Microemulsions Generation Using PGSS (Particles from Gas Saturated Solutions) Technique

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High pressure technology e.g. PGSS (Particles from Gas Saturated Solutions) allows to produce powders with properties difficult to achieve by classical methods like milling, crystallization or spray drying. In the last years, research for the PGSS process was focused on the production of single component systems[1, 2] but another very promising possibility is to use the PGSS process to obtain filled micro particles, solid - solid or solid–liquid composites.[3]

For powder production the shell and core materials are melted if necessary and pumped into a static mixer. Here these substances are mixed with supercritical carbon dioxide (CO_2). Subsequently the mixture is expanded through a nozzle into a spray tower. Due to the Joule-Thomson effect of the expanding carbon dioxide, a cooling of the droplets occurs and this leads to the formation of particles when they under-run the solidifying temperature. These particles can be gathered in the spray tower.

Encapsulation of sensitive substances forms an effective protection against stress factors. Besides protection, encapsulation opens furthermore new possibilities for the controlled release of active substances or for increased bioavailability.

This can be, for example, achieved in the case of micro emulsions. Thus an active substance can be solved in water that is subsequently encapsulated in a fatty matrix. The system can be stabilized with the help of an emulsifier. The obtained powderous emulsions have tailor made properties like bulk density, size, morphology and water content. The properties of the micro emulsion can be adjusted by the process parameters of the PGSS process.

INTRODUCTION

Powderous microcapsules can be produced by different well known chemical and physical processes. However, where very small particle sizes are required, or highly viscous substances have to be reduced to the micro-scale, the limits of traditional processes are fast reached. In such cases, the solution can be a high-pressure process like the PGSS (Particles from Gas Saturated Solutions) process which is suitable for the micronisation of different substances. In previous investigations it was already shown that fine polymer powders with different morphologies can be manufactured [2, 4, 5].

The process is not only applicable to polymeric systems, but allows to generate powderous composites of water encapsulated in fat or liquors in chocolate [6, 7].

It is also possible to obtain powder where liquid oil droplets are encapsulated in solid polyethylene glycols [8].

For the production of a powderous emulsion the shell material (fat) is used in molten form and is premixed with an emulsifier. This mixture and the second component (water or an active substance solved in water) are pumped and dosed into a mixing system were the two substances are intensively mixed in presence of heated CO_2 under high pressure. Thus micro droplets of the liquid are generated and are dispersed in the liquefied shell material. Subsequently the mixture is expanded very fast to ambient pressure through a nozzle into a spray tower. Simultaneously it is cooled down due to the

Joule-Thomson effect of the expanding gas. The shell material solidifies and forms a covering layer around the liquid droplets.

Dry and free flowing powders with a high content of the dispersed phase can be achieved. Additionally the micro encapsulation opens new possibilities for the control of release of active substances.

MATERIALS AND METHODS

Hydrogenated Castor Oil is a wax-like compound obtained by the controlled hydrogenation of refined Castor oil. It is a hard, brittle, high melting point (86 °C) product that is practically odourless and tasteless and it has a lot of applications especially in pharmaceutical and food industry.

Abimono 90N was used as an emulsifier. It is a distilled monoglyceride from fractionated Palm Oil with a melting point at 68 °C. Abimono 90N acts like a water in oil emulsifier.

The PGSS process is a high pressure spray process. The flow sheet of the PGSS process is shown in figure 1.

