CLEAN PROCESSING WITH SUPERCRITICAL FLUIDS

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ABSTRACT:
The way from fundamental properties to process verification for industrial application is most important. It is shown how flexible supercritical fluids can be used for processing materials. The application of supercritical fluids to mass transfer processes, phase transition processes, reactive systems, materials related processes, and nano-structured materials as has been reported in the last years shows a wide variety of processing steps, some already of industrial capacity, many other still under development. Beside extraction this includes impregnation and cleaning steps, multistage countercurrent separation, particle formation, coating and many reactive systems like hydrogenation, biomass gasification, and supercritical water oxidation. Polymers are modified with supercritical fluids and colloids and emulsions, as well as nanostructured materials show interesting phenomena which can be industrially exploited. To succeed herewith, the properties of supercritical fluids in combination with the materials processed must be clearly determined and fundamental knowledge of the complex behavior made easily available. Relying on a recent review [1], development and application to industrial processes in the context of own work is discussed.

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 [1].

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.

Advantages of processes using supercritical fluids comprise the properties of the product, processing conditions, handling of the solvent, expectations of customers and last but not least the expected profit. Supercritical fluids produce practically solvent free products and avoid deterioration. Process temperatures are low to very moderate, and it is in all cases feasible to create two phases. Solvent handling is favorable because it can be easily and totally removed, it is readily available and cheap, and it is accepted and part of the environment (water, carbon dioxide). Even then, solvent losses are minimal if compared to ordinary men´s activities for these substances, since the solvent is recycled.

A number of applications will be shortly addressed, like nano-materials using supercritical fluids, materials related processes, like polymer processing, application of supercritical fluids in the field of emulsions, micro-emulsions, and colloids. Phase transition processes for particle formation, anti-solvent processes, encapsulation, and coating are further fields for the application of supercritical fluids. Chemical reactions provide another wide field. Amongst the many reactions investigated to be carried out in supercritical fluids, reactions with enzymes, hydrothermal and hydrolytic biomass transformation to useful products and oxidation in supercritical water (SCWO), cleaning of soil and cleaning of bone material will be addressed. Mass transfer processes is the main field of application of supercritical fluids. Supercritical drying, cleaning, degreasing, impregnation, dyeing, and tanning are applications near-to or at industrial use, beside the most important separation processes. Processing at high pressures, continuous extraction, and large scale extraction will be discussed for single stage extraction. Countercurrent separation, chromatographic separation, and separation by adsorption conclude the discussed applications.

NANOSTRUCTURED MATERIALS USING SUPERCRITICAL FLUIDS

Supercritical fluids offer routes to functional nano-structured films and materials for next-generation microelectronic, energy conversion, and sensing devices, although no industrial 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. 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, exhibiting interesting properties for applications in fields such as catalysis, electronics, energy, and optics [1]. Supported metallic nanoparticles or metallic films are produced with a supercritical fluid deposition technique that involves the dissolution of a metallic precursor in a supercritical fluid and incorporation of the precurson on the substrate surface. Then, the metallic precursor is reduced to its metal form in the supercritical fluid, e.g. with a reducing agent, such as hydrogen. It is expect that supercritical fluids will soon be applied to industrial processes for manufacturing nanostructured materials [1].

MATERIALS- RELATED PROCESSES

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 investigated and results reviewed [1]. 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. Polymer foams created using supercritical carbon dioxide as a processing solvent have been of interest for industrial applications in recent years. An illustrative application is CO_2-assisted extrusion of polymers, another one is supercritical CO_2-assisted melt spinning. In addition, supercritical CO_2 can be utilized as a dispersion and transportation medium for manufacturing films from particles. Nano- or microparticles were dispersed in supercritical CO_2 and sprayed on substrates to deposit thin films. Polymer surfaces and templates can be modified.

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 [1].

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 [1]. 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. Therefore, the micro-emulsions can be broken down simply by controlling the temperature and pressure of the system, which leads to direct deposition of nanoparticles.

CO_2 can facilitate the formation of reverse micelles of polymers in organic solvents [1]. 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. Splitting of industrial emulsions was found to be effective with subcritical, i.e., liquid, propane at 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.

