

PARTICLES FROM GAS SATURATED SOLUTIONS (PGSS) – DRYING PROCESS: FUNDAMENTALS AND APPLICATION TO MICRONIZATION OF POLYETHYLENE GLYCOL

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Micronization of polyethylene glycol from aqueous solutions has been successfully performed with Particles from Gas Saturated Solutions (PGSS) - drying process, producing spherical PEG particles with average particle size of 10 μm and residual water content below 1 wt%. A detailed experimental analysis of the influence of different process and design parameters (temperature, pressure, flow rates, design of the static mixer used to put into contact aqueous solution and CO_2) has been carried out. Based on experimental results, an analysis of the fundamentals of the process has been developed, discussing mass and energy balances, phase equilibrium conditions, mass transfer rates and atomization mechanisms.

INTRODUCTION

The Particles From Gas Saturated Solutions (PGSS) process [1] is a particle formation method based on the use of supercritical carbon dioxide. This process consists in saturating a solution containing the solute of interest with supercritical carbon dioxide. The saturation is accomplished mixing the solution and the carbon dioxide at high pressure or supercritical conditions by means of a static mixer or other contacting device. Afterwards, the gas-saturated solution is expanded down to atmospheric pressure through a nozzle. During the expansion, the gas dissolved into the solution is suddenly vaporized, enhancing solution atomization. Moreover, the intense cooling due to Joule-Thomson effect during CO_2 expansion promotes particle formation. Both effects make possible to obtain particles with average sizes in the micrometer range and controlled particle size distributions. Many substances have been successfully micronized by PGSS, and this technology has entered industrial application [2].

The PGSS process can also be used to produce particles from aqueous solutions. An advantage of PGSS-drying of aqueous solutions over other drying process such as spray-drying is that it allows drying the solutions with a reduced thermal degradation or contamination of the product. This advantage was demonstrated in a previous work, in which a dry powder rich in polyphenols (natural antioxidants) was produced by PGSS-drying of green tea infusions [3].

PGSS-drying is a complex process in which interactions between different phenomena are influencing the properties of the final product. A detailed fundamental analysis of these phenomena is required for a rational design of PGSS-drying processes in order to achieve industrial application. The aim of this work is to contribute to the understanding of the fundamentals of PGSS - drying by a combined experimental and theoretical analysis of the PGSS – drying of aqueous polyethylene glycol (PEG) solutions.

MATERIALS AND METHODS

PEG with an average mol weight of 6000 g/mol was obtained from Clariant (Burghausen, Germany) and used without further purification. Distilled water was used to prepare solutions. Carbon dioxide was supplied by Yara (Germany). Gases were of technical quality and were used as obtained.

A schematic diagram of the pilot plant used for PGSS-drying experiments is presented in Figure 1. The aqueous solution and supercritical carbon dioxide are pressurized and preheated to pre-expansion conditions. Then they are intensively mixed using a static mixer (Sulzer SMX DN6, diameter 6 mm). This static mixer is constructed by adding mixing elements with a length of 6 mm. In experiments, static mixer configurations consisting in 0 to 10 elements were used, resulting in static mixer lengths of up to 6 cm. The resulting mixture is sprayed through a nozzle (Schlik type V121, inner diameter 1 mm – 1.4 mm, spray angle 90°) into a thermally insulated spray tower (height 1 m, diameter 0.6 m). Particles are collected at the bottom of the spray tower, and CO₂ together with evaporated water leave the tower through its upper part. A cyclone separator is used to recover fine powder entrapped in gas effluent.

Product was characterized by determining its particle size (Malvern Instruments Mastersizer 2000 laser diffraction system), particle morphology (LEO Gemini 1530 Scanning Electron Microscope) and residual humidity (determined gravimetrically according to the procedure described in DIN EN 827).