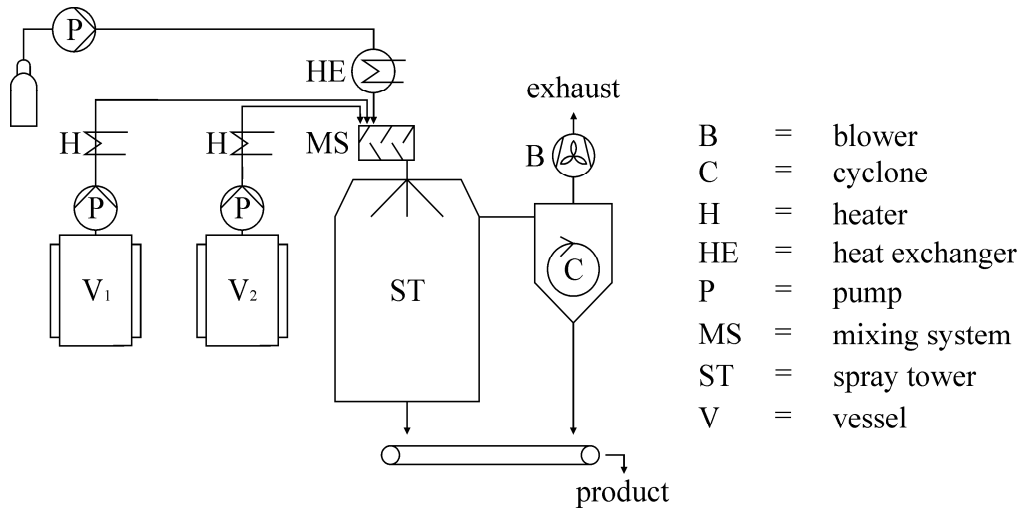


Figure 1. Flow sheet of PGSS process[8]

Using the PGSS process for the production of composites, a shell material is filled in and molten in vessel V_1. The shell material is premixed with the emulsifier (5 wt% of emulsifier in the shell material mass). The liquid is filled in vessel V_2. The materials are pressurized and dosed to a mixing system (MS) using two high pressure pumps (P). In the mixing system the two substances are mixed and homogenized. A supercritical fluid (CO_2) is added and partly dissolved in the formed emulsion. In the mixing system micro droplets of the core material are dispersed in the liquefied shell material. The dispersion is expanded to ambient pressure through a nozzle into a spray tower (ST). Fine droplets are formed by expansion. Simultaneously the drops are cooled by the expanding gas (Joule-Thomson effect). The shell material solidifies and forms a cover around the micro liquid drops, generating a powderous composite.

Maximum operating pressure and temperature of the used plant are 350 bar and 200 °C. Maximum mass flow is approximately 50 kg/h for shell material, 10 kg/h for core material and 150 kg/h for carbon dioxide.

Morphology and particle size of these powders can be adjusted by the operating process parameters (pre-expansion temperature and pressure, temperature in spray tower, mixing efficiency, gas to liquid ratio, nozzle geometry).

The particle size distribution of the produced powders was measured in dry state by laser diffraction, using a Malvern Mastersizer 2000. The bulk density was measured by weighing of a known powder volume. The particle morphology was observed using scanning electron microscopy (SEM). The mass fraction of water in the powder was calculated by the water mass flow divided by the sum of the water and the shell materials mass flow. The gas to product ratio (GPR) was calculated by the CO_2 mass flow divided by the sum of the water and the shell material mass flow.

RESULTS

PGSS experiments have been performed with different parameters. The pre-expansion temperature value was varied between 86 and 96 °C. The pre-expansion pressure was in the range of 59 to 152 bar. The gas to product ratio (GPR) reached values between 0.09 and 1.85. The temperature in the spray tower reached values between 25 and 34 °C. The mass fraction of the water in the final product was in the range of 17 to 52 wt%.

Particle size

Particle size (shown as mean diameter (d_{50}), which means 50 % of the particles are smaller than the indicated value) of different experiments shows a dependence on pre-expansion pressure and on gas to product ratio.

As can be seen on the left side of figure 2, an increase of pre-expansion pressure leads to a decrease of the mean particle size. Obviously at a pre-expansion pressure of 60 bar the mean particle size of the produced powders varied in a wider range than for higher spray pressures. Figure 2, right hand side, shows the dependency of the mean particle size of the gas to product ration for the same experiments. At spray pressures higher than 60 bar and with gas to product ratios over 0.4, the mean particle sizes are almost constant and smaller than 5 µm. The experiments with a spray pressure of 60 bar were carried out at gas to product ratios less than 0.5.