PHASE TRANSITION PROCESSES

Supercritical fluids (usually CO_2) can induce phase changes. 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 generation using supercritical fluids has pharmaceutical, neutraceutical, and food applications. It can also be applied in materials science with the creation of nano-particles or hydrothermal particles [1].

Particle Formation, Anti-Solvent 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 [1].

The variability in processing materials and conditions, as well as the various carrier materials available, has led to the development of many process steps. These include: Rapid expansion of the supercritical solution (RESS), supercritical anti-solvent (SAS), fluid-assisted micro-encapsulation (FAME), impregnation, concentrated powder formulation (CFP), and particles from gas saturated solutions (PGSS).

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. 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 [1].

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. Preparation of clinical lots and scale-up in compliance with GMP are possible [1].

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. A controlled delivery of the active ingredients can be achieved [1].

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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 [2]. In other investigations, polymers and stearyl alcohol were used as coating materials. Solid proteins can also be encapsulated. Two irregularly shaped proteins, one model (BSA) and one pharmaceutical (insulin), were coated by mixing the highly nonspherical protein particles with lactose. Tests revealed a favorable (uniform, prolonged) dissolution time [3].

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 as educt and processing fluid.

Supercritical fluids can be used in many reactions as a reaction medium or as a reactive component [1]. In many cases, phase equilibrium determines which reactions occur. Catalysis in supercritical fluids opens new opportunities because supercritical fluids are able to dissolve catalysts differently than typical reaction media. On one hand, enzymes can catalyze reactions in supercritical fluids. 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. Hydrolytic and hydrothermal reactions and oxidative reactions in supercritical water (SCWO) are under consideration for waste treatment and biomass processing. 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. 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. A systematic treatment of reactions with supercritical fluids has been published by Jessop and Leitner [4] and Arai et al. [5].

Reactions in supercritical fluids catalyzed by enzymes
Enzymes can catalyze reactions in supercritical fluids (see review by Knez [6]). The need of technologies that allow to separate optical isomers is increasing. Enzymes can distinguish substances on the molecular level very efficiently. They can catalyze a bio-transformation, where basically one of the enantiomers is preferably chemically modified. As a result, the reaction products differ in their physical behaviour more than the educts. This difference can be adjusted to the needs of subsequent separation processes by choosing appropriate compounds for modification of the enantiomers. Ideally, in a subsequent isomerization step, from the remaining enantiomer the original racemate is obtained, thus enabling a yield beyond 50 %. A complete process would then consist of an enzyme catalyzed reaction followed by a separation of the reaction compounds and an isomerization. Using supercritical carbon

dioxide as a reaction medium it would be advantageous to utilize the solvent power of carbon dioxide to separate the reaction products immediately after the reaction.

Stability and selectivity in supercritical fluids is a necessary condition. It was found that monomeric enzymes like α-chymotrypsin and trypsin, and the oligomeric enzyme penicillin amidase in supercritical CO_2 are partly denatured during the depressurization step. The degree of denaturation was larger in humid CO_2 than in dry CO_2. Enzymes with S-S-bridges (α-chemotrypsion, trypsin) were denatured to a lesser degree than the enzyme without cysteine (penicillin amidase). Results indicated that the denaturation was caused by partial unfolding during the depressurization step. [7, 8] The stability of immobilized soybean lipoxygenase-1 (LOX-1) LOX-1 was also significantly affected by the pressurization and depressurization steps during reactions in SCCO2, i.e. during working in batch mode, while stability was maintained during contiunuous feeding and removal of substrate and products. [9]. Under hydrostatic conditions, the enantioselectivity, stability and transferase / hydrolase activity of penicillin amidase (PA) from E. coli. At 3000 bar the activity of penicillin amidase for the hydrolosis of 6-nitro-3-phenylacetamidobenzoic acid (NIPAB) was two fold higher than at ambient pressure and was even higher at 4000 bar than at ambient pressure. Incubation experiments under pressure showed that denaturation occures at a pressure above 3000 bar The enantioselectivity for the hydrolysis of D- and L-phenylglycinamide (PGA) and D- and L-3-phenyglylamido-6-nitro-benzoic acid (PGNAB) and the kinetically controlled synthesis of amoxicillin were found to be markedly dependent on pressure [10].

