FORMATION AND DESIGN OF FINE PARTICLES USING SUPERCRITICAL FLUIDS

Željko Knez
University of Maribor, Faculty of chemistry and chemical engineering, Smetanova ul. 17,
SI-2000 Maribor, Slovenia;
e-mail: zeljko.knez@uni-mb.si, phone: +386 41 67 25 45, fax: +386 2 25 16 750

Particle formation and design of solid particles and powdery composites with unique properties is at the moment a major development of supercritical fluids (synonyms: dense gasses, dense fluids, high pressure) applications.

The unique thermo-dynamic and fluid-dynamic properties of supercritical fluids can be used for particle formation and particle design, for impregnation of solid particles, for formation of solid powderous emulsions, particle coating, e.g. for formation of solids with unique properties for the use in different applications.

This review will focus on fundamentals and on recent advances of particle formation and design processes using supercritical fluids, on their applications and the technological advantages and disadvantages of various processes.

INTRODUCTION

Conventional well-known processes for particle-size re-distribution of solid materials are crushing and grinding (which for some compounds are carried out at cryogenic temperatures), air micronization, sublimation, and recrystallization from solution. There are several problems associated with the above-mentioned processes. Some substances are unstable under conventional milling conditions, in recrystallization processes the product is contaminated with solvent, and waste solvent streams are produced.

Applying supercritical fluids may overcome the drawbacks of conventional processes, and powders and composites with special characteristics can be produced. Several processes for formation and design of solid particles using dense gases are studied intensively.

Particle formation processes and design of particles by PGSS™ process will be presented.

Rapid expansion of supercritical solutions (RESS)

Crystallization from supercritical solutions (CSS) is a special process where the fine particles are formed from the substances, which are soluble in supercritical solvents.

When the solute-laden solution is a supercritical fluid, supersaturation may be induced not only by varying the temperature but also by pressure variation. Thus pressure and pressure-gradients would be additional means for generation of particles with the desired size, form and morphology.

The formation of small particles is favoured when solids formation is maintained via primary nucleation throughout the batch crystallization.

Applying supercritical fluids in CSS allows one to obtain supersaturation and to control nucleation- and growth rates by temperature-induced variation of the concentration of the solute in systems where no volatile organic solvents are present.

The other way of performing the crystallization from SCF, is the rapid expansion of supercritical solutions, where small-size particles can be produced. In this process, a solid is dissolved in a pressurized supercritical fluid and the solution is rapidly expanded to some lower pressure level, which causes the solid to precipitate. This concept has been demonstrated for a wide variety of materials including polymers, dyes, pharmaceuticals and inorganic substances.

By varying the process parameters that influence supersaturation and the nucleation rate, particles can be obtained which are quite different in size and morphology from the primary material. Extremely high supersaturation can be obtained from density reduction caused by depressurization and the resulting expansion of supercritical solutions [1, 2, 3]. Several groups have studied the RESS process for substances, which may be applied in various fields, such as pharmacy, the electronics industry, cosmetics, and the food industry [1, 2]. Advantages of RESS are that with RESS process very fine particles are produced even of the size of some nanometres; controllable particle size and solvent-free. Disadvantages of RESS are: high ratios of gas/substance owing to the low solubility of the substance, high pressures (SC conditions) and sometimes temperatures; difficult separation of (very) small particles from large volumes of expanded gas and supercritical solutions established discontinuously, and thus there is the requirement for large-volume pressurized equipment.

Gas anti-solvent processes (GASR, GASP, SAS, PCA, SEDS)

The application of supercritical fluids as anti-solvents is an alternative recrystallization technique for processing solids that are insoluble in SCF. This method exploits the ability of gasses to dissolve in organic liquids and to lower the “solvent power” of the liquid for the compounds in solution, thus causing the solids to precipitate.

Gas anti-solvent processes (GASR, gas anti-solvent recrystallization; GASP, gas anti-solvent precipitation; SAS, supercritical anti-solvent fractionation; PCA, precipitation with a compressed fluid anti-solvent; SEDS, solution-enhanced dispersion by supercritical fluids) differ in the way the contact between solution and anti-solvent is achieved [1]. Advantages of GASR are: very small particles may be produced; the particle sizes are easily controlled; and applicability shown for a wide variety of substances [1, 2, 4]. Disadvantages of GASR are: it is a batch process and uses organic solvents; scale-up of the particle formation is not well known in spite of recent developments, and particle stripping from residual organic solvent is always required; highly diluted product streams; separation of gas and solvent may be required in an industrial process.

