CPF-TECHNOLOGY
A NEW CRYOGENIC SPRAYING PROCESS
FOR PULVERIZATION OF LIQUIDS

Sabine Grüner*, Frank Otto, Bernd Weinreich,
Adalbert-Raps-Zentrum, Am Forum 2, D-85350 Freising,
Fon/Fax: ++49 8161 713668, gruener@wzw.tum.de

INTRODUCTION

Compared to liquids, especially viscous liquids, powdery products have some advantages in their processing like dosing and mixing. The powder form can be obtained, as practised in traditional technologies, by combining liquids with solid powdery substances. Besides classical mixing processes spray technologies with an integrated drying step, like spray drying and fluid bed agglomeration, are used. In these processes liquid, powdery substance and solvent are dissolved resp. dispersed and homogenized in a premix. Afterwards the mixture is sprayed, the solvent is removed in a hot air stream and a powdery product is achieved.

CPF technology is a high pressure spray procedure which allows to spray liquids on powdery carriers using supercritical carbon dioxide. The processing is carried out in a gentle way, in an inert gas atmosphere and at low temperatures [1,2].

I – PRINCIPLE OF THE PROCESS

A principle flow scheme of a continuously operated plant is given in figure 1. The liquid is pumped from a vessel into a static mixer, where it is contacted with a dense gas, normally carbon dioxide. The mixing device is operated under pressures from 80 to 250 bar and temperatures from 20°C to 80°C. The conditions are mostly selected so that carbon dioxide is in the supercritical state ($p > 73{,}83$ bar, $T > 31{,}04$°C). The gas is dissolved under high pressure in the liquid and a gas-saturated solution is formed. A marked reduction in viscosity and surface tension of the liquid is caused by the solution of the gas. Therefore the spraying even of high viscous fluids, which was challenging in the past, is relieved. Moreover the forming of fine droplets is eased.

The gas-saturated solution is released to atmospheric pressure into a spray tower. The gas is set free and fine liquid droplets are formed. Moreover a remarkable lowering of the temperature in the spray tower is caused by the Joule-Thomson-Phenomenon. Fluidised carrier particles are dosed concurrently to the sprayed liquid. An intensive mixing of liquid droplets and carrier is obtained by the released gas. The liquid is bound to the carrier by adsorption on the surface, agglomeration of carrier particles and binding effects of capillary forces in the pores. As a result a free-flowing powder with liquid concentrations of up to 80% is obtained. The powder is removed from the bottom of the spray tower. Fine particles are removed from the gas by sedimentation, filtration and the use of a cyclone.

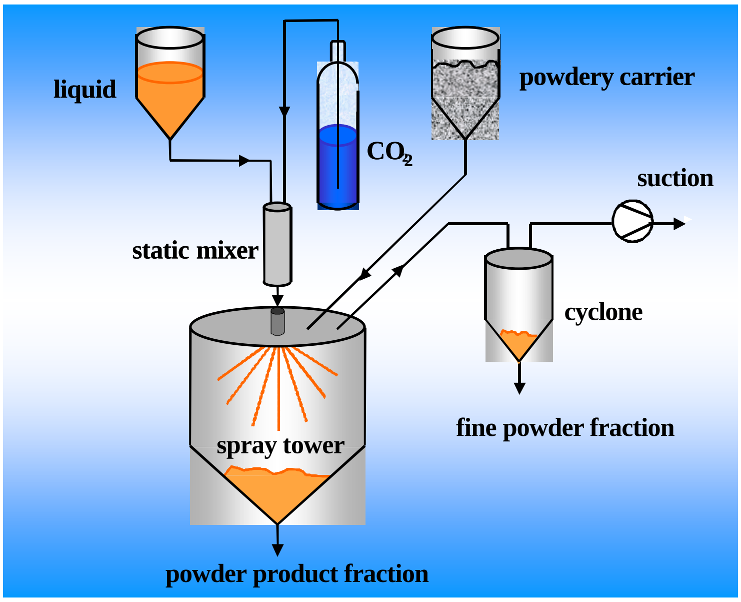

Figure 1: Flow scheme of CPF technology

II - MATERIALS

Generally all kinds of solid powdery substances can be used as carrier. To date more than 250 different carriers have been tested, mostly from food, cosmetic and pharmaceutical industry. Starches, celluloses, silicic acids, sugars, alumina and polymers have to be mentioned.

