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Title: **Chemical Conversions in Supercritical Media: Environmentally Sound Approaches to Processes and Materials**

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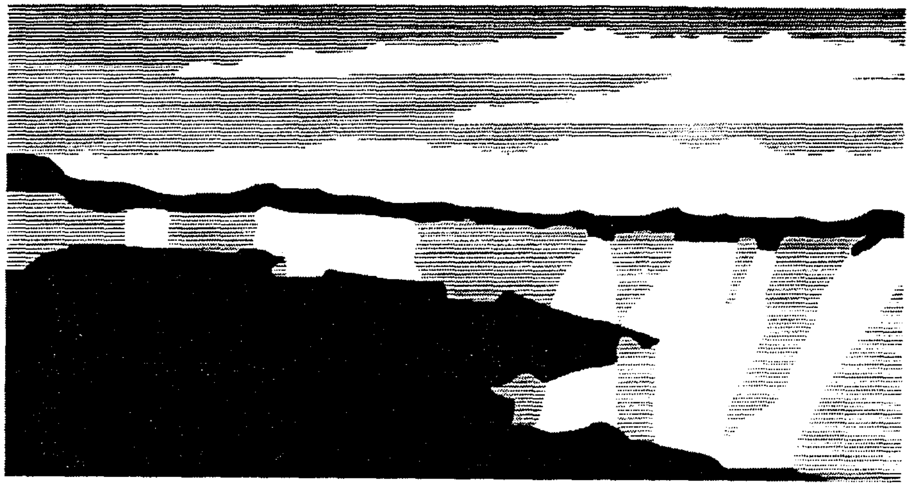

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Chemical Conversions in Supercritical Media: Environmentally Sound Approaches to Processes and Materials

Carol Burns*, Samuel Borkowsky, Steve Buelow, David Langlois, Richard LeLacheur, Mike Mitchell, Bill Tumas, Robert Waymouth (Stanford University), and Paul Williams

Abstract

This is the final report for a two-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). The aim of this effort was to evaluate the potential of supercritical fluids (SCF) as reaction media in an effort to develop new, environmentally-friendly methods for chemical synthesis or processing. The use of novel media creates the possibility of opening up substantially different chemical pathways, increasing selectivity (eliminating waste by-products), and enhancing reaction rates (decreasing hold-up times and saving energy). In addition, the use of SCF as reaction media facilitates downstream separations and mitigate or eliminate the need for hazardous solvents on scales from bench top to production. This project employed a highly interdisciplinary approach to investigate the utility of SCFs as reaction media for polymer synthesis and synthetic organic chemistry.

1. Background and Research Objectives

The need for environmentally friendly chemical processes both for manufacturing and remediation is increasing dramatically. It has recently been estimated that over 750 million tons of RCRA hazardous waste is generated annually in the United States [1]. Chemical manufacturing dominates this figure, accounting for more than 50% (nearly 400 million tons) of the total waste mass. The key to effective waste management is waste reduction, as established waste treatment technologies cannot provide an economically viable solution to this problem. Waste reduction may be realized in a number of ways, including producing more environmentally acceptable products, replacing hazardous or toxic reagents and solvents, investigating processes with higher yields or selectivities, and recycling by-products. Chemical manufacturers are seeking the technical means to realize these goals in clean production in order to reduce expenditures and remain competitive.

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The aim of this project was to evaluate the potential of supercritical fluids as reaction media for chemical synthesis in an effort to develop new, environmentally-friendly methods for chemical synthesis or processing. The use of novel media creates the possibility of opening up substantially different chemical pathways, increasing selectivity (eliminating waste by-products), and enhancing reaction rates (decreasing hold-up times and saving energy).

