Applications of Supercritical Fluids

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Key Words

separation processes, formulation, chemical reactions, biomass, supercritical water oxidation, polymers, nanostructures

Abstract

This review discusses supercritical fluids in industrial and near-to-industry applications. Supercritical fluids are flexible tools for processing materials. Supercritical fluids have been applied to mass-transfer processes, phase-transition processes, reactive systems, materials-related processes, and nanostructured materials. Some applications are already at industrial capacity, whereas others remain under development. In addition to extraction, application areas include impregnation and cleaning, multistage countercurrent separation, particle formation, coating, and reactive systems such as hydrogenation, biomass gasification, and supercritical water oxidation. Polymers are modified with supercritical fluids, and colloids and emulsions as well as nanostructured materials exhibit interesting phenomena when in contact with supercritical fluids that can be industrially exploited. For these applications to succeed, the properties of supercritical fluids in combination with the materials processed must be clearly determined and fundamental knowledge of the complex behavior must be made readily available.

INTRODUCTION

Although the properties of supercritical fluids are well known, they are as yet not fully exploited for industrial applications. The density of a pure supercritical fluid is easily changed by relatively small variations in pressure and temperature. In many cases, release of pressure drastically decreases temperature owing to the Joule-Thomson effect, which induces effects on phase behavior that can be the basis for many practical applications. The viscosity of a supercritical fluid is quite low but may increase with temperature. The surface tension of a supercritical fluid is essentially nonexistent. Diffusivity is high, which in combination with low viscosity induces interesting transport phenomena in condensed phases.

When very near to the critical point, fluids exhibit substantial deviations from normal behavior. Making use of these phenomena is difficult because control of process conditions to 1°C or 0.1 MPa is not easy to maintain. Furthermore, supercritical fluids are generally applied with other components to create at least a binary system that is far from the binary critical point.

Supercritical fluids, in particular CO_2, influence the properties of components with which they are mixed. Supercritical fluids dissolve substantially in condensed phases and are able to dissolve compounds far beyond their vapor pressure. Solubility in gaseous and condensed phases is one of the main useful supercritical fluid properties, but to design processes properly and to understand process phenomena if process conditions change, this property must be seen in context with thermodynamic phase equilibrium. Supercritical fluids drastically reduce the viscosity of condensed phases, sometimes making it possible to handle these materials in process equipment. The surface tension of liquids also decreases drastically with the amount of dissolved supercritical fluid, which enables mixtures containing supercritical fluids to move freely in small pores and tiny structures.

Far from being exhaustive, this short introduction suggests how flexible supercritical fluids can be in processing materials. This review covers recent industrial and near-to-industry applications; many other reviews have covered the fundamental properties of supercritical fluids.

Older areas of application are not reviewed here because they have been covered previously. Other areas not herein reviewed are supercritical fluid chromatography and enhanced oil recovery. Well-known industrial applications of supercritical fluids to the extraction of natural materials that are not covered include the decaffeination of coffee and tea, the defatting of cacao, and the production of extracts from hops, fruits, spices, nuts, and other natural materials; these processes are well documented elsewhere (1–5). Although the development of supercritical fluid chromatography for production on the preparative scale was successful (6, 7), its transfer to industrial processes has not yet been reported, although Taylor (8) recently reviewed the analytical aspects. Enhanced oil recovery with carbon dioxide has been a promising application for 35 years and may contribute to carbon capture and storage. Approximately 245,000 barrels per day of mineral oil were produced in the United States in 2008 with enhanced oil recovery techniques. This well-known technology is reviewed thoroughly elsewhere (9–11).

MASS TRANSFER PROCESSES

This section covers industrial applications of supercritical fluids to mass transfer processes in separation processes such as extraction from solids, multistage counter-current contacts, impregnation, dyeing, tanning of leather, and cleaning. In addition, topics directly related to industrial applications, such as optimization of extraction pressure and processing costs, and some process examples that are not yet commercialized are addressed. Information on industrial processes depends on the policies of companies using and selling supercritical fluid processes. Only open and accessible information can be reviewed.

Extraction of Essential Oils, Specialty Oils, and Edible Oils

Supercritical fluid extraction (SFE) from solids is carried out by continuously contacting the solid substrate with the supercritical solvent. The solid substrate is a fixed bed in most cases. The supercritical gas flows through the fixed bed and extracts the product components until the substrate is depleted. The loaded solvent is then removed from the extractor and fed to a precipitator or separator. Extraction and precipitation of the extract can be carried out in various devices, but in most cases one or more autoclaves are used as batch extractors and precipitation is achieved in a single step by reducing pressure and temperature (1). Globally, several companies supply standard design and customized plants. SFE technology is available for any size of plant and quantity of feedstock. Bertucco & Vetter (2), Brunner (3), and Pilz et al. (5) present fundamental information on the process and equipment. The contribution by Pilz et al. (5) is particularly helpful (although in German) because the extraction process with all its aspects is treated by major suppliers of supercritical fluid equipment. Furthermore, at any conference on supercritical fluids, dozens of papers are presented on the extraction of compounds from solids. Very few of these represent results that could be used to design a process because few aspects of the complex information needed to design a pathway from feedstock to product are covered.

Sesame oil. Most of the recently built industrial-size extraction plants are in Asia. For example, sesame oil is usually produced by roasting sesame seeds at more than 200°C and then extracting the oil by pressing at 180°C (12). The expressed sesame oil is prone to oxidation and loss of flavor. Extraction with CO_2, however, results in products without flavor loss. The active substances, sesamoline and sesamine, are soluble in CO_2 and are nearly completely present in the extracted oil. In 2004, a Korean venture company, UMAX Co., started to produce sesame oil in a large industrial SFE plant (~8000 liters of oil day^{-1}) in Korea (13). NATEX (Natex Prozesstechnologie GesmbH, Ternitz, Austria) designed and constructed the UMAX plant, which consists of two extractors with a capacity of 2500 liters and a design pressure of 55 MPa. The involved companies claim that the product is economically successful. NATEX reported calculated production costs for a plant with a capacity of 3 × 2.5 m^3 payload volume and a pressure of 32.5 MPa (55.0 MPa) as 0.635 €/kg feed (0.52 €/kg feed) for 38 weeks of operation per year and 0.53 €/kg feed (0.435 €/kg feed) for 50 weeks of operation per year (12).

