CAPILLARY NOZZLES IN THE RESS PROCESS: HYDRODYNAMIC MODELLING

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It is shown in few papers dealing with the RESS process simulation that particle size and morphology are functions of the capillary length (L) and diameter (D). Indeed, for such particle morphology and size, several authors gave criterions defining the appropriate ratio L/D. An hydrodynamic code is performed by treating the full Naviers-Stokes equations coupled with an accurate equation of state. Here, computations are done for bidimensional, instationnay, compressible and viscous carbon dioxide flow. Depending strongly on the inlet and the outlet pressures ratio, this kind of flow jet is accompanied by several right and oblique shocks. Thus, a Riemann solver basing on the Roe theory is implemented for capturing these discontinuities. From hydrodynamic point of view, profiles of different thermodynamic parameters and velocity in the capillary nozzle and the jet are given. These great gradients locate in someway the super-saturation region in nozzle where nucleation can be happened and relate it to the capillary dimensions. Therefore, this numerical study permits to avoid nozzle plugging in RESS process by choosing the optimal nozzle dimensions and thermodynamic operating parameters of the RESS process.

INTRODUCTION

The most researched process is the RESS process, where a product, initially dissolved in supercritical carbon dioxide, is deposited as micron sized particles by rapid expansion through a nozzle [1]. The formation of small particles of a substance, say of some µm dimension, with a narrow size distribution is an important process in the pharmaceutical and other industries. The alternative of milling can give a wider size distribution and also cause degradation of the substance, thermally or otherwise. RESS-modelling is focused on the flow through the nozzle, the supersonic free jet, the Mach disk, rarefaction shocks, and fluid transport properties in the expansion unit. From these calculations, particle size and morphology can be deduced. The expansion nozzle may be a short length of stainless steel capillary or a fine hole cut by a laser in a stainless steel plate. Various internal shapes of nozzle have been suggested in literature and different remarks were given where relation between particle size and nozzle dimnsions is shown. From hydrodynamic point of view, the supercritical fluid flow may be altered by the nozzle dimensions, [2]. Indeed, using a capillary nozzle diameter of 50 µm, for example, a focalised jet can be developed where particles of around few µm diameter of narrow size distribution are produced. Expansion to atmospheric conditions of a solution in carbon dioxide produces quantities of dry ice, so this has to be avoided by heating the solution before expansion and choosing a suitable geometry of the expansion nozzle.

Mathematical models aimed at a better fundamental understanding of the underlying thermo-physical phenomena are essential for rational design and scale-up of these technologies. In fact, an hydrodynamic code is performed by treating the full Naviers-Stokes equations coupled with an accurate equation of state. Here, computations are done for bidimensional, instationnay, compressible and viscous carbon dioxide flow, [3]. Depending strongly on the pressure ratio at both the inlet and the outlet of the nozzle, this kind of flow jet is presented as a succession of right and oblique shocks. Thus, a Riemann solver basing on the Roe theory is implemented for capturing these discontinuities and determining exactly different varibles at the nozzle orifice such as the pressure and the velocity. The code gives us the profiles of different thermodynamic and kinetic parameters in the capillary nozzle and the jet. These gradients locate in someway the supersaturation region in nozzle where nucleation can be happened and relate it to the capillary dimensions. Concerning the capillary nozzle dimensions effects, the length L and the diameter D were altered for the same numerical configuration. A new adimensional parameter is defined as the ration of the inlet gap pressure and the outlet one, and given as a function of the nozzle dimensions. We underline the hydrodynamic effects on the nucleation and coagulation conditions which can be computed after localizing the solute - solvent separation in RESS process.

Numerical simulation:

A numerical code has been developed to study the dynamics of the supercritical carbon dioxide expansion. This code solves the full time dependent the conservation laws of mass, kinetic quantity and energy of the flow using a specific equation of state. This set of equations is solved by using the Total variation Diminishing algorithm, introduced by Harten et al., [4]. Which is suitable for transonic and supersonic flows. Since we look for a steady a steady solution, we want to use as large a time step as possible, in this way, the convergence is accelerated by implicit linearisation using the ADI formulation. To capture the shock waves and discontinuities, we have used an approximate Riemann solver developed by Vinokur and Montagné et al. [5] who adapted the Roe's averaging to a nonconvex Riemann problem for a real gas,. The Naviers Stokes equations governing the instationary, bidimensional, axisymmetric, viscous, and compressible flow may be written in conservative form as :

$$\frac{\partial(yQ)}{\partial t}+\frac{\partial(yF)}{\partial x}+\frac{\partial(yG)}{\partial y}=0$$

