



Mini-Review: Green sustainable processes using supercritical fluid carbon dioxide

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Abstract

Environmentally benign carbon dioxide offers significant potential in its supercritical fluid phase to replace current reliance on a range of hazardous, relatively expensive and environmentally damaging organic solvents that are used on an extensive global basis. The unique combination of the physical properties of supercritical fluids are being exploited and further researched to continue the development and establishment of high efficiency, compact plant to provide energy and water efficient manufacturing processes. This mini-review is focused on the use and potential applications of supercritical fluid carbon dioxide for a selected range of key and emerging industrial processes as a sustainable alternative to totally eliminate or greatly reduce the requirement of numerous conventional organic solvents. Examples of the industries include: chemical extraction and purification, synthetic chemical reactions including polymerization and inorganic catalytic processes. Biochemical reactions involving enzymes, particle size engineering, textile dyeing and advanced material manufacture provide further illustrations of vital industrial activities where supercritical fluid technology processes are being implemented or developed. Some aspects relating to the economics of sustainable supercritical fluid carbon dioxide processes are also considered.

Key words: supercritical; extraction; synthesis; catalysis; enzymes; polymerization; particles; dyeing

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Introduction

The massive wide scale use of organic solvents by a diverse range of global industries represents a serious threat to the environment. In part response, the Montreal Protocol was introduced in 1987 with an initial objective to restrict or eliminate the manufacture and use of particularly damaging ozone depleting solvents such as chlorofluorocarbons (CFCs). The Montreal Protocol, considered as the most successful international treaty thus far by the former United Nations Secretary General, Kofi Annan, is dynamic and evolving with the manufacture and supply of solvents other than CFCs gradually being restricted. Years of negotiation fostered by the United Nations Environment Programme has now resulted in more than 170 signatory nations to the Montreal Protocol with its London (1990), Copenhagen (1992) and Beijing (1999) amendments. Consequently, world-wide there is pressure for industry to adopt new sustainable processes that do not require the use of environmentally damaging organic solvents. Supercritical fluids are characterized by gas like viscosities and solvating properties of a wide range of various organic solvents. In particular, environmentally benign carbon dioxide in its supercritical fluid (SCF) state is demonstrating significant potential for the development of a wide range of alternative processes that totally or

partially eliminate the use of some of the most commonly used organic solvents. Apart from this factor, the rapid mass transfer properties associated with the lower viscosity of SCF carbon dioxide can bring about more time efficient production capabilities for various types of important industrial processes. Hence, in appropriate circumstances more compact energy efficient plant can be constructed. Furthermore, in the textile dyeing industry the use of SCF dyeing techniques demonstrates considerable potential to reduce a significant global wastewater treatment and discharge pollution problem. This mini-review is designed to illustrate just some examples of the capability and potential of inexpensive SCF carbon dioxide to perform a range of important, sustainable industrial processes.

1 SCF carbon dioxide processes

1.1 Extraction using SCF carbon dioxide

Supercritical fluid extraction (SFE) has been successfully introduced for a range of industrial processes, examples include: coffee decaffeination, isolation of some flavouring components from hops, fatty acid refining and production of herbal products. The relatively low critical temperature of carbon dioxide (304.1 K) enables the extraction of thermally labile compounds whose isolation using traditional methods involving elevated temperatures pose problems. By controlling the density of SCF carbon dioxide it can imitate a range of organic solvents whose polarities range

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from *n*-pentane at lowest SCF density approaching pyridine at highest SCF carbon dioxide density. This property enables selective extraction, purification and fractionation procedures that exploit the tunable solvating strength of SCF carbon dioxide. In some instances, extraction and fractionation using SFE is the only way to meet product specifications (Brunner, 2005). Since SCF carbon dioxide rapidly penetrates and exits solid matrices, this results in more rapid and efficient extractions compared with the use of higher viscosity organic solvents whose solvating strengths SCF carbon dioxide can imitate. The principle limitation of SFE using SCF carbon dioxide is the limited solubility exhibited by polar compounds. However, it is also possible to add small amounts of organic solvents (modifiers) such as ethanol to SCF carbon dioxide to extend the range of its solvating strength to extract more polar compounds from matrices.

