PARTICLE GENERATION WITH SUPERCRITICAL CO2

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SUMMARY

Spray processes supported by dense gases allow the generation of powders and composites with characteristics that can hardly be obtained by classical methods. Process design for composites is strongly dependent on the ingredients which determine the functionality. Particle generation has already been investigated quite in detail for pure model substances, but interdependences between process design and ingredients are less known. Particle generation may be performed by expansion, e.g. RESS, PGSSTM, and CPFTM or by dilution of liquids by dense gases, e.g. GAS, SAS. This article illustrates new possibilities for the generation of powders and composites, gives some examples and is focused on the continuously operated PGSSTM and CPFTM processes. These two technologies offer tailor-made products and many application possibilities, e.g. for food, pharmaceuticals, cosmetics, paints or varnishes.

Keywords: Particle generation, powder generation, high pressure spray processes, supercritical fluids

1 PRINCIPLES

In Figure 1 a principal block diagram illustrates the required process steps for a high pressure spray process.



Figure 1: Block Diagram: Spray Process

The substance(s) must first be converted into a sprayable form by liquefaction or dissolution, which can be obtained by dissolution in a supercritical solvent (RESS), melting (PGSSTM types), dissolution in a solvent (GAS, SAS, PGSSTM) or by dispersing solids or liquids in a melt or solution to be powderized. A more or less sophisticated dosing system feeds the liquid to the mixing and powder generation system, where the fluid has to be dosed additionally. In case of coating or anti-solvent processes this is performed in autoclaves, while in other processes static or dynamic mixers, jet dispersers or homogenisers are used. The admixed ingredient can be required for the functionality of the final powder or as auxiliary compound necessary for stable process conditions. Admixing of SCF allows

processing of high viscous compounds, formation of emulsions, dispersions or blends, or increases subcooling after expansion. As mentioned before powder formation is induced by expansion or by dilution with a dense gas. The solidification of melts is very fast due to the direct heat transfer from particles into the coexpanded gas and therefore the thermal stress is lower compared to classical air drying. Because of this and the fact, that there is no contact with air/oxygen, these technologies are suitable for sensitive products as well. Separation of solids and particle formation are typically integrated into the equipment - in an autoclave for antisolvent processes and within a spray tower for others in order to separate the particles/composites either from liquids or the expanded gas. Post-processing for antisolvent processes, e.g. the removal of residual liquid from the precipitated particles, can be achieved by SCF drying. Coating, agglomeration, size fractionation, dispersion etc. may be considered for powdery products. On a case to case basis, depending on the used process and corresponding capacity, gas recycling has to be considered if feasible. $PGSS^{TM}$ and CPF^{TM} processes have relatively low or moderate gas consumption and consequently specifically designed gas recovery systems for such small or medium sized plants are more expensive than the use of fresh gas (CO₂).

1.1 Published Processes in Particle Design



Figure 2: Process Types

1.1.1 RESS Process

The product is dissolved in a compressed fluid and rapidly depressurised through a nozzle, which causes a rapid nucleation of the product into a dispersed powder. The process is limited to substances which are reasonably fluid soluble. The gas demand is high.

A schematic diagram is given in Figure 3.



Figure 3: Rapid Expansion of Supercritical Solutions

1.1.2 GAS/SAS (SEDS) Process

The product is first dissolved in an organic solvent and the precipitation of particles is performed by reducing the solubility through adding a dense gas as antisolvent, which dissolves partly into the solvent.

The gas and solvent are separated from the particles, whereby the gas disappears spontaniously, but the organic solvent needs an additional separation step.

Figure 4 shows the principle.



Figure 4: Gas (Supercritical Fluid) Anti-Solvent

1.1.3 PGSSTM Process [1]

This process produces particles by spraying of gas saturated solutions. The substance is melted and mixed with the dense gas, either in a high pressure vessel – discontinuous process – or by means of a static mixer – continuous process – and afterwards expanded via a nozzle into a spray tower. The dense gas dissolves partly in the melt and reduces the viscosity. After the expansion the solubility is immediately reduced and the volume increase of the disappearing gas causes the liquid to disintegrate into tiny droplets. Due to the Joule – Thomson effect the gas cools down and consequently the droplets solidify almost immediately. To some extent particles and gas are withdrawn separately in the spray tower. Finer particles are removed from the gas by means of a cyclone.