Particles from gas-saturated solutions (PGSS™)

This process allows to form particles from substances that are non soluble in supercritical fluid, but absorb a large amount of gas that either swell the substance or decrease the melting (for polymers glass transition temperature). This process can also be used for micronization of liquids, suspensions and emulsions.

In PGSS™ process the substance or the mixture of substances to be powderised must be converted into a sprayable form by liquefaction/dissolution. This can be achieved by melting or/and dissolving of the substance or mixture of substances in a liquid solvent, or by dispersing solids or liquids in a melt or solution, and saturation of the melt/solution/dispersion with the gas [5]. Then the gas-containing solution is rapidly expanded in an expansion unit and the gas is evaporated. Owing to the Joule-Thomson effect and/or the evaporation and the volume-expansion of the gas, the solution cools down below the solidification temperature of the solute, and fine particles are formed. The solute is separated and fractionated from the gas stream by a cyclone and electro-filter.

In PGSS™ process the content of the gas in the heavy phase is of great importance for process design.

When the liquefaction is achieved by melting, the knowledge of the P-T trace of the S-L-V equilibrium gives information on the pressure needed to melt the substance to be micronized and form a liquid phase at a given temperature, and to calculate its composition [6, 7, 8].

When the supercritical fluid has a relatively high solubility in the molten heavy component, the S-L-V curve can have a negative dP/dT slope [9]. The second type of three-phase S-L-V curve shows a temperature minimum [10]. In the third type, where the S-L-V curve has a positive dP/dT slope, the supercritical fluid is only slightly soluble in the molten heavy component, and therefore the increase of hydrostatic pressure will raise the melting temperature and a new type of three-phase curve with a temperature minimum and maximum may occur [11].

In general, for substances for which the liquefaction is achieved by melting, a system with a negative dP/dT slope and/or with a temperature-minimum in the S-L-V curve could be processed by PGSS™ [1, 2, 5].