In 2006 another Korean food company, Ottogi, started a commercial-scale SFE plant for the extraction of sesame oil from residues; Ilshin Autoclave Co. (Korea) constructed it (13). In this plant, all residual oil is extracted by SFE and then blended with the sesame oil extracted by pressing. Three extractors of 2300 liters each are used (13).

Cleaning of rice. Another new commercial application of SFE is cleaning rice. The Five King Cereal Industry Company Ltd. in Taiwan operates a rice-cleaning plant built by NATEX that includes three extractors of 5800 liters each (13). The average throughput is 4 tons hour^{-1}, and the total investment is U.S. $10 million. Further details on the operating conditions are not known. Five King Cereal Industry Company Ltd. claims that rice cleaned by supercritical CO_2 has advantages over the conventional product: Pesticides and heavy metals are removed, and germs and insect eggs are destroyed. The waxy layer and fatty acids are removed, which prevents degradation of the rice. Cooking time is shortened by 30%, and the shelf life of the bagged rice is extended.

Large-scale extraction. For huge quantities of solids, the literature discusses continuous processing. Continuous operation of equipment for extraction from solids eliminates downtime due

to batchwise changing the substrate in the vessel and thus enhances the production rate. Furthermore, the oscillation of pressure in the extraction vessel, which limits the number of operation cycles, is avoided. Large-scale extraction of soybean flakes with supercritical carbon dioxide was studied (14). For a product rate of 120,000 tons year^{-1} of soybean flakes, operating conditions and several process configurations were calculated using information based on long experience with the construction and operation of large-scale extractions. Optimum extraction pressure for the oil (triglycerides) is 40 MPa at 100°C with a solubility of 0.02 kg_{oil} $kg_{CO_2}^{-1}$, which is a compromise between economics and product quality. Solubility of the oil in CO_2 increases exponentially with pressure, thus lowering the energy costs for the CO_2 cycle but increasing the investment costs at the same time. The extracted oil was separated from CO_2 using reduction of density by reducing the pressure to 20 MPa at 100°C. For these conditions an economic analysis of the total extraction process found the lowest costs by considering various methods for the product separation, including isobaric separation and separation at pressures as low as 6 MPa. At recovery conditions, the residual loading of the CO_2 is approximately 0.0003 kg_{oil} $kg_{CO_2}^{-1}$. This value must be below the limit for the allowable residual loading (for this case approximately 0.0007 kg_{oil} $kg_{CO_2}^{-1}$), as derived from the accepted oil content remaining in the substrate at the end of the extraction after the oil in the remaining CO_2 in the substrate has been precipitated onto the substrate.

The process configurations include (*a*) several extractor vessels employing batch extraction; (*b*) an extractor that uses a carrier fluid; (*c*) a large extractor vessel with smaller feed and recovery vessels, as used for decaffeination of coffee beans; and (*d*) a continuous system similar to a chain extractor but modified for high pressures with special feed and removal systems.

Calculations showed that the total costs are lowest for the continuous extraction system, but the difference is small compared with the conventional batch extraction system with three extractors. The complex continuous system is not justified. Disappointingly, the cost advantage of continuous operation found for small-scale processes was not transferable to the large-scale extraction of oils from solids. The main reason is the larger amount of energy needed to introduce and remove the solid material at separate locations, necessary in continuous operation, compared with the time-sequenced operation steps in a conventional batch system.

The cost of the CO_2 extraction is 12 ¢/liter of oil, which is approximately twice as high as that for hexane (approximately 6 ¢/liter of oil) but still low. The CO_2 extraction produces soy flakes (also known as white flakes) that can be used for human food, whereas hexane-extracted flakes can only be used for animal food. Because the oil removed is only 20% of the feed, the residue of 80% determines the economics. Thus, because white flakes are more valuable, the total extraction process with CO_2 may be economically feasible, at least for the quantities needed for human food protein (14).

Very high pressures. Application of very high pressures (>100 MPa) in commercial extraction has been discussed recently (15, 16). Such high pressures pose no basic problems and may be of interest for the processing of pharmaceutical compounds that are difficult to dissolve. For example, in the extraction of rosemary, the concentration of the main components does not change much from 50 MPa to 150 MPa, with the exception of carnosolic extraction at 150 MPa, which also could be enriched from a 50-MPa extract. However, in the extraction of sliced nut kernels (*Juglans regia*) with an oil content of approximately 58 wt%, the extraction rate increases with pressure, but the yield does not change compared with extraction pressures of 30 or 50 MPa, and CO_2 consumption at 50 MPa is only 50% more than that at 150 MPa. The authors (15) claim that substances are selectively extracted in the pressure range 150–250 MPa. Enhancing the extraction pressure must be considered with care. With higher pressures the composition of the extract changes and may differ from that for a known and expected product. Whether higher pressures are

advantageous cannot be decided technically. Rather, the product must be accepted by customers and sold profitably.

Other Industrial Applications for Extraction

This section reviews some industrial applications of supercritical fluid extraction with CO_2 other than oil extraction.

Cork treatment. Cork stoppers are used for closing wine bottles. Sometimes, wines suffer from a defect that is attributed to the cork. Among the substances that can be blamed is 2,4,6-trichloroanisole (TCA). Even in very small quantities, approximately 4–5 ng liter^{-1}, TCA can contaminate wines (17). TCA levels from 0.13 to 2.11 ng/g of cork (18) can result in cork-tainted wines. In 2003 a new cork treatment process using supercritical CO_2 (19, 20) was presented. Operating conditions are from 10 to 30 MPa and 313 to 333 K. In a bench scale unit, residual TCA values of <0.5 ng g^{-1} (detection limit) were achieved while maintaining the shape of the cork stoppers. NATEX scaled up the process for a large industrial plant with a capacity of 2500 tons year^{-1}, which began to process cork granules in 2006 (21, 22). An interesting feature is the application of a compressor process for the CO_2 cycle.

Spent rubber tires. Another interesting extraction process is the application of supercritical CO_2 extraction to spent rubber tires to create new products from waste rubber granules (23). The supercritical CO_2 process eliminates the unpleasant rubber smell, improves leaching properties for components such as polycyclic aromatic hydrocarbons (PAHs), and by impregnation can add new features such as grass smell, fire retardants, and color. A minimum pressure of 26 MPa is required to achieve a reasonable extraction yield of compounds soluble in supercritical CO_2. Extracting too much of the soluble compounds makes the rubber granules brittle and unsuitable for many applications. By adjusting and controlling the extraction process conditions as well as by performing a proprietary separation, a selective removal of odor compounds can be achieved while substantially keeping the amount of extender oils and the level of antioxidants unchanged (23). Evaluation of the economics for a supercritical CO_2 plant with a capacity of 10,000–20,000 tons year^{-1} results in processing costs of 0.3 to 0.4 € kg^{-1}. This process is an interesting alternative to dumping or other waste processes.