Figure 1: Schematic diagram and picture of the PGSS- drying pilot plant

EXPERIMENTAL RESULTS

93 PGSS-drying experiments were performed varying the main operating conditions, including: pre-expansion temperature and pressure corresponding to the conditions in the static mixer (T_0 , P_0), solution and CO₂ flow rates (m_{Sol} , m_{CO_2}) and consequently gas/liquid flow rate (GLR), number of elements in the Sulzer SMX static mixer (ME) and nozzle diameter (d_{Nozzle}). Product properties analyzed included particle size and particle size distribution, residual humidity in the powder, particle morphology, and measured spray tower temperature T_e resulting from the expansion through the nozzle. In all experiments performed, the concentration of PEG in the initial aqueous solution was 50 wt%. With several combinations of process parameters, it was possible to successfully micronize PEG producing

particles with a mean particle size $d_{50} = 10 - 20 \mu\text{m}$ and a residual moisture content below 1 wt%, as shown in Figure 2.

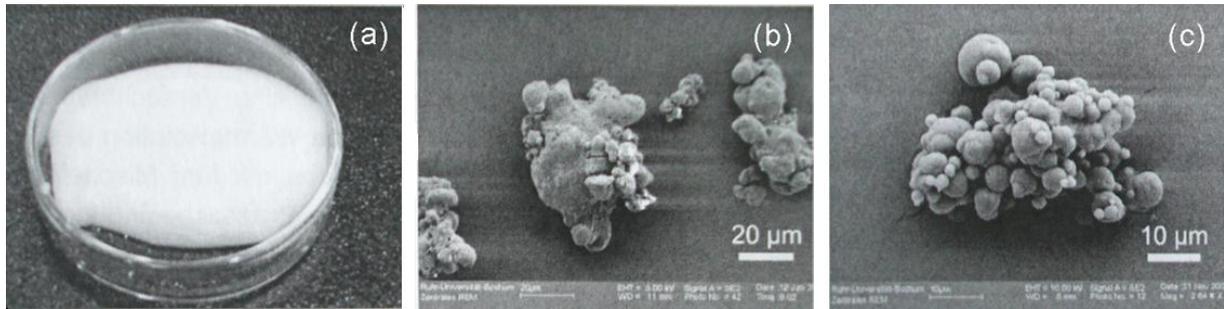


Figure 2: Product obtained by PGSS-drying of aqueous PEG solutions. (a) moisture content: 29.65 wt%, (b) moisture content: 3.01 wt%, (c) moisture content: 0.38 wt%

Both particle size and residual humidity in the final product decreased when the gas/liquid flow ratio GLR was increased, as shown in Figure 3. Particle size and residual humidity decreased when the pre-expansion temperature T_0 was increased. Smaller particles were obtained when the pre-expansion pressure P_0 was increased, but the residual water content was higher when the pre-expansion pressure was increased. Residual humidity in the final product showed no variation or decreased slightly when the number of elements in the static mixer ME and therefore the length of the static mixer were increased. Particle size decreased when the number of mixing elements was increased from 0 to 5, but small or no variations of particle size were observed when the number of mixing elements ME was further increased from 5 to 10, as shown in Figure 4.