On the laboratory scale the use of organic solvents also imposes a significant threat to the environment. Consequently, the United States Environmental Protection Agency have currently accepted and published three sample preparation procedures using SCF carbon dioxide. A SCF carbon dioxide method for measuring oil-in-water free from concerns about future evolving solvent legislation has been designed (Ramsey, 2008) and subsequently successfully evaluated by the United Kingdom Department of Trade and Industry. This is important since on a global scale many millions of oil-in-water measurements using particularly environmentally damaging and hazardous organic solvents are performed annually by a diverse range of industries. Hence, in 1994 the measurement of oil-in-water was the only analytical application identified by the United Nations Environment Programme for which an environmentally clean procedure has to be developed.

1.2 Organic synthetic reactions in SCF carbon dioxide

Two principle roles of organic solvents used to perform synthetic reactions are to dissolve and transport reactant species to one another and *via* solute-solvent collisions help impart activation energy such that if the reactants “collide” with correct orientation reaction proceeds.

Advances in the application of supercritical fluids for carbon-carbon bond formation in organic synthesis have been reviewed to year 2004 (Prajapati and Gohain, 2004) with 135 references cited. In general, it is reported that reaction rates within supercritical fluid media are enhanced due to the higher mass transfer of reactants within SCF media compared to organic solvent mediated synthetic reactions. Hence, this results in a reduction of energy demand compared with chemical reactions performed using traditional organic solvents where slower reaction rates are observed. Additionally, more frequent higher energy solute-solvent collisions within supercritical fluid media are also responsible for enhancing reaction rates though the role of this factor is often neglected. In addition, the role of heat transfer (Mantelis *et al.*, 2007) and micromixing (Carretier *et al.*, 2006) are other important parameters to be considered when performing chemical reactions within SCF carbon dioxide. Some examples of classical

organic synthetic procedures that have been successfully performed in SCF carbon dioxide include: Friedel Crafts, Diels-Alder, Aldol, Claisen rearrangement, Michael addition and Kolbe-Schmitt reaction in SCF carbon dioxide media. At the end of the reaction, as with SFE processes, the SCF carbon dioxide is simply expanded to waste further reducing energy demand compared to processes where organic solvent must be removed, perhaps several different organic solvents during a multi-stage synthetic procedure, to isolate the product. Also the use of SCF carbon dioxide as reaction medium eliminates other energy and further solvent demanding auxiliary processes that very frequently support synthetic reactions performed using organic solvents, e.g., crystallization that may also involve the use of anti-solvents, filtration, product drying and various mechanical procedures to produce particles of the correct size.

1.3 Catalysis in SCF carbon dioxide

The use of SCFs for catalytic processes has been shown to overcome many of the chemical, engineering and environmental difficulties associated with conventional chemical processes (Fahlman, 2002). An overview of heterogeneous and homogeneous catalysis (Subramaniam *et al.*, 2002) performed in SCF carbon dioxide describes the elimination or mitigation of pollution issues caused by the use of organic solvents. Homogeneous catalysis is generally preferred to heterogeneous catalysis since it offers greater rates and selectivities. However, the drawback of this methodology is the difficulty in separating products. By comparison, reactions involving SCF media offer the best opportunity for separation of reaction products and removal of the solvent, accomplished through simple depressurization. Many of the reports illustrate more efficient catalytic reaction rates especially for porous catalysts such as zeolites where active sites are mainly situated within the internal structure of the catalyst. In some instances catalysis performed in SCF carbon dioxide has been achieved in seconds rather than hours using conventional catalytic systems (Harrod *et al.*, 2001). For porous catalysts, high mass transfer of reactants within the catalyst pore structure is particularly important for increasing rates of catalysis. Additionally, many of the SCF catalysis reports describe enhanced catalyst lifetimes due to the elimination of the deposition of carbon species films, a phenomenon referred to as “coking” that ultimately renders the catalytic sites inaccessible leading to catalyst deactivation. Extended catalyst lifetimes using SCF carbon dioxide reaction media, apart from the convenience of keeping the catalytic system running longer, also provides other potential important economic benefits. It means for example, that relatively low cost catalysts such as those based on nickel that are especially prone to “coking” problems using conventional catalytic procedures may possibly be considered for use in SCF reaction media rather than relatively expensive palladium, platinum or ruthenium based catalysts that are more resilient to “coking” in conventional catalyst systems. Additionally, the SCF carbon dioxide removal of “coke” within the pore structures of zeolite catalysts