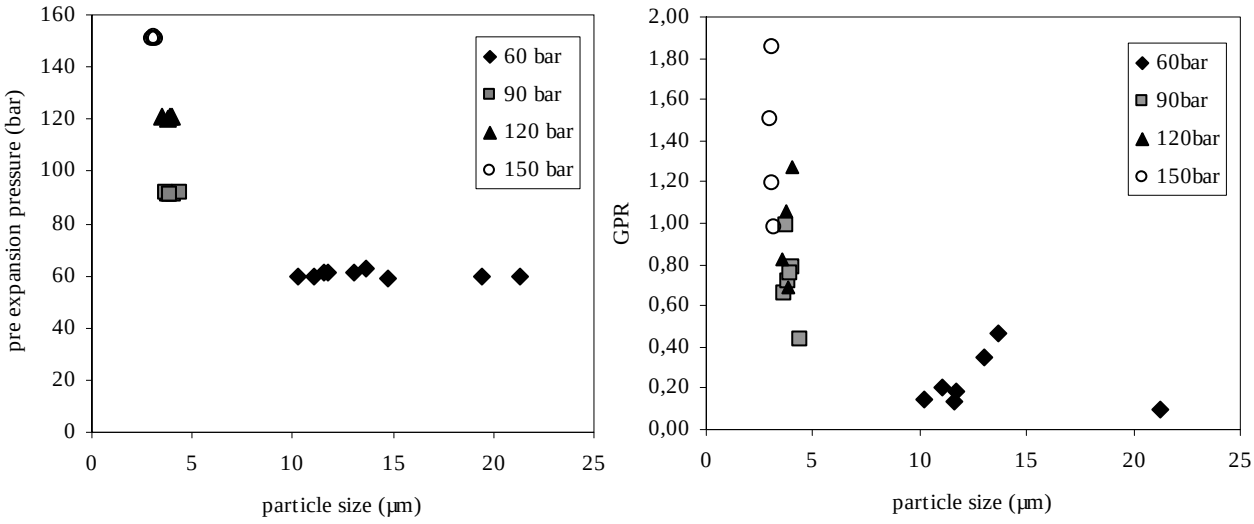


Figure 2. Influence of pre-expansion pressure (left side) and GPR (right side) on particle size

For the pre-expansion pressure of 60 bar an agglomeration of particles seems to occur. This can lead to an increase of particle size. An explanation can be the fact that at this pressure the Joule-Thomson effect is lower and the temperature in spray tower is higher.

Bulk density

Bulk density shows similar dependence like particle size on pre-expansion pressure and GPR. An increase of pre-expansion pressure leads to a decrease of bulk density (left side of figure 3.). A higher bulk density value will occur with a smaller gas to polymer ratio value (right side of figure 3.).

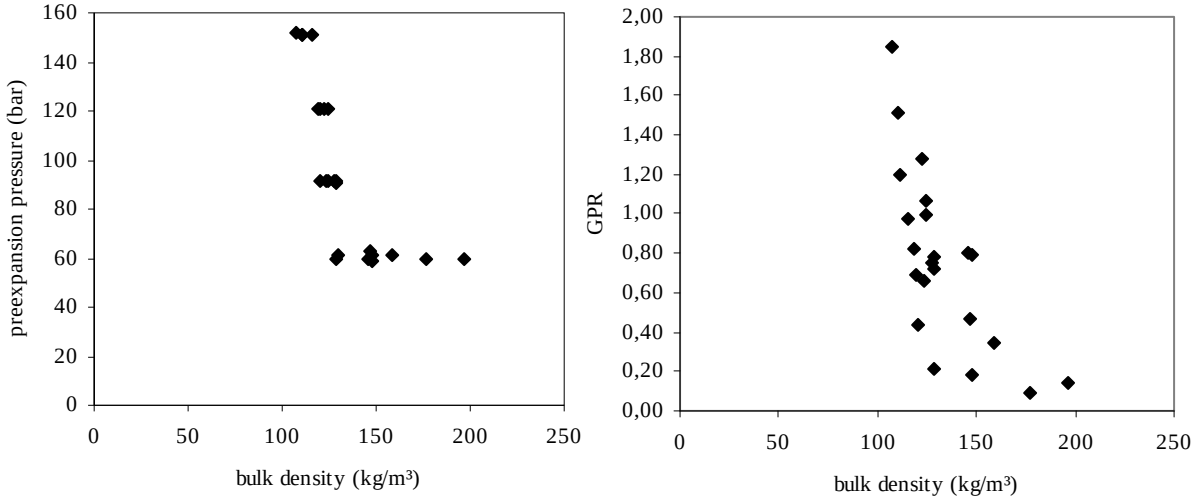
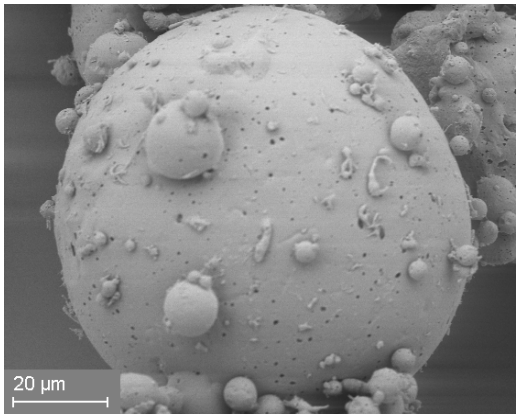