The separation of the racemic mixture of (R,S) 1 phenylethanol served as a model system for testing enymes as catalysts, reaction conditions, and product separation. The selective reaction of one of the isomers results in a product mixture that can be separated easier than the educt mixture. First, vinyl acetate was chosen as a reactant. A commercial enzyme, Novozym 435 proved to be the best enzymatic catalyst at constant pressure of 15 MPa with three times stoichiometric excess of vinyl acetate the optimum reaction temperature was 92 ^{o}C, but the enzyme was active up to 137 ^{o}C At a temperature of 100 ^{o}C the same reaction rate is obtained as at 40 ^{o}C [10, 11]. The thermal stability of immobilized Novozym 435 results from the low water concentration at which the reaction can be carried out in supercritical CO_2 and from the stabilizing effect of the solid support.

The product mixture of (R) 1-phenyl acetate, the non-reacted isomer ((S) 1-phenyl ethanol), vinyl alcohol, not reacted vinyl acetate, and secondary reaction product acetaldehyde was separated by stepwise depressurization and phase separation with hydrocyclones. But solubility differences of the product substances in supercritical CO_2 proved to be too low for a sufficient separation by simply reducing the pressure. A more efficient separation process like multistage counter current extraction would be more adequate. Other alternatives were to use ionic liquids (IL) for selective dissolving product compounds and to change the acylating agent [12]. In the IL--scCO2 -system one of the components should be preferably retained in the IL phase. Among the several ILs studied, only 1-ethyl-3-methy imidazolium ethylsulfate (ECOENG 212) increased the separation factor from 1 to 2.4, still too low to ensure a viable separation.

For the second alternative the acylating agent must incorporate a long alkyl chain to allow the separation of the ester product from the alcohol with scCO2. From reaction studies with different vinyl and methyl esters using Novozyme 435, the best proved to be vinyl laurate. The two main products of the reaction with this ester are (S)-phenylethanol and (R)-1-phenyl-ethyl laurate. The capability from scCO2 to separate these two products was evaluated by phase equilibrium measurements and calculations, resulting in a separation factor as high as 8. The reaction was carried out at 318.15 K and 16 MPa. The best separation results were

obtained using three separators at constant temperature and decreasing pressure from 13.3 MPa in the first to 10.1 MPa in the third separator. About 1% of the feed stream was recovered as (S)-1- phenyl-ethanol as gaseous product from the third separator with a purity of 86.1% [12].

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. Aternatively, 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. 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 [1].

Compounds from Biomass

Plant biomass consists of a number of compounds which can be processed by pressurized hot water, like sugars, starch, cellulose, hemi-cellulose, and lignin. Starch, cellulose, and hemi-cellulose are sugar-polymers and can be transformed to sugar-monomers. From starch, mono-sugars are produced straightforward by microorganisms or by hydrolysis and can be further transformed to ethanol, which is of some concern nowadays because of the competitive situation situation to food. Cellulose and hemi-cellulose, being available from agricultural sources without competition to food, can be transformed to mono-sugars, but so far scientific and technological development has not led to a commercial process, which has been installed. Nevertheless, this will be the future for bio-ethanol production [13].

Lignin: Lignin is also a major component of plant biomass. To make available the elemental chemical compounds of lignin for further application is still a task for research. During studies on the liquefaction of biomass, it was found that the biomass could be liquefied by hydrolysis up to 70–80%. The effluents were subsequently treated by biological degradation. Overall efficiency of COD removal increased to 90–95%. No toxic effects on the microorganisms were observed due to the prior hydrolytic treatment. The remaining compounds were attributed to lignin-derivates. They could not be reacted with water. Oxidation in near critical water by hydrogen peroxide converted all solid material, mostly to gaseous products. Only about 10% of the initial carbon load remained in the aqueous phase, with the main product being acetic acid [14].