such as mordenite zeolites (Petkovic *et al.*, 2005) extends the lifetime of this important class of catalysts. Due to its low viscosity, SCF carbon dioxide provides effective and continuous “rinsing” within porous catalyst structures.

Since 1999, amongst the most commonly studied catalytic reactions are: Fisher-Tropsch, hydroformylation, hydrogenation, Heck reactions, Suzuki reactions, oxidations and alkylation reactions. Colloidal catalysis, an intermediate between homogeneous and heterogeneous catalysis, due to high selectivity, high activity and ease of removal of reaction products has attracted attention. Only relatively recently has this class of catalysts been studied in conjunction with SCF carbon dioxide and it was reported (Niessen *et al.*, 2002) that this combination provided surprisingly high hydrogenation reaction rates, even at low hydrogen concentrations. Continuous hydrogenation reactions in SCF carbon dioxide that rely on the *in situ* decomposition of methanoic acid to provide SCF carbon dioxide solvent and hydrogen without the requirement of conventional compressed gas supplies represents an interesting development for this important catalytic process (Hyde *et al.*, 2005). Another development is the use of aerogels to prepare novel catalysts using SCF carbon dioxide to deposit metals such as nano-particles of palladium (Morley *et al.*, 2004) that produces efficient catalytic composites. However, it has been reported (Orlovic *et al.*, 2002) that for the production of a zinc chloride alkylation aerogel catalyst, care must be exercised with respect to the density of SCF carbon dioxide drying conditions. Low density SCF carbon dioxide providing a zinc chloride aerogel catalyst whose surface and pore coating was increased relative to high density SCF carbon dioxide drying conditions that resulted in increased removal of the zinc chloride catalyst from the surface and pores of the aerogel. In addition new inorganic catalysts using environmentally friendly ionic liquids, molten salts that are liquids at room temperature, in the presence of SCF carbon dioxide media for heterogeneous catalysis have been reported (Wang *et al.*, 2007).

1.4 Biotechnology using SCF carbon dioxide

The use of enzymes for organic synthetic procedures is accelerating with significant potential being demonstrated in the area of enantioselective chemical transformations (Salgin *et al.*, 2007). A general finding indicates that enzymatic reactions become less efficient as SCF pressure increases and SCF temperature decreases since these physical changes decrease the diffusion constants of the substrate to the enzymes active sites (Rezaei *et al.*, 2007). In agreement with the numerous reports concerning the use of SCF carbon dioxide with inorganic catalysts, the SCF reports involving enzymatic catalysis report superior reaction rates and efficiencies. In the case of a lipase-catalyzed esterification it has been determined (Ikushima *et al.*, 1996) that in a very limited range near the critical point of carbon dioxide, a drastic enzyme conformation change occurred. This caused the active sites to emerge close to the surface of the modified enzyme tertiary structure, increasing their accessibility thereby providing yet