Here, x represents the longitudinal axis; y refers to the radial axis. Q is the solution vector and F and G are fluxes in both directions including the Euler fluxes part and the dissipating terms.

$$Q=\begin{pmatrix} r \\ ru \\ rv \\ rE \end{pmatrix};\ F=\begin{pmatrix} ru \\ ru_2+P+t_{xy} \\ ruv+t_{yy} \\ (rE+P)u+ut_{xy}+vt_{yy}+k\frac{\partial T}{\partial y} \end{pmatrix}\text{; and}\qquad G=\begin{pmatrix} rv \\ ruv+t_{xx} \\ rv_2+P+t_{xy} \\ (rE+P)v+ut_{xx}+vt_{yy}+k\frac{\partial T}{\partial x} \end{pmatrix}.$$

Where $t_{xx}=\frac{2}{3}m\left(2\frac{\partial u}{\partial x}-\frac{\partial v}{\partial y}\right)$; $t_{yy}=\frac{2}{3}m\left(2\frac{\partial v}{\partial y}-\frac{\partial u}{\partial x}\right)$; $t_{xy}=t_{yx}=m\left(\frac{\partial u}{\partial y}+\frac{\partial v}{\partial x}\right)$.

Here r is the density, u and v are the components of the velocity in each directions and E is the total energy. The coefficients of the viscosity and the thermal conductivity are denoted μ and κ, respectively.

The Altinun and Gadetskii Equation of State was chosen to describe the thermodynamic properties of the pure carbon dioxide [6]. Both liquid and like gas states are represented accurately with this correlation. Except the critical region, the supercritical domain can also be included up to the high pressure domain. It is written as follows:

$Z=\frac{P}{rrT}=1+r_r\sum_{i=0}^{9}\sum_{j=0}^{6}b_{ij}(t-1)^j(r_r-1)^i$ where $\rho_r=\rho/\rho_c$ and $\tau=T_c/T$.

r is the perfect gas constant, ρ_c and T_c are both the critical density and temperature of the carbon dioxide, respectively. b_{ij} are tabulated constants given in [6]. Numerical simulations of supercritical carbon dioxide flow in the capillary nozzle and the supersonic jet are developed. The initial conditions are taken as given in table 1.

	State	**Pressure (bar)**	**Temperature(K)**	**Velocity (ms^{-1})**
Nozzle Inlet conditions	SCF	236.45	388	200
Nozzle Outlet conditions	Perfect gas	1.0	313	0.

Table 1 : Initial hydrodynamic conditions for all computation cases.

The cylindrical nozzle dimensions are taken as given in table 2. The recrystallization chamber diameter and length are 2cms and 4 cms, respectively. The grid takes in account the structure of the developed jet. So, curved meshes were chosen and calculus implementation was transformed from the Cartesian system to the curvilinear one. Due to the enormous difference scale between nozzle dimensions and those of the precipitation unit, refining meshing techniques were used. The time step was conditioned by the Courant Frederic Levy (CFL) number. At the beginning of the calculation, it was set at 10^{-9}s. The established algorithm permits to increase automatically the time step when flow instabilities became minors [3]. The numerical simulations were achieved when a stationary configuration of the flow is obtained. Here, any increasing of the iteration number can not alter the obtained results.

L D	**20**	**40**	**50**	**60**	**75**	**80**	**100**	**120**
0.1			x					
0.2			x					
0.3			x		x		x	
0.4			x					
0.5			x		x		x	
0.6			x					
0.7			x		x		x	
0.8			x					
0.9			x					
1.0	x	x	x	x	x	x	x	x

Table 2 : Different capillary nozzle dimensions used in computation cases (L in cm and D in µm).

NUMERICAL RESULTS:

Initially, the capillary nozzle and the recrystallisation chamber is filled by an immobile CO_2 at atmospheric pressure and ambient temperature, see table 1. In figure (1), isovalues of the longitudinal velocity are depicted. It shows a thin supersonic jet where the mach disk is captured accurately. The velocity oscillations along the jet were noticed. This phenomenon conveyed the succession of chocks along the flow. At the flat plate (deposition plate), the jet changes abruptly its direction.

