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Analysis of the Dynamics of Particles in a Precipitation Chamber by SAS Technique with Coaxial Injection System Using a One-Way Coupling Euler-Lagrange Approach

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Precipitation processes such as SAS - Supercritical Antisolvent - based on supercritical fluids have been extensively used in the crystallization of a wide variety of materials in a controlled manner allowing one to obtain nanoscale particles which are almost spherical in shape. The understanding of the dynamics of the particles inside the precipitation chamber allows the decision for operating conditions that are favorable to the precipitation of particles of small size, but there is still a great experimental challenge. In this paper, a Euler-Lagrange approach with one-way coupling was proposed to evaluate the dynamics of particles in a chamber of SAS precipitation prescribing one distribution of particle diameters, assuming values within ranges specified from experimental values. From the software ANSYS CFX used to obtain the solution of the mathematical model, the following variables were analyzed: mixture velocity, the time of trajectory, the dead zones and the average diameter of the precipitated particles. Under an operating pressure of 120 bar and an operating temperature of 313 K, the results showed that the flow pattern is quite complex. There is high speed of mixture at the outlet of the capillary injection. In this region were also observed large changes in the mixture density and large variations in the composition of the mixture.Were observed large particle diameters around the chamber outlet pipe, which suggests that a change in the outlet position of the camera can improve the process yield. The model proved to be a quick and economically versatile tool for a better understanding of the dynamics of particles and, consequently, to select conditions that can give a better control over the performance of the SAS process.

1. Introduction

The current cosmetic and food industry has invested widely in nanotechnology in new functional materials (nanomaterials) (Khare et al., 2014), processing in micro- and nano-scale, as nano-sensors for food preservation and nano-polymers as film formers (Morris, 2014), fixatives, emulsifiers, thickening agents and formulation in personal care products (Sanguansri et al., 2006). Thus, the development and improvement of techniques for obtaining high-quality particles in form and size, is of scientific and industrial interest. This is the case for the SAS (Supercritical Antisolvent) process, which employs supercritical fluids for precipitation.
With the SAS technique it is necessary to use an organic solvent in which the solute is soluble. The solute and organic solvent mixture enters through a capillary into a pressurized precipitation chamber that is pre-charged with the antisolvent. Once the solution interacts with the antisolvent (under supercritical conditions), which continues to be injected by the same capillary coaxially, there is an increase in the diffusion of antisolvent organic mixture, which causing precipitation of the solute (Bałdyga et al., 2010). To find the combination of parameters which results in the obtainment of particles that are best suited to each application properties, it is necessary to investigate the flow pattern at conditions of temperature and pressure above the critical values,

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and how this pattern influences the quality of the particles obtained at the end process. In this context, Computational Fluid Dynamics (CFD) were used as a low-cost alternative able to predict flow patterns in a short time (Henczka et al., 2005).

Some numerical approaches have been presented in the literature to describe the growth and dynamics of precipitated particles in the SAS process (Erriguible et al., 2013), but most of them are formulated for very specific systems of solutes and organic solvents (Badens et al., 2005), and a complete understanding of the phenomena involved in the process is still far from being reached (Jerzy et al., 2004).

Assuming small particle size and a dilute particle concentration (Martín et al., 2004), the particles exert a negligible force on the carrier fluid or other particles (Almeida, 2013). Hence, a Euler-Lagrange with one-way coupling approach is suitable to study the behaviour of a set of particles by solving a finite number of trajectories judged to be statistically representative of the particles moving over the calculation domain to obtain timely information about the particles such as residence time, distance and average diameter (Wörner, 2003).

This work deals with the formulation of a mathematical model for the fluid dynamics of the SAS process The particulate phase is considered from the Euler-Lagrange framework with one-way coupling its solution from computational and subsequent analysis of simulation is obtained by the use of the software ANSYS CFX.

2. Mathematical and numerical details

The chamber of precipitation considered in this study has an internal diameter of 80 mm and an internal length of 120 mm. The coaxial injection capillary has a length of 98 mm and a diameter of the inlet to the CO_2 of 0.9779 mm and a diameter of the inlet to the solution of 0.1 mm. The outlet of chamber is located in the chamber lid, being a pipe of 164 mm with an internal diameter of 6.34 mm (Franceschi, 2009).