Proteins, amino acids: Proteins are the other type of important bio-polymers. The reaction of hot pressurized water can be of interest for producing oligomers and amino acids as the building blocks of the proteins. In the hydrolysis reaction for proteins, first a proton is attached to the nitrogen atom of the peptide bonding. This leads to a splitting of the bonding, forming a carbo-cation and an amino group. In the next step, a hydroxide ion, from a

dissociated water molecule, attaches to the carbon-cation, forming a carboxy group. Hydrolysis of a model protein (BSA, bovine serum albumin) and sklero-proteins like feathers and hair, carried out in a continuous plug-flow reactor, resulted in a total liquefaction of the proteins and in the formation of amino acids. Production of amino acids depends mainly on reaction temperature, with an optimum at 310 $°$C. Pressure in the range of 15–27 MPa had no significant effect on the reaction. At 250 $°$C the amino acid yield increases up to a residence time of 300 s and then decreases due to decomposition reactions. Considerable quantities of glycine and alanine were produced from decomposition of complex amino acids. Other amino acids were only found in traces. Addition of carbon dioxide resulted in higher yields due to acid hydrolysis of the peptide bonds. At 250 $°$C and 25 MPa an amino acid yield of 150.3 mg/(g BSA) was obtained by sub-critical water being saturated with CO_2 to approximately 90%. The experiments with duck feathers (without the addition of CO_2) led to amino acid yields (122.0 mg/(g DFK) at 900 s) higher than for BSA without addition of CO_2 due to the shorter chain length of the sklero-keratin molecule. Thus, sub-critical water hydrolysis can be an efficient process for recovering amino acids from organic protein-rich waste-materials, such as hairs and feathers [15].

Oxidation in Supercritical Water
Supercritical water oxidation (SCWO) initially was seen as the best method to destroy toxic and dangerous compounds and to clean liquids and solids. 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. 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 [1].

Cleaning of soil with supercritical water and supercritical carbon dioxide
Cleaning of soil materials contaminated with hydrocarbons was effectively carried out with supercritical water in different processing modes [16]. In the semi-continuous fixed-bed extraction, a variety of weathered and heavily contaminated soil materials were completely cleaned. Supercritical carbon dioxide as an alternative solvent for the contaminants is only effective for fresh contaminations of hydrocarbons. Weathered soil materials cannot be treated by supercritical carbon dioxide. A continuous extraction with supercritical water in a tubular reactor can be carried out co-currently. Extraction time needed for cleaning could be reduced drastically, from 6 h for the semi-continuous extraction to less than 1 minute in the continuous extraction. At a temperature of 380 °C and a retention time of 45 s a 98 % degree of cleaning could be achieved. But solvent to feed ratio must be kept high, greater than 100, corresponding to about 1 wt.-% of soil material in the aqueous feed suspension. Alternatively, a longer tubular reactor (increased residence time) or a multiple treatment may be applied. Mixed contaminations consisting of heavy metals and hydrocarbons can be cleaned with

water at temperatures of 250 to 350 ^{o}C and a pressure of 25 MPa, if supercritical carbon dioxide is dissolved in the liquid phase. Evaluation of the results of this cleaning process are hampered by diverse analytical results. Fines, soil material with particle diameters < 63 μm, can be treated without additional problems and with the same success [16].

For a destruction of the extracted contaminants, the effluents were treated biologically. From weathered soil the contaminants were only partially degradable biologically. Supercritical water oxidation proved to be a good alternative. Oxidation of the hydrocarbons in the extract in supercritical water is fast and can be led to total oxidation of the organic compounds. Pro-ducts are confined to a controllable space. The necessary oxygen can be supplied in-line in an upstream high pressure electrolysis of water. The hydrocarbons removed from the soil materi-als are effectively oxydised in supercritical water by the electrolytically in-line supplied oxygen [16].

Cleaning of bone material
The organic matrix from animal-derived bone material can be removed with near-critical and supercritical water in a combined extraction and reaction process. The aim is a process to produce a biomedical implant material from animal bone material and hydrolysis products from collagen rich raw material. For milled bone material and larger bone fragments the residual protein and lipids content after the combined reaction and extraction at temperatures between 200°C and 350°C under constant pressure of 25 MPa and at varying the extraction time from a few minutes to hours, was below analytical detection limits [17].

For the reactor effluent the peptide and nitrogen concentration reveals that the rate of the combined extraction/reaction increases with temperature between 200°C and 350°C at a constant residence time of 22 min of water in the reactor. The maximum peptide yield at this operating conditions is 50 %. Comparing the peptide yield between 250°C and 350°C it can be seen that higher temperatures lead to increasing peptide yields while the total nitrogen yield decreases indicating the formation of gaseous degradation products. The amount of free amino acids in the reactor effluent at 250°C and 20 min was between 6 and 9.6 %. A maximum in yield of 5.3% is obtained at 200 ^{o}C and 600 s, 12.6% after 120 s at 250 ^{o}C, and 25% at 300 ^{o}C and 90 s. After 180 s at 300 ^{o}C all hydrolysis products passed through a membrane with 50 kD separation limit. Fractionation of the effluent by ultra-filtration into four fractions of < 650 D, 10 kD -- 650 D, 50 kD -- 10 kD, and >50 kD, revealed the variation of the amount of fractions with temperature and residence time [18].

