

MODELING OF MASS TRANSFER AND FLUID MECHANICS DURING THE DRYING OF PARTICLES PRODUCED BY SAS PROCESS

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ABSTRACT

This work presents a model of the drying stage in a crystallizer for the process SAS (Supercritical Anti Solvent) by means of the Computational Fluid Dynamics (CFD) program FLUENT 6. This stage is fundamental for obtaining products with adequate characteristics, and particularly its main aim is the elimination of organic solvent present in the crystals by means of a flow of supercritical CO₂, in order to avoid re-dissolution and agglomeration of particles due to solvent condensation in the depressurization, and also to reduce the concentration of the solvent in the particles below the acceptable limits when the product is intended for human consumption. A special emphasis is done in the identification of possible flow dead areas, the analysis mass transfer between solid crystals particles and fluid phase to determine the flow of CO₂ and the conditions in which it should be introduced. In addition an analysis of the parameters with stronger influence on the performance of the drying is presented.

INTRODUCTION

Several micronization technologies take advantage of the physical properties of supercritical fluids, among them, the gas or supercritical antisolvent (GAS or SAS) process and its variants, has received a considerable interest due to the wide range of materials that can be micronized with this technique [1-2], including explosives [3], polymers [4], superconductor precursors [5], pigments [6], pharmaceuticals [7-8], and natural compounds [9]. First, precipitation processes using a supercritical antisolvent allow solid particles to be obtained from a raw product with controlled size and morphology. Second, when carbon dioxide is used as the supercritical fluid, the process temperature is low ($T_C = 304.21$ K). Third, small quantities of organic solvent are required, and their removal from the final powder is complete. Finally, supercritical techniques do not require the final filtration step involved in the conventional method. In most cases, this recovery of the solid from the liquid solution constitutes a limitation of the process. These kinds of processes using supercritical fluids have mainly been developed for the pharmaceutical, nutraceutical, and cosmetic industries. The last step of a SAS precipitation experiment is the washing of particles with pure CO₂ for drying them and removing residual contents of the organic solvent. This step is important for a number of reasons, mainly: *to avoid redissolution and agglomeration of particles due to the presence of organic solvent and to eliminate small quantities of organic solvent that may be toxic from products which are going to be destined to human consumption.*

This work presents a simulation of the fluid mechanics and the mass transfer in the precipitator during the drying stage of a SAS experiment, performed with the commercial CFD package Fluent 6.

EXPERIMENTAL APPARATUS AND PROCEDURES

A schematic diagram of the pilot plant used for the supercritical anti-solvent precipitation is shown in Figure 2. The equipment used are two diaphragm pumps (Dosapro, Spain), one for the CO₂ (L-210) and the other for the solution (L-230); an isolated and jacketed AISI 316 stainless steel precipitator (H-110) with 2 L volume and with a porous metallic frit at the exit; an external stainless steel filter (H-310) from headline filters (UK), which has a screen size of 1 m; two back pressure regulator valves (K300 A/B) placed in parallel for safety reasons; and a separation flask (H-320) to achieve the separation of solvent and CO₂ after pressure release. Other elements are the heat exchangers required to cool CO₂ before pumping it (E-220) and for achieving the operating conditions (E-120), safety devices (safety valve and rupture disc), and instrumentation. A Pt-100 thermoresistance with an accuracy of $\pm 0.1\text{K}$ is placed inside the precipitation vessel. The inlet temperatures of SC-CO₂ and solution are also measured. For the pressure a DESIN TPR-10 digital pressure meter (DESIN Instruments, Spain), with an accuracy of $\pm 0.05\text{MPa}$, is used. The CO₂ mass flow is controlled with a coriolis flow meter (Sensor MICRO Motion Elite CMF010 NB, Transmitter MICROMotion Elite RFT91), with an accuracy $\pm 0.01\text{ kg/h}$.