Table 1: Boundary conditions for operating pressure and temperature : P_{0p}=120 bar and T_0=313.15 K

	Inlet	Outlet
Flow	**Mass flow rate** CO_2 inlet: 4.44×10^{-4} kg/s Solution Inlet: 4.656×10^{-5} kg/s	**Pressure:** p=0
Particles	**Mass flow rate:** 1.0×10^{-5} kg/s	
Turbulence Intensity	5%	5%
Walls	**No Slip**	

In the SAS chamber, under an operating pressure of P_{op}=120 bar and a temperature of T_0= 313.15 K, it is considered that initially the chamber is charged with CO_2 and that there is the ethanol and CO_2 injection from a coaxial capillary tube, where ethanol enters through the central tube and CO_2 enters from the outer tube. The capillary tube is located in the center of the chamber lid. The boundary conditions employed in the present model are summarized in Table 1.

Stokes number (St) is defined as the ratio of the characteristic time of a particle (or droplet) to a characteristic time of the flow. A preliminary calculation of Stokes number indicated that (under the operating conditions considered) the particles follow the streamlines of the fluid phase ($St \ll 1$) whereas for large Stokes number, the particle's inertia dominates and the particle will continue along its own trajectory as detailed in Rezende (2013). Currently in the literature, there various approaches for modelling multiphase flows (Rezende et al., 2015), the Euller-Lagrange approach Crowe et al. (1998), is used to describe a variety of multiphase flow processes as can be seen for example in Ricardo et al. (2013).

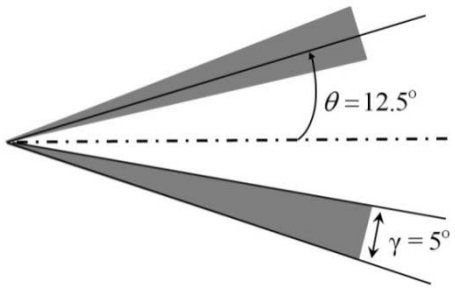

Figure 1: Scheme of the cone injection of particles: The region of injection begins in the outlet of the coaxial capillary

The most appropriate approach depends on the evaluation of number of Stokes, to determine the dynamics of the particles in the SAS chamber a Euller-Lagrange model with one-way coupling was employed. In the one-way coupled Euler-Lagrangian framework, the particles are modelled as a dispersed phase. The individual particles are treated as point-spheres governed by an equation for particle motion combined with a continuous phase described by the Navier-Stokes equations. The mathematical modelling of the one-way coupled Euler-Lagrangian approach can be seen in Mattson (2011).

Based on the assumption that the particle nucleation occurs at the outlet of the coaxial capillary of injection (Lengsfeld et al., 2000), a region of injecting particles was created for the simulation. This region has a conical shape and it was located at the exit of the coaxial capillary injection within the chamber. The particles are injected in a conical region around the solution jet formed in the capillary outlet with injection magnitude of velocity of 10 m/s previously evaluated to be approximately the same as the fluid phase.

The opening angle of the injection region has been chosen to be 25 ° (degrees) as in Figure 1, which was described in the literature as being approximately the opening angle for turbulent jets (Cushman-Roisin, 2013). From the external surface of the cone (grey region shown in Figure 1), it is assumed that, the particle dispersion region has an angle of dispersion of $\gamma = 5°$. This form of injection was chosen under the assumption that the nucleation region occurs at the boundary of the jet of solution.

A uniform distribution of particle sizes was selected, which produces an equal number of particles for all diameters between the specified minimum and maximum diameter. It was in the range of $1.5x10^{-7}$ to $1.0x10^{-6}$ m. For the transfer of linear momentum, we specified the drag model of Schiller-Neumann as in Rezende (2013). A mesh with a total cell number of $1.028x10^{6}$ was generated on ICEM 13.0 software and the system of equations was discretized and solved by the method of finite volumes based on elements (EbFVM) by ANSYS CFX 13.0 software. The assumptions of isothermal regime with the *k-ε* turbulence model were considered. Once the convergence is reached in the fluid field, the field for the particulate phase has been solved. We used an Intel Core i7 processor with 2.93 GHz speed and 16.0 GB of RAM, with operating system Windows 7 x 64, and it took around 4 h to complete the calculations. The total time of simulation was 90 s with time step of 0.1 s.