More detailed information on extraction with supercritical fluids. Many recently published reviews and book chapters cover the steps for extracting compounds from solid materials with supercritical fluids, primarily CO_2. A special issue of *The Journal of Supercritical Fluids* addressed the state of the art and developments in the past 20 years (24). Temelli (25), Temelli et al. (26), and Catchpole and coworkers (27) review the processing of lipid compounds. Detailed information can also be obtained from Reference 4, which contains contributions on tocopherols (28), fish oils (29), application to Chinese medicine (30), extraction from South American plants (31), and essential oils (32). King & Srinivas (33) present a broad view of the combination of process steps in production processes.

Surprisingly, information on industrial and commercial processes is scarce. Goedecke (5) presents the best compilation of supercritical fluid extraction knowledge regarding industrial processes and equipment. In the relevant chapter, industrial companies reveal essential information on technical processes that use supercritical fluids.

General Remarks on Extraction

These remarks summarize the reviewer's opinion on extraction from solids with supercritical fluids:

- Extraction from solids is by far the most important industrial application for supercritical fluids, primarily CO_2. Supercritical fluid extraction on a large scale is well known, and design improvements are always in progress; such changes include those due to safety concerns and investigations into the advantages of pressures beyond 50 MPa.

- Multiple extractors of appropriate size provide the most economic way to extract solids batchwise.

- Sequential extraction (multiple-stage counter-current operation) makes sense only if the loading of the extracting supercritical fluid is far from equilibrium solubility and if the extract is used as a single product containing all intermediate extract mixture compositions.

- Continuous extraction is in general not advantageous owing to the high effort required to transport solids to and remove them from a pressurized vessel. Nevertheless, decontamination of fine soil particles has been achieved successfully.

- Mostly the literature neglects that, in general, multiple compounds are extracted together. This multicomponent nature of the extract has at least two main effects: (*a*) During ongoing extraction the composition of the extract changes; in favorable cases the extract can be used for fractionation, and (*b*) the composition of the extract depends on the solvent-to-feed ratio because the equilibrium solubility of the compounds in a system containing more than two components depends on the solvent-to-feed ratio. Modeling such an extraction requires including the time-dependent composition change.

- Extraction with liquid hot water beyond 100°C (also known as subcritical water) is under investigation and probably has been applied in industry, but little information has been released. With liquid hot water, physical extraction is accompanied by chemical reactions. The higher the extraction temperature, the more reactions with water occur until at supercritical conditions most of the organic matter is broken down to simple molecules. This special topic is not covered here.

- Extraction with other gases, e.g., propane, may be advantageous because of higher solubility or selectivity with respect to their lower polarity as compared with CO_2. But, in contrast to CO_2, after removal from the processing facility, the products must be carefully degassed. Propane removal to a level well below 100 ppm requires a vacuum and many hours.

Supercritical Drying

Other processes in which components are removed from solids are desorption, drying, and cleaning. Desorption is a process for removing substances from porous surfaces.

Supercritical drying can advantageously produce aerogels, usually from silicon. An organic substance, e.g., ethanol, is removed from the gel by supercritical carbon dioxide. Disappearance of surface tension in supercritical fluids is essential for that process. The supercritical fluid is applied at conditions that are supercritical with respect to the substance removed and the supercritical solvent. Otherwise, e.g., during convective drying, the gel-like structure would collapse. Aerogels produced with supercritical CO_2 are not new, but recently they have been investigated for various purposes, e.g., as supports for catalysts and as carriers for pharmaceuticals. Materials other than silicon have been used to produce aerogels, e.g., polymers and biopolymers. In a project supported by the European Union, a consortium attempted industrial production of aerogels from cellulose (34). The cellulose solution was transformed into various gelled forms. The aerogel bodies were

immersed in a solvent that can be displaced by CO_2 at conditions of complete miscibility with the organic solvent. Otherwise, liquid remains in the structure, resulting in capillary forces that destroy the structure. The resulting highly porous material can be used to deliver active components. The cellulose aerogels have also been pyrolyzed to produce carbon aerogels useful for capacitors and electrodes in fuel cells. Aerogels are a promising field for industrial application because their use is manifold, e.g., in pharmaceutical applications (35).

Cleaning

With the aid of supercritical fluids, substances can be removed from surfaces, similar to an extraction process, but intended for cleaning. The low surface tension of supercritical CO_2 makes it possible to enter the smallest structures. CO_2 also reduces the surface tension and viscosity of contaminating oils, which can then be removed in either liquid or gaseous phases. At the end of the cleaning process, no solvent residues remain on the solid material. This process has been applied to the cleaning of semiconductor wafers as well as to the removal of photosensitive resins and residues following lithographic steps. Prototypes have been set up that allow the development of processes with supercritical CO_2 at a preindustrial scale (36, 37).

Degreasing

With the ban on ozone-depleting solvents, cleaning by supercritical CO_2 has become an alternative to conventional industrial cleaning with organic solvents or water and detergents. CO_2 must show the necessary solvent power for the components adhering to metal parts; tests showed that very low solubilities are not a drawback for cleaning metal parts because an additional solvent must be added to achieve acceptable results. According to Dahmen et al. (38), pure CO_2 or CO_2 with a cosolvent are suitable solvents for a variety of cleaning applications, e.g., cleaning metal parts. Although commercial-scale tests show good cleaning efficiency, close to reference cleaned parts, a very thin film of unextracted lubricant remains on the surface of the parts (39). For a high-level cleaning, oxygenated solvents must be added and used in combination with ultrasound, as in the degreasing system (39) already used in industry. CO_2 achieves an appropriate cleaning quality at a reasonable cost while substituting for chlorinated organic solvents.

Impregnation with Supercritical Fluids

Much work has been conducted on the removal of components from solid materials. The reverse direction also provides some interesting applications for supercritical fluids, including wood impregnation, fabric dyeing, and leather tanning. Specific properties of supercritical CO_2 that allow a high and fast penetration into the cores of solid materials include its viscosity as low as 10^{-2} to $9 \cdot 10^{-2}$ mPa s^{-1}, which is 30 to 100 times lower than the viscosity of a liquid, and its high diffusivity coefficient of 10^{-2} to 10^{-1} m^2 s^{-1}. The small supercritical fluid molecules diffuse into porous and natural materials, such as wood, cork, leather, and fabric fibers, carrying molecules such as fungicides, polymers, and dyes.