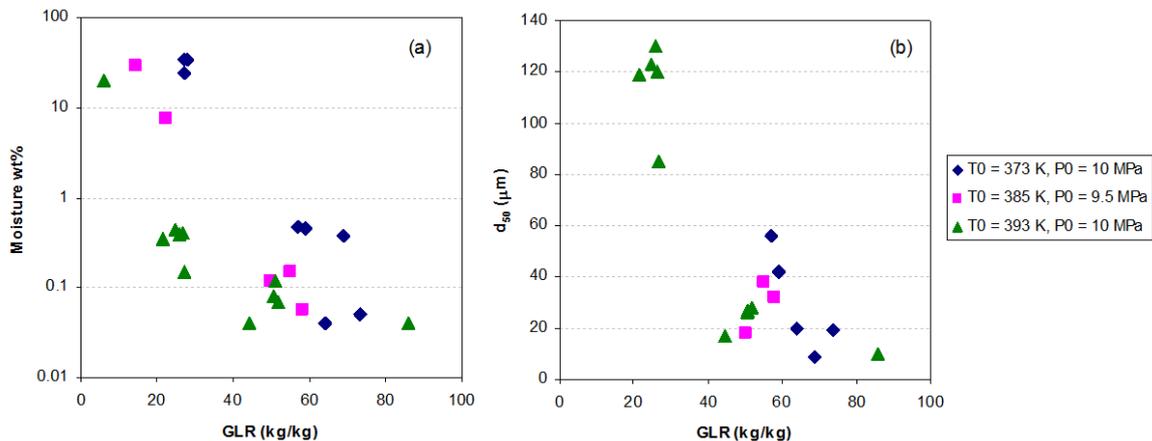


Figure 3: Variation of (a) residual moisture content and (b) mean particle size with GLR with different pre-expansion pressures and temperatures. A logarithmic scale is used in the ordinate axis of diagram (a). In all experiments represented in this figure, a static mixer configuration with 5 elements was used

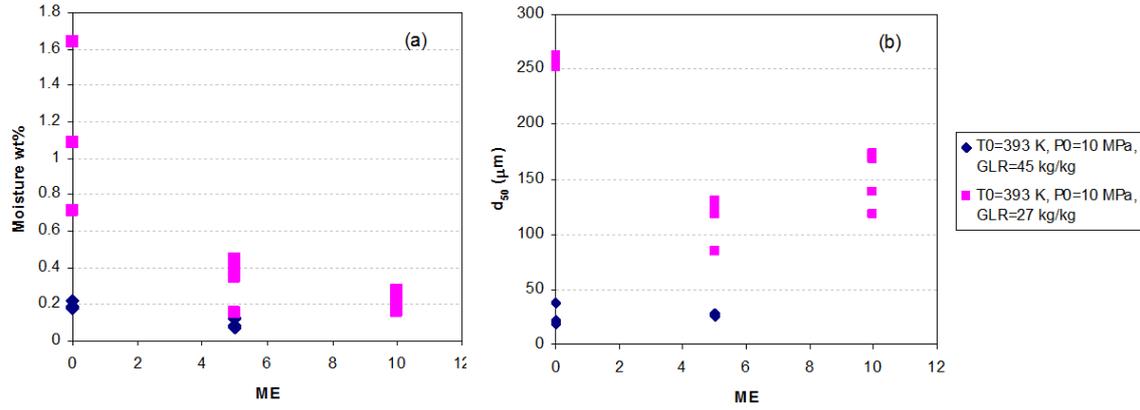


Figure 4: Variation of (a) residual moisture content and (b) mean particle size with the number of elements in the static mixer ME.

DISCUSSION

Moisture concentration in powder

The gas/liquid ratio GLR required for reducing water concentration in the powder down to a specified volume can be obtained by performing a mass balance. Global mass balances to CO_2 , water and PEG result in Eqs. (1-3):

$$m_{CO_2} = m_G \cdot w_G \quad (1)$$

$$m_{sol} \cdot w_{sol} = m_G \cdot w_G + m_P \cdot w_P \quad (2)$$

$$m_{sol} \cdot w_{sol} = m_P \cdot w_P \quad (3)$$

Where m represents mass flowrate, w water mass fraction, CO_2 the initial gas stream, sol the initial solution, G the gaseous effluent of the spray tower, and P the particles produced.

In addition to mass balances, the following equilibrium relationships hold: if GLR is high enough for completely removing liquid water, concentration of water adsorbed in particles and water concentration in the gas phase are related by the adsorption equilibrium condition. If GLR is too low for completely removing liquid water, water concentration in the gas phase is equal to the saturation concentration. Resolution of Eqs. (1) – (2) together with the appropriate equilibrium condition allows calculating m_G , w_G , m_P and w_P , and therefore the expected residual moisture concentration in particles.

