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REVIEW

Applications for supercritical fluid technology in food processing

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The application of supercritical fluid technology in a range of industrial and experimental food processing systems, employing dense carbon dioxide in its supercritical, near-critical or liquid state as a solvent, is reviewed. The principles of supercritical fluid technology are discussed in relation to actual and potential applications. A summary of commercial applications, patented processes and published research studies is presented, together with a more detailed consideration of selected examples of some recent developments.

INTRODUCTION

This review is intended to provide an update of the application of supercritical fluid technology in experimental and industrial food processing systems employing dense carbon dioxide, in its supercritical, near-critical or liquid state, as a solvent. Additional information on many of the subjects discussed in this paper may be found in recent reviews by McHugh and Krukonis (1986), Rizvi *et al.*, (1986*a,b*), Hierro and Santa-Maria (1992), King and Bott (1993), and Hung and Unger (1994), as well as in specific studies cited herein.

Supercritical fluid technology exploits the solvent power and inherent physical properties of a pure compound or mixture at temperatures and pressures at or near its critical point in phase equilibrium. The location of the critical point of a pure compound on its pressure–temperature phase diagram is shown in Fig. 1. The critical point in this simplified example lies at the end of the vaporisation curve, where the gas and liquid phases merge to form a single homogeneous fluid phase. Beyond this point is the supercritical fluid region. Supercritical fluids are characterised by high densities, low viscosities, and diffusivities intermediate between gases and liquids (Rizvi *et al.*, 1986*a*). These unusual properties make supercritical fluids potentially very good solvents. The solubility of a compound in a supercritical solvent is dependent on the density of the solvent, as well as on the physicochemical affinity of the solute for the solvent.

Dissolved compounds can be recovered from supercritical fluids simply by decreasing the pressure and/or increasing the temperature, both of which reduce fluid density. Supercritical fluid density is characteristically very sensitive to small changes in temperature and/or pressure in the vicinity of the critical point and, provided that the relevant phase equilibria are understood, this provides an opportunity for relatively efficient and inexpensive process control steps in practical applications. However, most practical applications of supercritical fluids involve binary, ternary or multicomponent mixtures, which are characterised by phase equilibria of much greater complexity than that illustrated for a single component system, as in Fig. 1. The physicochemical interactions which occur in these systems are still very poorly understood. Until quite recently, this, together with the expense and practical problems associated with the construction and operation of industrial-scale pressure vessels, has constituted a significant barrier to the application of this technology to the extraction and fractionation of complex matrices such as foods and natural products (McHugh, 1986; McHugh & Krukonis, 1986; Rizvi *et al.*, 1986*a*; King & Bott, 1993).

FOOD PROCESSING APPLICATIONS OF SUPERCRITICAL FLUIDS

Research into the solvent properties of dense gases, near-critical and supercritical fluids over the last 130 years has led to the characterisation of a wide range of solvent systems. In some cases, notably in the mining and petroleum industries, this has led to the development of commercially important extraction and fractionation processes (McHugh & Krukonis, 1986). However, with the notable exception of the Solexol process for purifying fish oils using near-critical propane (Dickinson &

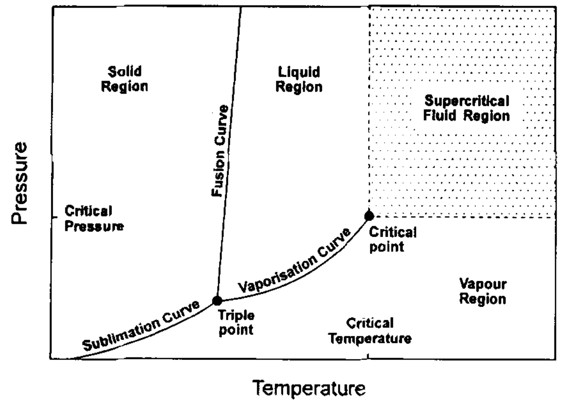

Fig. 1. Theoretical pressure–temperature phase diagram for a pure compound.

Myers, 1952), research and development of food processing applications of supercritical fluid technology has been confined largely to the last 20 years. Significant milestones were reached with the establishment of the first commercial supercritical fluid process for decaffeination of green coffee beans, by Hag A.G. in Bremen, Germany, in 1978 (Lack & Seidlitz, 1993), and the liquid carbon dioxide process for extraction of hop flavours, by Carlton and United Breweries, (CUB) in Melbourne, Australia, in 1980 (Clark & Mailer, 1981). Both of these applications have been successful commercially, and have given rise to numerous variations and improvements which have also been developed to an industrial scale (Gardner, 1993; Lack & Seidlitz, 1993).