The selection criteria enclose differences in material attributes, particle form and size, bulk density, pourability, porosity and wetting behaviour. Particle size of carriers used ranges from 5 µm to 2 mm, bulk density reaches from 50 kg/m^3 to 1400 kg/m^3.

A wide range of different liquids has also been tested and versatile use of this process was found out. Beneath low and highly viscous liquids CPF technology can be applied to lipophilic and hydrophilic liquids. Highly viscous plant extracts as well as thermal sensitive etheric oils, oxygen sensitive oils and fats and high volatiles were successfully processed. Moreover vitamins, emulsions and dispersions were pulverized.

III - BINDING

First the liquid is bound to the carrier particle surface by adsorption when liquid droplets and fluidised carrier are brought into contact. Therefore the particles are coated with a thin liquid film. For a higher liquid loading the liquid is bound by capillary forces in liquid bridges between carrier particles. Hence agglomeration occurs. When carrier with porous particles are used, the pores are filled with liquid also caused by capillary forces [3].

Due to the release of carbon dioxide very fine droplets of the sprayed liquid are generated in the CPF technology. Therefore also non-wetting liquids can fill the pores of the particles because the internal pressure of the droplets (Laplace pressure) is high enough. Binding mechanisms and the infiltration of a non-wetting liquid droplet into a pore are shown in figure 2.

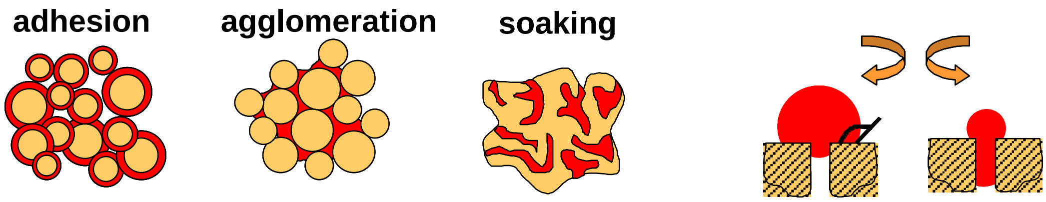

Figure 2: Binding mechanisms

IV - INFLUENCING FACTORS

One field of investigation was to find out the influencing factors on the maximum liquid ratio in the final powder. The maximum liquid ratio is understood to be the maximum amount of liquid which can be bound to the carrier without losing the powdery structure. It was found out in experiments that the liquid characteristics have nearly no influence on the maximum liquid ratio.

A carrier can be loaded with the same volume of a liquid substance independent from the kind of liquid. On the one hand the binding between liquid and carrier is a physical process, meaning the filling of cavities and the coating of surfaces. On the other hand the liquid properties, which affect the processing in other spray technologies, take a back seat due to the use of supercritical carbon dioxide. The dense gas causes a marked reduction of the viscosity, meaning that high viscous liquids can be sprayed as well as low viscous liquids. Moreover very fine droplets are generated by the released gas, so that non-wetting liquids can fill the pores of the carrier particles. An influence of the liquid characteristics on the maximum liquid ratio was only found when the liquid changes the structure of the carrier, e.g. the carrier is dissolved or swollen by the liquid.

But the maximum liquid ratio, which can be realized, depends strongly on the properties of the carrier. Different liquid capacities were found for the carriers, because each carrier features a different surfaces or porous structure for binding a liquid.

In order to find out the specific attribute of the carrier which causes such a strong influence, different material properties like particle size, porosity, BET surface, bulk density and tapped density were investigated with regard to the maximum liquid ratio. A dependency of the maximum liquid ratio was detected only for the tapped density of the carrier [2,4]. The correlation is given in figure 3. In principle maximum liquid loading increases with a decreasing tapped density.

In practise an estimation of the maximum liquid ratio is feasable by this correlation and therefore the number of necessary trials is distinctly reduced.