Supercritical fluid-based processing of wood to protect it from deterioration owing to environmental exposure went into large-scale operation in Denmark in March 2002 (40). In the CO_2 process, a harmless organic fungicide is used to protect the wood.

Wood 1.1 m wide and 2.4–6 m long is placed in a vessel pressurized with CO_2 to approximately 15 MPa and at 40–60°C. Problems with groove formation were solved and led to an understanding

of procedures for maintaining the mechanical integrity of the wood. Key data for the plant are: vessel size 3×8 m^3, cycle time 2–5 h, and annual capacity 60,000 m^3.

Dyeing

The textile-finishing industry has investigated dyeing of poly(ethylene terephthalate) (PETP) fibers in supercritical carbon dioxide for economic efficiency and practicality in a pilot plant (41). Swelling and mass transport of CO_2 and of dyes have been studied for PETP and other glassy polymers. Diffusion of disperse dyes strongly depends on the type of dye (42, 43).

Dyeing of natural fibers such as cotton has problems that arise from the inability of carbon dioxide to break hydrogen bonds, which seems to hinder the diffusion of dyes into the interior of hydrogen-bond cross-linked fibers such as cotton and viscose, as well as wool and silk (41). Disperse dyes require too much time for dyeing, whereas the reactive, direct, and acid dyes used in conventional water dyeing are nearly insoluble in supercritical carbon dioxide. This could be overcome with modified CO_2-soluble disperse dyes with functional groups that are able to react with the fiber (41). Natural fibers can be dyed in supercritical CO_2 without pretreatment of the fiber using special compounds. High color yields and excellent dyeing were obtained with 2-bromoacrylic acid. Results were even better for protein fibers (44).

Water seems to improve the dyeing process. Maximum color uptake was obtained when both the supercritical CO_2 and the textiles were saturated with water but no liquid water was present (45). At the saturation point, deep colors were obtained with a vinylsulphone dye for polyester, nylon, silk, and wool; fixation percentages were 70–92% when the dyeing time was 2 h. Experiments with a dichlorotriazine dye in water-saturated supercritical CO_2 at 22.5–27.8 MPa and 100–116°C also showed enhanced coloration (38).

Tanning

Making leather from hides requires several stages; the main one is tanning. Today, 90% of world leather production involves tanning with chromium, which uses approximately 0.7 m^3 water/metric ton of hides. Compressed carbon dioxide can be used to shorten tanning times, to reduce water effluents and pollution, and to save leather-finishing fats (46). Typically, approximately 30 h are needed to tan skins with chromium. The same tanning result is obtained in only 5 h if the process is performed with CO_2 at a pressure between 3 and 10 MPa (46, 47). Tanning with supercritical CO_2 begins with a quick increase in the chromium content of the hide, followed by a moderate impregnation rate, another quick increase in the chromium content, and finally an upper limit (48). Pressure has no influence on tanning time at less than 3 MPa and between 10 and 30 MPa. Dyeing of leather in supercritical CO_2 results in uniform dyeing, good dye penetration, and good dimensional stability (49). Successful tests have been conducted in a 100-liter autoclave. However, this process will be successfully applied only if most of the process steps can be carried out in the same pressure vessel (49).

Countercurrent Separation

The use of supercritical fluids to separate mixtures of components with low volatility has been developed to full commercial scale. The powerful separation process is carried out at moderate temperatures, thus avoiding thermal degradation of components. Competitive processes are vacuum distillation and short path distillation, which are well known and can be ordered from various suppliers. Countercurrent multistage separation with supercritical fluids, again usually CO_2,

however, needs to be designed for each specific problem; the necessary knowledge has not diffused to all members of the chemical engineering community, let alone to decision-making managers. Therefore, the actual number of applied countercurrent separations with supercritical fluids is low.

Enrichment of natural tocopherols. One repeatedly investigated problem is the enrichment of tocopherols from natural sources, mainly the distillates from edible oil processing, i.e., deodorizer distillates (DODs) (50, 51). The purification of synthetic tocopherols and tocopherol acetate using supercritical fluids was developed long ago and is available for industrial-scale operation (52, 53). The enrichment of tocopherols from DODs using supercritical fluids has been commercialized after extensive investigations (48). Tocopherols were concentrated from methyl-esterified DOD with supercritical CO_2 in a semicontinuous countercurrent process using a fractionation column with a height of 2.4 m, an inner diameter of 20 mm, and a total volume of 750 ml. Fatty acid methyl esters were removed at 16 MPa with a column temperature gradient of 313–348 K, and natural tocopherols (>50%) were obtained with high yield (>80%). After scale up experiments with an 18-liter column (54, 55), a commercial-scale fractionation system of 2×350 liters was erected in China in 2000 with an annual capacity of 750 tons of methyl ester-DOD (56).

De-oiling of raw soy lecithin. De-oiling of raw soy lecithin was for years industrially carried out by countercurrent separation with propane. Because of problems with propane, an alternative process was developed using supercritical carbon dioxide (57). The target product is a free-flowing powder with an acetone-insoluble matter minimum content of 95%. Scale up in a small-scale production plant was performed to verify results from experiments conducted in a pilot plant at 40 MPa and 60°C with specific CO_2 flow rates ranging from 100 to 200 kg CO_2 kg feed h^{-1}. An economic investigation proved the commercial feasibility of the process. A production plant was designed for de-oiling 200 kg h^{-1} of raw soy lecithin, which, assuming 62% acetone-insoluble matter in the raw material, corresponds to a production capacity of 120 kg h^{-1} of pure lecithin powder. The plant began operating in 2007 (57).

PHASE TRANSITION PROCESSES

This section reviews the process steps necessary for supercritical fluid (usually CO_2)–induced phase changes. Again, the discussion here is restricted to industrial and near-industrial processes. The use of supercritical fluids for particle generation or formulation has pharmaceutical, nutraceutical, and food applications. It can also be applied in materials science with the creation of nanoparticles or hydrothermal particles, which are covered in later sections.

Phase transition processes with supercritical fluids aim to create more useful formulations than do conventional methods that rely on solvents such as acetone, methylene chloride, and dimethylsulfoxide. Total or partial replacement of these solvents provides a bright prospect for the application of supercritical fluids if the conditions of industrial application can be met.