Almost all food processing applications of supercritical fluid technology employ carbon dioxide as the solvent. Dense carbon dioxide is not only a powerful solvent for a wide range of compounds of interest in food processing, but it is also relatively inert, inexpensive, non-toxic, non-flammable, recyclable, readily available in high purity, and leaves no residues. With a critical point at 31·1°C and 7·38 MPa, near-critical and supercritical carbon dioxide can be used at temperatures and pressures which are relatively safe, convenient and particularly appropriate for the extraction of a range of more volatile and/or heat-labile compounds. These properties are particularly significant when compared to the safety, toxicity and increasing expense of operation and regulatory constraints associated with some traditional food solvents, such as hexane and dichloromethane.

The range of applications listed in Table 1 reflects the fact that, as a solvent, dense carbon dioxide tends to be selective towards lower molecular weight (below *c.* 500 Da) lipophilic compounds, such as hydrocarbons, halocarbons, ethers, esters, ketones and aldehydes (Rizvi *et al.*, 1986*b*; King & Bott, 1993). Early systematic studies on the carbon dioxide solubility of a range of lipophilic natural substances, for example by Schultz and Randall (1970) and Stahl *et al.* (1984), as well as trends that are emerging from numerous recent studies (summarised by Rizvi *et al.*, 1986*a*, and Sanders, 1993), show that, generally, solubility decreases with increasing molecular weight within a homologous series, and decreases with the addition of polar groups such as hydroxyl, carboxyl or nitrogen. Some selectivity and fractionation within this range may be achieved by controlling solvent temperature and pressure, thereby exploiting differences in solute molecular weight and vapour pressure. The partial fractionation of cholesterol, triglycerides, fatty acids and other lipids from foods such as dried egg yolk (Froning *et al.*, 1990) and anhydrous milk fat (Arul *et al.*, 1987; Bhaskar *et al.*, 1993) illustrates this effect. In the latter study, Bhaskar *et al.* (1993) separated anhydrous milk fat into five fractions, over the pressure range 24·1–3·4 MPa, at 40–75°C. They were able to partially fractionate the short-chain (C4–C8) and medium-chain (C10–C12) fatty acids from the long-chain and unsaturated fatty acids (C14–C18), together with partial fractionation of the corresponding triglycerides. Cholesterol content of the raffinate was decreased by 51%, and beta-carotene content increased by 145%. The melting point of the raffinate increased from 40°C to 45°C; each of the remaining four fractions had a different melting point, ranging from 30 to 38°C. It is a common observation in such processes that carotenoids, and polar substances such as sugars, polysaccharides, amino acids, proteins, phosphatides, glycosides and inorganic salts are relatively insoluble in dense carbon dioxide, and are largely retained in the raffinate (Schultz & Randall, 1970; McHugh & Krukonis, 1986; Rizvi *et al.*, 1986*b*; King & Bott, 1993).

In many supercritical fluid systems, a retrograde phenomenon (lowering of solubility on increasing temperature) occurs, at relatively low pressures, close to the critical region, where the increase in solute vapour pressure is insufficient to fully compensate for the loss of solvent power caused by reduction in solvent density (Mansoori *et al.*, 1988). When temperature is increased at higher pressures, the corresponding increase in solute vapour pressure can more than compensate for the reduction in solvent density, resulting in an overall higher solubility. This relationship is sometimes apparent as a 'crossover' effect in solubility isotherms, as illustrated in Fig. 2. In this example, Schmitt and Reid (1986) found that, at pressures above *c.* 16 MPa, the solubility

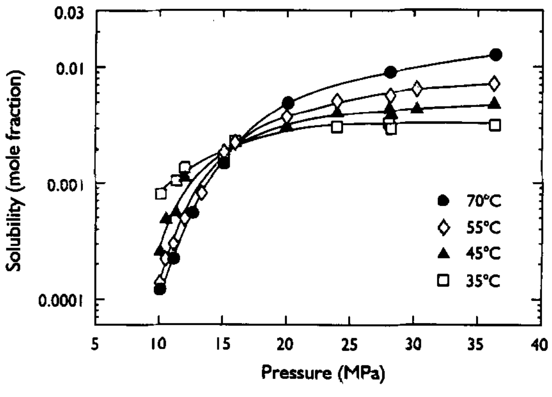

Fig. 2. Solubility isotherms for benzoic acid in supercritical carbon dioxide, showing the 'crossover point' at *c.* 16 MPa. Data from Schmitt and Reid (1986).