Figure 5 shows the minimum GLR required for achieving a certain moisture concentration in particles calculated with the global mass balance as a function of spray tower temperature, T_e . Experimental conditions are also represented in this figure showing if dry powder, agglomerated particles or wet product was obtained. It can be seen that with few exceptions, in all experiments in which powder was produced, GLR was above the minimum value calculated with the mass balance. Also in all experiments in which a wet product was obtained, GLR was below the minimum value. On the other hand, it can be seen that agglomerated particles were obtained both experiments performed with GLR close to the

minimum value, and in experiments with relatively high spray tower temperature ($T_e > 310$ K), which indicates that proximity to melting conditions is another parameter together with residual moisture content which promotes agglomeration.

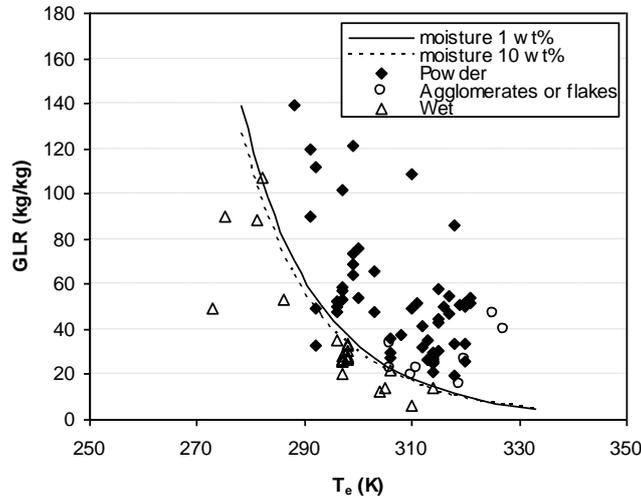


Figure 5: Mass balance calculations of required GLR for achieving a certain moisture content in particles, together with experimental conditions classified according to the type of product obtained

Mass balance calculations can also be used to obtain quantitative predictions of expected moisture concentration. Figure 6 shows a comparison of experimental and calculated moisture concentrations in all experiments performed. It can be seen that in most experiments in which moisture concentration is high, experimental concentration is higher than the concentration calculated with the mass balance, as it may be expected considering that mass balance results represent the optimum situation corresponding to equilibrium, and that in reality a lower efficiency of drying, and therefore a higher moisture concentration, is expected. On the contrary, in most experiments in which moisture concentration was low (< 1 wt%), experimentally observed concentration is lower than expected from mass balance calculations.

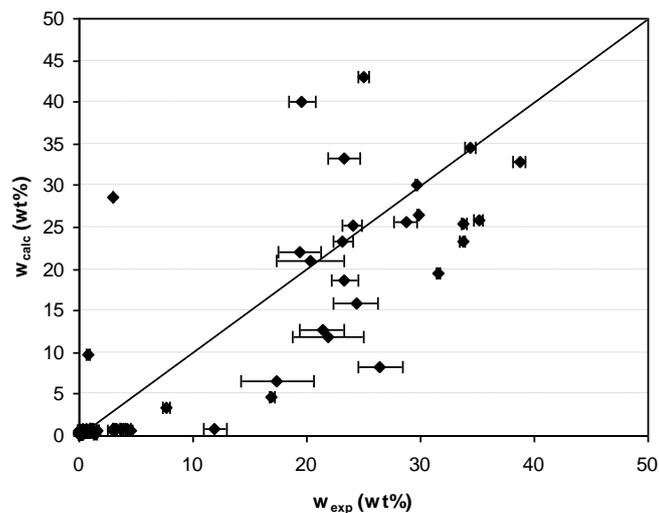


Figure 6: Comparison between measured and calculated moisture concentration

Phase equilibrium and mass transfer in the static mixer

The phase equilibrium model based on the PC-SAFT equation of state developed in a previous work [4] can be used to calculate the limits to mass transfer between aqueous solution and supercritical fluid in the static mixer imposed by phase equilibrium conditions. Results are presented in Figures 7 and 8 as a function of pre-expansion temperature T_0 and gas/liquid ratio GLR . Figure 7 shows the equilibrium concentration of CO_2 in the liquid phase, and Figure 8 shows the fraction of water which can be extracted by CO_2 in the static mixer β , defined in Eq. (4).