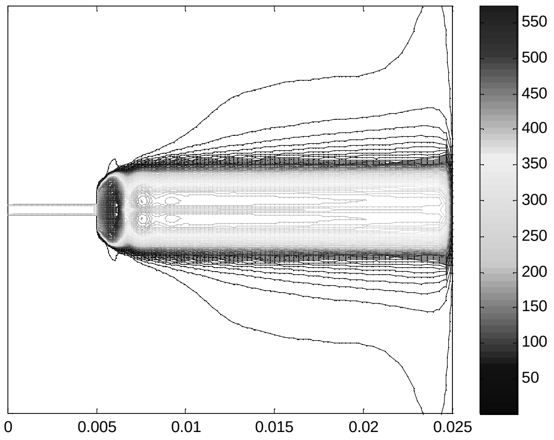


Figure (1)- Velocity isovalues of the expansion

Obviously, important gradients of temperature are detected in the flow field. Figure (2) shows a very cold jet where temperature exceeds 200K. Also, gradients of pressure show the abrupt expansion of the supercritical CO_2 where solvating properties are loosed near the orifice nozzle, figure (3). Here, the supersaturation ratio exceeds the unity and nucleation of molecular particles of the solute happens.

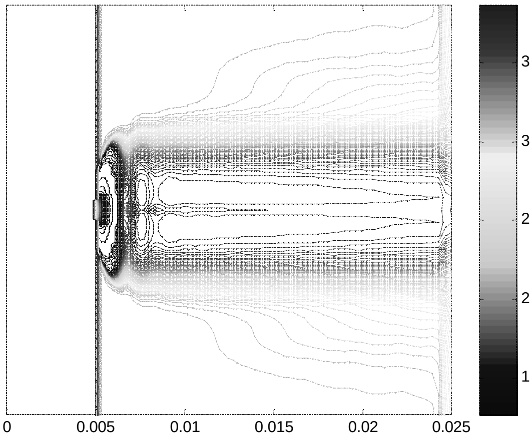
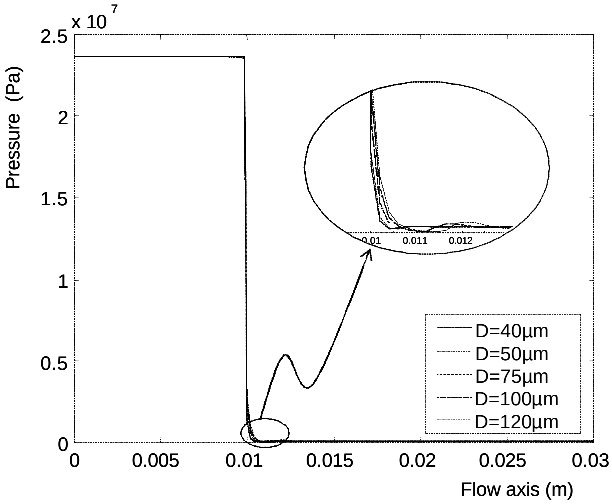


Figure (2) – Temperature isovalues of the expansion

The velocity along the jet axis is given as a function of capillary diameter in figure (4). We notice the variation of the Mach disk position with diameter and amplified oscillations along the jet especially in the jet axis are related to the orifice diameter. At the precipitation unit limits and the flat plate, there is no change concerning hydrodynamic variables. At the beginning of the nozzle, constant hydrodynamic quantities were conserved except at the boundary layers where dissipation is localised.



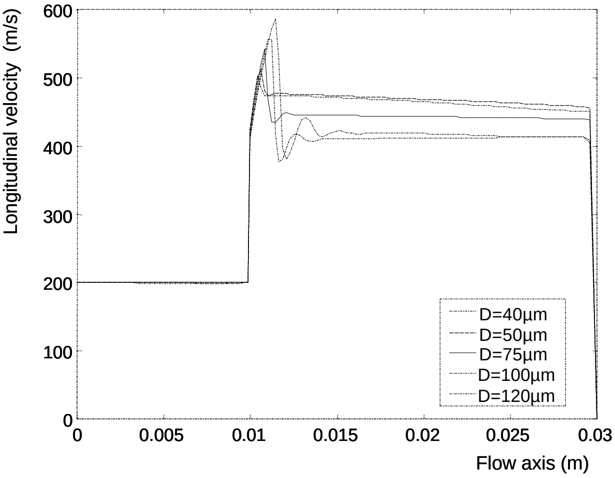
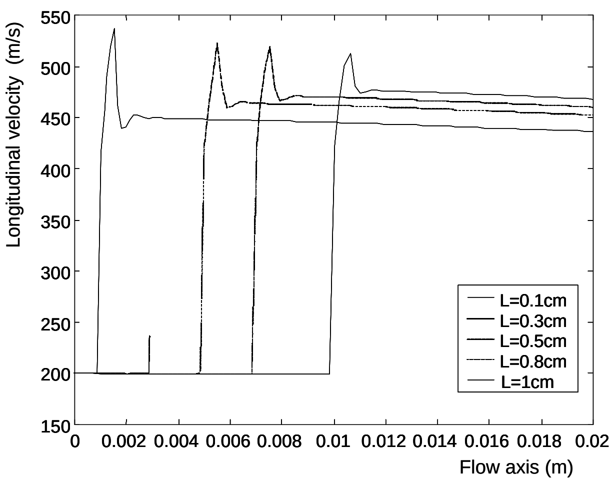