3. Results and discussion

3.1 Velocity field

The velocity field can be observed in the central cutting plane in Figure 2 (a) and the vector field in the central cutting plane in Figure 2 (b). Due to the large velocity difference between the jet and the ambient mixture, a thin shear layer is created, which is subjected to flow instabilities that eventually lead to the generation of turbulent fluctuations and the shear layer continuously grows downstream (Cushman-Roisin, 2013). This turbulent shear flow drags the bulk fluid into the jet and improves the flow mixing. At the exit of the nozzle, the jet spreads laterally outward with high velocity which decreases downstream reaching the bottom still with a speed of approximately 7.5 m/ s and rising again.

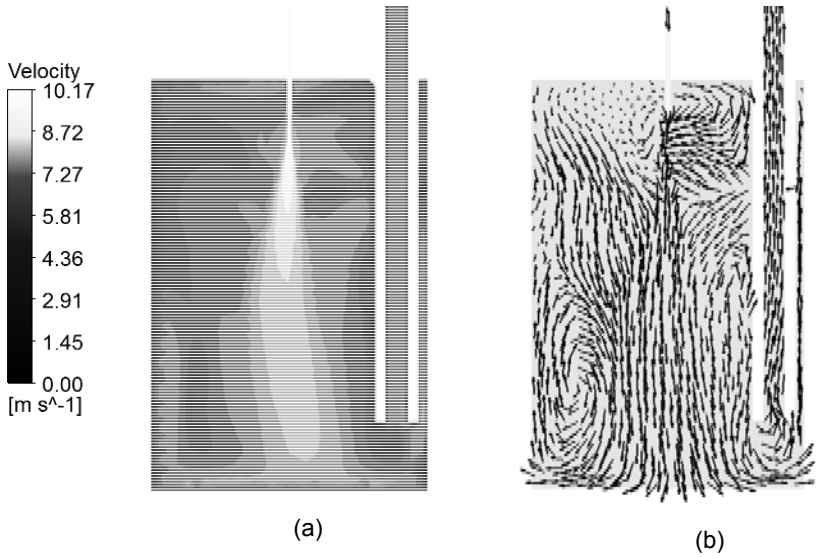

Figure 2: Fields of average velocity for a cutting plane through the center of the chamber. (a) Contour map of the magnitude of average velocity; (b) Average velocity vectors field

The chamber has a small length (120 mm), and recirculation zones like those of Figure 2 (b) occur near the wall and around the outlet pipe. The velocity reaches its minimum value at the laterals of the chamber and close to the lid, where portions of fluid are swallowed up by the jet as seen in Figure 2 (a) and (b).

3.2 Density and mixture

The flow of the mixture in supercritical state is compressible. For predict the high compressibility of the mixture, the density of the mixture was calculated with the equation of state of Peng-Robinson, but with the ideal mixing rule. This thermodynamic approach is simpler than those usually employed in the literature such as Bałdyga et al. (2010), or in Jerzy et al. (2004) which employed mixing rules as van der Waals; and Sierra-Pallares et al. (2012) which employed Wong and Sandler mixing rule, but also, the use of such mixture rules result in greater computational cost.
Figure 3 shows the density distribution of the mixture and the mass fraction of ethanol in a plane passing through the center of the precipitation chamber. Near the critical point of the mixture droplets formed in the chamber SAS exhibit high sensitivity to variations in the density of the mixture, since the smaller the density difference between CO_2-rich regions and organic solvent-rich regions, smaller particle sizes are observed (Imsanguan et al., 2010). The density of CO_2 and ethanol obtained in the present study is consistent with that observed in the experimental work reported by Petit-Gas et al. (2009) under similar conditions of operation. It is observed that the largest variation in density occurs at the outlet of the coaxial capillary injection, where the ethanol that goes through the center of the capillary tube comes in contact with the surrounding CO_2 which also enters from the outside the capillary tube. In the remainder of the interior of the chamber there is a homogeneous distribution of the mixture density, 670 kg/m^3. It is also observed from the mass fraction distribution of the ethanol in capillary outlet region, that there is a homogeneous mixture containing approximately 18% of ethanol, this is in agreement with the value reported by Martín et al. (2004) under similar conditions in their numerical work.

