, and other industry focus areas determined by the DOE and the EPA. Because the first two technical working programs are in research areas where Los Alamos is a critical technical leader and focal point for industry interactions, Los Alamos was selected to lead the formation of the technical program.

A major objective of this proposal is to couple the chemical studies with a larger international program that will involve LANL, a number of academic collaborators and industrial partners. With guidance from the EPA, DOE, other Federal agencies our academic and industrial partners, we will develop an industry roadmap and technical program plan. The roadmap and technical program plan provide the technical basis for the Dense Phase Fluids program. The objectives for the program are as follows:

- o The main objective is to provide the leadership, technical collaborations and resources necessary for spearheading the rapid development and implementation of advances in supercritical fluid technology where environmental and/or energy advantages, as well as economic advantages, can be realized consonant with sustainable development.
- o The program will provide a platform for academic, national laboratory and industrial leaders in basic science, technology and engineering of supercritical fluids to work together with industrial problem holders to define the areas that would best benefit from advances in SCF's, to define specific collaborative research projects in these areas, to acquire and distribute the necessary resources and to disseminate technical information.
- o Program participants will work together to ensure adequate federal and industrial funding as well as efficient utilization of resources.
- o Through development of an industry roadmap, the program will provide a mechanism for industry to guide and monitor technical developments in scientific understanding, scope of application and engineering implementation.
- o The research and development program will provide member companies with access to state-of-the art science and technology as well as mechanisms for utilizing equipment and expertise for industry and/or-company specific projects.

The program roadmap development effort will focus on a number of aspects of supercritical or dense phase fluids, primarily:

1. Cleaning
   - Drywash
   - CO_2 Snow
   - Precision Cleaning
2. Extraction/Separation
   - Pharmaceuticals from Fermentation
   - Heavy Metals from Waste Water and Soil
   - Waste Processing and Recycling
   - CO_2 Separations
3. Polymer Synthesis and Processing
   - CO_2-Modified Extrusion Processes
   - Dyeing Processes
   - Impregnations and Residual Monomer
   - Polymer Modifications
4. Materials Synthesis and Modification
   - Cementation
   - Fly Ash
5. Chemical Synthesis and Catalysis
6. Delivery Technologies
7. Reaction Engineering
8. Theory, Computation, and Modeling
9. Equipment Technology

LANL Expertise

LANL possesses a unique combination of expertise and facilities to conduct research and manage the national program development. Reactor systems are available for use in both batch and flow experiments designed to test the efficiency of chemical reactions, and analytical protocols have been developed for both on- and off-line product analysis. Scientists in the Hydrothermal Processing Project (CST Division) have extensive experience in the design, construction, and operation of supercritical reactors, and have developed characterization techniques for *in situ* analysis of these complex systems. This experience extends to the operation of pilot-scale reactors used in hydrothermal waste treatment experiments. Expertise exists within CST Division in mechanistic organic chemistry, as well as synthetic inorganic, organometallic, and materials chemistry. No comparable combination of expertise in supercritical fluid engineering and chemical synthesis is available elsewhere. In addition, LANL has been developing a strong partnership with several universities and a number of companies from several industry sectors in the area of dense phase fluids.