another mechanism apart from improved substrate mass transfer and heat transfer that further enhanced the rate of biocatalysis. However, this early reported phenomenon has not been generally reported subsequently and consequently the effect may be limited especially if the enzyme active site is composed of amino acids some distance apart, e.g., first and last amino acid residues in lactate dehydrogenase forming components of the active site are 142 amino acid residues apart that are brought together in close proximity by the unmodified enzyme tertiary structure. Membrane reactors have been widely used for enzyme reactions conducted in SCF carbon dioxide and can advantageously enable enzyme recovery and product isolation as a one-step process (Gumi *et al.*, 2007). Furthermore, the use of ionic liquids has been demonstrated to increase the selectivity of a recirculating enzymatic reactor (Rios *et al.*, 2007). Various studies have been conducted using immobilized and non-immobilized enzymes using SCF carbon dioxide with several types of SCF reactors including: batch, stirred-tank, extractive semibatch, recirculating, semi continuous flow, packed bed, continuous-bed, continuous-membrane and cross-flow membrane reactors. Enzymes such as lipases can work extremely efficiently at temperatures in excess of 373 K in dry SCF carbon dioxide. In comparison, enzymes are frequently denatured at such higher temperatures in aqueous media due to hydrolysis. Enzyme stability in SCFs does not appear to be a problem. Consequently, a high throughput enzyme packed column using a continuous flow of SCF carbon dioxide modified with toluene system has been developed and it was reported (Osanai *et al.*, 2006) that enzymatic activity of the lipase used remained stable for at least 6 months. The addition of zeolites to lipase catalyzed esterifications has been found (Peres *et al.*, 2005) to promote enzymatic activity and this is attributed to an ion exchange mechanism promoting the enzyme active site becoming negatively charged as required by the catalytic mechanism.

The downstream processing costs and production cost for a one-step enzymatic conversion in SCF carbon dioxide have been projected (Aatonen, 1999), stemming from which it was concluded that enzymatic reactions in SCF carbon dioxide can be commercially utilized in the fine chemical industry where high specificity is required but that the technology may be limited to the production of only a few tons of product per annum. This is because enzyme catalytic rates are generally slower than inorganic catalytic rates. Often, low solubility of polar substrates in SCF carbon dioxide imposes a limitation of enzymatic catalysis in SCF carbon dioxide. However, further developments in enzymatic reactions performed within aqueous media (Ramsey *et al.*, 2000) or ionic liquids (Miyawaki and Tatsuno, 2008) followed by *in situ* extraction of relatively non-polar products using SCF carbon dioxide may provide a partial solution, in some instances, to at least eliminating the use of organic solvents for final product isolation. Criteria to design green enzymatic processes in five different ionic liquids including stability studies that indicated an improvement in the half-life, over a prolonged period of time, of the enzyme *Candida antarctica* lipase B

at 323 K have been published (Lozano *et al.*, 2004). These studies involved the continuous synthesis of alkyl esters in the presence of SCF carbon dioxide.

1.5 Polymerization using SCF carbon dioxide

SCF carbon dioxide has provided a successful reaction medium for the production of some polymers including: amorphous fluoropolymers, polysiloxanes, some hydrocarbon polymers, polybutylacrylate and polystyrene. Additionally SCF carbon dioxide has been used to synthesize polymers that would otherwise be difficult to prepare (Wood *et al.*, 2007). The use of SCF carbon dioxide to produce polymers provides polymers free of solvents, in many cases also water, that are required for many applications. Also in chain transfer reactions SCF carbon dioxide does not intimately participate hence no complications are anticipated with solvent complexes formed with monomer or macro radicals that may otherwise occur in conventional organic solvent reaction media (Steffen *et al.*, 2004). A dedicated text (Kemmere and Meyer, 2005) provides a comprehensive overview and guide for further polymer research programmes using SCF carbon dioxide.

1.6 Particle engineering using SCF carbon dioxide

Particle design using SCF carbon dioxide is demonstrating significant potential in applications involving the pharmaceutical, nutraceutical, cosmetic and specialty chemical industries. For example, modern day drug delivery systems rely on crystallographic purity and control of polymorphism as an integral part of the process. SCF carbon dioxide has been demonstrated as a means for the preparation and control of specific physical morphology of pharmaceutical compounds (Bettini *et al.*, 2003). A particle design survey using supercritical fluid technology involving a literature and patent search to year 2000 has been published (Jung and Perrut, 2001). Particle engineering using SCF carbon dioxide can overcome thermal and chemical degradation problems that can occur with traditional methods for the micronization of powders that rely on grinding, crushing, milling and sieving.