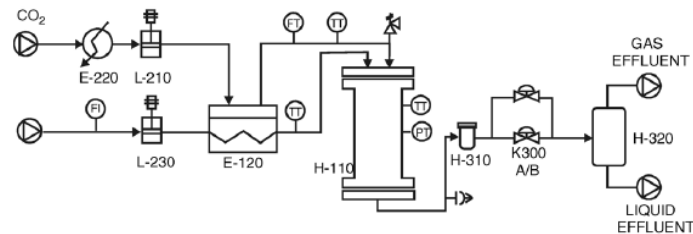


Figure 1. Schematic diagram of the pilot plant

A standard experiment is as follows: the experiment starts by pumping pure CO₂ into the crystallizer. When the desired operating conditions (temperature, pressure and flow rate) are achieved and remain stable, the solution is fed to the precipitator during a fixed time until a fixed solvent concentration is achieved. When the desired amount of solution has been injected (aprox. 400 mL), the liquid pump is stopped and only pure CO₂ is pumped. The flow of CO₂ is maintained during a period long enough for the complete removal of solvent from the precipitator and to dry the particles obtained. The minimum amount of CO₂ required for this step was determined experimentally, and an amount of 1 kg (roughly equivalent to 1.5 times the volume of the precipitator) is normally used in the experiments.

MODEL DESCRIPTION

FLUENT 6 is a computational fluid dynamics (CFD) software package to simulate fluid flow problems. It uses the finite-volume method to solve the governing equations for a fluid. It provides the capability to use different physical models such as incompressible or compressible, inviscid or viscous, laminar or turbulent, etc. Geometry and grid generation is done using GAMBIT which is the preprocessor bundled with FLUENT. The model presented in this work has been developed using this commercial CFD simulator.

The model includes the mass, energy and momentum transport equations. For the description of the mass transfer we're going to adopt species transport model which includes inlet diffusion and diffusion energy source. The standard k- ϵ model with standard wall functions has been used to model turbulence. We have solved our model both for steady-state and non-stationary state due to the fact that the system which is being modeled is time dependent.

The physical properties required by the model are the volumetric, thermal and transport properties of the mixture of the two species that constitute the system: carbon dioxide and ethanol.

- Density of the mixture is calculated with the Peng-Robinson Equation of State with Huron-Vial mixing rule, implemented into a User Defined Function (UDF) of Fluent.
- Viscosity of a mixture can be estimated from the viscosity of the pure components at the same temperature and pressure applying the Arrhenius equation:

$$\eta_{\text{mix}} = \eta_1^{x_1} \eta_2^{x_2} \quad (1)$$

Where η is the viscosity and x is the mole fraction.

- Diffusivity of CO₂ in EtOH, D_{12} is calculated by Catchpole and King [10].
- Thermal conductivity of solution EtOH–CO₂ is approximated by the thermal conductivity of CO₂ due to the fact we are working with high concentration of CO₂ ($c_{\text{CO}_2} > 0.95$).

RESULTS AND DISCUSSION

The SAS crystallization from its dilute EtOH–CO₂ solution has been considered in the present work to identify the possible flow dead areas and to determine the flow of CO₂ and the conditions in which it should be introduced. In addition an analysis of the parameters with stronger influence on the performance of the drying is presented. The simulation has been performed at fixed pressure and temperature (100 bar and 313 K) and SC CO₂ flow rates of 5–20 kg/h for several designs.

- Design Type 1:* Figure 1 show several Type 1 models which present cylindrical nozzles.