Particle Formation, Antisolvent Processes

Phase transition processes use a supercritical fluid in connection with substances that are to be brought by the supercritical fluid into a certain shape and functionality for application. The active components may be dissolved in organic solvents. Such systems consist of at least a gaseous phase and a liquid phase. The liquid phase may be homogeneous, but all variations including homogeneous liquids, self-structuring liquids, (micro) emulsions, and suspensions are possible. A

substantial amount of the supercritical fluid is present in all phases; by changing its concentration (by changing temperature, pressure, or the amount of supercritical fluid in the phase) this phase is partly transformed to the formulated useful solid form. The driving force of this solidification is the high, rapid, and homogeneous temperature decrease that occurs when a CO_2-containing solution is depressurized to ambient pressure. The variability in processing materials and conditions, as well as the various carrier materials available, has led to the development of many process steps, many of them characterized by acronyms intended to promote their uniqueness despite not being very different from each other. These include:

- Rapid expansion of the supercritical solution (RESS): Compounds dissolved in the supercritical fluid, usually CO_2, are precipitated by expansion.
- Supercritical antisolvent (SAS): A supercritical solvent is dissolved in a liquid solution to create either neat particles or microspheres embedded in a carrier, or complex particles with carrier materials.
- Fluid-assisted micro-encapsulation (FAME): A suspension of fine particles of a compound dispersed in a liquid carrier leads to composite microcapsules/microspheres.
- Impregnation: The active compounds are carried by a supercritical fluid and are adsorbed on a porous carrier.
- Concentrated powder formulation (CPF): During the cosolidification of the liquid and solid phases, the liquid penetrates the pores of the carrier and is adsorbed.
- Particles from gas saturated solutions (PGSS): A molten substance is fed with a pressurized gas into a static mixer and is expanded in a nozzle to ambient pressure, forming particles.

Phase transition processes for creating particles using the unique properties of supercritical fluids are entering industrial application on the basis of results from almost 30 years of basic research on thermodynamics and mass transfer. Many process ideas have been developed for solidification in the presence of supercritical fluids. Selected antisolvent and PGSS processes have been scaled up and are successfully applied. New concepts had to be generated for a successful introduction of new processes in the food area (58). For drug formulations based on supercritical fluid technology, some innovative process steps have been scaled up and may be introduced into industry, especially for manufacturing inhalable and sustained-release particles (59).

Intensive research and development have yielded many attractive results, but also too many patents that complicate the intellectual property situation. In addition, the process complexity connected with high investment costs has delayed the introduction of supercritical fluid formulation techniques despite their proven performance (59). Several reviews cover these topics and provide detailed information. Weidner (58) reports on selected antisolvent and PGSS processes whereas Perrut et al. (59) report on pharmaceutical applications in compliance with current Good Manufacturing Practice (cGMP). Türk (60) focuses on the RESS process for creating particles with improved dissolution behavior. Cocero et al. (61) review supercritical encapsulation and co-precipitation processes to form composites or encapsulates. Reverchon et al. (62) cover the use of supercritical fluids in polymer processing to form polymer-drug microparticles, to produce simple or loaded membranes, and to form temporary scaffolds for pharmaceutical and medical applications.

In the following, efforts toward producing formulations for pharmaceutical processes and food applications are described in some detail because they have reached industrial scale.

Pharmaceutical applications: from lab- to commercial-scale experience. Acceptance of particle generation with supercritical fluids is improved by the design and operation of the necessary equipment in a compliant environment with clean room techniques, efficient control, supervision

and documentation, and protection of operators (59). Preparation of clinical lots and scale up in compliance with GMP are possible. Several process steps must be considered separately.

Particle generation. For nucleation of solid particles from liquid droplets (antisolvent, nebulization, and microencapsulation processes), the droplet size is a basic parameter. When attempting to increase equipment size (scaling up) while maintaining particle characteristics from laboratory-size results, the simplest rule is to keep nozzle diameter and liquid velocity constant, i.e., to keep both Re and We numbers constant, which leads to a multi-nozzle system. Experience has shown that the key parameter is the liquid velocity.

Maintaining a constant residence time before particle collection leads to consistent final particles when all other parameters are kept constant. The morphology of the solid depends on the temperature at which the particles are formed and maintained. Careful design and operation are required for large-scale production to obtain reproducible particle size and morphology.

Particle collection. Particle collection and harvesting are important and difficult issues when micro- or submicroparticles are produced. Very fine particles can only be collected by filtration or liquid scrubbing. For a semibatch process, the particle-loaded fluid is directed to one of at least two collection vessels operated alternately. Particle collection has also been achieved by depressurizing a stream of liquid CO_2 into the particle-loaded gas stream, which leads to a dry powder of microparticles that exhibits no agglomeration after sublimation.

Residual solvent stripping. Particles formed by processes using an organic solvent in addition to supercritical carbon dioxide contain precipitated organic solvent adsorbed onto the particles. Removal of the organic solvent down to an acceptable concentration requires long-time application of vacuum or the percolation of substantial volumes of pure carbon dioxide—or some other inert gas—through the particle bed. If a fluid is used, it can be recycled and reused only after the organic solvent taken up has been removed from the fluid by depressurization followed by carbon bed adsorption.

Scale up. Samples of less than 1 g can be processed on equipment consisting of 10-ml process vessels placed in a glove box. Larger samples (1–20 g) are processed with apparatus that can be installed inside a hood. Clinical lots (10–100 g) need a pilot plant operated inside a clean room, in compliance with GMP.

Improving delivery of active pharmaceutical ingredients. Supercritical fluid micronization may lead to a significant increase in the dissolution rate of poorly water-soluble active pharmaceutical compounds (63, 64). Dissolution rates not only depend on the surface area and particle size of the processed powder but are also much affected by morphology and wetting properties. Supercritical fluid processes can lead to optimized formulations that take advantage of the resulting specific surface area increase. Composite particle generation by supercritical fluid processes incorporating hydrophilic polymers, cyclodextrines, and their derivatives leads to size-controlled particles that enhance the dissolution rate.