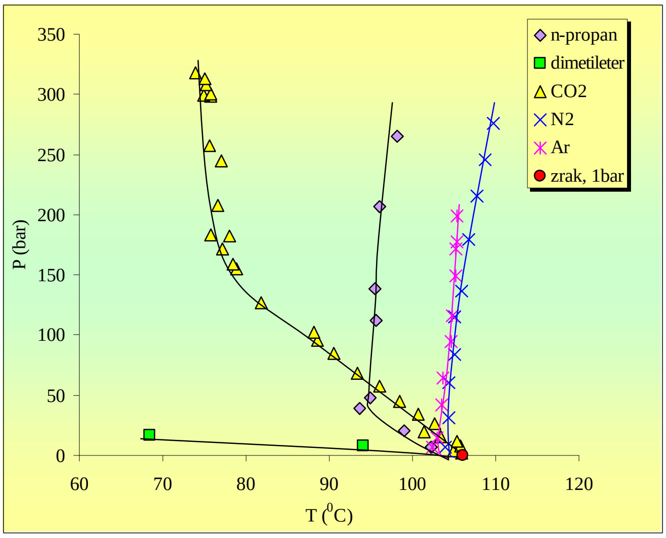

Figure 1: S-L-G behaviour of K3 vitamin in various gasses

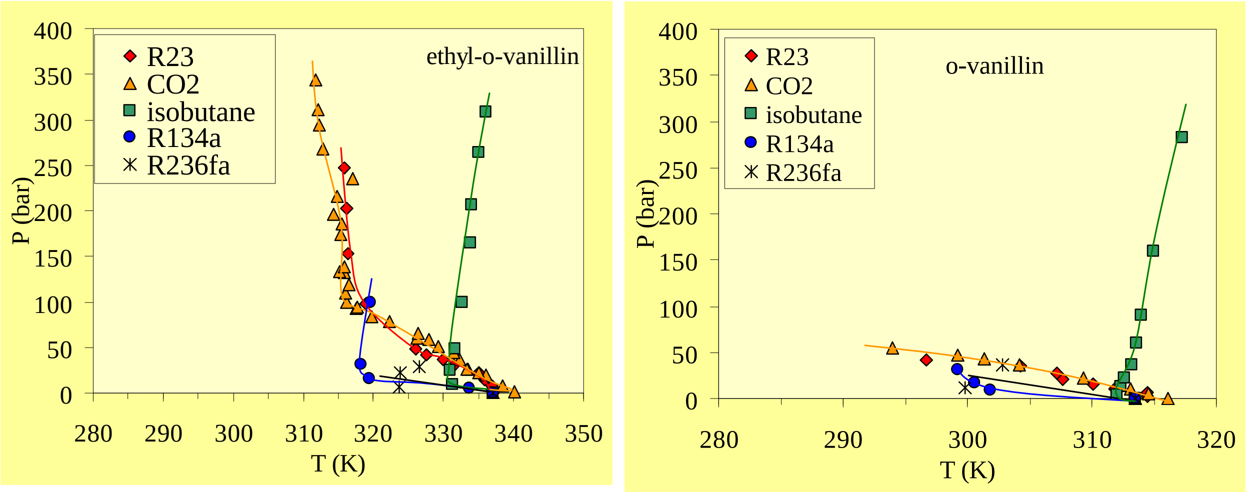

Figure 2: S-L-G lines for o-vanillin and ethyl-o-vanillin in various gasses

On figure 3 the basic scheme of PGSS™ apparatus is presented. Detailed description of apparatus and experimental procedures is presented in [1, 2, 5].

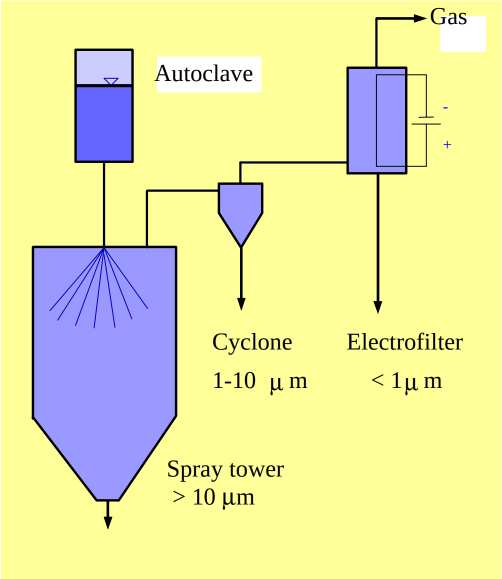

Figure 3: Basic scheme of apparatus for PGSS™ micronisation

The PGSS™ process was tested in the pilot- and technical size on various classes of substances. Up to the present time the application of the PGSS™ process has been investigated for polymers, waxes and resins, natural products, fats and fat derivatives, pharmaceuticals, synthetic and natural antioxidants, surface-active compounds, UV-stabilizers, etc. [1, 2, 5].

The highly compressible fluids which have been used were carbon dioxide, propane, butane, dimethyl ether, freons, nitrogen, alcohols, esters, ethers, ketones and mixtures of above-mentioned gasses and solvents.

The powders produced show narrow particle-size distributions, and have improved properties compared to the conventional produced powders.

The material structure of the substance to be micronised (crystalline-amorphous, pure or composite), the process parameters (pre-expansion pressure, temperature, gas to substance ratio(GSR), viscosity of melt/solution/dispersion) of the PGSS™ process and geometry of the process equipment influences particle size, particles size distribution, bulk density, the morphology (particle shape) (Figures 4, 5) and ratios crystalline/amorphous of the processed substances.

For polyethylene glycols the mechanism of powder generation in an expanding jet of mixture of gas and melted polymer were identified and quantified. Calculations o heat conductivity, heat transfer, solidification rsp. crystallization, nucleation and growth of gas bubbles indicate, that the morphology is controlled by different mechanisms.

It was determined that with increasing GSR smaller particles are formed. At such high ratios (GSR) the influence of pressure on particle size of polyethylene glycols is less pronounced, then at low GSR. The pre-expansion temperature has a strong influence on the morphology of fine particles. At T_r=1. 12 (T_r =$T_{experimental}$/$T_{fussion\ of\ polymer}$) the microfoams were only obtained at higher pressures, while at T_r=1 or lower than 1 the pressure region, where microfoams were generated is much lower and starts already at pressures of 60 bar [12, 13].

Based on the results from laboratory-scale equipment and the first production plants, the basic economics of the process were calculated. The processing costs are between 0.15 and 0.60 Euro/kg (composition of costs: investment ~ 20%, personell ~ 37%, and operating ~ 43%) and vary depending on the substances to be micronized, the scale of the equipment, etc.

