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PLENARY LECTURE*

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INDUSTRIAL APPLICATIONS AND CURRENT TRENDS IN SUPERCRITICAL FLUID TECHNOLOGIES

Supercritical fluids have a great potential for wide fields of processes. Although CO₂ is still one of the most used supercritical gases, for special purposes propane or even fluorinated-chlorinated fluids have also been tested.

The specific characteristics of supercritical fluids behaviour were analyzed such as for example the solubilities of different components and the phase equilibria between the solute and solvent. The application at industrial scale (decaffeination of tea and coffee, hop extraction or removal of pesticides from rice), activity in supercritical extraction producing total extract from the raw material or different fractions by using the fractionated separation of beverages (rum, cognac, whisky, wine, beer, cider), of citrus oils and of lipids (fish oils, tall oil) were also discussed.

The main interest is still for the extraction of natural raw materials producing food ingredients, nutraceuticals and phytopharmaceuticals but also cleaning purposes were tested such as the decontamination of soils, the removal of residual solvents from pharmaceutical products, the extraction of flame retardants from electronic waste or precision degreasing and cleaning of mechanical and electronic parts. An increasing interest obviously exists for impregnation purposes based on supercritical fluids behaviour, as well as for the dyeing of fibres and textiles.

The production of fine particles in the micron and submicron range, mainly for pharmaceutical products is another important application of supercritical fluids. Completely new products can be produced which is not possible under normal conditions.

Supercritical fluid technology has always had to compete with the widespread opinion that these processes are very expensive due to very high investment costs in comparison with classical low-pressure equipment. Thus the opinion is that these processes should be restricted to high-added value products. A cost estimation for different plant sizes and different applications was also analyzed.

Supercritical fluids have a great potential for wide fields of processes. For different applications, industrial scale production plants are already in operation and the acceptance of supercritical fluids as an alternative to conventional processes is increasing more and more. CO₂ is based on its good properties, the availability in large amounts and, therefore, low price, and so, CO₂ is still one of the most used supercritical gases. For special purposes, propane or even fluorinated-chlorinated fluids have also been, giving the advantage of much higher solubility of substances compared to CO₂.

SOLUBILITY AND PHASE EQUILIBRIA

The basics for all process design is the knowledge of solubilities and phase equilibria. Phase equilibria can be calculated based on a given set of experimental data by different equations of state, which have been further developed as well as mixing rules. For a large number of compounds, which is normally the case for the extraction of natural materials, solubilities are still described by density-based equations, e.g. the Chrastil equation.

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SUPERCRITICAL FLUID EXTRACTION (SFE)

Supercritical fluid extraction (SFE) from solid materials is the most developed application. In this field the largest industrial scale plants are in operation, such as the decaffeination of tea and coffee (100 kt/year), hop extraction (60 kt/year) or the removal of pesticides from rice (30 kt/year).

Many different materials have been tested. These materials must have to be divided into two groups:

- The purified solid material is the product of interest. In this case no changes of the particle size of the raw material may be done and the material must be treated as is. Special interest must be focused on the expansion step after extraction. A too fast pressure decrease will lead to an overpressure of the fluid, which is included inside the cells, and can destroy the solid particles.

- The extracted substances are the product of interest. For this case the size of the raw material can be adjusted with the aim of achieving high extraction rates with short extraction time and energy input. The optimal particle size ranges from 0.4 to 0.8 mm giving the advantage of short diffusion length for the supercritical fluid and therefore high extraction rates.

Smaller particles must be pelletised to avoid blocking of the filters, which can destroy the filters and is a further safety risk for operation. For the same reason a uniform particle size distribution is also required.

The best situation arises if well purified solid materials as the extracts are products of interest. This is the

case for the decaffeination of coffee and tea, where beside the decaffeinated material, the extracted caffeine is required for beverage industries.

More and more fractionated separation is used if the extract is the product of interest. By stepwise decrease of the pressure from the extraction level down to the separation pressure, the substances are separated according to their solubility behaviour in the supercritical fluid. In the first separator at higher pressure level these compounds are removed from the fluid, which are only soluble at the high pressure level of the extraction step, while fats, waxes, aroma, ... remain solved in the fluid. At the low pressure of the subsequent separator, all compounds are removed from the extraction gas, so it can be recycled to the process. For the case that very light volatile substances are present, a subsequently activated carbon filter completely removes these compounds from the extraction gas before its recycling. These light volatile compounds would decrease the difference in concentration at the extractor inlet, because the fluid is already preloaded and part of the solvent power is lost.