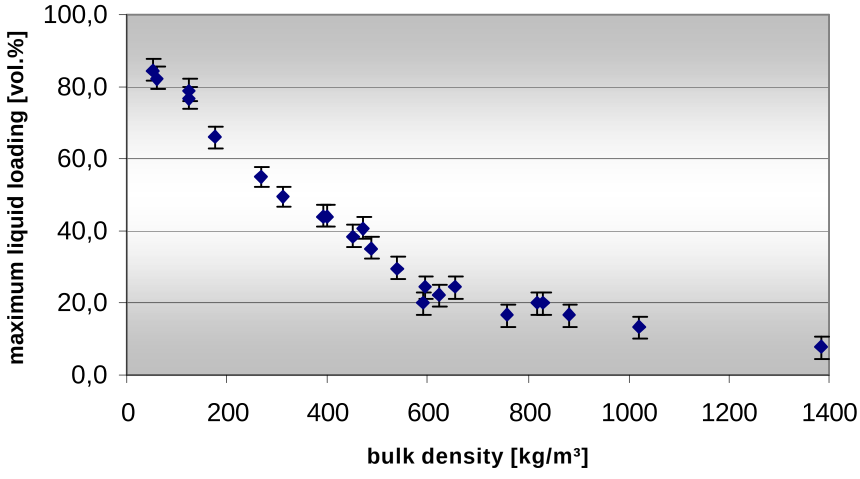

Figure 3: Correlation between maximum liquid ratio and tapped density of carriers

V - APPLICATION

Citrus flavour

In order to prove the mild process conditions of CPF technology, some sensitive flavours were selected for pulverization. To demonstrate the absence of oxygen during the whole process, flavours highly sensitive to oxygen were sprayed. As an example a citrus flavour, which contained 90% limonene, was processed. Limonene reacts rapidly to carvone in the presence of oxygen. Therefore an increasing content of carvone is an obvious pointer for oxidation. In food products already small amounts of carvone aren´t acceptable because a disturbing caraway-like taste is caused.

In the diagramm (figure 4) the carvone content of the original flavour (represented in the proportion to the content of citrale) and of powders from CPF technology, spray drying and fluid bed agglomeration is given. The results verify that in case of CPF no increase of carvone could be detected, meaning that no oxidation has occured. The inert gas atmosphere in the CPF-process is sufficient to pulverize oxygen sensitive liquids without degradation. Both processes, spray drying and fluid bed agglomeration, oxidation was detected due to the use of a hot air stream [5].

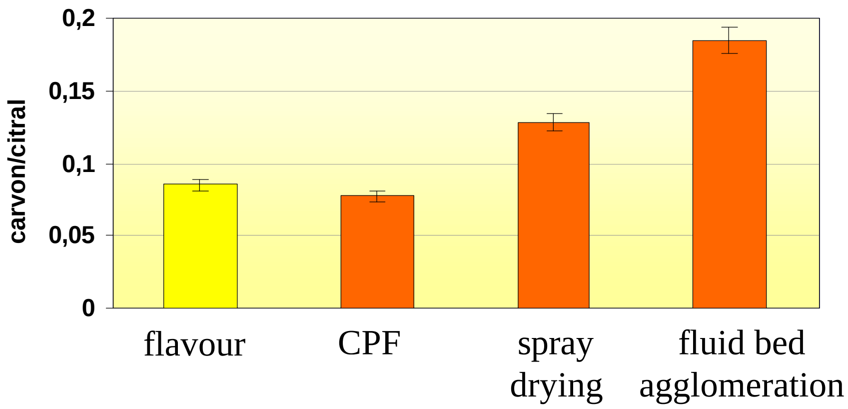

Figure 4: Citrus flavour pulverized with CPF, spray drying and fluid bed agglomeration

Emulsions

Using CPF technology liquids remained unchanged in their composition during processing. They are just fixed to the carrier in the form of fine droplets. But spraying of emulsions is associated with the risk of changing the liquid structure due to occurring shear stress. Thus it was investigated whether droplet size distribution is changed during the spraying or not. In figure 5 microscopic pictures and the measured droplet size distribution of an emulsion before and after spraying is given. From the results it is obvious that the emulsion was not changed in its structure by the procedure.

