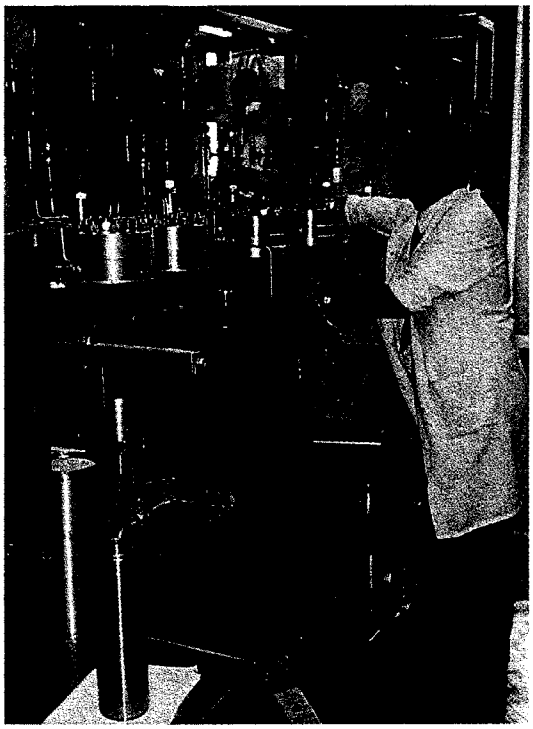
Critical Fluids Support Sustainable Technologies

This "green" technology using natural agents finds niches in reaction chemistry, materials science, and natural product isolation.

Critical fluid technology, which embraces gases and liquids under compression near or above their respective critical temperatures, continues to find widespread applications in a number of fields. With more than 30 processing plants worldwide—including hops, flavors, and natural oil production in the UK—critical fluids are finding niches that complement "green" and sustainable technologies. This article takes a look at the organizations active in transferring new critical fluid technology that may impact the commercial sector during the next century.



At Leeds' Express Separations a supercritical fluid pilot plant is routinely used to extract a variety of natural products and treat solid materials.

One of the key UK groups involved in critical fluid technology is at the Univ. of Leeds under the leadership of Tony Clifford and Keith Bartle. Research in supercritical fluids began at Leeds in 1984 in the area of analytical chemistry and led to the start up of Express Separations Ltd., Leeds, UK, a company devoted to transferring technology to both private and governmental sectors. R&D at Leeds has seen the application of supercritical fluid carbon dioxide (SC-CO_2) for the fractionation of polymers, dyeing of textiles and paper, production of fine particles by dissolving and precipitating metal carbonyls, and isolation of naturally occurring pesticides from plant matter. In conjunction with the BLC Leather Technology Centre, Northampton, UK, an Express research team recently explored the feasibility of replacing kerosene with SC-CO_2 for degreasing hides.

An offshoot of the Leeds effort via a collaboration with the Univ. of North Dakota Energy Research Center, has been the use of hot, pressurized water (i.e. subcritical water) for extracting plant materials. The Leeds/Express group has successfully de-terpenated essential oils and extracted rosemary or cloves using pressurized water. The extractions and fractionations are typically done at a water temperature of about 150°C and reduce energy use. Scaling up the processes is routine at Express, which is aided by agreements with Separex in France (pilot plant facilities) and other European and Asian partners.

A collaboration between Clifford and Chris Rayner at Leeds has created another consortium with industry known as the Leeds Cleaner Synthesis Group. This effort is based on the principle of "solvent tuning"—the adjustment of the pressure and temperature of the critical fluid, to produce a desired reaction product via conducting synthesis in SC-CO_2. Recent studies in Rayner's group have involved the oxidation of organic sulfides to sulfoxides using a hydroperoxide catalyst in conjunction with a sulfonium ion exchange resin. For example, a chiral sulfoxide synthesis, the sulfoxidation of methyl cysteine methyl ester, has produced more than a 95% yield of one specific diastereoisomer by adjusting the density of the CO_2, a result which could not be achieved in organic solvent media. This result implies significant advantages for the synthesis of chiral compounds for the pharmaceutical industry.