$$\beta = \frac{(n_{sol} \cdot w_{sol} - m_m \cdot w_m)}{m_{sol} \cdot w_{sol}} \cdot 100 \quad (4)$$

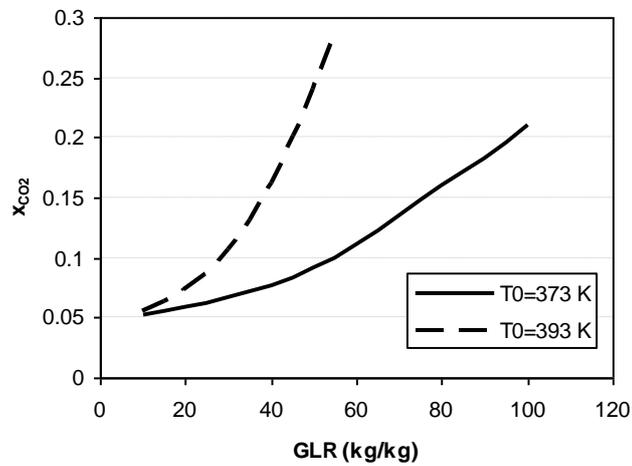


Figure 7: equilibrium concentration of CO_2 in the liquid phase in static mixer effluent calculated with PC-SAFT EoS as a function of pre-expansion temperature T_0 and gas/liquid ratio GLR

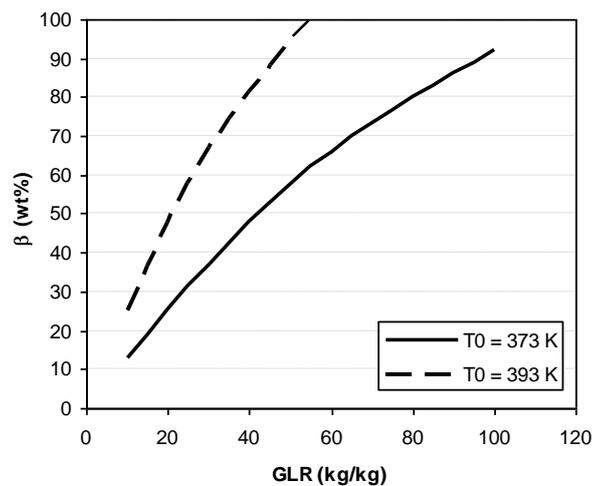


Figure 8: Fraction of water extracted to the gas phase in the static mixer in equilibrium conditions calculated with PC-SAFT EoS as a function of pre-expansion temperature T_0 and gas/liquid ratio GLR

Results presented in Figure 8 demonstrate that a characteristic feature of the PGSS-drying process is that in general a significant fraction of water is extracted in the static mixer. With this, it is possible to reduce the evaporation duty of the spray tower, therefore making possible either to reduce the required size of the spray tower, or to increase the capacity of an existing tower by increasing the amount of water extracted in the static mixer. Additionally, and as in any PGSS application, the saturation of the liquid phase with CO₂ is the primary function of the static mixer, and results presented in Figure 7 demonstrate that although the solubility of CO₂ in pure water is low ($x_{\text{CO}_2} = 0.01258$ at $T = 369.7$ K and $P = 8.34$ MPa [5]), high CO₂ solubilities can be obtained if the aqueous solution contains a compound that promotes CO₂ solubility, such as PEG.