Table 1. Examples of food extraction systems employing supercritical or near-critical carbon dioxide

Process and food type	Reference	Process and food type	Reference
1. Extraction of fats and oils		5. Flavour/aroma extraction	
Fish	Zosel (1978)	Hops	Gardner (1993)
Rice bran	Ramsey *et al.* (1991)	Ambrette, Angelica, Aniseed, Anise	
Evening primrose	Favati *et al.* (1991)	Basil, Capsicum, Caraway, Cardamom,	
Soybean	List & Friedrich (1985)	Carob, Carrot, Cassia, Celery, Cinnamon,	
Peanuts	Goodrum & Kilgo (1987)	Clove, Cocoa, Coffee, Coriander, Cumin,	
Sunflower	Stahl *et al.* (1980)	Cubeb, Fennel, Fenugreek, Ginger,	
Canola	Lee *et al.* (1986)	Juniper, Lovage, Mace, Marjoram,	
Rice, rice koji	Taniguchi *et al.* (1987*a*)	Nutmeg, Oregano, Parsley, Pepper, Pimento	
Beef	Chao *et al.* (1991)	Rosemary, Sandalwood, Sage, Savoury,	
Oats	Fors & Eriksson (1990)	Thyme, Turmeric, Vanilla, Vetiver	Moyler (1993)
Potato chips	Hannigan (1981)	Onion	Sinha *et al.* (1992)
Corn germ	List *et al.* (1984*a*)	Dried botino (Katsuobushi)	Hamatani & Takahashi (1988)
Cottonseed	List *et al.* (1984*b*)	Apple	Bundschuh *et al.* (1988)
Egg yolk	Froning *et al.* (1990)	Passion fruit	Raasch & Knorr (1991)
Krill	Yamaguchi *et al.* (1986)	Wine	Carnacini *et al.* (1989)
Wheat germ	Taniguchi *et al.* (1985)	Dried mushroom	Valle & Aguilera (1989)
Mustard	Taniguchi *et al.* (1987*b*)	Citrus fruits	Temelli *et al.* (1988)
Olive	Giovacchino *et al.* (1989)	Cheese	Gmuer *et al.* (1986)
Cocoa	Rossi *et al.* (1989)	Elderberry	Eberhardt & Pfannhauser (1985)
Yeast extract	Duwe *et al.* (1986)	Caraway, wormwood	Stahl *et al.* (1984)
Biscuit wastes	Nakazono (1987)	Lactones from milk fat	Rizvi *et al.* (1993)
		Peppermint oil	Goto *et al.* (1993)
2. Cholesterol extraction			
Beef	Chao *et al.* (1991)	6. Miscellaneous extractions	
Milkfat	Fujimoto *et al.* (1987)	Bixin pigment from annatto seeds	Degnan *et al.* (1991)
Egg yolk	Froning *et al.* (1990)	β-Carotene, lutein from leaf extracts	Favati *et al.* (1988)
Fish	Hardardottir & Kinsella (1988)	β-Carotene from sweet potatoes	Spanos *et al.* (1993)
		Pesticides from contaminated senna leaves	Stahl *et al.* (1984)
3. Fractionation of fats and oils		Antioxidants from sage extracts	Djarmati *et al.* (1991)
Milkfat	Arul *et al.* (1987)	Antioxidants from Labiatae herbs	Nguyen *et al.* (1991)
Sunflower oil	Stahl *et al.* (1980)	Fractionation of glucose/fructose mixtures	Bracey *et al.* (1991)
Rice bran oil	Saito *et al.* (1991)	Inactivation of orange juice pectinesterase	Balaban *et al.* (1991)
Fish oil	Zosel (1978)	Off-flavours from textured vegetable proteins	Sevenants (1987)
Citrus oils	Temelli *et al.* (1988)	Debittering of citrus juices	Kimball (1987)
Fatty acid esters	Liong *et al.* (1992)	Decaffeination of coffee, tea	Lack & Seidlitz (1993)
Canola oil	Temelli (1992)	Concentration of alcohol and other fermentation products	Saito *et al.* (1987)
4. Refining of fats and oils			
Deodorisation of soybean, palm kernel and peanut oils	Zosel (1979) Ziegler & Liaw (1993)		
Deacidification of olive oil	Brunetti *et al.* (1989)		
De-oiling of soybean lecithin	Heigel & Hueschens (1983)		
Hydrogenation of vegetable oils	Zosel (1976)		
Deodorisation of rosemary extract	Muehlnikel (1992)		
De-oiling of bleaching clays	Waldmann & Eggers (1992)		
Extraction of tocopherols from soybean sludge	Lee *et al.* (1991)		