MASS TRANSFER PROCESSES

Mass transfer processes comprise 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 [1].

Drying: 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.

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. 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.

Degreasing: Pure CO_2, or CO_2 with a cosolvent are suitable solvents for a variety of cleaning applications, e.g., cleaning metal parts. For a high level cleaning, oxygenated solvents must be added and used in combination with ultrasound, as in the degreasing system.

Impregnation with supercritical fluids:
The reverse direction to the removal of components from solid materials 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.

Dyeing: The textile-finishing industry has investigated dyeing of poly(ethylene terephthalate) (PETP) fibers in supercritical carbon dioxide for economic efficiency and practicality at least at pilot plant scale. Natural fibers can be dyed in supercritical CO_2 without pretreatment of the fiber using special compounds, e.g. 2-bromoacrylic acid. Results were even better for protein fibers.

Tanning: Compressed carbon dioxide can be used to shorten tanning times, to reduce water effluents and pollution, and to save leather-finishing-fats. Typically, are needed to tan skins with chromium. The same tanning result is obtained in only 5h, compared to approximately 30h in classical processing, if the process is performed with CO_2 at a pressure between 3 and 10 MPa. However, this process will be successfully applied only if most of the process steps can be carried out in the same pressure vessel.

Extraction
Beside well known processes for decaffeination, production of hops-extracts, the extraction of edible oils and of spices, fragrances, and contaminations, more recently there have been some new applications in the field of oils, e.g. sesame oil, the processing of rice, and the cleaning of cork for cork-stoppers [1]. Some aspects of interest are discussed below: Very high pressures, extraction profiles in a fixed bed extractor, large scale- and continuous-extraction.

Very high pressures: Application of very high pressures (>100 MPa) in commercial extraction has been discussed recently with the goal of lower solvent ratios (CO_2/feed), additional fractionation during product recovery, and enhanced solubility of certain compounds [19]. 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. In this case, carnosolic acid could also be enriched from a 50 MPa-extract. 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 .

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.

Extraction profiles in a fixed bed extractor [20]: Extraction curves representing yield are the result of all the extraction processes in a fixed bed extractor. In a plug-flow extractor, the resulting extraction-yield curves should be independent on the radius in the fixed-bed extractor. Due to enhanced void volume at the rim of the fixed bed and inhomogeneous distribution of the solid materials, significant differences in the loadong of the extracting fluid can be determined. The higher the flow rate of the extracting fluid, the more the extraction profile is represented by plug-flow. Nevertheless, near the rim, due to an enhanced local flow rate, the loading is higher. In addition, channelling can be observed. Modeling of the extraction can be achieved by applying a two-zone model with enhanced flow rate in the rim zone. The problem is not very serious in practical applications since the extract from different positions at the end of the extractor is mixed and calculations are related to mean values of flow parameters, where even substantial deviations caused by channelling are levelled out.

Continuous extraction: Extraction results with supercritical fluids from a fixed bed are excellent, but extraction times may be very long, e.g. up to 6 hours for decontaminating of soil material with near- and supercritical-water [21]. Productivity may be improved by continuous operation in co-current flow for solvent and soil material. Laboratory results proved, compared to semi-continuous extraction, residence times can be reduced remarkably by continuous operation. In the continuously operated apparatus the degree of extraction can be brought up to 100 % within a residence time of only 28 s at the cost of a high solvent to soil ratio. Due to extraction in the co-current mode, solvent to soil ratios must be high for a high concentration gradient

Similar results were found for the extraction of oils from bleaching earth. This material is a bulk waste that is dumped and can cause problems to self-ignition, beside others. Although the solvent to feed ratio is much higher for continuous operation, the calculated extraction costs are definitely lower. Therefore, the continuous extraction is an economic alternative for fine-particle solids. The question, whether this conclusion is true for large scale extraction led to the investigation of extraction of oil from soy-flakes.