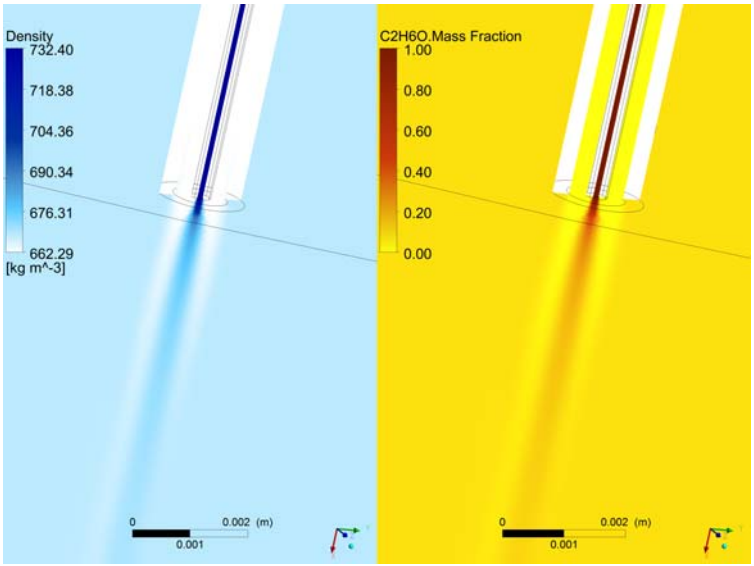

Figure 3: The chamber region where there is greater variation in density and ethanol mass fraction: the region at the outlet of the capillary injection

3.3 Particles dynamic

In Figure 4 the tracking of the particles, colored by the mean particle diameter, is shown. The trajectories of the particles are quite complex. As can be observed in Figure 2, the jet of mixture reaches the bottom of the chamber with high velocity. In Figure 4 observes that the mean particle diameter in the jet region is large (t=1.6 s). Next to the bottom of the chamber there is an increasing in the particle diameters (t =10 s) as well as at the top near the outlet tube and in the walls after being recirculated for the bottom and rise again at the top of chamber, as can be seen in the time range of 16.4 s to 90 s.
Concerning the particle traveling time, it was observed that there is a greater residence time to particles surrounding the outlet pipe of the chamber. This is a region that is observed largest particles diameters, see

Figure 5, that showing the distribution of mean diameters by a horizontal line, at the 23 mm from the top, near the outlet tube. These patterns of particles would not be observed if one considers the outlet located at the bottom center of the chamber. In this case, the streamlines would be observed more evenly distributed as shown in Almeida (2013) in a two-dimensional analysis with a chamber of the same dimension.