of benzoic acid in supercritical carbon dioxide increased with increasing temperature. Below this pressure, which corresponds to the solubility isotherm crossover point in this system, increasing temperature resulted in a decrease in solubility. Some food processing systems have succeeded in controlling and exploiting this complex thermodynamic behaviour, to effect simultaneous extraction and fractionation at relatively low pressures. In practice, this is usually achieved by operating two or more separation vessels in series, with the secondary or tertiary separator set at a slightly higher temperature than the primary extraction vessel and the final evaporator/condenser. For example, in the fractionation of anhydrous milk fat, Bhaskar *et al.* (1993) used five separation vessels in series, operating at 40°C/24·1 MPa, 60°C/24·1 MPa, 75°C/17·2 MPa, 60°C/6·9 MPa and finally 60°C/3·5 MPa. Retrograde condensation of lipid fractions in the second and third separators was achieved by first increasing process temperature at constant pressure, then further increasing temperature while commencing pressure reduction. Additional examples include the fractionation of sunflower seed oil (Stahl *et al.*, 1980), wormwood (Stahl *et al.*, 1984), rice bran oil (Saito *et al.*, 1991), fish oil (Zosel, 1978), citrus peel oil (Shin *et al.*, 1992), and fatty acid esters (Liong *et al.*, 1992).

Carbon dioxide cannot be regarded as a simple substitute for organic solvents, as there will usually be commercially significant qualitative and quantitative differences between the two types of extracts. Hexane-extracted vegetable oils and fish oils, for example, may be rich in phosphatides (lecithin), whereas carbon dioxide-extracted oils usually contain little or no phosphatides. This results in the two types of extracts, and their corresponding raffinates, having very different processing characteristics (List & Friedrich, 1985; Yamaguchi *et al.*, 1986; Ramsay *et al.*, 1991). Commercially significant differences in yield and chemical composition are also apparent in many carbon dioxide-extracted flavours and fragrances, compared to the corresponding traditional steam-distilled or ethanol-extracted products, and relate, for example, to differences in the proportions of particular water-soluble or volatile/heat-labile components in the extracts. This can result in carbon dioxide extracts, such as some of the more complex essential oils, being regarded as superior in quality to steam distillates, in that their composition more closely resembles that of the headspace odour of the botanical source (Schultz & Randall, 1970; Moyler, 1993). Conversely, carbon dioxide extraction of flavours such as carob, which includes important high-molecular weight, water-soluble components, may yield a product which is functionally inferior to the traditional ethanol–water extract (Moyler, 1993). Consequently, the commercial success of adoption of carbon dioxide as an alternative extraction solvent often depends on the associated development of new ancillary processes for the handling and utilisation of new types of product. In hop extraction, for example, the commercial success of the CUB liquid carbon dioxide process depended not only on the development of an efficient process for extraction and carbon dioxide recovery, but also on the development of a new secondary process for the separation, concentration and isomerisation of hop alpha-acids from the extract, and recovery of the base flavour component, without the use of organic solvents (Clark & Mailer, 1981).

An additional consideration in the development of a new carbon dioxide extraction process is that the conventional form of the material to be extracted may be unsuitable with respect to the solvent characteristics of carbon dioxide and the design of the pressurised extraction vessel. In the CUB process, for example, it was found that neither dried, baled hops, nor the traditional pelletised hops used in wort processing, were entirely suitable for carbon dioxide extraction. The CUB process was therefore further modified by developing a hop pretreatment process that produces a type of dried, milled and pelletised hop material that is ideally suited to carbon dioxide extraction. This resulted in significant improvements in extraction efficiency and product quality, and is now an integral part of the overall process (Clark & Harold, 1983).

