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, PGSS™, and CPF™ 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 PGSS™ and CPF™ 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.

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 (PGSS™ types), dissolution in a solvent (GAS, SAS, PGSS™) 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 sub-cooling 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 co-expanded 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 anti-solvent 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 anti-solvent 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™ and CPF™ 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

- **RESS**
  Rapid Expansion of a Supercritical Solution
- **SAS**
  Supercritical Fluid Anti-Solvent
- **GAS**
  Gas Anti-Solvent
- **SEDS**
  Solution Enhanced Dispersion by SCF
- **ASES**
  Aerosol Solvent Extraction System
- **PLUSS**
  Polymer Liquefaction Using Supercritical Solvation
- **VAMP**
  Ferro, Powder Coating Formulation
- **CPF**
  Concentrated Powder Form
- **SFDD**
- **SFT-CD**
- **UNICARB®**
  from Union Carbide, PGSS™ related Process
- **PGSS™**
  Particles from Gas Saturated Solutions
- **CPCSP**
  Continuous Powder Coating Spraying Process

**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 disperse 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 anti-solvent, which dissolves partly into the solvent.

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

Figure 4 shows the principle.

**Figure 4: Gas (Supercritical Fluid) Anti-Solvent**

1.1.3 **PGSS™ Process**

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™ process.

**Discontinous PGSS™ Process**

**Continuous PGSS™ Process**

**Figure 5: Particles from Gas Saturated Solutions**
1.1.4 CPCSP Process

This modified PGSS™ 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.

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

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

1.1.6 CPF™ Process [2]

The above mentioned processes are used to produce powders from liquids which are solid at ambient temperature. The CPF™ 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 powdery 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.

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

2 THE PGSS™ 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, pre-expansion 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.

$$F = 6.9 \cdot 10^{-11} \cdot \frac{(T[K])^{4.247}}{p[bar]^{0.403} \cdot GTP^{0.105}}$$

Relative deviation = 14%

Valid for:
323 K < T < 373 K
50 bar < p < 350 bar
0,1 < GTP < 10

Figure 10 demonstrates a corresponding result with a constant GTP ratio and shows the influence of pressure and temperature on morphologies.
Figure 11: Areas of equal particle-size, -density and – morphology [3]

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

Figure 12: Particle sizes

The possible applications of the PGSS™ process are listed in Table 1.

<table>
<thead>
<tr>
<th>Emulsifiers</th>
<th>Fat/Fat Derivatives</th>
</tr>
</thead>
<tbody>
<tr>
<td>– Soya lecithin</td>
<td>– Chocolate</td>
</tr>
<tr>
<td>– Sunflower lecithin</td>
<td>– Cocoa butter</td>
</tr>
<tr>
<td>– Phosphatidy/cholesterol</td>
<td>– Butter</td>
</tr>
<tr>
<td>– Phosphatidyethanolamine</td>
<td>– Butter fat and fractions</td>
</tr>
<tr>
<td>– Alkylpolyglucoside</td>
<td>– Palm and other vegetable fats</td>
</tr>
<tr>
<td>– Monoglyceride</td>
<td>– Stearic acid</td>
</tr>
<tr>
<td>– Diglyceride</td>
<td>– Fatty alcohols</td>
</tr>
<tr>
<td>– Lamegin</td>
<td>– Stearlystearate</td>
</tr>
<tr>
<td>– Vitamines/Antioxidants/</td>
<td>– Natural waxes</td>
</tr>
<tr>
<td>Fragrances</td>
<td>– Phytosterol</td>
</tr>
<tr>
<td>– Citric acid</td>
<td>– Encapsulation of water in fat</td>
</tr>
<tr>
<td>– Rosmarin extract</td>
<td>– Nifedipin, felodipin</td>
</tr>
<tr>
<td>– Watersoluble vitamins</td>
<td>– Acetyl salicylic acid</td>
</tr>
<tr>
<td>– β-Carotene</td>
<td>– Ibuprofen</td>
</tr>
</tbody>
</table>

| Natural waxes            | Synthetic antioxidants                   |
| – Phytosterol            | – Menthol                                |

Table 1: PGSS™ Applications

<table>
<thead>
<tr>
<th>Liquid content: 64 wt%</th>
</tr>
</thead>
</table>

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

Figure 13: Open structure – microcavities [4]

Figure 14: Agglomeration – liquid bridge [4]

Figure 15: Fat encapsulated water [4]

In Table 2 the PGSS™ process features are given.

<table>
<thead>
<tr>
<th>Applicable for a multitude of substances</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Low melting compounds</td>
</tr>
<tr>
<td>- High-viscous products</td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th>Mild Process Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>- 40 to 200 bar, solvent-free, inert atmosphere</td>
</tr>
<tr>
<td>- Typically 0.1 to 2 kg gas per kg powder</td>
</tr>
<tr>
<td>- “Small” spray towers</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Adjustable particle size, morphology and application profiles</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Spheres, hollow spheres, microfoams, fibres, irregular particles</td>
</tr>
<tr>
<td>- Encapsulations, solid solutions, reactive compounds</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Easy Scale-up</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Production plants with capacities of some hundred kg/hour</td>
</tr>
<tr>
<td>- Competitive, especially if operated continuously</td>
</tr>
</tbody>
</table>

Table 2: Features – PGSS™ Process [4]
Finally the production cost is presented in Figure 16 to complete the overview of the PGSS™ process.

![Figure 16: Production cost](image)

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

![Figure 18: Applicable Carriers for CPF™](image)

### 3 POWDEROUS LIQUIDS - THE CPF™ 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](image)

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.

### 3.1 Powderous Emulsions via CPF™ Process

As shown before the product quality can be influenced by size, composition and morphology. The CPF™ 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.

![Figure 19: Continuously operated CPF™ process for powderous emulsions](image)

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 CPF™ 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].

![Water in Oil Emulsion](image)

![Oil in Water Emulsion](image)

**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 CPFTM process are summarised in Table 3.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dosage of carrier</strong></td>
<td>Pneumatic by inert gas</td>
</tr>
<tr>
<td></td>
<td>Carrier typically between 10 μm and 500 μm</td>
</tr>
<tr>
<td><strong>Dosage of liquids and gas</strong></td>
<td>High pressure pumps and inline mixers</td>
</tr>
<tr>
<td></td>
<td>Integrated formation of emulsions under high pressure</td>
</tr>
<tr>
<td></td>
<td>Rapid “immobilizing” of the emulsion</td>
</tr>
<tr>
<td></td>
<td>Sprayability of high viscous liquids due to dilution with SF</td>
</tr>
<tr>
<td><strong>Stress</strong></td>
<td>-20 to +25°C, minimized loss of aroma, no oxidative stress</td>
</tr>
<tr>
<td><strong>Liquid content in powders</strong></td>
<td>Up to 90 wt%</td>
</tr>
</tbody>
</table>

*Table 3: Features of the CPFTM 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

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Both PGSS™ – and CPFTM – processes are exploited in cooperation between the inventors of said processes, Raps and Natex.

5 REFERENCES

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