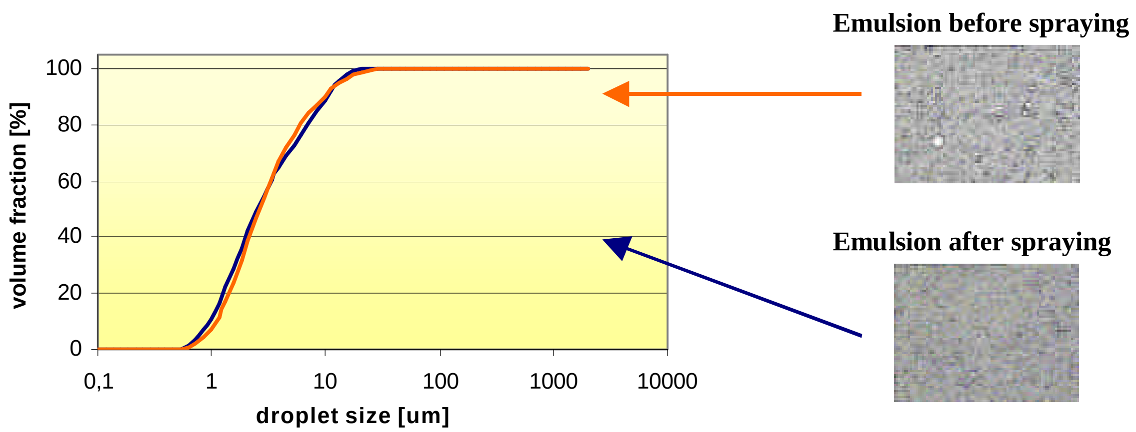

Figure 5: Influence of CPF technology on droplet size distribution

In following experiments the pulverized emulsion is released in water. The droplet size distribution is measured and compared to the result of the basic emulsion, to find out whether a change during storage of the powdered emulsion occured or not. The droplet size distribution of the basic emulsion is given in figure 6 left side. The results of the processed emulsion, meaning sprayed and released, are shown on the right side.

The droplet density in the re-dispersed emulsion (microscopic picture) is lower than in the basic emulsion caused by a dilution effect of the release in water. But the original droplet size isn´t changed during re-dispersion. Compared to the basic emulsion the droplet size distribution of the released emulsion is a bit closer, this might be caused by the dilution in water. In both cases the average droplet size is nearly the same [6].

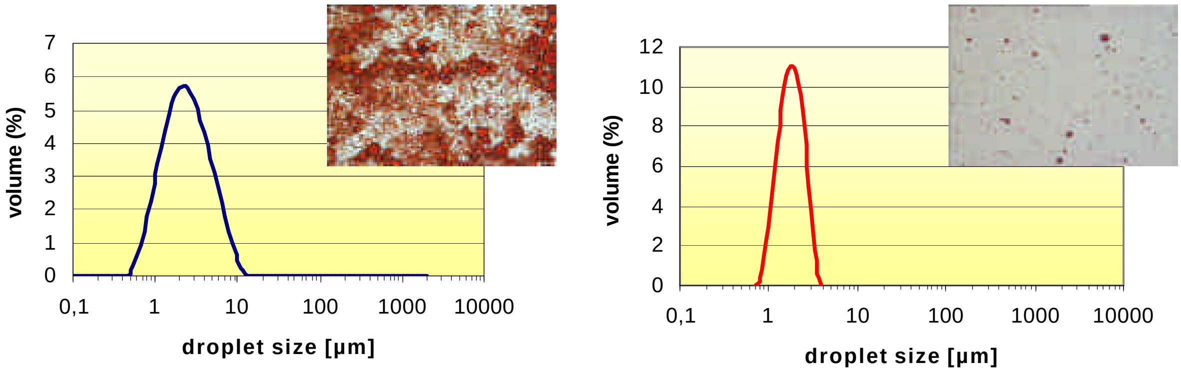

Figure 6: Droplet size distribution of basic emulsion and re-dispersed emulsion

CONCLUSION

CPF technology is a versatile procedure to pulverize liquids. Supercritical carbon dioxide is used to generate fine droplets by a marked reduction of viscosity and surface tension. Moreover the process conditions are gentle due to an inert gas atmosphere and low temperatures. Compared to traditional technologies the use of CPF technology is particularly advantageous in case of viscous, temperature and oxygen sensitive liquids.

REFERENCES :

[1] WEINREICH, B. et al., WO 99/17868, 1999

[2] GRÜNER, S., Entwicklung eines Hochdrucksprühverfahrens zur Herstellung hochkonzentrierter flüssigkeitsbeladener Pulver, Thesis, Erlangen, 1999

[3] DÖRFLER, H., Grenzflächen- und Kolloidchemie; VCH, Weinheim, 1994

[4] LANKES, H., Maximale Flüssigkeitsaufnahmekapazität von dispersen Trägerstoffen beim Beladen und Tränken, Thesis, München, 2002

[5] GRÜNER, S. OTTO, F., WEINREICH, B., CPF-Technology – Application in Food Industry, 6th Conference on Supercritical Fluids and their Applications, Maiori, Italy, 09.-12.09.01

[6] Wingenfeld, J., Herstellung und Eigenschaften pulverförmiger Emulsionen, Thesis, Bochum, 2002