

POWDER COATING IN A HIGH PRESSURE FLUIDIZED BED PROCESS

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In this contribution a novel fluidized-bed coating process is introduced to microencapsulate heat sensitive materials with particle sizes below 100 μm . Supercritical carbon dioxide is used as solvent for the coating material as well as carrier fluid for the core material. The behaviour of the high pressure fluidized-bed was investigated for different process parameters and materials. It is shown that the fluidization starts at lower fluid velocities if the pressure is increased and it was possible to fluidized particles with a mean size below 10 μm . The coating of glass beads with stearyl alcohol was carried out and layers with a thickness of 1 to 8 μm were achieved.

1 INTRODUCTION

Solid particles are microencapsulated for use in various products, including pharmaceuticals, processed food and fertilizers, and energetic materials. To microencapsulate particles, a fluidized-bed coater equipped with a spray nozzle such as a Wurster Coater is commonly used [1]. Conventional coating processes involve layering a liquid coating material usually in the form of atomized droplets through the nozzle onto a fluidized bed of particles. After the atomized droplets of coating material come into contact with the core particles, the solvent must evaporate quickly. If excess droplets are present in the bed, agglomeration takes place, leading to particle growth and defluidization. Therefore, proper droplet atomization and drying are essential to avoid unplanned agglomeration of solid particles. In case of fine particles ($< 100 \mu\text{m}$), however, agglomeration becomes a serious problem because of their strong cohesive force. The feed liquid acts as a binder for the fine particles.

A novel fluidized-bed coating process using the Rapid Expansion of Supercritical Solutions (RESS) is described for the microencapsulation of fine particles [2, 3]. This process exploits the capability of supercritical fluids to act as a selective solvent. Supercritical fluids are noteworthy in that their density is like that of a fluid (thus they are effective solvents) while their viscosity and diffusion coefficient are like that of gases (thus they exhibit good mass transport behaviour). These properties make supercritical fluids effective as an extractant. Via the RESS process, particles and droplets in the submicron range can be produced by atomizing a supercritical solution through a nozzle. These fine droplets make it possible to improve the deposition onto the particles, so that a thinner and more even coating layer can be achieved [4, 5]. In addition, because the cohesion and adhesion forces are small compared to organic solvents, the capillary forces are considerably reduced, making it possible to encapsulate particles smaller than 100 μm without forming agglomerates. In this process, the supercritical fluid is used both as solvent for the coating material and as carrier fluid for the formation of the fluidized-bed.

2 APPARATUS AND MATERIALS

2.1 High Pressure Fluidized-Bed Device

The experiments were conducted in a laboratory scale device. A schematic view of a high pressure fluidized-bed coating apparatus is shown in Figure 1. The apparatus consists essentially of three subsections: the CO₂ supply, the extractor (in which the CO₂ becomes saturated with coating) and the high pressure reactor (where the coating takes place). The maximum allowable pressure in the device is 30 MPa at a maximum temperature of 373 K. The reactor has a volume of 500 cm³ and an internal diameter of 60 mm. The diameter can be reduced by different glass tubes. The fluidized-bed can be observed through two windows in the high pressure vessel.