A further description and applications are given later in the article.

Figure 5 shows the flow diagrams for the discontinuous and continuous $PGSS^{TM}$ process.

Discontinous PGSSTM Process



Continous PGSSTM Process



Figure 5: Particles from Gas Saturated Solutions

1.1.4 CPCSP Process

This modified PGSSTM process was developed to powderize reactive 2-compound powder paints. The molten binder and the setting agent are pressurized and mixed in a static mixer together with a cold dense gas (temperature below their melting points). Due to the short contact time a reaction can be avoided. The gas induced decrease of the melting point maintains the compounds in a liquid state. The composites are obtained in a "frozen" powderized form.

Continuous processing allows easy adjustment of all conditions.

Figure 6 shows a principal flow diagram.



Figure 6: Continuous Powder Coating Spraying Process

1.1.5 Suitability of the Mentioned Processes

When comparing the above mentioned processes one recognizes that only the anti-solvent processes use an organic solvent as a utility, which must be removed from the powder in a further expensive step. Other processes use only a gaseous or supercritical fluid, which disappears after expansion and can be easily separated from the powder because of the density difference.

RESS and PGSSTM processes are similar in design, but limitations become obvious when the conditions of the 2 component solution are considered. The essential parameters for powder formulation are mass-flow ratio between the solvent and the substance (or solvent to total mass-flow) as well as pressure and temperature of the mixture before expansion. Figure 7 shows the influence of pressure versus composition.

The left curve represents the composition of the solvent poor liquid phase and the right one the solvent rich gas phase.

The RESS process is limited by the solubility of the substance in the gas or supercritical phase and requires high gas demand.

The PGSSTM process is limited by the solubility of the solvent in the substance and needs much less gas.

Contrary to continuous PGSSTM the solvent ratio can therefore not be chosen freely for the discontinuous processes.



Figure 7: Operation Areas of Spraying Processes

1.1.6 CPF^{TM} Process [2]

The above mentioned processes are used to produce powders from liquids which are solid at ambient temperature. The CPFTM process generates powders from liquids, which are not solidified during spraying. Liquid and gas are pressurized, mixed together and expanded into a spray tower. A powderous carrier is dosed into the produced fine droplet spray and a powder with a liquid content of up to 90 wt.-% is formed.

A further description and applications are given later in the article.

Figure 8 shows a principal flow diagram.



Figure 8: Concentrated Powder Form

In the following sections attention is paid to the PGSS^{TM} and CPF^{TM} process.

2 THE PGSSTM PROCESS

Polyethylene glycols (PEG) were used as model substances to demonstrate the dependence of particle size, size distribution, morphology and bulk density on process parameters like pre-expansion pressure, preexpansion temperature and gas to product ratio (GTP). The different molecular weights demonstrate the influence of the melt viscosity on the product quality.

Numerous evaluated experiments showed that smaller particles are formed with increasing GTP ratio. At such high ratios the pressure influence is less pronounced than at lower values.

From Figure 9 it can be seen that different morphologies are formed, depending on applied processing conditions. The morphology factor is set arbitrarily [1] at values between 0,2 and 1 and increases with decreasing void volume ratio. A model to calculate the factor is given below.



Figure 9: Morphologies of PEG 6000 [3]

The pre-expansion temperature has a strong influence on the morphology. At 100 °C microfoams are obtained at pressures above 250 bar, while at 60 °C the pressure range is much larger, e.g. is starting at pressures of about 60 bar already. Spheres are formed at high preexpansion temperatures and/or lower mixing pressures and GTP ratios. The diameters of the produced spheres are between 20 to 200 μ m.

Especially at temperatures higher than $100 \,^{\circ}C$ spheres molten together are observed. The reason is obviously that the formed droplets collide before complete solidification.