Two popular methods of particle engineering using SCF carbon dioxide include rapid expansion of supercritical fluid solutions (RESS) and supercritical fluid anti-solvent (GAS) procedures. RESS is well suited for those applications in which the compounds exhibit sufficient solubility in carbon dioxide. Although RESS offers advantages of being able to manufacture nano and micro sized particles without the use of any organic solvent at low temperature it suffers from the disadvantages of limited solubility of many compounds in SCF carbon dioxide, especially polar pharmaceuticals, and high carbon dioxide consumption. The RESS process involves depressurizing the SCF solution through a nozzle of appropriate geometry such that extremely rapid nucleation of the product creates a highly dispersed material. In situations where solubility limitations prevent the use of RESS then GAS has been successfully developed. The basic GAS procedure involves dissolving the compound in an appropriate organic solvent in a partially filled vessel and then introducing SCF carbon dioxide into the vessel such that the volume of organic

solvent is expanded as it becomes super saturated with SCF carbon dioxide. This lowers the organic solvent strength that results in solute precipitation within the vessel. At the end of the precipitation process the organic solvent saturated with SCF carbon dioxide is transferred to another vessel which is depressurized such that the separated solvent and carbon dioxide can be recycled. A chiral resolution process involving GAS for the separation of enantiomers represents yet a further interesting development (Martin and Cocero, 2007). The obvious disadvantage of the GAS procedure is the use of organic solvents though it does help overcome problems associated with traditional micronization. One form of GAS, solvent enhanced dispersion by supercritical fluids (SEDS) uses various SEDS expansion nozzle configurations in which SCF carbon dioxide is introduced to the organic solvent solution to dynamically control the morphology of the products and as such SEDS is more sophisticated compared to basic particle production within a GAS vessel. SCF carbon dioxide has also been used to produce composite micro and nano particles for the sustained and controlled release of drugs from impregnated polymer particles. The polymer supercritical fluid extraction of emulsions (PSFEE) method (Chattopadhyay *et al.*, 2005) uses a counter current flow of SCF carbon dioxide through a column whose opposite inlet is equipped with a fine nozzle that introduces the drug polymer emulsion. As the dispersed emulsion descends the column under gravity, SCF carbon dioxide impregnates the polymer removing the solvent. The resultant carbon dioxide-solvent stream is led to waste collection with the dried drug impregnated polymer particles being collected. Different procedures involving SCF carbon dioxide have also been used to produce microspheres, microcapsules and liposomes.

1.7 Textile dyeing using SCF carbon dioxide

Large-scale water pollution caused by the textile dyeing industry is a global environmental problem. In the United States, the textile industry has invested more than one US billion dollars in the past decade to introduce environmental technologies designed to prevent byproducts of textile manufacturing polluting the environment. This level of investment is paralleled in other parts of the world, most notably Korea and Taiwan. Quality standards of industrial effluents will continue to be raised leading to increase in costs of industrial wastewater treatment in particular those involving the disposal of dye house effluents. Also, apart from significant wastewater treatment costs there is the initial problem of obtaining a water supply of acceptable quality since the water may be too hard and there may be insufficient suitable water supply to establish dyeing houses. It is estimated that with even the most economical use of water up to 100 litres of water are required to produce 1 kg of dyed material. As a consequence, the dyeing of fabrics using SCF carbon dioxide as a dye solvent has been the focus of increasing research.

General findings concerning the use of SCF to dye textiles are as follow: dyeing time is reduced, up to 3 h in the case of fluorotriazine dyed cotton (Fernandez Cid *et al.*, 2006), small amounts of water placed in the dyeing