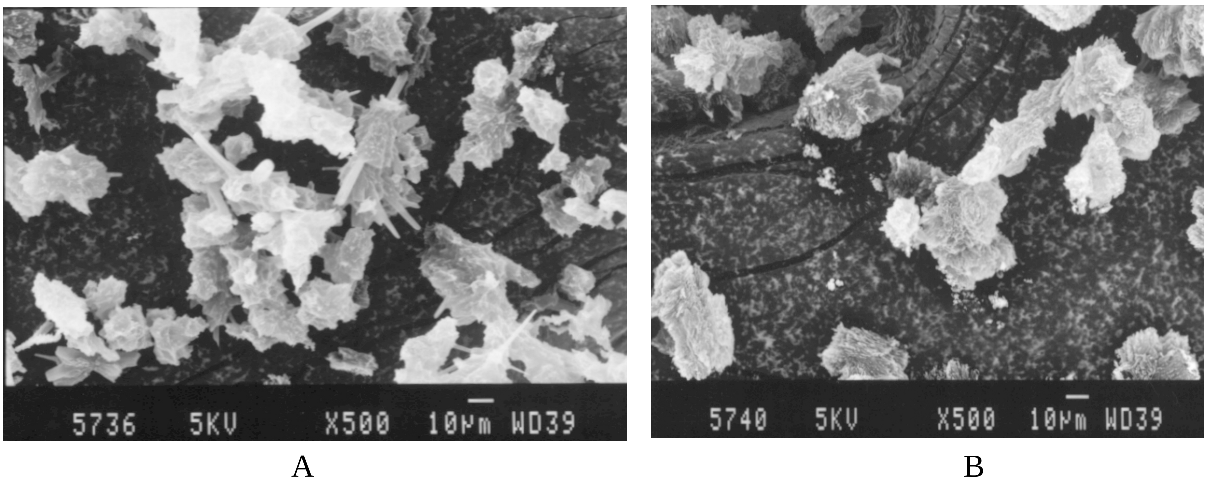

Figure4: PGSS™ micronised vanillin in freone R134 (A) and in freone R236fa (B)

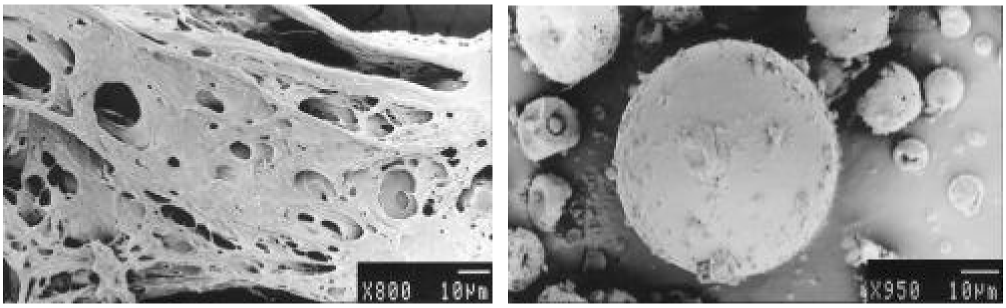

Figure5: Polymer processed by PGSS™ process at different process conditions

Based on the results from laboratory-scale equipment and the first production plants, the basic economics of the process were calculated. The processing costs are between 0.15 and 0.60 Euro/kg (composition of costs: investment ~ 20%, personell ~ 37%, and operating ~ 43%) and vary depending on the substances to be micronized, the scale of the equipment, etc.

The advantages of the PGSS™ process over conventional methods of particle-size reduction are numerous.

- It is a versatile process, applicable for several substances,
- it uses moderate pressures
- has low gas consumption,
- gives solvent-free powders,
- is suitable for highly viscous or sticky products,
- gives fine powders with narrow size-distribution,
- different morphologies, and
- is easy to scale-up.

Through the choice of the appropriate combination of solvent and operating conditions for a particular compound, PGSS™ can eliminate some of the disadvantages of traditional methods of particle-size redistribution in material processing. Solids formation by PGSS™ therefore shows potential for the production of crystalline and amorphous powders with a narrow and controllable size-distribution, thin films, and mixtures of amorphous materials. Due to the low processing costs PGSS™ can be used not only for highly valuable, but also for commodity products.

CONCLUSION

One goal of RESS/CSS, the anti-solvent processes such GAS, and the PGSS™ process, is to obtain submicron- or micron-sized particles. Although several features concerning RESS and GAS-processes scale-up are not yet very well known, it is probable that these processes are, or may be, used for producing relatively small amounts of high-value-added substances.