Figure (3)- Evolution of pressure along the jet axis

Figure(4)- Evolution of velocity along the jet axis

The axial velocity of the jet as a function of capillary length is depicted in figure (5). At every length case, we have obtained exactly the same profile of velocity. There are simply translations of the expansion when different velocity profiles are drawn together. Similarly to the velocity, the pressure is drawn as a function of capillary length along the flow axis. An accurate capture of the expansion shocks is remarked, figure (5). Numerical simulation proved that abrupt decreasing in pressure is localized at the capillary outlet orifice and there is no considerable effect of the capillary length on the pressure falling. The zooming shows that oscillation of pressure after expansion is quite the same for all cases.



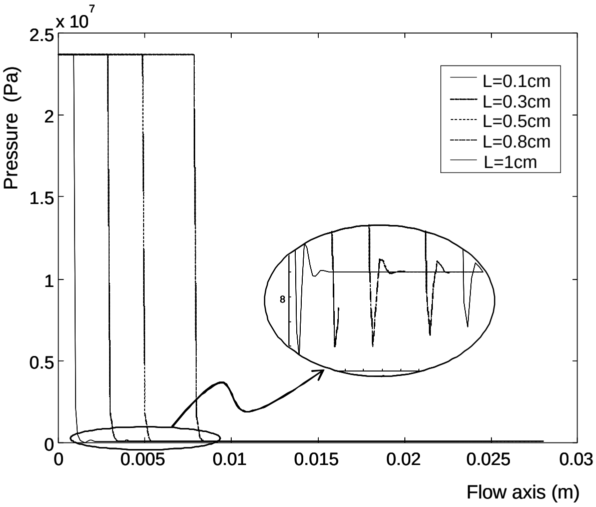


Figure (5)- Evolution of velocity along the jet axis

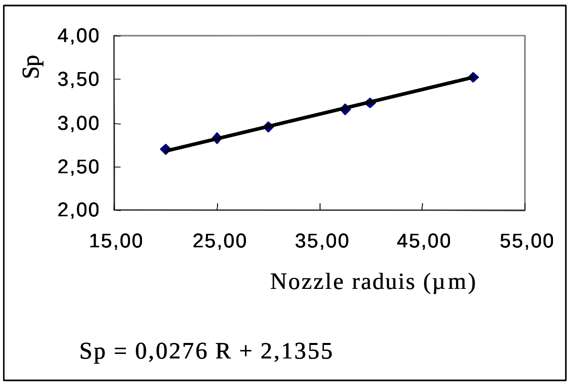
Figure(6)- Evolution of pressure along the jet axis

From these calculations, we define the parameter S_p which represents the ratio between the pressure gap at the inlet and that at the outlet of the nozzle. The pressure gap is calculated as the difference between pressure at a given region and the critical pressure of carbon dioxide. This parameter S_p is defined explicitly as follows:

$S_p=\frac{P_{in}-P_c}{P_c-P_{out}}$; where P_c, P_{in}, and P_{out} are critical, inlet, and outlet pressures, respectively.

When the supercritical carbon dioxide flow crossed the nozzle orifice, an abrupt decreasing of pressure and an enormous increasing of the velocity is noticed. Crossing the critical pressure means the loosing of the solvatating power of the supercritical state. Hence, the carbon dioxide can be considered as a light gas and the solute is separated from CO_2. We define the nucleation region as the zone where super-saturation ration overcomes the unity and the solute is nucleated. Depending strongly on the pressure level, the pressure slope S_p and therefore the super-saturation ratio can localize, in someway, the nucleation zone.

From different computations, S_p is depicted as a function of capillary diameter, figure (7). The pressure slope S_p is proportional to the nozzle radius. Indeed, increasing diameter of the capillary orifice decreases the outlet pressure gap. We conclude that abrupt expansion crosses the critical pressure very close to the nozzle outlet orifice when important capillary diameters were used.