Smaller industrial plants have been designed as multipurpose plants, where extracts from different raw materials are produced. For these plants cleaning is one of the most important time consuming operations, which is very often underestimated during cost estimation. The cleaning issue is extremely important and must be considered at the very beginning of any equipment design, especially for those intended for food or pharmaceutical products. Dead ends and dead zones should be avoided and adequate installation must be considered for cleaning the whole unit with liquid solvents or water steam. After the cleaning step these solvents must be removed carefully from the whole plant to avoid contamination of the products.

The applications of SFE are very wide spread, so that a complete overview is not possible. The main interest is still for the extraction of natural raw materials. The focus is for special plants available in South America, but also for Chinese herbs, where especially pharmaceutical companies are interested in highly concentrated extracts containing no solvents.

For different raw materials the combination of SFE and liquid extraction using polar solvents is of interest. By SFE mainly the non-polar compounds are extracted, only at high pressures do some polar compounds also have certain solubilities. These SFE extracted solids still contain highly polar substances, which now can easily be extracted by polar solvents like water or alcohols. For a direct extraction of the polar compounds, the non-polar substances will produce emulsions, which are difficult to handle and reduce the extraction efficiency.

CLEANING PURPOSES

For many pharmaceuticals the production process cannot be changed because of the very long lasting pe-

riod of permission. The most difficult step is solvent removal from the final product, because evaporation or vacuum drying is limited to given temperatures not to destroy the active compounds. For this purpose supercritical fluids are a good alternative, where the final concentration of solvents in the product can be decreased dramatically. It only must be taken into account that the solvent may act as a modifier. So the correct extraction conditions must be chosen not to remove or change the active compounds from the pharmaceutical.

The decreasing and cleaning of mechanical and electronic parts is a further promising application of supercritical fluids. For the cleaning of very fine and complicated three-dimensional structures with liquid solvents the problem arises that these solvents remain in these structures. The use of compressed gases, mainly in the liquid state because of higher density to also remove solid particles, gives the advantage that after the cleaning step no solvent remains in the purified parts and no further treatment for solvent removal must be performed. Beside this, especially for electronic parts cleaning, the viscosity of normal solvents is too high so that they cannot penetrate the very fine structures. Liquefied gases offer low viscosities at high densities and can overcome these problems.

A further application of liquid CO₂ are so called "dry washing machines" for textile cleaning. Different products have already been introduced into the market with the aim of replacing traditional washing machines, which are still operated with perchlorethylene.

SUPERCRITICAL FLUID FRACTIONATION (SFF)

Supercritical fluid fractionation (SFF) of liquid mixtures combine the benefit of the very high selectivity of supercritical fluids with the advantage of a continuous process. As opposed to the SFE of solid materials, which is always operated in batch mode, liquids are continuously introduced and withdrawn from the extraction column. The design criteria for supercritical extraction columns are similar to those of liquid-liquid extraction. The separation takes place by a counter current flow of the feed and the supercritical fluid along the column height. It must be taken into account that the difference in the density of the phases is reduced because the fluid dissolves into the liquid phase, thus reducing the liquid density dramatically. For special cases the supercritical fluid even represents the heavy phase and must be introduced at the top of the column. Applications are available for the SFF of beverages (rum, cognac, whisky, beer, wine, cider), of citrus oils and of lipids (fish oils, tall oils).

IMPREGNATION

The basics of supercritical impregnation are the high diffusivity and the tuneable solvent power of supercritical fluids. In the supercritical state the fluid is a powerful solvent, so that the impregnation compounds have a high solubility in the fluid and based on the low viscos-

ity and high diffusivity are transported even into the smallest pores of the matrix. In the case of polymeric non-porous materials the supercritical fluid causes swelling of the polymer and thus easy and complete impregnation of the mixture into the material. During the decompression step the solute precipitates because of the reduced solvent power of the supercritical fluid. The conditions of the decompression step must be adjusted for each material separately in this way that the solute remains in the matrix and does not follow the fluid. By slow depressurisation the danger of destroying the matrix structure, based on an over pressure inside the pores, is also reduced.