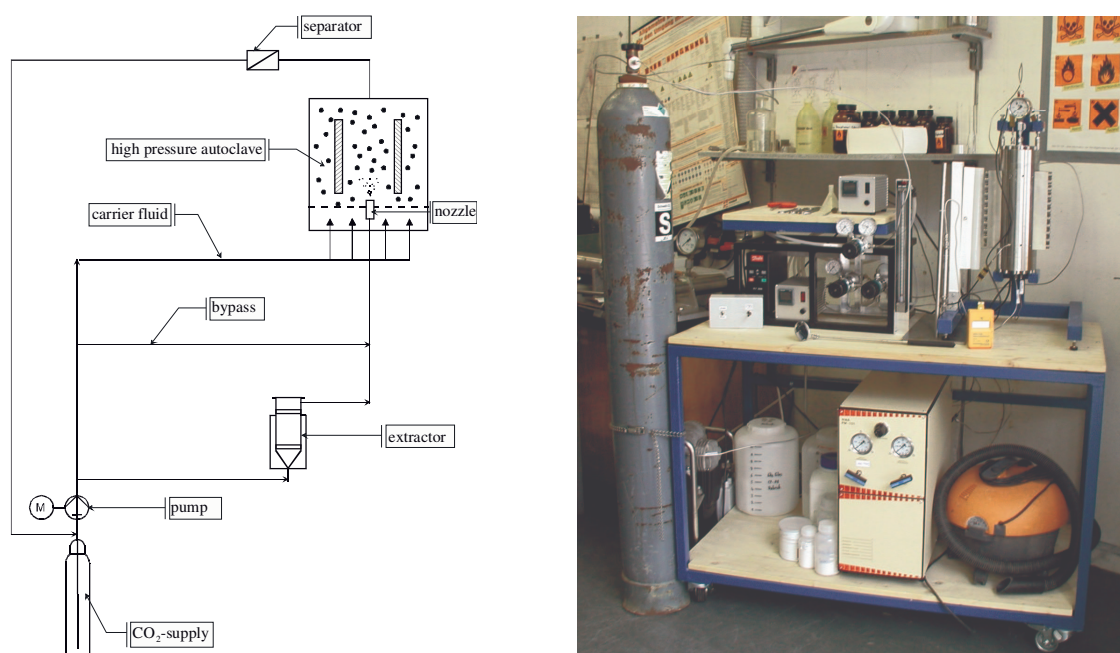


Figure 1: A schematic view and picture of the high pressure fluidized-bed apparatus

In each experiment, the fluidized-bed reactor was filled with the core material. The bed was fluidized by adding pure carbon dioxide via the line identified in Figure 1 as “carrier fluid”. The reactor floor consisted of a perforated plate. When the reactor reaches thermal stability, the microencapsulation process is initiated. CO₂ flows through the extractor, saturated by the coating material, and then expands through a nozzle into the fluidized-bed reactor. The expansion produces a fine aerosol of droplets that deposit onto the core particles, spread out as a film and then harden, yielding a solid layer of coating on the particles. Nozzles with different diameters (50, 100 and 150 μm) were used. At the end of each experiment the connection between the extractor and nozzle was flushed by opening the bypass, at which time the product was subjected to post-drying.

2.2 Materials

The first experiments were conducted using stearyl alcohol (C₁₈H₃₈O, obtained from Merck) as the coating material and different core materials (see Table 1). The melting point of the stearyl alcohol was 328 K. The different glass beads have a very high sphericity whereas the salt crystals are irregular shaped.

Table 1: Properties of the used core materials

Material	Density [kg/m ³]	Mean particle size [μm]
Glass beads 1	2485	7.39
Glass beads 2	2483	69.9
Glass beads 3	2487	124.6
Glass beads, hollow	1124	13.4
KNO ₃ crystals	2098	143.0

The phase equilibrium of the binary system stearyl alcohol/CO₂ was measured in a high pressure view cell (own design) according to the synthetic method by Teipel et al. [6] and presented in Figure 2. The curves represent the border between the homogeneous and two phase region; above the curve a homogeneous solution is present, below two phases exist. It is seen that 2.1 wt.-% stearyl alcohol are complete soluble in sc-CO₂ at 60 °C and 200 bar.