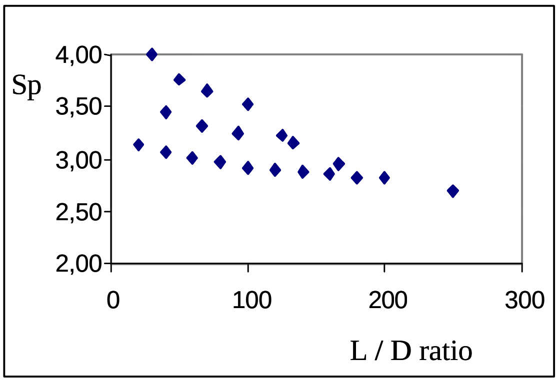
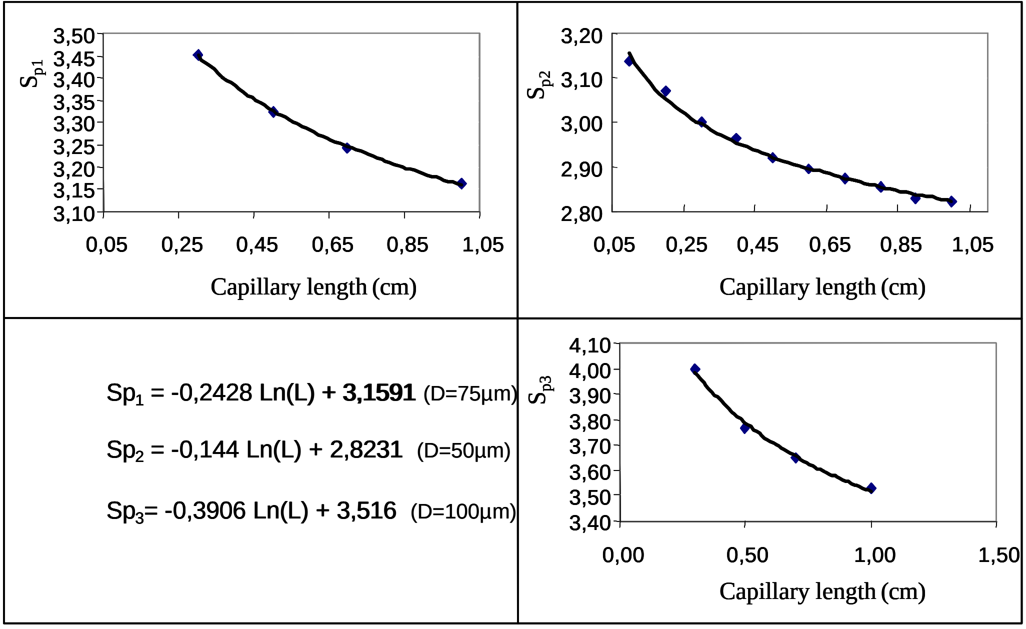


Figure (7)- S_p as a function of the diameter at L= 1cm

Figure(8)- S_p as a function of the L/D ratio

At a given diameter, SP is depicted as a function of capillary length, figure (9). The pressure slope Sp is drawn as a logarithmic function. Indeed, length of the capillary orifice has a little effect on the outlet pressure gap. We conclude that abrupt expansion crosses the critical pressure very close to the nozzle outlet orifice. There is no significant influence of the capillary length on the flow. Perhaps, L is a significant parameter of jet stability when turbulence is considered. Finally, the pressure gap is showed as a function of the nozzle geometrical parameter L/D given in several studies, figure (8). Effectively, we combine effects of diameter and length of the nozzle. Whereas, the effect of the capillary diameter is more significant.



$Sp_1 = -0{,}2428 \ Ln(L) + 3{,}1591$ (D=75µm)

$Sp_2 = -0{,}144 \ Ln(L) + 2{,}8231$ (D=50µm)

$Sp_3 = -0{,}3906 \ Ln(L) + 3{,}516$ (D=100µm)

Figure (9)- Pressure slope S_p as a function of capillary length

CONCLUSION

The rapid expansion of supercritical solution is studied numerically from hydrodynamic point. Profiles of different thermodynamic parameters and velocity in the capillary nozzle and the jet are given. These great gradients locate in someway the super-saturation region in nozzle where nucleation can be happened and relate it to the capillary dimensions. A new parameter based on the pressure gap is defined. This factor is proportional to the diameter but there is no significant effect of the length. The brutal expansion comes closer as much the opening of the nozzle. Therefore, this numerical study permits to avoid nozzle plugging in RESS process by choosing the optimal nozzle dimensions and thermodynamic operating parameters of the RESS process. A comprehensive model that accounts for expansion in the nozzle and in the jet along with nucleation, growth, and agglomeration remains a challenge.

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