The research and technology transfer efforts of the Clean Technology Group under the direction of Martyn Poliakoff at the Univ. of Nottingham embrace an equally diverse number of applications of critical fluid technology. Supported by funding from government research councils and industrial sources, the Nottingham group has conducting pioneering efforts, particularly in reaction chemistry and the synthesis of unique materials under sub- and supercritical conditions. Poliakoff and associates' research on rapid hydrogenation reactions deserves special mention, having been initiated on small-scale, modular reaction systems, and having been more recently scaled up with help from industrial collaborator, Thomas Swan & Co. Ltd., Consett, UK.

The Nottingham group recently demonstrated the potential of hot, pressurized water as an environmentally benign medium for conducting reductions of organic compounds with hydrogen generation using Zn in the aqueous media. Similarly, hydrogen-deuterium exchange in aromatic compounds has been affected in superheated D_2O. Other novel synthetic routes have been developed using an anti-solvent in conjunction with SC-CO_2 to create "buckyballs" and the hydroformylation of olefins in SC-CO_2 using rhodium phosphine complexes as catalysts.

Poliakoff's colleague, Steven Howdle, conducts research on materials synthesis and modifications using sub- and supercritical agents. Most notable are the efforts in conjunction with Ferro Corp., Cleveland, in the production of powder coatings at low temperatures using Ferro's "VAMP" powder coating process. Here a designated polymeric matrix is mixed with a pigment moiety and suitable cross-linking and polymerization initiators in an autoclave with stirring to produce a foam induced by swelling of the polymer. Reduction of pressure and venting of the mixture permits polymer-coated particles to be obtained that can be used in coatings.

The Univ. of Nottingham's miniature and modular approach to conducting reactions in critical fluid media allows considerably flexibility in changing reaction conditions under pressure.

A technology spin-off of research conducted at the Univ. of Bradford by Peter York and Mazen Hanna is Bradford Particle Design Ltd., Bradford, UK. Using a patented process known as SEDS (solution enhanced dispersion by supercritical fluids), which can produce unique particle size, shape, and morphology, the firm has focused its initial efforts on producing materials for pharmaceutical companies. Features of the SEDS process include initiating particle formation in an oxygen- and light-free atmosphere as well as permitting solvent-free, uncharged particles to be generated. The micron-sized powders are used in controlled release technology, pulmonary delivery, and needle-free injections. The technology permits dehydration and synthesis using compressed CO_2 in conjunction with organic anti-solvents.

Startup funding has been provided by the Biotechnology and Biological Sciences Research Council and a Dept. of Trade and Industry LINK biochemical engineering project as well as industrial sponsorship via GlaxoWellcome. More than 12 commercial licensing relationships are in place with 20 pharmaceutical companies, including a collaboration with PowderJect Technologies Ltd., Oxford, for a needle-free drug delivery system.

Research on the application of supercritical fluids for coatings has recently started at the Univ. of Surrey in Guildford under the direction of John Hay. Hay and colleagues are extending applications of a Union Carbide UniCarb coating process developed during the 1980s in the US in conjunction with the Nordson Corp., Westlake, Ohio. Initial research at the Centre for Supercritical Coating Technologies, Guilford, UK, is focused on the use of organosilicone agents as polymerization stabilizers, rather than fluoro-containing additives. Hay also cites the benefits of SC-CO_2, not only as a substitute for organic solvents, but as an effective plasticizing agent for polymers used in coating applications. Recent studies have shown that a poly-(dimethylsiloxane) grafted into a methacrylate monomer is an effective polymerization surfactant.

A similar theme involving useful polymerizations conducted in SC-CO_2 has been pursued by Andrew Cooper at the Univ. of Liverpool. The focus of this research concerns production of monolithic and emulsion/suspension polymers using SC-CO_2 as a reaction medium aided by the presence of fluorinated additives, similar to those used by DeSimone in the US.

As noted previously, critical fluid technology using natural agents such as CO_2 or water is a key contributor to sustainable "green" technologies. In this regard, the efforts of James Clark and colleagues at the Univ. of York to propagate a Green Chemistry Network in the UK deserves mention. With sponsorship from the Royal Society of Chemistry, Clark has established not only the network, but a new journal called *Green Chemistry*. Although a number of green agents have been emphasized, other critical fluids can be used profitably for extracting and fractionating natural product mixtures. Toward that end, the Advanced Phytonics Corp., Ossett, UK, has demonstrated the efficacy of a CFC-substitute (1,2,2,2-tetrafluoroethane) for use as a low-temperature and pressure extracting agent for a variety of natural products and nutraceuticals.

—Jerry King

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