2. Importance to LANL's Science and Technology Base and National R&D Needs

One aspect of the area of environmental stewardship is waste minimization, or pollution prevention. The development of new technologies for pollution prevention (by process or product modification/substitution) is of key importance in addressing problems both within the DOE and in the private sector. In both practical and economic terms, pollution prevention is the best way to mitigate the environmental impact of technology. Therefore, the best way to address the national need to ensure responsible environmental management in the future (in activities addressing both national defense and economic security) is heavy investment in technology to prevent the generation of waste. This is recognized in the DOE's strategic plan; waste minimization or "clean" processing is incorporated explicitly as an integral part of many of the technical goals for the major business areas (in environment, energy, defense, and economic competitiveness). This project is an ideal example of LANL's multidisciplinary, highly integrated approach to science, bringing together LANL's expertise in hydrothermal processing, reactor design/engineering, in-situ spectroscopy, inorganic synthesis, polymer synthesis and processing, and mechanistic organic chemistry. It forms a part of a larger LANL effort in supercritical fluid technology and engineering (including SCF extraction/cleaning and hydrothermal processing) coordinated through joint meetings. The individual programs have a synergistic relationship: knowledge in SCF engineering, phase behavior, and diagnostics developed previously in the cleaning and hydrothermal programs contributes materially to efforts to study process chemistry, while reactivity knowledge gained in the course of this project will likewise enhance efforts to develop advanced waste treatment technologies. Successful execution of this program relies on a strong multi-organizational and interdisciplinary collaboration, and contributes to core LANL capabilities in complex experimentation and measurement and earth and environmental systems.

3. Scientific Approach and Results to Date

The areas of chemical synthesis and processing in which application of SCF technology can make a profound impact are too numerous to list. We chose to concentrate our efforts on a relatively small number of critical areas, representing both adaptations of chemical processes conducted in conventional media (to demonstrate solvent substitution and evaluate process performance) and experimental syntheses designed to take advantage of the unique properties of supercritical fluids to facilitate unprecedented reaction pathways. Three research areas were chosen for investigation. These areas are:

1. Metal-catalyzed polymerizations: Palladium and nickel catalyzed polymerizations of butadiene and copolymerizations of dienes with carbon monoxide. This research was conducted in collaboration with Stanford University.
2. Radical Polymerizations: Styrene polymerization, acrylate foam production, and cationic ring opening polymerizations in supercritical CO_2 for the production of polymers of industrial interest.
3. Synthetic Organic Chemistry: Design of experimental and analytical procedures to investigate anionic nucleophilic substitution. Initial focus on synthesis of fluoroaromatic compounds with extensions to other aromatic compounds and unactivated, unsaturated systems.

We established capabilities for supercritical fluids synthesis and processing (with synthetic, analytical, and reactor systems), and made significant technical progress in each of the three research areas. Some of the technical results are summarized below.

We have been investigating the use of supercritical CO_2 as an environmentally benign replacement solvent for conventional hydrocarbon and halocarbon solvents for a variety of chemical transformations. Initial efforts in the area of metal-catalyzed polymerizations focused on establishing benchmark systems for the comparison of polymerization systems in both conventional media and supercritical CO_2. The systems chosen for investigation were nickel- and palladium-based catalytic processes for the polymerization of 1,3-butadiene or copolymerization of butadiene and carbon monoxide. Complexes of the formula $[(C_3H_4R)Ni(O_2CCF_3)]_2$ (R = Me, H) are known to serve as catalysts for the 1,4-polymerization of butadiene with varying steroregularities [2]. In collaboration with Prof. Robert Waymouth (Stanford University), we investigated the effect of solvent on this reaction.

The table on the following page summarizes relevant results from an investigation of the polymerization of 1,3-butadiene using $[(p\text{-allyl})Ni(CF_3CO_2)]_2$ in supercritical CO_2.

Entry #	Solvent	C_4H_8/Ni	Pressure psi	Temp C	Time h	Yield	% *cis*	% *trans*
1	neat			55			68	32
2	toluene	860		55	48		69	31
3	heptane	1200		55	44	85%	93	7
4	CO_2	790	1100	55	54	76%	77	23
5	CO_2	725	2000	55	48	78%	85	15
6	CO_2	800	3000	55	45	75%	83	17

A comparison entry 4 with entries 5 and 6 show that the *cis-trans* stereochemistry is affected somewhat by a change in reaction pressure. In addition, we have obtained data at other pressures and temperatures and have investigated the polymerization chemistry of a cobalt catalyst which has been reported to polymerize 1,3-butadiene regiospecifically to syndiotactic 1,2-polybutadiene.