vessel or sprayed on the fabric, found to be essential for dyeing silk, generally increase textile colouration. This is attributed to water, that is sparingly soluble in SCF carbon dioxide, causing swelling of the fibres leading to increased SCF carbon dioxide dye solution impregnation (van der Kraan *et al.*, 2007). Also it is noted that since dyeing using SCF carbon dioxide takes place using a quasi-type gaseous phase, that the dyestuff is homogeneously distributed leading to a high degree of evenness of fabric dyeing quality. In comparison some water based dye processes require the use of dispersants to evenly solubilise the dye in water; these dispersants also give rise to further wastewater treatment problems. Solubilities of dyes can be controlled by selecting appropriate SCF carbon dioxide density and this allows a simple and convenient method to produce fabrics of selected dye intensity. At the end of the dyeing period the carbon dioxide and excess dye, otherwise forming part of the wastewater effluent in aqueous dyeing processes, can be separated and recycled. If necessary the textile can be rinsed with a solvent such as acetone to remove excess dye that is deposited when the SCF carbon dioxide is expanded back to its non-solvating gaseous phase. However, "rinsing" the finished dyed fabric with pure SCF carbon dioxide is from an environmental and safety perspective a more logical option. Fabrics that have been successfully dyed using SCF carbon dioxide include polyesters, nylon, silk, cotton and wool. Apart from more rapid SCF carbon dioxide dyeing time, shorter times are also required to heat and prepare SCF carbon dioxide dyeing solutions, dyeing being generally conducted at 333 to 415 K, compared with aqueous dyeing solutions. In addition to these energy saving factors, SCF carbon dioxide dyed textiles are produced predominantly or totally dry. Consequently, this eliminates an energy demanding drying stage following textile dyeing in aqueous media, approximately 3800 kJ/kg water evaporated to dry the textile. Hence, apart from providing potential to solve major dyeing industry wastewater treatment issues that represent a significant global pollution problem, SCF dyeing processes are also energy efficient. The major problem in gaining widespread industrial acceptance of SCF dyeing procedures appears to stem from the initial high investment to construct production scale SCF dyeing plant. However, SCF pilot scale dyeing plant is currently available from several vendors in order to pave the way forward.

1.8 Advanced materials manufactured using SCF carbon dioxide

Ionic liquids are molten salts at room temperature with negligible vapour pressure hence they do not evaporate even when exposed to vacuums. In many respects ionic liquids have physical properties, with the exception of volatility, that parallel environmentally benign SCF carbon dioxide. Ionic liquids are: non-flammable, odourless that provide an environmentally benign medium to perform chemical reactions and separations. Furthermore, ionic liquids can be recycled without leading to organic solvent emissions. Ionic liquids have a large variety of applications including electrolytes in batteries, lubricants, plasticizers,

extraction, inorganic and biochemical catalysis. A review of ionic liquids towards supercritical fluid applications has been published (Keskin *et al.*, 2007). In many respects ionic liquids seem the perfect companions to SCF carbon dioxide, e.g., reactions performed within ionic liquids can be subjected to SFE such that solvent free products can be recovered. Despite the various environmental advantages, ionic liquids have been manufactured using volatile organic solvents. However, it has now been demonstrated (Wu *et al.*, 2005) that ionic liquids, 1-butyl-3-methylimidazolium bromide and 1,3-dimethylimidazolium trifluoroethanesulfonate, can be synthesized in SCF carbon dioxide with 100% yield with excess reactants being extracted *in situ* by SCF carbon dioxide thus avoiding any cross contamination and the use of organic solvents. In fact two of the challenges facing the use and applications of ionic liquid-SCF carbon dioxide systems appear how to make ionic liquids soluble in SCF carbon dioxide to enable the solubilising of more polar species within the SCF phase and solute recovery from ionic liquids using SCF carbon dioxide.

Aerogels are the lightest and lowest density solids known to exist. Aerogels are typically 50%–99.5% composed of air yet possess remarkable strength-to-weight ratios being able to support up to several thousand times their own mass. Additionally, aerogels provide large surface-area-to-volume ratios. Due to their high air content aerogels such as blue silica aerogels are translucent whose appearances have been described as "frozen smoke" like. At present most aerogels are fabricated from silica or pyrolyzed organic polymers (Bryning *et al.*, 2007). The main focus of attention for silica aerogels stems from their incredible insulating properties, superior to organic foams such as polystyrene, polyurethanes and polyethers etc. that are produced using organic solvent systems. The eventual disposal of these organic foams also represents a significant environmental problem. Silica aerogels made of inexpensive silicon dioxide that are non-flammable can be fabricated in slabs or pellets and by mass or by volume are the best insulators ever discovered, however despite their strength-to-weight ratios silica aerogels are brittle and also structurally decompose on contact with water. As a consequence of these limitations, one application coupled with their transparency is the potential manufacture of energy efficient windows whereby silica aerogels are supported between two panes of glass. Since silica is environmentally benign, the eventual disposal of silica aerogel insulating materials unlike organic foams poses no significant environmental problems since they can be crushed to produce very fine particles of sand.