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 soy-bean flakes with supercritical carbon dioxide was studied [22]. For a product rate of 120,000 tons·year^{-1} of soy-bean 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 $kg_{oil}·kg_{CO2}^{-1}$, 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 $kg_{oil} \cdot kg_{CO2}^{-1}$. This value must be below the limit for the allowable residual loading (for this case approximately 0.0007 $kg_{oil}\ kg_{CO2}^{-1}$), as derived from the accepted oil content remainingin the substrate at the end of the extraction after the oil in the remaining CO_2 in the substratehas 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.

General Remarks on Extraction [1]:

- 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 batch-wise.
  - 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 multi-component 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.

- 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, contrary 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.

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. Counter-current multistage separation with supercritical fluids, again usually CO_2, however, needs to be designed for each specific problem.

Capacity of a separation device with respect to throughput, often determined by the diameter of a separation column. This part is related to hydrodynamic behavior in the separation equipment and strongly depends on the type of the internal equipment of the separation column and on the amounts of the countercurrently flowing phases.

Flooding [23]: For the design of countercurrent columns knowledge about the hydraulic capacity and the flow regimes of the packed column is required. Correlations would allow to reduce experiments. Most sophisticated semi-mechanistic models for the hydraulic capacity use the interdependence of liquid holdup and pressure drop to quantify the flooding point. These models follow a modular approach. First the dry pressure drop and the holdup below the loading point are described. That means the interaction of a single phase with the packing is modeled. Then the holdup beyond the loading point and the pressure drop of the irrigated packing are specified. These two phenomena are coupled, i. e. the pressure drop depends on the holdup since this determines the free area available to the gas flow and the holdup depends on the pressure drop because this is a measure for the shear force the gas flow exerts on the liquid. A consequence of the coupled equations is, that the solution is cumbersome because it involves iterations. Easier and more successful is the semi-empirical correlation of the flooding points as shown in the following equations.

$$j_G^* = f\left(j_L^*\right) \quad with \quad j_G^* = \frac{u_G}{\varepsilon}\sqrt{\frac{\rho_G}{g\,d_H\left(\rho_L-\rho_G\right)}} \quad and \quad j_L^* = \frac{u_L}{\varepsilon}\sqrt{\frac{\rho_L}{g\,d_H\left(\rho_L-\rho_G\right)}} \quad (1)$$

With u_L for the superficial liquid velocity and ε the fractional void volume which is unity for a falling film column but smaller than unity for packed columns. j_G^* and j_L^* are modified Froude-Numbers rating the respective impact pressure to the difference between liquid head and buoyancy.

$$\sqrt{j_G^*} + K_1 \sqrt{j_L^*} = \sqrt{K_2} \quad \Leftrightarrow \quad j_G^* = \frac{K_2}{\left(1 + K_1 \sqrt{\Phi}\right)^2} \tag{2}$$

with K_1 and K_2 as dimensionless parameters.

The flooding points for a wide variety of geometries (structured packings, random packings and falling film columns), substances, and states (temperature, pressure) had been determined experimentally. A liquid layer of 50 mm height on the uppermost packing element was the indicator for a flooding point. For the correlation of the data the values K_1=0.4222 and K_2=1.1457 resulted in a relative standard deviation of 19% (compared to 17.5 % for the detailed approach).

Membrane Separation [24]: An unsolved problem of the SFE process remains the high energy demand required to close the loop of the solvent cycle. After lowering the pressure, which is necessary to recover the extracted compound from the solvent, the recycled CO_2 has to be recompressed to the desired extraction pressure and cooled to extraction temperature. The relatively high energy demand for the regeneration of CO_2 has a negative influence on the competitiveness of the SFE process. In order to improve the economics of the this process, the regeneration of CO_2 by means of membranes is an interesting alternative, since the bulk amount of CO_2 can be regenerated without an intense depressurisation step. In order for this process to be successful, a highly selective membrane which at the same time exhibits a high permeability to CO_2 as well as a sufficient stability under the supercritical operating conditions would be necessary. Cellulose acetate and Teflon AF2400-PEI membranes were identified as suitable membranes for the separation of sea buckthorn oil and rice bran oil from supercritical CO_2. Membrane modules for membranes with total active areas of 300 cm² and 0.4 m² resulted in experimental data on which an economical analysis was based, revealing a 50 % reduction in processing costs.