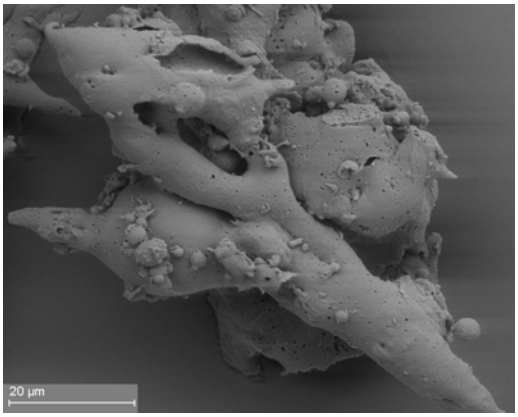
Figure 3. Influence of pre-expansion pressure (left side) and GPR (right side) on bulk density

Morphology

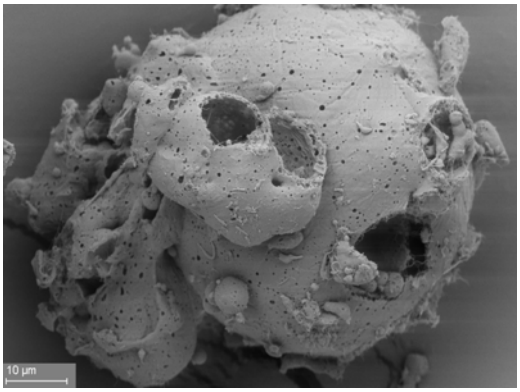
The SEM pictures in figure 4 give an exemplarily overview of the morphology of the obtained particles. In the legend to the pictures the water fraction in wt% of the produced powder and the spray pressure is given.



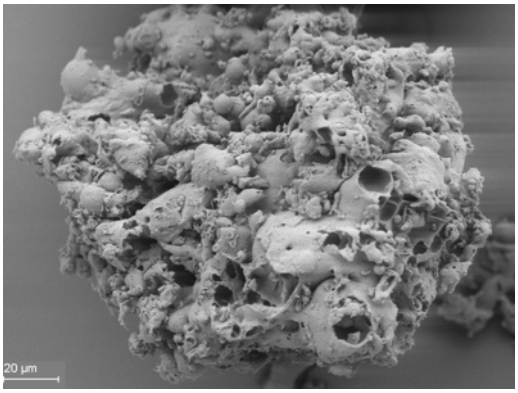
40 wt % water, pressure 60 bar



33 wt % water, pressure 90 bar



42 wt % water, pressure 120 bar



35 wt % water, pressure 150 bar

Figure 4. SEM pictures of fat-water composites

The shown particle morphologies vary between agglomerates, foam-like structures and spheres in outer shape. Open structures as well as closed structures can be found. In some pictures pinholes can be seen on the surface. One can guess that these pinholes are caused by CO_2 which leaves the droplets shortly after leaving the nozzle. This effect occurs due to the decrease of solubility of CO_2 in the melted fat with decreasing pressure [9]. In the same time the solidification occurs very fast due to Joule-Thompson effect. With the increase of pre-expansion pressure a stronger cooling effect will occur. This will lead to a more porous morphology and even to a foam.

CONCLUSIONS

The PGSS process can be applied with success to a combination of fat and emulsifier as shell materials and water as core material. The PGSS process can be used to produce open and closed particles.

High pressure encapsulation can be used to design particles with tailor made properties like size, size distribution, morphology and bulk density. The properties of the powders can be adjusted by changing the process parameters.

An increasing pre-expansion pressure will lead to a decreasing particle size and bulk density of the powder.

Dry and free flowing powders with a mass fraction of more than 50 wt% of water were achieved. The encapsulation of a water soluble active substance opens new possibilities for the controlled release and also for protection of active substances.

Acknowledgement

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