PGSS and CPF for food applications. The PGSS process has been realized in the laboratory and pilot plant as well as on a production scale (58). The substance to be transformed into a powder is mixed in molten form with a pressurized gas (usually CO_2) in a static mixer and then expanded in a nozzle to ambient pressure. Because of the Joule-Thomson effect, the gas cools extremely rapidly, removing heat from the droplets formed from the molten solute with the assistance of the

pressurized gas, and transforms the droplets into a solid state in a very short time, approximately 10 ms to a few hundreds of milliseconds. The high concentration of gas in the liquid phase leads to a considerable reduction in melting point, viscosity, and interfacial tension, which helps to render substances liquid and able to be sprayed via a nozzle. An industrial plant began operation in mid-2008 at the Fraunhofer Institute UMSICHT (Fraunhofer-Institut für Umwelt-, Sicherheits- und Energietechnik) in Oberhausen, Germany, with a capacity of up to 300 kg h^{-1}.

The CPF process is similar. It generates dry, free-flowing powders containing an unusually high liquid content (65, 66). The liquid to be transformed into a powder is contacted with a pressurized gas and expanded in a nozzle. This forms a fine dispersed spray of liquid droplets. A solid carrier material is blown into that spray using an inert gas. The expanding gas causes a zone of high turbulence where the droplets and the solid carrier are intensively mixed. The liquid droplets agglomerate the carrier material. The agglomerates may contain up to 90 wt% (in a few cases more than 90 wt%) of liquid and are withdrawn continuously from the bottom of the spray tower. The CPF process has been applied to more than 100 liquids and approximately 60 solid carriers.

Encapsulation and Coating

Many formulations are composites or encapsulates composed of a core material (the active component) surrounded by a coating material or carrier (typically a biopolymer or a fat). Composites are frequently produced by simultaneous precipitation of the core and coating materials, which leads to a dispersion of core particles into a matrix of coating material, whereas encapsulates are produced when the coating material is precipitated as a thin shell around a core particle (61). A controlled delivery of the active ingredients may thus be achieved.

A special aspect is the production of solid formulations in a high-pressure fluidized bed. Nearly all processes described here create solid formulations by expanding mixtures to ambient pressure. A fluidized bed, especially at higher pressures, created with the formulation gas (CO_2) offers numerous options for the process, including precipitation, encapsulation, coprecipitation at controllable conditions, and continuous removal of formulated particles. Furthermore, high values of heat and mass transfer result in constant process conditions throughout the receiving vessel. As a model system, silica particles and glass beads were encapsulated with a wax, which is common in technical coating applications (67). In other investigations, polymers and stearyl alcohol were used as coating materials (68, 69). Solid proteins can also be encapsulated. Two irregularly shaped proteins, one model (bovine serum albumin) and one pharmaceutical (insulin), were coated by mixing the highly nonspherical protein particles with lactose. Tests revealed a favorable (uniform, prolonged) dissolution time (70, 71).

REACTIVE SYSTEMS

Reactions in and with supercritical fluids have attracted special attention for approximately 25 years, but only a few reactions carried out at production scale have been reported. Nevertheless, the largest production process is the well-known polymerization of ethylene at high pressures to polyethylene. In the 1980s Mitsubishi introduced the production of methyl-ethyl-ketone (MEK) using supercritical butene as an educt and processing fluid.

Supercritical fluids can be used in many reactions as a reaction medium or as a reactive component (72–75). In many cases, phase equilibrium determines which reactions occur (76). Catalysis in supercritical fluids opens new opportunities (77) because supercritical fluids are able to dissolve catalysts differently than typical reaction media. On one hand, enzymes can catalyze reactions

in supercritical fluids (78). On the other hand, sub- and supercritical CO_2 can inhibit biological reactions and be used for sterilization. Supercritical fluids also have been considered for recycling polymers (79). Hydrolytic and hydrothermal reactions and oxidative reactions in supercritical water (SCWO) are under consideration for waste treatment and biomass processing (80–82). A systematic treatment of reactions with supercritical fluids can be found in Jessop & Leitner (83) and Arai et al. (84).

The application of supercritical fluids to reactions, especially when using continuous flow systems, can have several advantages owing to efficient process intensification, lower operation costs, and a safer operation as a result of the smaller quantities of material involved. Important reactions that could be carried out in supercritical CO_2 in continuous flow systems include Friedel-Crafts alkylation, hydroformylation, and transesterification of triacylglycerides (85) and simple esters (86).

Hydrogenation

Hydrogenation is frequently used in the fine chemicals industry. Problems arise because of the low solubility of hydrogen in liquid substrates and the low mass transfer rate. In combination with supercritical CO_2, hydrogen is transported into the liquid phase much more easily because CO_2, which is readily soluble in liquid substrates, acts as a carrier. This application is used on an industrial scale (87). Another application that will probably become large scale is the hydrogenation of edible oil components. Hydrogenation of fatty acid methyl esters to fatty alcohols is carried out in a single gaseous phase by adding propane, which dissolves both substrate and hydrogen (88). Single-phase conditions have been achieved at a loading of 15–20 wt% for different lipids at a total pressure of 15 MPa. Reaction time is in the range of seconds if the hydrogenation reactions are carried out in continuous flow reactors. A pilot plant began operation in 2002, but it seems that collaboration of specialists in different areas is necessary to develop this technology to a standard industrial hydrogenation process (88).

Hydrothermal Biomass Gasification

In the context of renewable resources, biomass is under consideration for the production of energy and basic chemicals. Biomass can be gasified to produce synthesis gas or hydrogen, which requires breaking down all the biomass compounds. Alternatively, biomass can be liquefied to produce gaseous and liquid fractions. The liquid fraction is sometimes called bio-oil and could be used as fuel, but it would need to be refined differently than the current route for mineral oil.

Hydrothermal biomass gasification processes are under development and have reached demonstration size, which is bigger than most production processes for specialty chemicals. Biomass containing its natural water content can be converted to H_2, CO, CO_2, and CH_4 (82). However, technical solutions are needed before large-scale production facilities can be built. Fast hydrolysis of biomass in sub- and supercritical water causes a rapid degradation of the polymeric structure of biomass and leads, together with consecutive reactions, to a gaseous product at relatively low temperatures. The high solubility of the intermediates in water under sub- and supercritical conditions inhibits the formation of tar and coke.

A plant for hydrothermal biomass gasification with a throughput of 100 kg h^{-1} slurry and 20% dry matter was built at the Research Center in Karlsruhe, Germany; various biomass feedstocks were converted to gas. The plant is designed for approximately 700°C and 35 MPa. Biomass is crushed and its water content adjusted before it is pumped with membrane pumps and heated by a tube-in-tube heat exchanger having an efficiency greater than 80%. In a preheater, the temperature

of the aqueous flow is further increased. Conversion mainly takes place downstream in the reactor. The product mixture is cooled in the heat exchanger and an additional cooler. The gas phase is separated from the liquid phase while still under pressure. CO_2 is removed from the hydrogen-rich gas phase in a scrubber (82).