Enrichment of natural tocopherols and purification of synthetic tocopherolacetate: One repeatedly investigated problem is the enrichment of tocopherols from natural sources, mainly the distillates from edible oil processing, i.e., deodorizer distillates (DOD). The enrichment of tocopherols from deodorizer distillates using supercritical fluids has been commercialized after extensive investigations. Tocopherols were concentrated from methyl-esterified DOD with supercritical CO_2 in a semicontinuous countercurrent process using a fractionation column. 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%). 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 [1].

The purification of synthetic tocopherols and tocopherol acetate using supercritical fluids was developed long ago and is available for industrial-scale operation [25]. Purification of crude synthetic tocopherol acetate by means of supercritical fluid extraction with supercritical CO_2 was carried out with two fully automated columns of packing height of 13.6 m and diameters of 35 mm and 50 mm, equipped with regular packings, Sulzer CY (35 mm),

Montz A3-500 (50 mm) at 323--343 K and 16--28 MPa. Crude tocopherolacetate (TA) with a content of 87 wt.-% TA was purified in a single extraction step up to a minimum of 92 wt.-% TA with a yield of 90-99 %. In a second separation step, product of the first step was purified up to a minimum content of 97 wt.-% with a yield of 90 - 97 %. Production costs in this case can be significantly reduced by adsorption of the product on silicagel at high pressure and producing a formulated high quality end-product.

Supercritical Fluid Chromatography
Preparative chromatographic techniques for the production of substances with high purities are well established. Nearly all of the preparative separations are carried out using liquid solvents as mobile phase. However, the used organic solvents could be often replaced by supercritical fluids, resulting in less costly solvent recycling. The chromatographic separation with supercritical fluids can be operated as a discontinuous Batch-SFC process or as a continuous Simulated-Moving-Bed process (SMB-SFC). For three of the four investigated separation systems, the specific productivity of the SMB-process is significantly higher than the productivity of the batch-process. Although specific productivity is related to the same amount of stationary phase in both cases, the total amount of stationary phase needed is about 4—6 times higher for the SMB-SFC mode than for the batch-mode. Therefore, economic comparison of the two processes showed that the batch-process is less costly in the range of the investigated production rates from 0.4 and 5 t/a [26].

Although the separation potential of chromatographic processes is very high, productivity in general is very low compared to fluid extraction or single stage fixed-bed processes. Therefore, the separation with the aid of solid surfaces, as provided by adsorbents, is worth while to be looked at. In most cases, products need not to be really pure substances.

Separation by Adsorption – Desorption
Adsorption and following selective desorption in a supercritical CO_2-environment is a separation process that can provide high selectivity between groups of compounds. This process was found feasible for the deterpenation of citrus peel oils, i.e. the separation of limonene from the original oils, increasing the concentration of the fragrant oxidized compounds [27]. In this process, the oil is adsorbed and selectively desorbed with supercritical CO_2 at varying conditions similar to solid extraction. The components with a higher affinity to the adsorbent are retained. The feed-oil can be directly mixed with the adsorbent or first dissolved in CO_2 and then brought in contact with the adsorbent and deposited. At different conditions to adsorption, extraction with CO_2 induces selective desorption.

Silica gel is a very versatile adsorbent. About 80 % of its surface is constituted by polar heads via unreacted or residual silanols. The other 20 % are nonpolar methyl groups. Polar compounds are adsorbed by the polar sites. Non-polar components can thus be separated by extraction with CO_2 or other supercritical fluids. The course of desorption is analogue to an extraction from a solid matrix. In such a process, e.g. tocopherols can be separated from sterols, or carotenes from tocopherols [28].

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 under development, 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.

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 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 on the properties of mixtures is necessary for process design. Experts in process design have not yet absorbed this fundamental knowledge.

Furthermore, there are aspects of supercritical fluids application which probably only can be treated successfully in cooperation with process engineers. Some of these aspects are:

- Combining classical separation processes with SFE,
- combining two process steps in one SFE-plant,
- effective regeneration of the supercritical solvent, and product removal,
- effective integration of SFE-processes in a process scheme.

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