Although the use and applications of silica aerogels is still at a relatively early stage of research and development, as previously described silica aerogels have been successfully impregnated with various metals and metal complexes using SCF carbon dioxide to produce new inorganic catalysts. Aerogel-drug formulations for the rapid release of drugs including ketoprofen, griseofulvin and miconazol have been studied (Smirnova, 2002) and that work also reports increased rate of aerogel formation in the presence of SCF carbon dioxide. Another application

of silica aerogels may involve shock-proofing delicate instrumentation since upon impact silica aerogels shatter compared with organic foams currently used for shock-proofing that produce a significant amount of rebound energy when they are impacted. The transfer of a portion of the rebound energy back into the object that the organic foam is designed to protect may give rise to damage.

The most common aerogels are silica aerogels and these are now generally synthesized by polymerization of silicon alkoxides in alcohols to produce a wet gel precursor. The problem arises in drying the gel since removal of solvent using conventional drying techniques brings about collapse of the aerogel pore network due to the liquid surface tension pulling the sides of the aerogel pore network structure together causing shrinkage as the liquid is progressively replaced with air. As a means of initially solving this problem wet gel processes involving the conversion of alcohols into their low viscosity supercritical phase were developed. However, these procedures due to flammability issues are dangerous. Hence, SCF carbon dioxide processes to displace the liquid solvent and dry the gel have been successfully developed as safe replacement technology. Although SCF technology is widely used to dry aerogels, freeze drying techniques have now also been introduced. However, freeze drying often has disadvantages including, the gel aging period has to be prolonged for stabilization of the network and in some cases the pore network structure may be destroyed by initial crystallization of the solvent within the pores. It has been reported (Zhao *et al.*, 2007) that using the two different drying techniques for the preparation of zirconia aerogels, two different products with respect to pore size and morphology were formed, freeze drying producing a powder termed to be a cryogel.

Polyimides are hard wearing materials that have many applications, including the aerospace and electronic industries, have been prepared using SCF carbon dioxide (Said-Galiyev *et al.*, 2003). Unlike polymers that can be easily impregnated with substances using conventional techniques, once formed polyimides are impervious to many materials. However, infusing additives into polyimides greatly increases their applications. Hence, a SCF carbon dioxide method for infusing a highly reflective silver additive into polyimides for aerospace applications has been developed (Boggess *et al.*, 1998).

2 Conclusions

There is no doubt that the industrial activity of mankind has generated too much carbon dioxide giving rise to an imbalance in the biosphere with the massively developing Asian economy serving to exacerbate the situation. However, this review of a selection of key industrial processes confirms, perhaps ironically, the use of SCF carbon dioxide can significantly help reduce further carbon dioxide emissions since the need to eventually transport and incinerate waste organic solvents from manufacturing processes is not required. SCF carbon dioxide processes have also been demonstrated on many occasions to be more efficient, rapid sustainable substitutes for some

processes that currently rely on the use of hazardous environmentally damaging organic solvents. This means that SCF processes are also energy efficient, particularly when they can replace organic solvent based processes that at some stage(s) require removal of organic solvents by energy consuming procedures. The cheap, ubiquitous, inexhaustible world supply of carbon dioxide that has given rise to global warming can be harnessed to provide a wide range of environmentally friendly, energy efficient, economically attractive sustainable processes. Additionally, in the case of the textile dyeing industries, the use of alternative SCF carbon dioxide dyeing procedures provide significant potential to eliminate a current and enormous global wastewater pollution problem. Advantageously, the infrastructure for the isolation and distribution of carbon dioxide for industries including drink carbonation and welding operations is already well established on a global basis. If mankind can fully exploit and seek to limit its own carbon dioxide emissions, perhaps the major problem that has given rise to global warming can be exploited to provide a diverse range of sustainable industries of which only a selection are briefly described within this report.

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