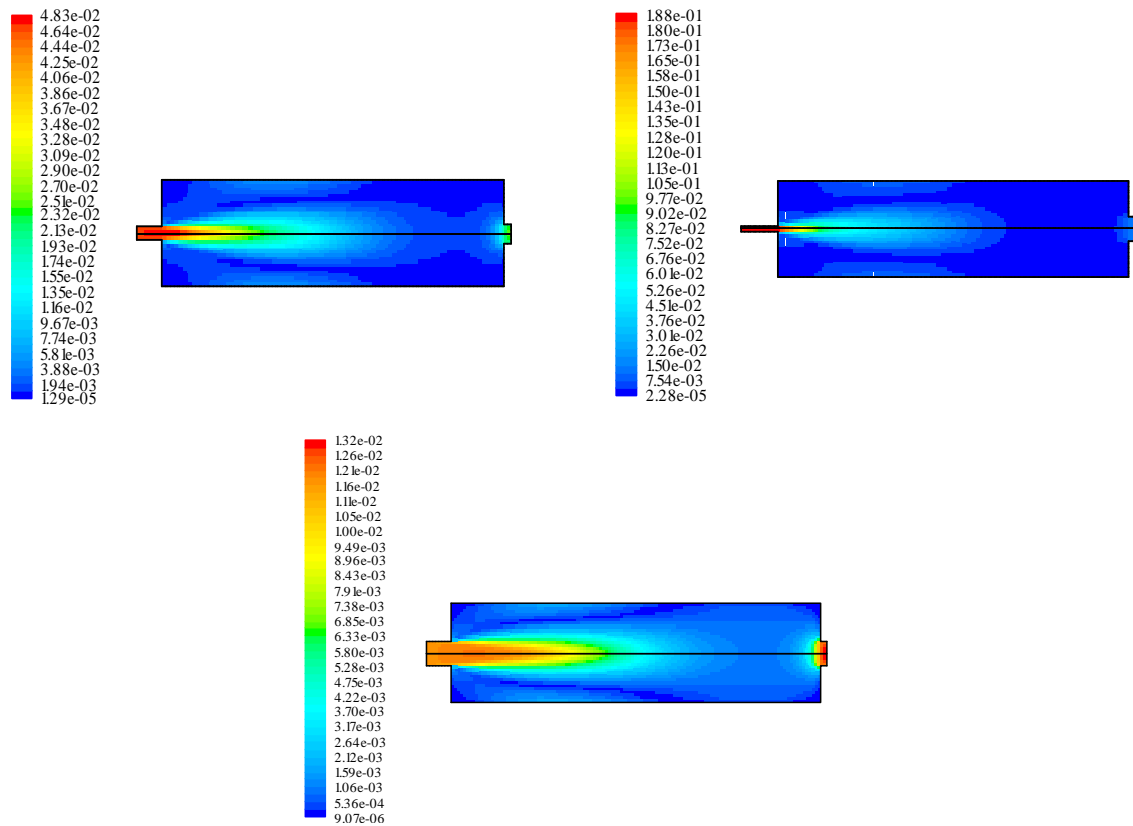


Figure 1. Contours of velocity magnitude for different d_{NOZZLE} (3,5,12 mm)

For the same flow rate, different *diameter nozzle* has been tried to see the influence of this parameter in velocity field which has a great influence in mass transfer. The calculated operation times required for a 99 % elimination of organic solvent are presented in Table 1. This table also shows the estimated times required for an equivalent removal assuming that the precipitator behaves as a perfectly-mixed tank and a plug flow reactor compared with simulated times obtained with Fluent. Also, the results have been evaluated in terms of average percent recovery solvent (EtOH) vs. the time required for the complete recovery of it as presented in Figure 2.

G (kg/h)	τ_{FP} (min)	τ_{CSTR} (min)	τ_{CFD} (min)
5	3.6	66.7	125
10	1.8	33.4	75
20	0.9	15.4	50

Table 1. Comparison of residence time between ideal and simulated flow model

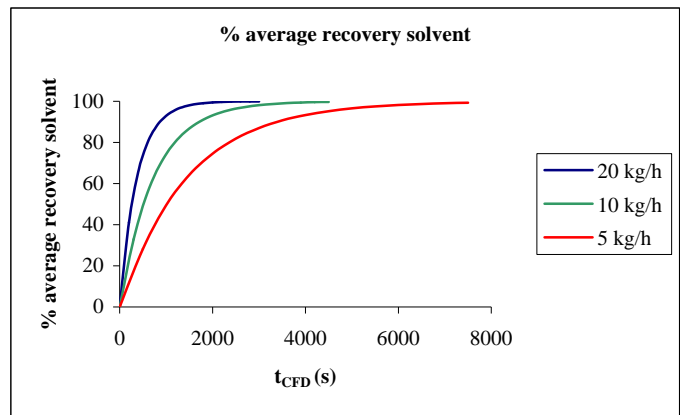
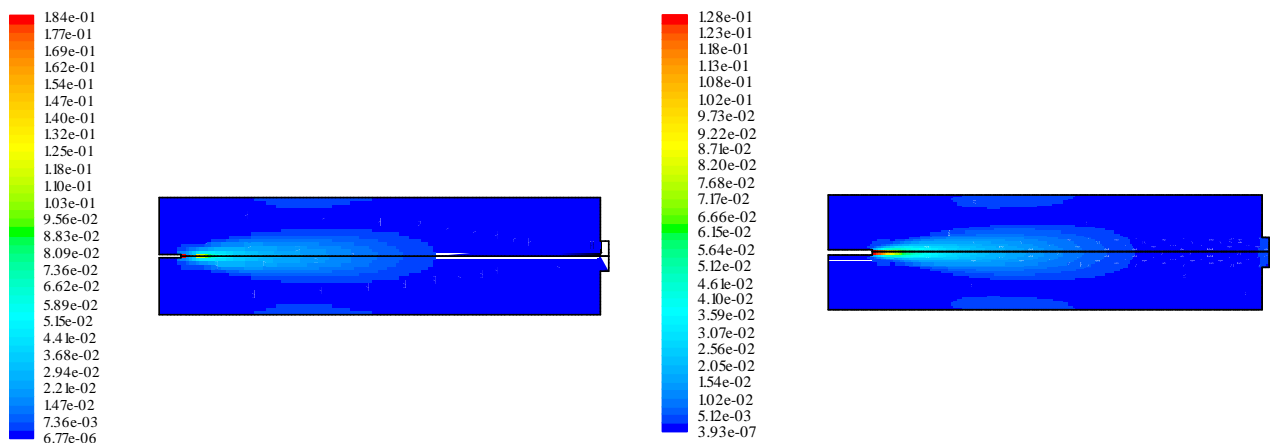