The solubility range, selectivity and versatility of supercritical carbon dioxide systems can be extended and modified dramatically by the use of entrainers and adsorbents. An entrainer is commonly a cosolvent, with intermediate volatility between that of the primary supercritical fluid and the solute to be extracted. The cosolvent is miscible with the primary supercritical fluid, and usually constitutes only a small percentage of the overall fluid composition. Although most cosolvents are liquids at ambient conditions, gases can also be used. Among the relatively few theoretical studies of supercritical fluid cosolvents that have been published, the observations of Dobbs and Johnston (1987) provide an interesting example of both qualitative and quantitative effects of a cosolvent (3·5 mol% methanol) on the solubility of two structurally similar solutes (benzoic acid and hexamethyl benzene) in supercritical carbon dioxide. Their data, shown in Fig. 3, indicate

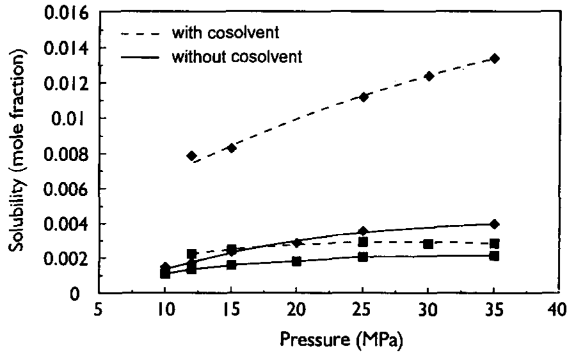

Fig. 3. Cosolvent effect of methanol in supercritical carbon dioxide. Solubility of both benzoic acid (♦) and hexamethyl benzene (■) increases, and selectivity for benzoic acid is improved, when 3·5 mol% methanol is added to the benzoic acid/hexamethyl benzene/carbon dioxide system. Data from Dobbs and Johnston (1987).

that, under these conditions, the methanol cosolvent increased the carbon dioxide solubility of both solutes, as well as greatly improving the selectivity for benzoic acid. Cosolvents in systems such as these are thought to enhance solute solubility by physical interaction with the solvent, possibly to increase solvent density, as well as by specific chemical interaction with the solute, for example by hydrogen bonding (Dobbs *et al.*, 1987; Ting *et al.*, 1993*a,b*).

In food processing applications, ethanol, water and various gases are particularly suitable cosolvents. Such cosolvents have been used to enhance the solubility in carbon dioxide of materials such as annatto pigments (Degnan *et al.*, 1991), rice bran oil (Ramsay *et al.*, 1991), monosaccharides (Bracey *et al.*, 1991), egg yolk lipids (Rossi *et al.*, 1990), fish oils (Hardardottir & Kinsella, 1988), gluten lipids (Hammam *et al.*, 1987), caffeine (Lack & Seidlitz, 1993), juniper berry oil (Moyler, 1993), cholesterol (Wong & Johnston, 1986), triglycerides (Ikushima *et al.*, 1985) and canola lipids (Temelli, 1992). Some entrainer-based systems, however, may suffer from the disadvantage that it is necessary to strip the entrainer from the product after extraction.

Adsorbents have been used in a range of supercritical carbon dioxide extraction and fractionation systems, and have the potential to greatly improve the selectivity and efficiency of separations by a variety of mechanisms, usually by specific interaction with solutes or solute impurities at the extraction, separation or collection/evaporation stages. Examples include the use of a silica gel–silver nitrate column to fractionate fatty acid esters of rice bran oil (Saito *et al.*, 1991), silicate, or a mixture of activated carbon and celite, to remove cholesterol from anhydrous milk fat (Fujimoto *et al.*, 1987), and activated carbon to trap commercially valuable caffeine extracted during decaffeination of tea and coffee (Lack & Seidlitz, 1993). Adsorbents, such as activated carbon, may also have an important role to play in removal of toxins, pollutants or other undesirable components from the carbon dioxide at the final stage of an extraction process, before the gas is recycled or vented to atmosphere.