Kappler [3] developed a regression analyses in his research in order to determine the morphology factor as follows:

$$F = 6.9 \cdot 10^{-11} \cdot \frac{(T[K])^{4,247}}{p[bar]0,403 \cdot GTP^{0,105}}$$

Relative deviation = 14 %

Valid for:

323 K < T < 373 K

50 bar < p < 350 bar

$$0, 1 < \text{GTP} < 10$$

Figure 10 demonstrates a corresponding result with a constant GTP ratio and shows the influence of pressure and temperature on morphologies.



Figure 10: Areas of equal morphologies (GTP = 4)

It was realized from experiments that significant trends exist regarding dependences of processing conditions on the bulk density as well. By means of a regression analyses the corresponding bulk densities can be calculated as follows [3]:

$\rho_{S}[g/ml] = 5.2 \cdot 10^{-17} \cdot \frac{(T[K])^{6.574}}{(p[bar]^{0.552} \cdot GTP^{0.106}} \pm 0.047[g/ml]$	
Relative deviation = 15 %	
Valid for:	
323 K < T < 373 K	
50 bar < p < 350 bar	

0,1 < GTP < 10

The 3-dimensional graph resulting from calculated values shows that the:

- bulk density decreases with increasing GTP ratio and increasing pressure,
- for particle size pressure dependence is of higher significance than temperature,
- bulk density decreases strongly at low pressures and GTP ratios and
- decreases hardly at high pressures and GTP ratios.

The summary of all results is shown in Figure 11. Areas of equal particle sizes together with areas of equal bulk densities and areas of equal morphologies can be seen related to the process parameters pressure, temperature and GTP ratio. By means of Figure 11 it is possible to determine the required processing conditions in order to obtain the desired particle characteristics.

As a consequence from the above it is possible that particle characteristics can be tailor-made in a range between approximately 3 μ m up to 500 μ m and with bulk densities from about 90 kg/m³ up to about 600 kg/m³.



Figure 11: Areas of equal particle-size, -density and – morphology [3]

A distribution of typical particle sizes can be seen in Figure 12 below.



The possible applications of the $PGSS^{TM}$ process are listed in Table 1.

Emulsifiers	Fat/Fat Derivatives		
 Soya lecithin 	– Chocolate		
 Sunflower lecithin 	 Cocoa butter 		
 Phosphatidylcholine 	– Butter		
 Phosphatidyethanolamine 	 Butter fat and fractions 		
 Alkylpolyglucoside 	 Palm and other vegetable 		
 Monoglyceride 	fats		
 Diglyceride 	 Stearic acid 		
 Lamegin 	 Fatty alcohols 		
	 Stearylstearate 		
Vitamines/Antioxidants/	 Natural waxes 		
Fragrances	 Phytosterol 		
 Citric acid 	 Encapsulation of water in 		
 Rosmarin extract 	fat		
 Watersoluble vitamines 			
 β-Carotine 	Pharmaceuticals		
 Synthetic antioxidants 	 Nifedipin, felodipin 		
– Menthol	 Acetyl salicylic acid 		
	– Ibuprofene		
77.4			

Table 1: PGSSTM Applications

Figures 13, 14 and 15 show particles of composites, agglomerates and fat encapsulated water.



Liquid content: 64 wt%





Figure 14: Agglomeration – liquid bridge [4]



number of micro-pores rises with increasing portion of water

Figure 15: Fat encapsulated water [4]

In Table 2 the PGSSTM process features are given.

Applicable for a multitude of substances - Low melting compounds - High-viscous products
Mild Process Conditions - 40 to 200 bar, solvent-free, inert atmosphere - Typically 0,1 to 2 kg gas per kg powder - "Small" spray towers
Adjustable particle size, morphology and application profiles - Spheres, hollow spheres, microfoams, fibres, irregular particles - Encapsulations, solid solutions, reactive compounds
Easy Scale-up - Production plants with capacities of some hundred kg/hour - Competitive, especially if operated continuously
Table 2: Features – PGSS TM Process [4]

Finally the production cost is presented in Figure 16 to complete the overview of the PGSSTM process.