Figure 2. Solvent recovery for several flows

This enormous difference is due to the fact that flow dead areas exist in the top and bottom corners of our crystallizer (see Figure 1). From results of Table 1, due to these dead areas it is only possible to moderately reduce the required drying time by increasing CO₂ flow rate. So, for that a new design is proposed with a holed inlet to spread inlet flow and avoid flow dead areas. This new model is shown in Figure 3.

2. Design Type 2:

With this modification in the nozzle shape, and a smaller distance from the top, a small decrease of simulated residence time is achieved as it is presented in Figure XXX.



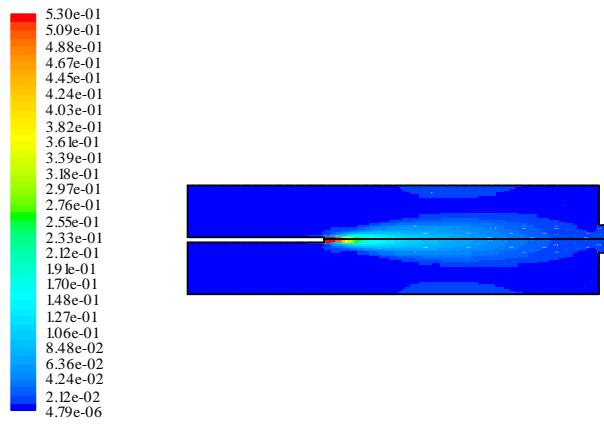


Figure 3. Contours of velocity magnitude for different distance from the top

3. Design Type 3:

Flow dead zones of the top corners have been achieved that disappeared but still flow dead zones in bottom corners of the crystallizer exist. For this reason, our next challenge has to be to eliminate it, so the bottom of the precipitator has been modified for having a conic shape. With this new shape in the bottom of the crystallizer, a high decrease of simulated residence time is obtained as it is shown in Table 2.

On the other hand, in Figure 4 it is observed how bottom flow dead areas has been eliminated by means of c_{EtOH} variation along precipitator

