Supercritical Fluid Technology:
Green Chemistry for the 21st Century

Currently, the U. S. produces millions of tons of pollution each year, and spends billions of dollars controlling this pollution.[1] This data clearly indicates that sustainable economic growth will require more than end-product environmental monitoring of existing industrial processes. Rather, the worldwide focus on technology development must include new industrial processing methodology that supports pollution prevention at the source. Such a change in production methodology will effect numerous immediate and long-term benefits, including financial, as fewer capital investments will be necessary for future environmental remediation.

The Green Chemistry program of the Environmental Protection Agency (EPA) was recently created to support *benign by design* principles in the design, manufacture, and use of chemicals and chemical processes.[2] This Design for the Environment (DfE) program features R & D efforts related to innovative technologies, in order to assist industries with the development of environmentally benign products and processes. Such an initiative harmonizes with the Pollution Prevention Act of 1990 that was created to focus on *source reduction* of pollutants; a concept that is often overlooked due to the industrial focus on waste management and pollution control.

In 1992, the EPA's Office of Pollution Prevention and Toxics (OPPT) teamed up with the National Science Foundation (NSF) to jointly fund worldwide green chemistry research. Since its inception in 1977, the OPPT has been responsible for assuring that chemicals for use or sale do not pose any adverse effects to human health or the environment. To date, the OPPT-NSF partnership has awarded tens of millions of dollars in the form of grants for fundamental research in green chemistry to groups throughout the world.[1] Much of the recent funding has been directed to research that exploits the unique properties of supercritical fluids (SCFs), as a alternative to traditional solvents.

Under the Federal Resource Conservation and Recovery Act (RCRA), industries that use organic solvents must comply with strict regulations concerning on-site storage, recycling/disposal, and off-site waste transport.[3] Together with the Federal Clean Air Act (CAA), these regulations are intended to suppress pollution that would occur through excessive solvent evaporation, or improper disposal to contaminate soil and/or water resources. It would be an extremely attractive proposition to have media that would serve as a versatile solvent, without carcinogenic properties or the potential for environmental degradation. Indeed, this goal has been brought to fruition with the advent of supercritical fluid technology.

Supercritical fluids possess properties that are intermediate between liquids and gases. This unique phase is obtained through the exertion of pressures and temperatures greater than the critical point (Figure 1). Near the critical point of a fluid, minute changes in pressure or temperature significantly alters the physico-chemical properties of the SCF (*e.g.*, density, diffusivity, or solubility characteristics). This is especially important for synthetic applications, where reaction conditions (*e.g.*, selectivities, rates, pathways) may be sensitively manipulated. Such reaction control is impossible using traditional organic-based solvents. Further, due to the deleterious effects that many organic solvents have on the environment and/or one's health, media such as halogenated hydrocarbons (*e.g.*, chloroform, dichloromethane) are being phased out of use, and benign replacements are being developed. Supercritical carbon dioxide (sc-CO_2) is an attractive alternative, since it is extremely inexpensive and poses no threat to the environment or human health. However, depending on the application, a variety of other SCFs may be more attractive; Table 1 lists common fluids that have been utilized for applications as diverse as extraction/chromatography, inorganic/organic synthesis, catalysis, materials processing, and even dry-cleaning.

Extraction and Chromatography

Although SCFs were discovered over 100 years ago, the first commercial applications for SCFs were only realized in the late 1970's, with reports of coffee decaffeination. Since then, SCF
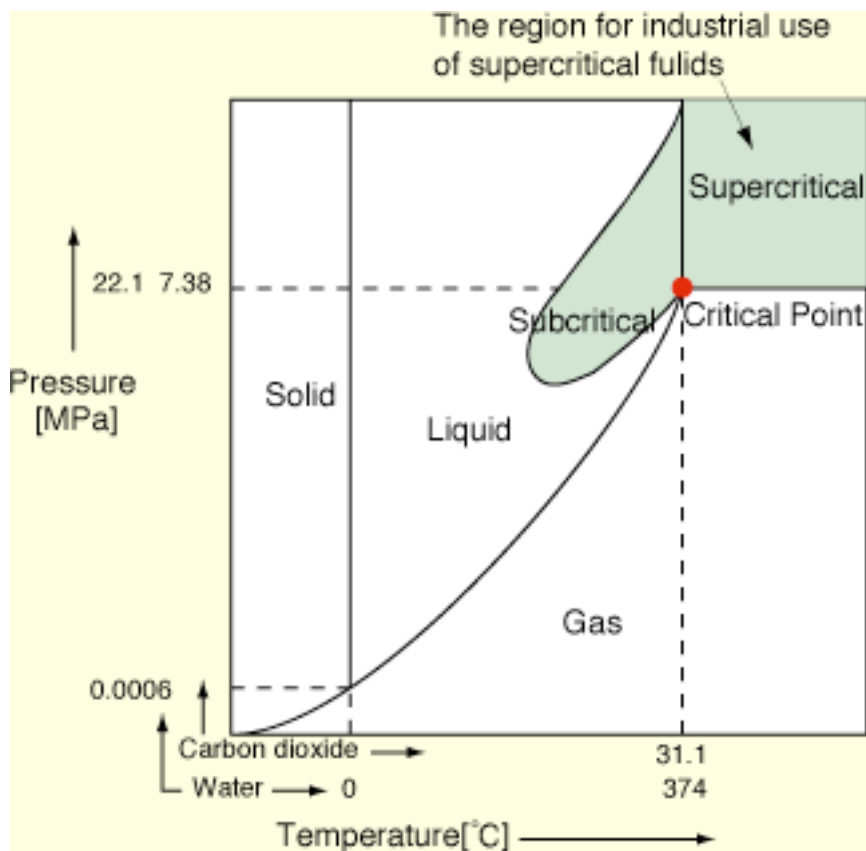
Figure 1. Phase diagram and critical constants for carbon dioxide and water.[4]

Table 1. Comparison of the critical constants for commonly used fluids.