The impregnation of wood has already been industrially applied in a plant in Denmark. Beside a better impregnation compared to steam impregnation the further advantage is that the impregnation cycle time could be dramatically shortened. A combined extraction – impregnation process was developed for the treatment of old books. In the first step the acids, responsible for destroying the paper, were extracted by supercritical CO₂. Afterwards the books were impregnated again using supercritical CO₂.

Our department is involved in developing an impregnation process for the polymeric parts of artificial hips and knees. These polymers are impregnated by special substances so that no negative reactions in the human body occur after implanting.

In the field of pharmaceutical products supercritical fluids are applied for new drug delivery systems. These pharmaceuticals exist as biodegradable polymer impregnated by a drug. By decomposing the polymer in the human body the active substance is set free for a longer period, where it is necessary to achieve the right concentration of the drug, because at too low concentrations no effect is present and at too high concentrations it might be toxic. For the impregnation of the polymer supercritical fluids offer the advantage that the concentration of the drug can be adjusted and, further, this concentration is accurate over the whole polymer diameter based on the high diffusivity of the supercritical fluid.

DYEING

The dyeing of fibres is still a high water polluting process and difficulties are present for dyeing certain synthetic fibres. To use the benefits of supercritical fluids for a wide application it was necessary to develop a new family of colorants, which are soluble in supercritical CO₂ and have an excellent affinity with these synthetic fibres. The advantage of the supercritical fluid dyeing process is that intensive dyeing of the whole fibre occurred and not only of the surface, as in aqueous processes. After the supercritical fluid penetrated into the fibres and was decompressed, the coloured material could easily be separated from the dry excess colorants, which could be reused for the next dyeing cycle. Special

interest is indicated if the supercritical fluid causes swelling of the synthetic materials and thus can lead to a change of fibre properties.

PARTICLE DESIGN

The use of supercritical fluids for the production of ultra fine particles is a relatively young field of research. Beside the production of particles of micron und submicron size, these techniques offer the advantage of a very narrow particle size distribution, which is of high importance for many applications. Depending on the material to be processed, different processes including supercritical fluids have been developed. Different overview articles have already been published [1–3].

RESS Process

The RESS-process (**R**apid **E**xpansion of **S**upercritical **S**olutions) has been studied for many different substances, mainly pharmaceutical ones. The basics for this process are that the substance to be processed must have a certain solubility in the supercritical fluid. The substance is first solved into the supercritical fluid and this mixture enters the spraying chamber by a nozzle, causing a rapid expansion of the saturated solution. By this the solvent power of the fluid decreases rapidly and therefore different kinds of particles are produced. The advantage is a completely solvent free product and, depending on the operation parameters, different kinds of particle can be formed.

The negative effect of this process is that the substances must to be solved in the supercritical fluid, which is the case at relatively high pressure levels. Even under these conditions the solubility is relatively low so that a high amount of fluid is necessary. By expanding the mixture, a problem arises that a low amount of extremely fine particles must be separated from a huge amount of gaseous fluid without particle agglomeration, which is very difficult to handle.

To overcome the problems of particle separation from the gas flow for some products, the expansion of the saturated mixture into liquids is supposed, which act as non-solvent (**RESSN**) or antisolvent (**RESS-AS**). By this a suspension of liquid including the fine particles is produced, which prevents agglomeration of the fine particles and increases the separation efficiency of the particles from the gaseous fluid.

GAS-processes

The disadvantages of the low solubility of solids in supercritical fluids are overcome by **GAS**-processes (**GAS** = **G**as **A**nti **S**olvent, **SAS** = **S**upercritical **A**nti **S**olvent). The substance to be powdered is solved in an organic solvent and this mixture is contacted with the supercritical fluid. At this contact either the fluid dissolves into the liquid causing a strong volume increase or the whole liquid is solved in the supercritical fluid re-

sulting in a single fluid phase. In both cases the solvent power of the organic solvent is reduced dramatically, which results in a sudden supersaturation producing ultra fine particles.

The necessary pressure level for all GAS-processes is much lower in comparison with the RESS-process because the volume expansion takes place at low pressures. Beside this advantage, also the necessary amount of fluid is much lower. The disadvantages are that in most cases organic solvents are used which must be removed from the final product.