Figure 16: Production cost

3 POWDEROUS LIQUIDS - THE CPFTM PROCESS

A short description and principal flow sheet were already presented in article 1.1.6. In the following the principal morphologies and the corresponding binding mechanisms, demonstrated in Figure 17, will be discussed.



Figure 17: Morphologies and Binding Mechanism [5]

In the spray the carrier is intensively contacted with the liquid droplets through the expanding gas and the liquid can adsorb onto the carrier. Depending on the size of the carrier and the thickness of the adsorbed layer, only a certain percentage can be bound. With increasing liquid concentrations the carrier particles agglomerate and such agglomerates can hold high concentrations by capillary and interfacial forces. In case a porous carrier material is used, very fine droplets – formed during the gas driven expansion – can penetrate into rather small pores and impregnate the carrier consequently.

Different types of carriers which can be used, are given in Figure 18.



Figure 18: Applicable Carriers for CPF^{TM} [5]

3.1 Powderous Emulsions via CPFTM Process

As shown before the product quality can be influenced by size, composition and morphology. The CPF^{TM} process also allows to generate new types of composites.

Examples are powderous emulsions. In Figure 19 a schematic picture of such a plant is given.



J. Wingenfeld, phD-Thesis, Bochum 2002

Figure 19: Continuously operated CPF^{TM} process for powderous emulsions [6]

The oil- and water phase are dosed from different vessels, pressurized and both immiscible liquids are emulsified and mixed with the dense gas in the mixer. The mixture is suddenly expanded, a carrier is admixed to the sprayed emulsion and a powderous agglomerate is formed. The morphology is different from standard CPFTM products. In case an oil/water emulsion is formed and a hydrophilic carrier is used, liquid oil droplets are dispersed in a continuous water phase. The oil droplets will hardly adsorb to the carrier surface, but will either coalesce or remain as droplets. In case of a lipophilic carrier for such an emulsion, the probability of adsorption is higher. Similar considerations can be applied for water/oil emulsions.

An example for the release properties of such an emulsion is given in Figure 20 below [4].



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Figure 20: Redispersion of powderous oil (paprika extract) in water emulsion and water in oil emulsion [6]

Both emulsions in Figure 20 are redispersed in water. The W/O emulsion is rather bad, although a suitable emulsifier is used. The re-dispersed O/W emulsion, shown in the lower row, is very homogeneous, because the continuous water phase in the emulsion causes an easy and fast break-up of the agglomerate and the small oil droplets disperse evenly and immediately.

The features of the $\mbox{CPF}^{\mbox{\scriptsize TM}}$ process are summarised in Table 3.



Table 3: Features of the CPF^{TM} Process

4 CONCLUSION

- High pressure spray processes with supercritical fluids allow to generate a multitude of special particle morphologies and composites
- Reduction of melting temperatures allows to - mix and dissolve sensitive, reactive and/or immiscible substances in a liquid
- Fast dissolution rates, reduced viscosities and surface tensions allow to
 - reduce the solubility of crystallizing substances in classical solvents rapidly
 - mix/dissolve liquid compounds even with high viscosities e.g. by static mixers

- generate sprays from gas containing liquids with a broad range of viscosities
- Large volume increase during expansion allows to
 - generate small droplets in sprays
 - admix and agglomerate additives at high turbulence in expanding sprays
- Rapid and large temperature reduction by expansion and direct heat transfer allows to
 - solidify droplets very quickly
 - establish a high degree of supersaturating, which helps to powderize substances that are difficult to crystallize
 - "freeze" and powderize immiscible liquid compounds
 - reduce losses of compounds with high volatility

ACKNOWLEDGEMENT

The author wishes to thank his co-workers who contributed to the design and technical realization of processes and products. Research and development was supported by the Adalbert Raps Stiftung for many years, as well as by Raps and Yara. The lab-scale and pilot work was performed at the universities in Bochum (Prof. Weidner), Maribor (Prof. Knez) as well at the Adalbert Raps Zentrum (TU München, Weihenstephan).

Both $PGSS^{TM}$ – and CPF^{TM} – processes are exploited in cooperation between the inventors of said processes, Raps and Natex.

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