The universal problems in hydrothermal biomass gasification are corrosion, salt precipitation, and catalyst poisoning if a heterogeneous catalyst is used. Plugging may occur in parts with smaller diameters and at low flow velocity. The efficiency of heat exchange (recovery) is the most important parameter for the process. Without heat recovery in a heat exchanger, the gasification process with water is energetically inefficient. Furthermore, the heating rate of the feedstock should be high, which can only be achieved by mixing high-temperature water with biomass (82).

Experience from the development of coal gasification and liquefaction plants shows that a continuous process will only be feasible for very large installations. Smaller facilities, which are more likely to be built, can be operated with similar efficiency in a semibatch mode by feeding the biomass as a batch to one or several reactors that are in contact with a continuous flow of heated water.

Oxidation in Supercritical Water

SCWO initially was seen as the best method to destroy toxic and dangerous compounds and to clean liquids and solids (89, 90). Process development and various applications soon showed that several problems are connected with SCWO including salt precipitation, plugging, and severe corrosion. Salt precipitation was treated by different reactor designs, including a tank reactor with fresh water introduced near the reactor walls, tubular reactor designs with cleaning by balls or high flow velocity, and reactors that introduce fresh water at the internal walls (transpiring wall reactor). Corrosion was fought using zirconium-based ceramics, nickel-based alloys, noble metals, and other materials, with no general success. Only in recent years has systematic information accumulated such that measures can be taken against corrosion (91). The most severe corrosion occurs in the heating and cooling section of the plant, whereas the reactor itself experiences much less corrosion. Because there is no generally applicable solution for this problem, a corrosion-resistant material must be chosen for each feedstock. Alternatively, existing SCWO plants need set specifications for the feedstock and for fresh water that detail the compounds or elements that must be contained within certain limits or not at all. Two examples are mentioned here: a solid waste treatment plant (92) and a plant for treating wastewater (93).

A hybrid SCWO system was designed that consists of two reactors: a vessel-type batch reactor and a continuously operated tubular reactor (92). The first reactor consists of a pressure vessel with a reaction cartridge. The reaction cartridge supplies solid waste contaminated with polychlorinated biphenyls (PCBs) to the reactor. When the reactor and reaction cartridge are heated to 270–300°C, subcritical water dechlorinates and neutralizes as well as liquefies KOH and organic compounds. The effluent from the reaction cartridge is discharged to the tubular reactor maintained at 600°C and 24 MPa, where SCWO completely decomposes it. Finally, the first reactor is heated from 300 to 600°C to decompose residues in the reaction cartridge. A pilot plant with a capacity of 200 kg day^{-1} of solid waste was built in 2002. After treatment of wood soaked in 1,2-dichlorobenzene (DCB) in the pilot plant, no organic residue was detected in the reaction cartridge. Very low dioxin concentrations in the effluent and exhaust gas fully satisfied emission standards. The hybrid SCWO system completely decomposed DCB and all organics.

In Korea in 2006, a SCWO plant was constructed for treatment of wastewater from manufacturing plants for terephthalic acid (TPA) and liquid crystal displays (LCDs) (93). This industrial wastewater is produced in large volumes and has high toxicity (Cr and N concentrations of LCD

wastewater are approximately 3500 mg liter^{-1} and between 11,000 and 54,000 mg liter^{-1}, respectively. The LCD wastewater was decomposed in a tubular reactor at 25–29 MPa and 396–615°C. In-situ formation of chromium oxide nanoparticles in the 200–400 nm size range was observed owing to decomposition of ammonium chromate in the wastewater. SCWO provides an effective means for oxidizing wastewater from TPA and LCD manufacturing plants. Almost 100% conversion, based on chemical oxygen demand (COD), can be achieved in wastewater from the TPA plant at sufficiently long contact times, high temperatures, or high concentrations of oxygen. Conversion greater than 99.99%, based on COD, can be obtained within 10 s at 615°C for LCD wastewater.

MATERIALS-RELATED PROCESSES

This section summarizes some industrial and near-industrial applications that are named after the materials used or their phenomenological behavior, such as polymers, emulsions, microemulsions, colloids, and nanostructured materials.

Polymers

The properties of supercritical CO_2 make it ideally suited to replace organic solvents in polymer processing. The miscibility, phase separation, and morphological modifications of polymer solutions in supercritical fluids at high pressures have been reviewed (94). Carbon dioxide is an effective dilution agent for polymer melts that significantly increase free volume and thus improve the ability to process materials through reductions in viscosity and interfacial tension. Many examples in the literature demonstrate the unique capabilities of CO_2, which range from the production of fine particles to diffusive impregnation to continuous blending and extrusion processes (95). Polymer foams created using supercritical carbon dioxide as a processing solvent have been of interest for industrial applications in recent years and have been reviewed recently (96).

An illustrative application is CO_2-assisted extrusion of polymers. In an extrusion process a raw material is converted into a product with desired properties by forcing it through a die in an extruder. This process, which is already used industrially for polymeric foams, can be effectively modified with supercritical CO_2 to achieve micro-structured polymeric foams. Cell density and pore diameter are affected primarily by temperature. An increase in temperature enhances the expansion rate, average diameter, and pore coalescence. The CO_2 concentration, which is determined by the CO_2 volumetric flow rate, is only significant at concentrations of <0.1% CO_2 for the structure of the polymeric foam. Nucleation may be dominant at very low concentrations ($1.9 \cdot 10^{-3}$%); this is followed by growth and coalescence until constant levels of cell density and pore diameter are reached at greater than 0.1% CO_2. When the solubility limit for CO_2 is exceeded, heterogeneous nucleation leads to macropores (97).

Another application is supercritical CO_2-assisted melt spinning (98). It has been demonstrated that supercritical CO_2 assists in the reduction of the melt viscosity of a styrene copolymer, styrene-iso-butylene-styrene (SIBS), by several orders of magnitude. Supercritical CO_2 swells into the polymer matrix and extracts low-molecular-weight solvent from the polymer-rich phase. Carbon dioxide is then easily removed from the polymer through evaporation, and the physical properties of the original polymer matrix are obtained.