For the discontinuous GAS-process the solvent with the dissolved solids is filled in an autoclave and afterwards contacted with the supercritical fluid, causing the precipitation of the solids, which are retained by a filter plate at the bottom of the autoclave. In the subsequent separator the supercritical fluid and the solvent are separated and can be recycled for the process. Solvent free particles are produced for the case that after precipitation the whole amount of solvent is extracted by the supercritical fluid

Continuous operating GAS-processes allow operation over a longer time period until the precipitated solids must be removed from the spraying chamber.

As well for the ASES-process (**Aerosol Solvent Extraction System**) as for the PCA-process (**Precipitation with Compressed Fluid Antisolvent**), the solvent with the dissolved solid material is sprayed into a spraying chamber, where the phase contact of fine droplets with the supercritical fluid takes place. Beside the nozzle design, pressure and temperature conditions the phase ratio of solvent to fluid flow, as well as the solute concentration in the solvent, also influence the size and size distribution of the produced particles.

In the SEDS-process (**Solution Enhanced Dispersion by Supercritical Fluids**) the contact of liquid mixture and supercritical fluid takes place inside the nozzle. Although the time of contact of the two phases is in the range of milliseconds, volume expansion takes place inside the nozzle. At the outlet of the nozzle the supercritical fluid acts further as an expanding agent which results in much smaller droplets and subsequently in smaller particle sizes.

For the CAN-BD-process (**Supercritical Carbon Dioxide Assisted Nebulation Bubble Drying**) the contact of the solution with the supercritical fluid takes place in a branch connection and is expanded to atmospheric pressure so that extremely fine droplets are produced. These very small droplets are dried in a hot inert gas flow, in most cases nitrogen and by this fine particles are produced. The difference of the SAA-process (**Supercritical Assisted Atomisation**) is that the contact of solution and solvent takes place in a mixing chamber, so that a much longer contact time of phase contact is present. The liquid phase can be enriched with supercritical fluid up to saturation, depending on the pressure and temperature conditions in the mixing chamber.

In the DELOS-process (**Depressurisation of Expanded Liquid Organic Solutions**) only this amount of fluid is introduced into the liquid mixture so that volume expansion takes place but no solid particles precipitate. During the expansion of this mixture, extremely fine droplets and subsequently fine particles are produced. The difference to the other processes is that spraying as well separation of the solvent and fluid take place at atmospheric pressure.

PGSS-process

The PGSS-process (**Particles from Gas Saturated Solutions**) was developed for substances which can be melted in the presence of a fluid. The compressed fluid is solved at moderate pressure and temperature conditions in the melt, which results in many cases in lowering of the melting point of the substance. This gas saturated melt is expanded by a nozzle in the spraying chamber. The temperature decrease takes place because of evaporation of the compressed fluid and because of the Joule-Thomson effect. Under cooling solid particles are produced which are separated in different fractions according to particle size.

The advantage of this process is that no solvents are used and, therefore, do not have to be removed from the final product. For powdered substance no solubility in a supercritical fluid or a solvent is necessary, but the other way round high CO₂-concentrations of 10 to 40 wt% can be achieved at low pressure levels. The limitation for this process is that only substances with moderate melting temperatures can be treated and those that do not decompose or transform before reaching the melting temperature.

CPF-process

In comparison to the previous processes of the CPF-process (**Concentrated Powder Form**) no decrease of the particle size is achieved. The goal of this process is to reach high concentrations of a liquid in a solid carrier. The liquid and the CO₂ phases are mixed in a static mixer so that the viscosity of the liquid is reduced dramatically. With the help of a nozzle this mixture is sprayed parallel with the solid carrier into the spraying chamber. The result is a powdery material with extremely high contents of liquids, up to 80 % liquid.