Examples of food-related applications of carbon dioxide extraction are summarised in Table 1. Most of these applications are still at the research or process development stage. Commercially successful hop extraction plants have been established in several countries, including Australia, UK, Germany and USA. There are several commercial plants for the decaffeination of coffee and/or tea, notably in Germany, UK, Japan, USA and Austria. The third area of significant commercial development in this field has been in the flavour and fragrance industry, with commercial plants operating in several countries, including UK, France, Germany, USA and Japan. These industrial plants are commonly batch or semi-batch systems, and vary in capacity according to the nature of the product and the operating requirements of the process. Some relatively small extraction plants (100–500 litre extraction volume), have been used successfully by the Japanese food industry to process a range of high-value food ingredients and medicinal compounds, such as katsuobushi and octosanol (Hung & Unger, 1994). Several commercial flavour extraction plants, such as those used by Universal Flavors Ltd (UK) and CUB (Australia) are designed to extract approximately 500 kg at a time, with three to five extraction vessels in series, in a semi-batch process (Clark & Mailer, 1981; Moyler, 1993). In the CUB process, this allows up to 4 t of pelletised hops to be processed, yielding up to 800 kg of hop extract, per day. The use of even larger extraction vessels, such as the four 4000-litre vessels comprising the BXT tea decaffeination and hop extraction plant in Wolnzach, Germany, can result in even greater production capacities.

FUTURE PROSPECTS

The successful commercial developments described above share some common characteristics. First, they involve the processing of relatively high-value, low-volume products. The decaffeination processes have the unusual advantage of producing a valuable extract (caffeine), as well as a valuable raffinate (decaffeinated coffee beans). Many extraction processes for essential oil/oleoresin-type flavours have had the advantage of being applicable not only to the food industry, but also to highly profitable sectors of the perfume and fragrance industry. Secondly, these areas have had the benefit of ten years or more of thorough research and development. Thirdly, they consist of relatively simple extraction processes, exploiting the inherent solubility and selectivity characteristics of carbon dioxide, in relation to certain types of lower-molecular-weight organic compounds, in batch or semi-batch systems. According to these criteria, commercial developments in the near future might be expected to continue in the area of food flavours, as well as in the extraction and refining of 'natural' food ingredients, functional foods, alternative medicines and specialty oils.

Recent developments in the production of industrial fine powders and thin films, by the rapid non-equilibrium precipitation of non-volatile compounds from dense gas solutions upon expansion, may also find applications in food processing (Matson *et al.*, 1987; Lee *et al.*, 1990; Tom *et al.*, 1993). In rapid expansion of supercritical solution (RESS) processes, a non-volatile solute is dissolved in a supercritical fluid at high pressure, then precipitated mechanically, rather than thermally, by fast decompression. This allows rapid establishment of uniform nucleation conditions within the solution, minimising temperature and pressure gradients, and results in particles with a narrow size distribution. The sensitivity of supercritical fluids to small changes in temperature and pressure in the highly compressible region offers the potential to control both particle size and morphology over a wide range, with only small adjustments to process conditions. In a related application, gas anti-solvent (GAS) crystallisation, solids may be dissolved in a liquid, and a supercritical fluid (having a low solvent power with respect to the solids, but miscible with the liquid) is added to precipitate the solids. Rapid addition of the supercritical fluid results in a sudden reduction in liquid density, and the rapid precipitation of small and uniform particles. The GAS technique may be particularly useful in processing solids such as polypeptides and proteins, which are difficult to solubilise in supercritical fluids or sensitive to mechanical handling. Both RESS and GAS technologies are being investigated in relation to microencapsulation and controlled release formulations for drugs, particularly as alternative processes for compounds which are prone to degradation or denaturation by heat, oxygen or mechanical stress (Tom *et al.*, 1993). Parallel problems and similar opportunities exist in the development of improved food ingredient formulations, such as controlled release flavours and preservatives. The commercial feasibility of some of these developments may be more promising than many of the separation systems investigated previously, in that they involve the processing of relatively small quantities of high-value components.

Research and development in supercritical fluids is also being extended to cover such diverse processes as chemical and enzymatic reactions, and recrystallisations (Caralp *et al.*, 1993), non-thermal sterilisation (Kamihira *et al.*, 1987) and extrusion technology (Rizvi & Mulvaney, 1992). As our knowledge and experience in the chemistry, thermodynamics, phase behaviour, engineering, scale-up and economics of supercritical and near-critical fluid systems improves, this technology may well find application in the processing of some lower-value, higher-volume products, such as vegetable oils, milk fat, and food industry by-products. Additional pressures to develop this type of alternative technology are likely to come from the increasing costs and constraints of traditional solvent extraction systems, and of the management and minimisation of industrial wastes.

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