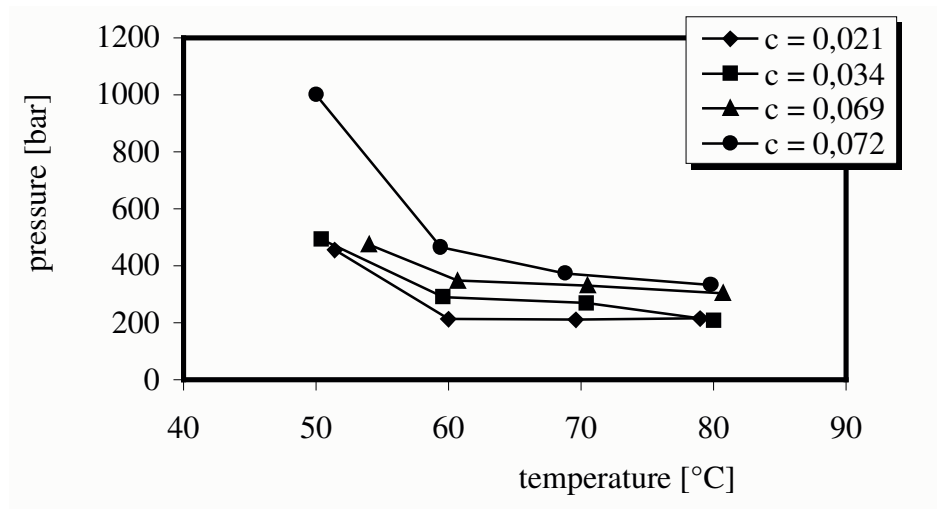


Figure 2: Phase equilibrium of the system stearyl alcohol/CO₂

3 EXPERIMENTAL RESULTS

3.1 Fluidization

Before starting with the microencapsulation the fluid dynamic of the high pressure fluidized-bed was investigated. Figure 3 shows the porosity ϵ (bed voidage; $\epsilon = V_l/V_g = 1 - V_p/V_g$) of the fluidized-bed (glass beads 3 are used) at different pressures (corresponding to different fluid densities). As expected the porosity increases if the fluid velocity is increased. At low velocities a sharp increase of the porosity is seen. This point represents the transition between the fixed-bed and fluidized-bed regime. The minimum velocity which is necessary to fluidize the particles decreases if the pressure is risen. At 20 bar and 80 bar this velocity is 0.08 m/s and 0.029 m/s, respectively.

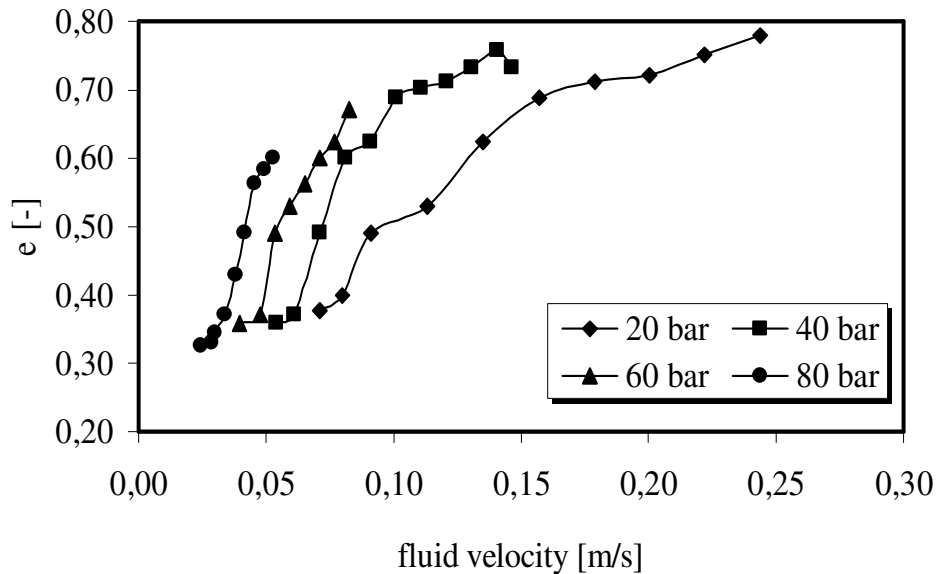


Figure 3: Bed voidage of glass beads (mean particle size: 124.6 μm) versus fluid velocity at different operating pressures ($\vartheta_{\text{R}}=55\text{ }^{\circ}\text{C}$)

The fluidization of smaller particles started at lower velocities and the influence of the pressure on the minimum velocity was reduced. Using the glass beads 1 this velocity was 0.0095 m/s at 20 bar and 0.0067 m/s at 60 bar. Table 2 summarizes the influence of pressure on the minimum fluidization velocity for the glass beads 1 and 2.