ECONOMIC EVALUATIONS

The supercritical fluid technology has always had to compete with the widespread opinion that these processes are very expensive due to very high investment costs in comparison with classical low-pressure equipment. Thus, the opinion is that these processes should be restricted to high-added value products. Depending on the material to be treated the plant capacity must be adjusted and even then for low price products like coffee, tea, hops, rice, cork, sesame, etc. these processes become economical. Especially legal restric-

tions for the solvent residue in the product make supercritical fluid processes more and more attractive because in most cases no further energy and cost intensive purification processes are necessary. A cost estimation for different plant sizes and different applications has been published by Perrut [4,5], based on pump processes including all the necessary apparatus, piping, valves and instrumentation for turnkey plants. As shown in Figure 1 all prices are nearly a straight line according to the following equation:

$$PI = A (10 V_T Q)^{0.24}$$

with PI = the dimensionless price index, V_T = the total volume and Q = the solvent flow rate

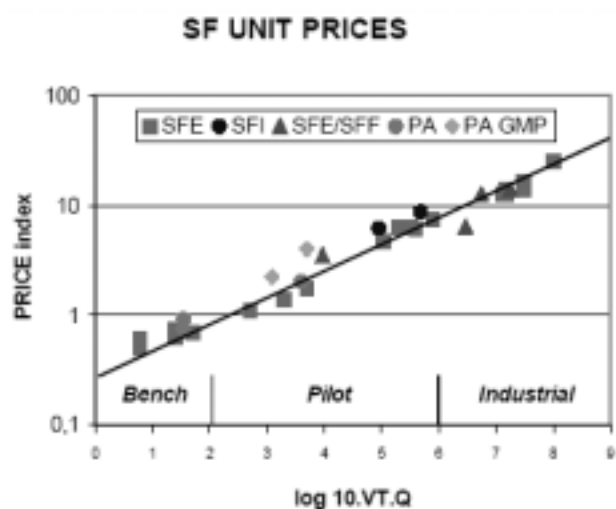


Figure 1. Supercritical unit prices [4,5]

This price index represents with high accuracy the prices for autoclaves from 0.5 to 500 litres. The bench scale equipment is underestimated and much larger units are much less costly than predicted by this rule. Further it must be considered that depending on the pressure level, which is necessary for the process, beside the pump process, the compressor process is also available, where no condenser and undercooler is required, thus reducing the investment costs. Up to now each industrial scale plant has been designed individually because all the apparatus have had to be adapted to the special requirements depending on the raw materials to be treated and on the optimised parameters based on preliminary experiments (pressure, temperature, solvent flow rate, batch time, ...).

The following table shows the industrial scale plants delivered by the NATEX company (until 1992 executed by SCHOELLER BLECKMANN).

REFERENCES

- [1] J. Jung, M. Perrut, J. Supercritical Fluids **20** (2001), pp.179-219
- [2] T. Gamse, F. Miguel, M.J. Cocero, Proceedings CHISA 2004 16th International Congress of Chemical and Process Engineering, 22.-26.8.2004, Prague / CZ, CD-ROM 0323.pdf

Table 1. Industrial plants delivered by NATEX company

Year	Supply	Plant Size	Country
1983	multipurpose plant	30 L, 300 bar	Austria
1985	multipurpose plant	3 X 35 L, 300 bar	Austria
1987	turn-key plant	35.000 L total, 325 bar	Germany
1989	turn-key plant	63.000 L total	Italy
1993	multipurpose plant	200 L, 550 bar	Czech Republic
1995	multipurpose plant	2 x 800 L, 550 bar	India
1995	multipurpose plant	2 x 250 L, 550 bar	India
1996	multipurpose plant	3 x 300 L, 550 bar	India
1997	rice treatment plant	3 x 5800 L, 325 bar	Taiwan
2000	plant components	3 x 17.000 L horizontal extractor	Denmark
2001	multipurpose plant	3 x 1000 L, 500 bar	New Zealand
2003	industrial extraction plant	3 x 2500 L, 550 bar	South Korea
2004	industrial extraction plant	3 x 8300 L, 150 bar	Spain

- [3] T. Gamse, S. Schwinghammer, R. Marr, CIT 77, **6**, 2005, p. 669-680
- [4] M. Perrut, Proceedings 2nd International Meeting on High Pressure Chemical Engineering, 7.-9.3.2001, Hamburg / DE, CD-ROM I_op03.pdf
- [5] M. Perrut, Proceedings 5th International Symposium on Supercritical Fluids, 8.-12.4.2000, Atlanta /USA, CD-ROM 354984.pdf

Further recommended literature:

Books:

- [1] High Pressure Process Technology, Edts. A. Bertucco, G. Vetter, Elsevier Sciences, ISBN 0444504982, 2001
- [2] Gas Extraction, G. Brunner, Springer, ISBN 0-387-914773, 1994.
- [3] Extraction of Natural Products Using Near-Critical Solvents, Edts. M.B. King, T.R. Bott, Blackie A&P, ISBN 0-7514-0069-6, 1993
- [4] Dense Gases for Extraction and Refining, E. Stahl, K.-W. Quirin, D. Gerard, Springer-Verlag, ISBN 0-387-18158-X, 1987.
- [5] Supercritical Fluid Cleaning: Fundamentals, Technology and Applications, Edts. J. McHardy, S.P. Sawan, Noyes Publications, ISBN 0-8155-1416-6, 1998
- [6] Supercritical Fluid Processing of Food and Biomaterials, Edt. S.S.H. Rizvi, Blackie A&P, ISBN 0-7514-0184-6, 1994.

Proceedings:

- [1] Proceedings of the 3rd International Symposium on High Pressure Chemical Engineering, 7.-9.10.1996, Zürich / CH, Edts. Ph. R. von Rohr & Ch. Trepp, Elsevier Science, ISBN 0-444-82475-8.
- [2] Proceedings of the 4th International Symposium on High Pressure Technology and Chemical Engineering, 22.-25.9.2002, Venice / I, Edt. A. Bertucco, AIDIC ISBN 88-900775-1-4
- [3] Proceedings of the 5th Meeting on Supercritical Fluids, 23.-25.3.1998, Nice / F, Edts. M. Perrut & P. Subra, ISBN 2-905-267-28-3.
- [4] Proceedings of the 6th Meeting on Supercritical Fluids, 10.-13.4.1999, Nottingham/UK, Edts. M. Poliakov, M.W. George, S.M. Howdle, ISBN 2-905-267-30-5.

- [5] Proceedings of the 7th Meeting on Supercritical Fluids, 6.–8.12.2000, Antibes / F, Edts. M.Perrut & E.Reverchon, ISBN 2–905–267–33–10.
- [6] Proceedings of the 8th Meeting on Supercritical Fluids, 14.–17.4.2002, Bordeaux / F, Edts. M.Besnard & F.Cansell, ISBN 2–905–267–34–8
- [7] Proceedings of the 7th Italian Conference on Supercritical Fluids and Their Applications and the 9th Meeting on Supercritical Fluids, 13.–16.6.2004, Trieste / I, Edts. I.Kikic & M.Perrut, ISBN 2–905267–42–9
- [8] Proceedings of the 5th International Symposium on Supercritical Fluids, 8.–12.4.2000, Atlanta / USA, Edt. D.Bush
- [9] Proceedings of the 6th International Symposium on Supercritical Fluids, 28–30.4.2003, Versailles / F, Edts. G.Brunner, I Kkic, M.Perrut, ISBN 2–905–267–37–02
- [10] Proceedings of the International Symposium on Supercritical Fluids ISSF2005, 1.–4.5.2005, Orlando / USA,

Journals:

- [1] Journal of Supercritical Fluids, Elsevier
- [2] Fluid Phase Equilibria, Elsevier
- [3] Journal of Chemical Engineering Data, American Chemical Society

IZVOD

INDUSTRIJSKE PRIMENE I TREND RAZVOJA TEHNOLOGIJA BAZIRANIH NA NATKRITIČNIM FLUIDIMA

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Natkritični fluidi imaju veliku mogućnost primene u mnogim procesima. Ugljen (IV)–oksid u natkritičnom stanju je još uvek jedan od najčešće korišćenih fluida ali se za specijalne namene testiraju i drugi kao na pr. propan i fluorovano–hlorovani fluidi, koji imaju prednost u odnosu na CO₂ zbog mnogo veće moći rastvaranja.

Za projektovanje svih procesa u ovoj oblasti osnovno je poznavanje rastvorljivosti određene supstance u natkritičnom fluidu i fazne ravnoteže između rastvarača i rastvorka. Ravnoteža faza se može izračunati na osnovu datog seta eksperimentalnih podataka primenom kubne jednačine stanja. Za veliki broj jedinjenja rastvorljivost se još uvek opisuje jednačinama baziranim na gustini ugušćenog ili natkritičnog fluida.