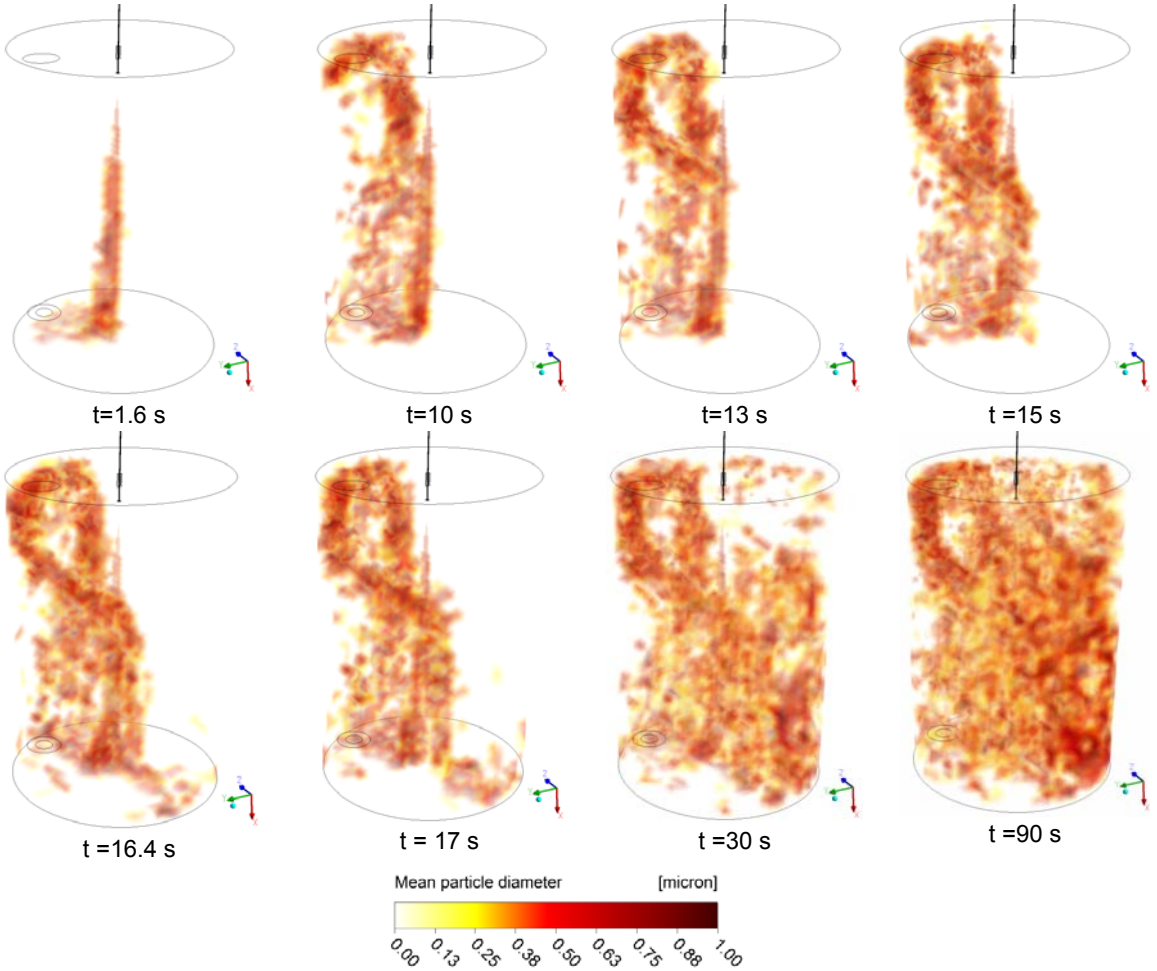

Figure 4: Flow particle patterns by a volume rendering colored by the mean particle diameter in different times of simulation

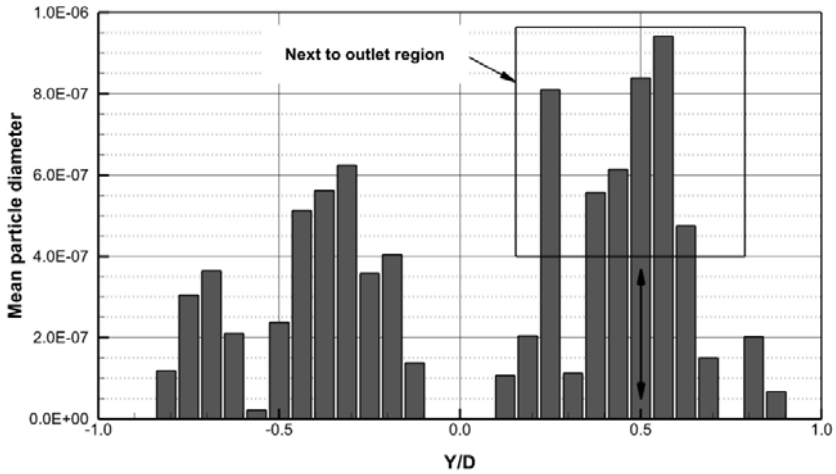

Figure 5: Mean particle diameters on a horizontal line next to the chamber exit pipe with zoom in a region of the larger mean particle diameter. The Line is located at the 23 mm below of the chamber lid and D is the diameter of the chamber

4. Conclusions

This study proved to be an efficient methodology for information about of the flow patterns of a supercritical mixture in an SAS chamber of precipitation. The computational time is cost-efficient, about four hours. There was agreement on the distribution of the mixture density and mass fraction of ethanol with works presented in the literature. The analysis of tracking of the particles showed that there is a complex pattern of trajectories inside the chamber. The outlet located at the chamber lid made the trajectory of the particles difficult, increasing their residence time and the mean particles diameter in this region. A chamber with an outlet located at the bottom center could minimize this tendency and must to be considered in a future work, in which this numerical methodology will be implemented and validated in a wide range of operating conditions.

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