Table 2: Influence of pressure on fluidization velocity for different glass beads ($\vartheta_{\text{R}}=55\text{ }^{\circ}\text{C}$)

Pressure [MPa]	u_{mf} [cm/s]	
	Glass beads 1 ($d_{50,3}=7.4\text{ }\mu\text{m}$)	Glass beads 2 ($d_{50,3}=70\text{ }\mu\text{m}$)
0.1	1.1	3.0
2	0.86	2.7
4	0.9	2.5
6	0.74	1.8
8	0.3	0.82

3.2 Microencapsulation

In first coating experiments glass beads with a mean particle size of 70 μm were encapsulated with stearyl alcohol. The layer thickness was measured at different coating times. Figure 4 presents these results for different pressures before the nozzle. The condition inside of the fluidized-bed reactor were constant ($\vartheta_{\text{R}}=55\text{ }^{\circ}\text{C}$, $p_{\text{R}}=8\text{ MPa}$). As nozzle we used a 100 μm Laval nozzle which was heated up to 80 $^{\circ}\text{C}$. The extraction condition were equal to them at the nozzle (80 $^{\circ}\text{C}$; 16-19 MPa). The coating thickness varies from 1 to 8 μm , depending on the coating time, and that, at long times, the thickness approaches a constant value. It is seen that at higher pre-expansion pressure the layer thickness increases. One reason for that is the higher solubility of stearyl alcohol if extraction pressure increases so that more coating material reaches the reactor. This tendency is supported by an increase of the mass flow rate of carbon dioxide through the nozzle at elevated pressures. Furthermore, Kröber et al. showed

that the droplet size of the aerosol of stearyl alcohol behind the nozzle is independent of the pressure before the nozzle [7].

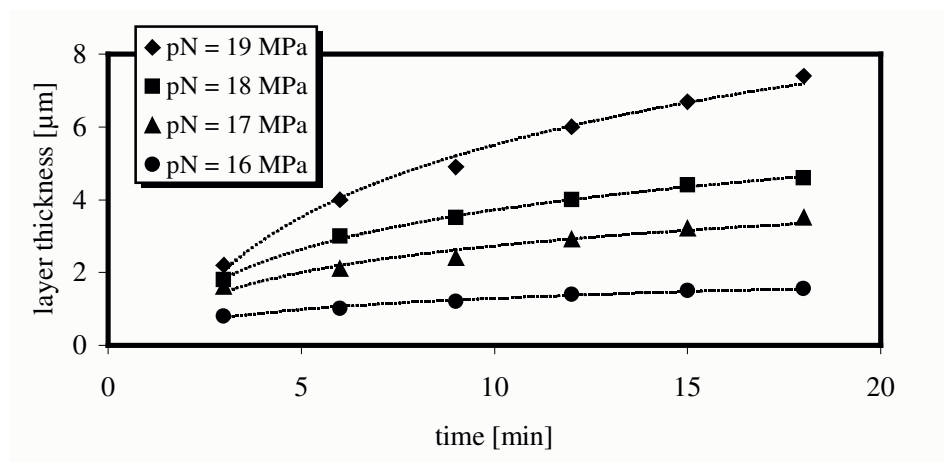


Figure 4: Thickness of the coating in dependency of coating time for different pre-expansion pressures ($d_{50}=70 \mu\text{m}$, $p_R=8 \text{ MPa}$, $\vartheta_R=55 \text{ }^\circ\text{C}$, $\vartheta_N=80 \text{ }^\circ\text{C}$, $d_N=100 \mu\text{m}$)

SEM pictures of the microencapsulated particles show that the coating layer is uniform and smooth. In Figure 5 a coated glass particle is presented and compared with untreated material.