Saturation in the static mixer is further limited by the kinetics of the mass transfer process. Mass transfer of water and carbon dioxide between gas and liquid phases in the static mixer can be calculated by means of differential mass balances using global mass transfer coefficients. Eq. (5) shows a mass balance in the liquid phase. The global mass transfer coefficient in the liquid phase, $K_L a$, depends on individual film coefficients in the gas and liquid phases k_{GA} and k_{LA} and on the slope of the equilibrium relationship K^* , as shown in Eq. (6). An equivalent set of equations can be written for the gas phase.

$$\frac{dm_i}{dz} = K_L \cdot a \cdot \rho_L \cdot A \cdot (x_i^* - x_i) \quad (5)$$

$$\frac{1}{K_L \cdot a} = \frac{1}{k_L \cdot a} + \frac{K^*}{k_G \cdot a} \quad (6)$$

Mass transfer coefficients can be calculated with the correlations presented by Streiff et al. [6] for Sulzer SMX static mixers, following the approach described by Ruivo et al. [7] for calculating mass transfer in static mixers operating with a droplet dripping flow mechanism under supercritical conditions.

Figure 9 show the results obtained with the model as a function of gas/liquid ratio GLR and pre-expansion pressure and temperature P_0 , T_0 . Part (a) of this figure presents calculated CO₂ molar fraction in the liquid phase, and part (b) calculated water molar fraction in the gas phase. Calculations have been performed considering a static mixer consisting of 10 mixing elements (and therefore a length of 6 cm) and a fixed liquid flow rate of 1.5 kg/h, typical of experiments. By comparing results obtained with the mass transfer model with the phase equilibrium conditions, it can be calculated that according to the mass transfer model CO₂ concentration in the liquid phase ranges from 60% to 75% of saturation concentration, and H₂O concentration in the gas phase ranges from 30% to 50% of equilibrium concentration, depending on process conditions.

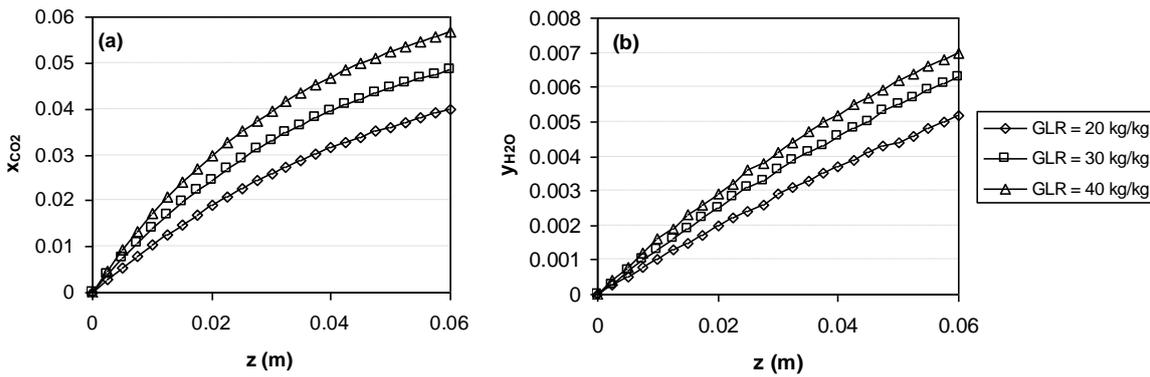


Figure 9: Results of the mass transfer model of the static mixer at $T_0 = 373$ K and $P_0 = 10$ MPa: (a) CO_2 molar fraction in the liquid phase, (b) H_2O molar fraction in the gas phase

Atomization mechanism

The effluent of the static mixer entering into the expansion nozzle is a biphasic mixture consisting of a liquid phase close to saturation with CO_2 , and a gas phase partially saturated with water. When this mixture is depressurized down to ambient conditions, gas phase undergoes a considerable volume expansion (from about 200 kg/m^3 to 1.4 kg/m^3), and CO_2 dissolved into the liquid phase is suddenly vaporized as well. During this process, water is evaporated. Both processes promote droplet atomization and particle formation.