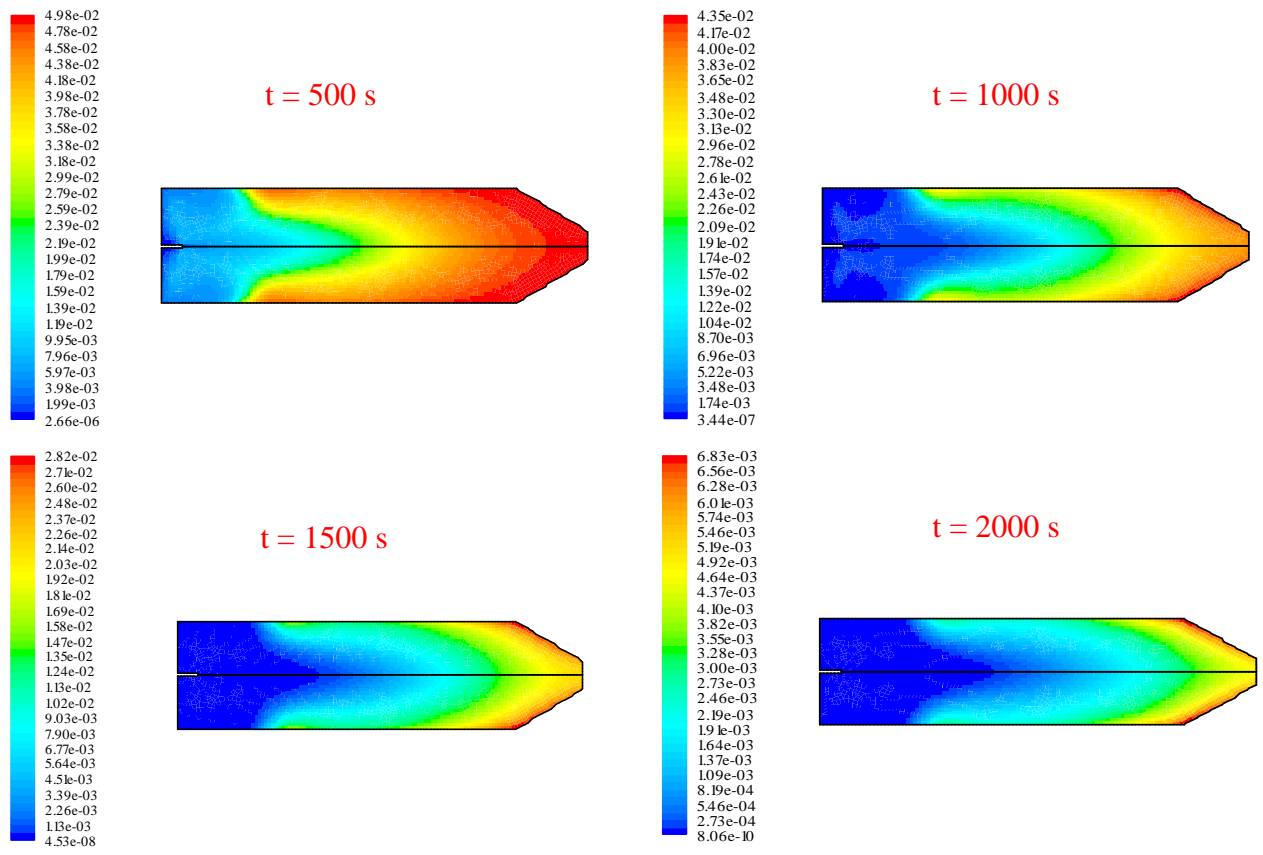


Figure 4. Contours of solvent concentration for different times

G (kg/h)	τ_{FP} (min)	τ_{CSTR} (min)	τ_{CFD} (min)
5	3.6	66.7	58.3
10	1.8	33.4	33.3
20	0.9	15.4	12.5

Table 2. Comparison of residence time between ideal and simulated flow model

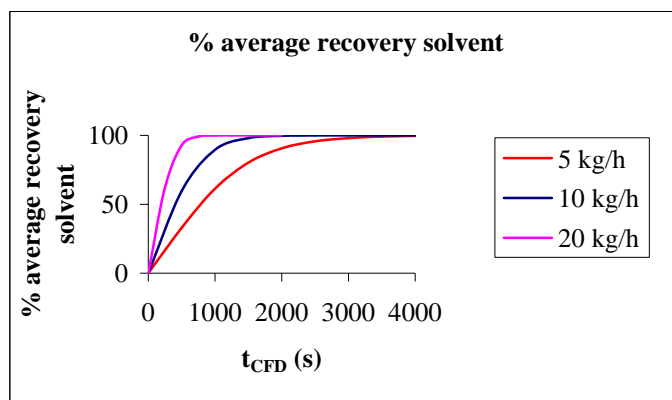


Figure 5. Solvent recovery for several flows

CONCLUSIONS

Precipitation processes based on supercritical fluids present several advantages over conventional methods, as they allow obtaining small particle sizes with control of the morphology and particle size distribution, and without contamination or degradation of the product. For this purpose, a detailed knowledge of the fundamentals and mechanisms of the process is necessary. The SAS crystallization process has been modelled based on the mechanism of mass transfer with hydrodynamics above the mixture critical condition of the CO₂-EtOH system. The final model for the crystallizer shows us a simulated residence time of 58.3 min. for a flow of 5 kg/h, which is 1/2 times than first model (see Table 1). This residence time is high compared to the results obtained assuming plug flow ideal due to the dead volumes inside the precipitator but show a good agreement when we assumed ideal perfectly-mixed behaviour (see Table 2)

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