Restrictions arising from the difficult product- and gas-recovery in the RESS and GASR, GASP, SAS/PCA/SEDS processes are avoided by the PGSS™ process.

The PGSS™ process has several advantages, which favour its use for large-scale applications. This process has promise for the processing of low melting, highly viscous, waxy, and sticky compounds, even if the obtained particles are not of submicron size. The process already runs in plants with a capacity of some hundred kilograms per hour. New possibilities for generation of particles and composites based on PGSS™ and CPF™ processes are [12]:

- microfoam particles via the continuously operated PGSS™ process,
- powderization of reactive compounds and immiscible substances,
- powderous liquids via the CPF™ process,
- powderous emulsions via jet dispersion and the CPF™ process.

Numerous other processes for particle formation and design of composites and particle coating using supercritical fluids have been developed (UNICARB™, VAMP™, SAA, reactions in supercritical media leading to particle formation) are additionally described in the literature [1, 2, 12, 14]. The specific properties of dense gasses allow obtaining fine dispersed solids, especially of substances with low melting point temperatures, high viscosities and very waxy or sticky properties. Economic evaluation of the process shows that these compounds cannot be efficiently and economically processed by conventional mechanical processes and there is a big advantage of the use of supercritical fluids.

AKNOWLEDGEMENTS

The author wish to thank his co-workers and his students. Special thank to Prof. Dr. Rudolf Steiner at the University of Erlangen and Prof. Dr. Eckard Weidner and his co-workers from the University of Bochum.

REFERENCES

[1] KNEZ, Ž., WEIDNER, E., Precipitation of solids with dense gasses, in *High pressure process technology: fundamentals and applications*, Bertucco, A. and Vetter, G. (eds) (Elsevier, Amsterdam, London), **2001**, p. 587

[2] JUNG, J., PERRUT, M., J Supercrit Fluid, 20(3), **2001**, p. 179

[3] DEBENEDETTI, P.G., TOM, J.W., KWAUK, X., YEO, S.D., Fluid Phase Equilibria, 82, **1993**, p.311

[4] GALLAGHER, P.M., COFFEY, M.P., KRUKONIS, V.J., KLASUTIS, N., Gas antisolvent recrystallization – new process to recrystallize compounds insoluble in supercritical fluids, ACS Sym Ser, 406, **1989**, p.334

[5] WEIDNER, E., KNEZ, Ž., NOVAK, Z., European Patent EP 0744 992, 1995 PatentWO 95/21688, **1995**

[6] FUKNE-KOKOT, K.,KÖNIG; A., KNEZ, Ž., ŠKEGET, M., Fluid Phase Equilibira, 173, **2000**, p.297

[7] FUKNE-KOKOT, K., ŠKEGET, M., KÖNIG; A., KNEZ, Ž., Fluid Phase Equilibrium, 205, **2003**, p.233

[8] ŠKERGET, M., NOVAK-PINTARIC, Z., KNEZ, Ž., KRAVANJA, Z., Fluid Phase Equilibrium, 203, **2002**, p.111

[9] De SWAAN, A. J., DIEPEN, G.A.M., Rec. Trav. Chim. Pays-Bas 82, **1963**, p. 249

[10] TUMINELLO, W.H., DEE, G.T., McHUGH, M.A., Macromolecules, 28, **1995**, p.1506

[11] WEIDNER E., WIESMET, V., KNEZ, Ž., ŠKERGET, M., J. Supercrit. Fluids, 10, **1997**, p.139

[12] WEIDNER, E., Powderous composites by high pressure spray processes, in *Proceedings of the 6th International Symposium on supercritical fluids*, Brunner, G., Perrut, M., Kikic, I. (eds) (Tome 3. Vandoeuvre Cedex: Institut National Polytechnique de Lorraine, Versailles, France), **2003**, p. 1483

[13] KAPPLER, P., LIENER, W., PETERMAN, M., WEIDNER, E., Size and morphology of particles generated by polymer- meltswith carbon dioxide, in *Proceedings of the 6th International Symposium on supercritical fluids*, Brunner, G., Perrut, M., Kikic, I. (eds) (Tome 3. Vandoeuvre Cedex: Institut National Polytechnique de Lorraine, Versailles, France), **2003**, p. 1891

[14] REVERCHON, E., SPADA, A., Ind. Eng. Chem. Res., 43, **2004**, p.1460