Fluid	Critical Temperature (°C)	Critical Pressure (atm)
Carbon dioxide (CO_2)	31.1	72.8
Methane (CH_4)	-82.1	45.8
Ethane (C_2H_6)	32.3	48.2
Propane (C_3H_8)	96.7	41.9
Argon (Ar)	-122.3	48.0
Nitrous oxide (N_2O)	36.5	72.5
Water (H_2O)	374.1	218.3

media has been used to successfully extract analytes from a variety of complex compounds through manipulation of system pressure and temperature. By comparison, conventional methods (*e.g.*, Soxhlet extraction and vacuum isolation) are more complicated and time/energy intensive. In general, these latter methods also suffer from the production of crude extracts that consist of deteriorated constituents, or feature the premature removal of volatile components.

The limiting property of sc-CO_2 is that this medium is only capable of dissolving nonpolar organic-based solutes. However, the addition of small amounts of a co-solvent such as acetone, has been shown to significantly improve the solubility of relatively polar solutes.[5] More recently, solubility of ionic compounds such as aqueous metal salts have been enhanced through inverse micelle formation using fluorinated surfactants. DeSimone and coworkers have performed much of the research related to surfactant design which has been exploited for "solvent-free" dry-cleaning applications.[6]

Supercritical fluid extraction has also been applied to environmental remediation such as the extraction of PCBs and other organics from water and soil.[7] For the extraction of metal contaminants, a chelating agent is commonly added to the fluid, with the soluble metal complex being removed from the SCF following system depressurization.

Applications in Catalysis

The use of SCFs for catalytic processes such as hydrogenations, oxidations, hydroformylations, and etherifications, has been shown to overcome many of the chemical, engineering, and environmental difficulties associated with conventional processes. In general, homogeneous catalysis is preferred over heterogeneous reactions due to greater rates and selectivities. However, the drawback of this methodology is the difficulty in separating products. By comparison, reactions involving SCFs offer the best opportunity for separation of reaction products and removal of solvent from the system, accomplished through simple system depressurization.

Since both hydrogen and organic substrates are soluble in SCFs, a single phase is created which eliminates mass-transfer considerations. The complete miscibility of supercritical fluids with permanent gases, the enhanced mass-transfer properties, and the additional safety provided by a nonflammable solvent, are aspects that make SCFs, especially sc-CO_2, very attractive as a benign solvent for hydrogenations and other catalytic processes. Even biphasic catalysis has made use of SCF technology, with the co-addition of organic salts known as ionic liquids to assure catalyst miscibility.[8]

Applications in Materials Synthesis

Nanometer metal powders are expected to have applications as burn rate modifiers in propellants, as well as components in fuel air explosives, energetic structural materials, and high-density explosives.[9] Powders of some transition metals and their alloys are used in thick-film technology for the production of conductive pastes for hybrid integrated circuitry and for the metallization of multilayer ceramic (MLC) capacitors.[10] Metal powders are prepared by a variety of methods such as powder mixing/calcination, metal-organic decomposition from nonaqueous solutions, and precipitation from aqueous solutions of metal salts.[11] However, these methods generally give a nonuniform size distribution that requires milling of the agglomerated powders. Spray pyrolysis has also been utilized to generate metal alloy particles possessing diameters in the range 100-1000 nm.[12] However, only in the last two years have researchers begun to utilize SCFs as a medium for nanoparticle growth.

Once a component is dissolved in a supercritical fluid, the particles may easily be isolated from the fluid by decreasing the system pressure. If the medium is sc-CO_2, gaseous CO_2 is released from the system (often being recycled), and the dissolved components are deposited as extremely fine particles, due to the rapid expansion of the supercritical solution (RESS). Another method for nanoparticle formation uses microemulsions, whereby an aqueous metal salt solution, reducing agent, and surfactants are added to the SCF. The resultant metal nanoparticles are deposited by RESS after the SCF is vented from the system. Particles formed through this simple

procedure are shown to be free of atomic incorporation and are extremely homogeneous in size.[13]

Recently, chemical vapor deposition (CVD) has also utilized SCF technology for the growth of thin films. Supercritical fluid transport CVD (SFT-CVD) allows relatively nonvolatile precursors to be introduced into the deposition chamber, as long as they are soluble in the SCF.[14] By comparison, traditional thermal CVD methods may only use volatile precursors. Complex films such as $BaTiO_3$ and YBCO have been successfully deposited using SFT-CVD by dissolving stoichiometric amounts of metal β-diketonate precursors within the SCF. The deposition of these films using traditional CVD processes is much more complex since more than one solid/liquid precursor must often be used, each possessing a unique volatility.

Safety Considerations and Future Development

The obvious unappealing aspect of dealing with supercritical fluids is the relatively high-pressure conditions that must be used. However, this problem has been circumvented by the use of flow reactors analogous to those reported by the Poliakoff research group at the University of Nottingham.[15] Flow reactors also offset the problem created by altering the critical temperature of the fluid by dissolution of solutes. That is, with batch reactors, the critical temperature of the reaction mixture may change significantly as the reaction proceeds. Further, if one uses an autoclave, it is typically small in size to reduce the danger associated with large volumes at high pressure. To scale up a reaction carried out in a flow reactor, one would simply run the reactor for a longer period of time, with *in situ* real-time spectroscopic monitors, if desired.

Hence, one can no longer claim that reactions in supercritical fluids are either too dangerous and/or expensive to carry out. Improvements in both areas have allowed the improvement of present technology, and will continue to open this field to include many unexplored areas of chemistry.

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