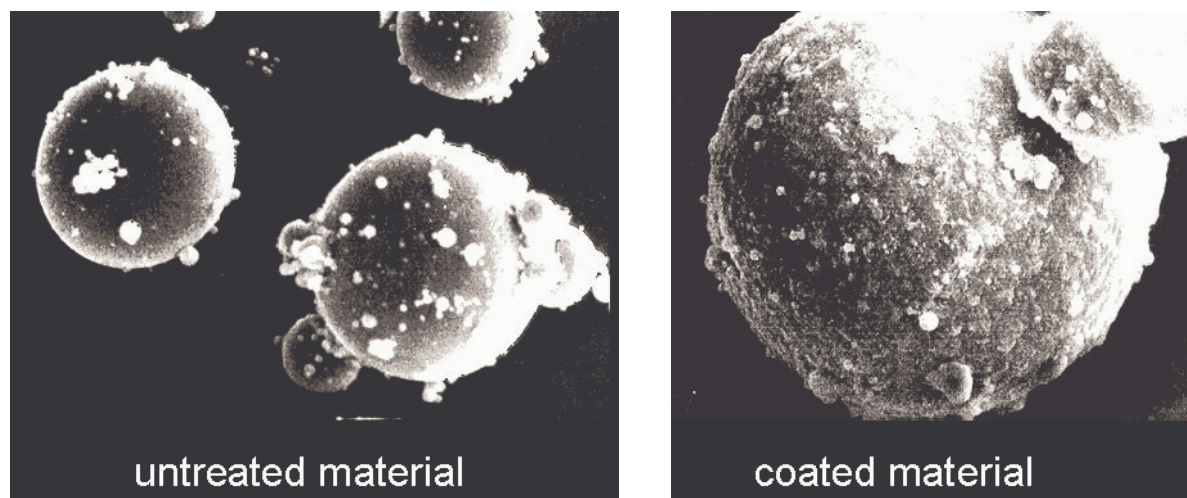


Figure 5: SEM pictures of untreated glass beads (left) and with stearyl alcohol coated particles (right)

4 CONCLUSIONS

A new fluidized-bed coating process was introduced to encapsulate fine and heat-sensitive particles. It was shown that the fluidization of particles under sub- or supercritical conditions is different from that under atmospheric pressure. With increasing pressure the minimum fluid velocity which is necessary to start the fluidization decreases. It was possible to fluidize glass beads with a mean particle size of $7.4 \mu\text{m}$. Stearyl alcohol was used for first coating

experiments with glass particles of a mean particle size of 70 μm . Complete coatings with a layer thickness between 1 and 8 μm can be achieved depending on the coating time and process conditions.

Further investigations of the particle coating in a high pressure fluidized-bed will be carried out. Especially, variations of the particle and coating material as well as coating conditions like pressure and temperature will be performed. The encapsulation of particles smaller than 10 μm with very thin layers without agglomeration is a challenge of this project. Therefore, the hydrodynamic of the high pressure fluidized-bed has to be characterized by experiments as well as calculations.

The costs of this process can be estimated with some assumptions. The costs of a coating of 50 μm core particles with a density of 2,500 kg/m^3 and a layer thickness of 2 μm are estimated to 170 € per kg core material. Herein, a solubility of 1 wt.-% of the coating in supercritical CO_2 and a fluid velocity of 3 cm/s are assumed. The efficiency of the decomposition is assumed to 70 % and the costs of a plant are 500,000 € and 150,000 €/a. From these data it becomes clear that this process is only economically if high expensive substances are used.

5 REFERENCES

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