In addition, supercritical CO_2 can be utilized as a dispersion and transportation medium for manufacturing films from particles (99). Nano- or microparticles were dispersed in supercritical CO_2 and sprayed on substrates to deposit thin films. Miniature structures such as microelectrodes of $LiCoO_2$, $LiMn_2O_4$, and graphite could be generated using patterned masks, but the fabrication

of copper and aluminum conductive films was not successful. The Cu and Al particles melted on the substrate surface at high collision velocities, but conductive films could not be formed on ceramic and plastic substrates. Reverchon et al. discuss the modification of polymer surfaces and templates (62).

Emulsions and Microemulsions, Colloids

Attaining homogeneous solutions is a goal in industrial processes, including those with CO_2. However, emulsions, microemulsions, and colloids provide many more possibilities to process insoluble compounds. In recent decades, these structures have been investigated in connection with supercritical fluids, and several possible applications to production processes have been identified, as recently reviewed by Johnston & da Rocha (100) and Zhang & Han (101).

Many nonvolatile solutes are insoluble in CO_2. Therefore, many recent projects have utilized colloids in CO_2 to include insoluble phases. Whereas the solvent strength of CO_2 is limited, water-in-CO_2 (W/C) and CO_2-in-water (C/W) emulsions and microemulsions solubilize high concentrations of polar, ionic, and nonpolar molecules within the dispersed and continuous phases. These emulsions may be separated easily for product recovery simply by depressurization, unlike conventional emulsions. W/C or C/W dispersions in the form of microemulsions and emulsions offer new possibilities for replacing organic solvents in many fields (100). Colloids including microemulsions, emulsions, polymer latexes, proteins, and metal and metal oxide nanoparticles may be stabilized in supercritical fluids with a variety of surfactants, adsorbed ligands, and particle stabilizers. Particle-stabilized emulsions in CO_2–water systems may be used to produce particles with special morphologies such as mesoporous hollow silica spheres. The stability of the dispersions can be controlled with CO_2 density (100). Therefore, the microemulsions can be broken down simply by controlling the temperature and pressure of the system, which leads to direct deposition of nanoparticles (101).

Various inorganic nanoparticles have been successfully synthesized in W/C microemulsions (101). They have also been applied to chemical reactions, for example the preparation of nanometer-sized metallic palladium particles in a W/C microemulsion by hydrogen reduction of Pd^{2+} and subsequent in-situ hydrogenation of olefins (96). High concentrations of both hydrophilic and hydrophobic reactants can be dissolved in microemulsions, and reaction rates can be tuned by the microproperties of the microemulsion, which in turn can be controlled by compressed CO_2 (101), similar to the reduction of the solution viscosity upon CO_2 addition.

CO_2 can facilitate the formation of reverse micelles of polymers in organic solvents. Reverse micelles begin to form at a specific elevated pressure defined as the critical micelle pressure (cmp). The unique advantage of this kind of reverse micelles is that their formation and breakage can be repeated easily by changing the pressure (101).

Splitting of industrial emulsions was found to be effective with subcritical, i.e., liquid, propane (102). At conditions of 40–80°C and 4 MPa, very fast phase separation was observed. After removing propane from the phases, water and the original organic mixture can be further processed. The process was tested in a pilot plant with 40 kg h^{-1} capacity and a 1000 kg h^{-1} industrial plant (102).

NANOSTRUCTURED MATERIALS USING SUPERCRITICAL FLUIDS

Supercritical fluids offer routes to functional nanostructured films and materials for next-generation microelectronic, energy conversion, and sensing devices (103), although no industrial-scale processes appear to have been carried out so far. The physicochemical properties of

supercritical fluids will drive their use in device fabrication, as the absence of surface tension, favorable transport properties, and liquid-like densities enable solution-based processes in an environment that behaves much like a gas (103).

Techniques for preparing nanostructured materials have been reviewed recently (104, 105). Cansell & Aymonier (104) describe how specific properties of supercritical fluids have been exploited for synthesizing functional nanostructured materials such as nanorods, nanowires, conformational films, core–shell structures, supported nanoparticles, polymers impregnated with nanoparticles, and particles with organic coatings. These advanced nanostructured materials exhibit interesting properties for applications in fields such as catalysis, electronics, energy, and optics.

Erkey (105) reviews supercritical fluids as a promising technique to prepare supported metallic nanoparticles or metallic films. The supercritical fluid deposition technique involves the dissolution of a metallic precursor in a supercritical fluid and the exposure of a substrate to the solution. After incorporation on the substrate surface, the metallic precursor is reduced to its metal form by a wide variety of methods that result in films or particles. The reduction methods employed include chemical reduction in the supercritical fluid with a reducing agent, such as hydrogen or an alcohol, thermal reduction followed by thermal decomposition in an inert atmosphere, and chemical conversion with hydrogen or air after depressurization (105).

Watkins (103) describes the application of films in three areas: deposition of conformal metal oxide films by hydrolysis of β-diketonate-based precursors in supercritical fluid solution, deposition of conformal metal films by reduction of organometallic compounds in supercritical CO_2, and formation of ordered mesoporous films by 3D replication of block copolymer templates in supercritical carbon dioxide.

All these authors expect that supercritical fluids will soon be applied to industrial processes for manufacturing nanostructured materials. But introduction of the technique will depend not only on excellent research results but on scalability. This requires experts in other fields who are willing to cooperate and learn. In the past, lack of knowledge has hindered the transfer of supercritical fluid techniques. Extremely flexible as this technique is, it requires knowledge of thermodynamics, in particular phase behavior; of the properties of supercritical fluids; and of the properties of mixtures of the materials to be processed with the supercritical fluid. In addition, knowledge of the changes supercritical fluids induce in the properties of mixtures is necessary for process design. Experts in process design have not yet absorbed this fundamental knowledge.

CONCLUSION

Supercritical fluids are a unique class of solvents. In combination with components occurring in nature, in chemical processes, and in materials design, including all structures of matter from gas to solid, from homogeneous to nonhomogeneous, the variety of possible applications for supercritical fluids is endless. This review has described many applications now used industrially or just before that stage. It may be assumed that this development will continue. The transfer of knowledge concerning effects on the design of process steps must be emphasized. The practical application of supercritical fluids requires the design of technical components and plants for production. Compared with other technical systems, supercritical fluid production plants are relatively simple from the mechanical and control points of view. The background is complex, however, and must be transferred to process designers, process engineers, and all who want to use supercritical fluids for production of a desired project.

DISCLOSURE STATEMENT

The author is not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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Contents

Errata

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