Considering phenomena occurring in the expansion nozzle, certain parallelisms can be established with the flash-boiling atomization mechanism [8]. Flash-boiling atomization consists in expanding a superheated liquid through a nozzle, so partial evaporation of the liquid occurs and the expansion of gas bubbles promotes liquid atomization. Alternatively, gas nucleation can be induced by releasing a gas previously dissolved into the liquid.

This atomization mechanism is intensified by the peculiar physical and phase equilibrium properties of systems with supercritical carbon dioxide. The drastic variations in the density of CO_2 near the critical point enable a higher volume expansion than possible when subcritical gases are employed: when CO_2 is expanded from 10 MPa to 0.1 MPa at 313 K, the volume it occupies is increased by a factor of approximately 370. When nitrogen or air, the two most frequently used gases in flash-boiling atomization, are expanded in the same conditions, gas volume is increased only by a factor of approximately 100. At the same time, the amount of CO_2 that can be dissolved in an aqueous solution containing a polymer such as PEG is very high. CO_2 concentration in the liquid phase is higher than CO_2 solubility in pure water at the same pressure and temperature by a factor of 2 to 4, depending on process conditions, and the difference is even higher if a gas with a lower solubility in water than CO_2 such as N_2 or air is used. The increased efficiency of both atomization mechanism enabled by the use of supercritical carbon dioxide justifies the good experimental results obtained in terms of particle size.

It can be noted that the identification of flash evaporation of dissolved CO_2 as a major parameter influencing atomization allow explaining all trends of variation of particle size with process conditions observed in experiments:

1. When GLR is increased, the concentration of CO₂ dissolved into the liquid phase increases because the liquid is enriched in PEG by water extraction. Due to this, atomization is more efficient and particle size decreases.
2. When temperature is increased or pressure is increased, the solubility of CO₂ in the liquid phase increases as well, leading to more efficient atomization and smaller particle size.
3. When the number of elements in the static mixer is increased, the concentration of CO₂ in the liquid phase increases and therefore a smaller particle size is obtained. However, when saturation concentration in the liquid phase is approached, a further increase in the number of mixing elements does not cause significant variations in fluid composition and therefore in atomization and particle formation.

CONCLUSIONS

Polyethylene glycol has been successfully micronized by PGSS-drying. Moisture concentration in the powder could be reduced below 1 wt%, and spherical particles with average particle sizes of 10 – 20 μm and regular particle size distribution were consistently obtained. An experimental study of the influence of main process parameters has been performed. It has been observed that smaller particle size is obtained when pre-expansion pressure, pre-expansion temperature, gas/liquid flow ratio or the number of elements in the static mixer is increased. A lower moisture concentration is achieved when pre-expansion temperature, gas/liquid flow ratio or the number of elements in the static mixer is increased, and when pre-expansion pressure is decreased.

It has been shown that a global mass balance can be used to calculate the minimum gas/liquid flow ratio required for producing dry powder. In experiments in which final moisture concentration was lower than 1 wt%, measured moisture concentrations were smaller than expected from mass balance calculations.

With a mass transfer model of the static mixer, it has been shown that CO₂ concentration in the liquid phase leaving the static mixer ranges from 60% to 75% of saturation concentration, and water concentration in the gas phase ranges from 30% to 50% of equilibrium concentration.

It has been proposed that atomization of the biphasic mixture leaving the static mixture occurs by a flash-boiling atomization and effervescent atomization. This processes is enhanced by the physical properties of CO₂, particularly the high volumetric expansions achieved when CO₂ is depressurized from supercritical to ambient conditions and the high solubility of CO₂ in the liquid phase. By application of this mechanism, all trends of variation of particle size with process conditions observed in experiments can be explained in function of CO₂ concentration in the liquid phase: any modification in process parameters which causes an increase of CO₂ concentration in the liquid phase, promotes a more efficient atomization and therefore a reduction of particle size.

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