Procesi dekafeinacija čaja i kafe, ekstrakcija hmelja ili izdvajanje pesticida iz pirinča koji se zasnivaju na primeni natkritičnih fluida realizovani su i na industrijskom nivou. Još uvek su mnoge istraživačke grupe aktivne u oblasti natkritične ekstrakcije, ne samo u cilju proizvodnje ukupnog ekstrakta iz određene sirovine već i kod razvoja frakcionog razdvajanja na osnovu promene različite moći rastvaranja natkritičnog fluida. Glavni interes je još uvek kod ekstrakcije prirodnih sirovina iz kojih se dobijaju hranljivi sastojci, nutraceutikalije i fitofarmaceutikalije, ali se ispituju i neki drugi procesi kao na primer: čišćenje ili odmašćivanje uz pomoć natkritičnih fluida, dekontaminacija zemljišta, uklanjanje zaostalih rastvarača iz farmaceutskih proizvoda, ekstrakcija zapaljivih jedinjenja iz elektronskog otpada ili precizno smanjenje onečišćenja mehaničkih i elektronskih delova. Takozvane "mašine za suvo pranje", koje koriste tečni CO₂ uvode se na tržište sa ciljem zamene mašina za hemijsko pranje koje koriste fluorovano–hlorovane rastvarače. Kontinualno frakcionisanje tečnosti natkritičnim fluidima ima prednost u odnosu na druge procese frakcionisanja, a testirano je za frakcionisanje pića (rum, konjak, viski, vino, pivo, jabukovača), ulja tropskog voća i masti (riblje ulje, kalofonijum).

Veliki značaj imaju natkritični fluidi koji se koriste za impregnisanje. Tako se kod tretmana starih knjiga prvo uklanja kiselina, a zatim izvrši impregnisanje. Bojenje vlakana i tkanina pomoću natkritičnog CO₂ ima prednost u tome što se u ovom procesu ne pojavljuje zaprljana (otpadna) voda, a zaostala boja se može ponovo iskoristiti. Impregnisanje drveta se već industrijski primenjuje u jednoj fabrici u Danskoj. Radi boljeg manipulisanja sa proizvodom, CO₂–ekstrakti, koji su u većini slučajeva lepljivi proizvodi, učvršćuju se na različitim nosačima.

Poslednjih godina razvijena je proizvodnja finih čestica veličine mikrona ili manje, uglavnom za farmaceutske proizvode. Primenjuju se različiti procesi kao RESS (brza ekspanzija zasićenih rastvarača), GAS (gas antisolvent) ili PGSS (formiranje čestica u zasićenim rastvorima natkritičnog fluida), zavisno od prirode rastvorljivosti sirovine koju treba prevesti u prah. Lekovi sa produženim dejstvom, koji se sastoje od biološki razgradljivog polimera koji uključuje aktivnu supstancu, mogu se, proizvodi ovim metodama, čija je prednost u vrlo homogenoj raspodeli proizvoda.

Reakcije sa ili u natkritičnim fluidima se ispituju za različite namene. Katalizatori koji se koriste u cilju ubrzanja nekih hemijskih reakcija mogu se modifikovati kako bi se uvećala njihova rastvorljivost u natkritičnom fluidu. Time se povećava brzina procesa koji se u izmenjenim uslovima rastvorljivosti realizuje u pseudo–homogenim uslovima. Na taj način se mogu dobiti potpuno novi proizvodi koji nisu mogući kada se sinteza realizuje pod normalnim uslovima.

Reakcije katalizovane enzimima se koriste za vrlo specifične proizvode zbog dve povoljnosti: na jednoj strani je visoka selektivnost enzima, a na drugoj moguće promene moći rastvaranja natkritičnog fluida. Pored veće brzine reakcije i konverzije, prednost je i jednostavna separacija proizvoda kao i mogućnost izdvajanja i ponovnog vraćanja natkritičnog fluida u proces.

Ključne reči: Natkritični fluidi • Ekstrakcija • Frakcionisanje • Reakcija • Nutraceutikalije • Hrana •

Key words: Supercritical fluids • Extraction • Fractionation • Reaction • Nutraceuticals • Food •