Efforts in radical polymerizations for polymer production in supercritical CO_2 investigated three areas: styrene polymerization, acrylate foam production, and cationic ring opening polymerizations. These areas coincide with general industrial interest for the production of polymers in an environmentally responsible manner, for new coatings methods to reduce emissions of VOCs (volatile organic compounds), and for the production of foams without the use of hazardous blowing agents. Knowledge of surfactant design and use obtained in this work is directly applicable to supercritical (SC) fluid cleaning technologies.

Styrene polymerizations met with limited success. Highlights of our discoveries: benzoyl peroxide is a superior initiator, lower pressures of carbon dioxide are preferred, styrenic monomers with electron withdrawing groups polymerized better, and an adequate steric stabilizer was not found. (Work by others in the field indicate that block copolymers of PDMS (poly(dimethylsiloxane) and styrene are useful stabilizers.)

Acrylate foam production has been successful. We have found that comb polymers containing PDMS teeth on an acrylate backbone make superb stabilizers for the polymerizations of acrylates. Also, we are very near the production of foams in liquid carbon dioxide. (For the production of emulsions, the higher viscosity of a liquid phase is preferred to a SC phase - but the advantages of carbon dioxide still apply.) We routinely obtain high yields of acrylate polymer and produce foam-like materials. Problems still remain with incomplete emulsification.

Finally, we have examined the potential of supercritical and near-critical water as a reaction medium for ionic organic chemistry. Our investigation of nucleophilic substitution reactions in high-temperature, high-pressure water have continued, and yielded considerable information on the behavior of both substrates and nucleophiles under these conditions. Early studies demonstrated that hydroxide was a potent base under near- and supercritical conditions. Halogenated aromatic substrates (bromo, chloro, fluoro) all reacted quantitatively with hydroxide to yield phenolic byproducts. A marked difference between substrates was noted however. Chloro- and bromo-substituted substrates react via a benzyne mechanism, and yield cine substituted phenolic products. The fluoro substrate reacts only via direct substitution (e.g., S_NAr mechanism) to yield ipso-substituted phenolic products.

Changing from hydroxide to halogen nucleophiles demonstrated that the mechanism of substitution also depended on the nucleophile. Reactions between sodium chloride and bromotoluene substrates gave 50-80% yields of ipso-substituted chlorotoluenes, with only minor yields (generally <5%) of hydroxy- or hydrogen-substituted products (cresols, toluene). Both the product distribution and substitution patterns changed dramatically when fluoride salts were used as the nucleophiles. Reactions of potassium or cesium fluoride with bromotoluenes led to hydroxy-substituted compounds as the major products (40-80% yields), and fluorotoluenes as relatively minor products (<10% yield).

The effects of varying solvent density (and therefore dielectric constant) were examined for the reactions of fluoride salts with chlorotoluene substrates. Under the usual baseline conditions described above, a density of 0.5 g/mL was used and a temperature of 400 °C. By reducing the amount of water in the reactor, densities of 0.3 and 0.2 g/mL were also examined. This type of reaction led to low yields of the desired fluorinated byproducts at 0.5 g/mL, and high yields of hydroxylated byproducts. The ratio of fluorinated:hydroxylated was about 0.2 for these conditions. By decreasing density to 0.3 g/mL, this ratio was increased to 0.6. A further decrease in solvent density to 0.2 g/mL increased the ratio to about 1. This reduction in density also resulted in formation of a two phase medium (liquid-vapor) at an overall density of 0.2 g/mL. Phase separation occurred almost exactly at 0.3 g/mL, as observed in a high pressure diamond window cell.

The overall results of this work indicate that the concept of conducting nucleophilic substitution reactions between ionic species and aromatic substrates is valid. This is most clear for the reactions between sodium chloride and bromoaromatic compounds. However, the reactions are complicated by the presence of basic species such as fluoride and hydroxide, which can lead to the benzyne mechanism. Benzyne chemistry leads both to a loss of regiochemical control and to likely solvent participation and formation of hydroxylated products. Manipulation of the solvent through changes in pressure and possibly phase results in a change in product distribution, and may provide a means of optimizing a desired chemical transformation.

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