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Modeling of particle formation processes using gas saturated solution atomization

Matteo Strumendo *, Alberto Bertucco, Nicola Elvassore

DIPIC "I. Sorgato", University of Padova, Padova, Italy

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Abstract

In the PGSS process, a gas saturated solution is atomized through a nozzle and a spray is formed; afterwards, the gas (carbon dioxide) evaporates and droplets solidify.

In this work, the behaviour of a carbon dioxide super-saturated solution drop in a low pressure environment is investigated. A mathematical model, based on the general multi-component equations of change and on the Stefan conditions to account for the moving boundaries, is solved numerically providing the spatial and temporal profiles of temperature, composition, mass flow inside and outside the droplet.

The time required to attain the solid–liquid equilibrium condition at the droplet boundary decreases monotonically when the initial carbon dioxide content is increased, and increases together with the initial solution temperature. These trends are consistent with experimental data, showing that the average final particle size decreases if the mixing vessel pressure is raised and increases together with the spray temperature.

Keywords: Gas saturated solutions; Moving boundary problem; Particle formation; Particle size; Solid–liquid equilibrium

1. Introduction

In recent years, a growing interest has been paid to supercritical fluids and their industrial applications. Taking advantage of supercritical fluids peculiar properties [1], new techniques have been developed and existing ones have been improved in many fields, i.e. separation processes, polymerization/depolymerization processes and particle production.

Particularly, the use of supercritical fluids has been attractive for particle formation [2–4], above all for applications in the pharmaceutical, cosmetic, food, particle coating and fine chemistry industries. Some advantages of supercritical fluids-based processes are: the possibility of avoiding (or at least minimizing) the use of organic solvents; the flexibility to treat a wide range of materials, including thermolabile ones; the ability to produce particles with a wide range of sizes, shapes and morphologies; the possibility of loading the particles with an active ingredient [2], which can be dispersed in a matrix (microspheres) or surrounded by a shell (microcapsules).

The more important processes for particle production using supercritical fluids are RESS, SAS (and its implementations) and PGSS (Particles from Gas Saturated Solutions); comparisons among the three processes are presented in the review papers [2–4].

In PGSS [5], the material to be processed is melted and mixed at high pressure with the supercritical fluid (typically carbon dioxide) in a mixing unit. In this way, a gas saturated solution is obtained, which is then flowed through a nozzle to an expansion unit (at low pressure and temperature) so that a spray is formed. Carbon dioxide evaporates very quickly from the droplets, which eventually solidify due to the temperature decrease and to the carbon dioxide loss. Finally, solid particles are separated from the carbon dioxide by means of filters, cyclones and electrostatic separators.

One of the key features of PGSS is the strong reduction of the melted substance viscosity once it is mixed with the supercritical fluid. A second effect of mixing the melted substance with the supercritical fluid is the melting point temperature depression; this phenomenon prevents the solidification inside the nozzle as well.

Another interesting feature concerns the decrease of the temperature and the subsequent droplets solidification. This is usually ascribed [5] to a combination of the Joule–Thompson

* Corresponding author. Present address: Department of Chemical and Environmental Engineering, Illinois Institute of Technology, Chicago, IL, USA. Tel.: +1 312 567 3066; fax: +1 312 567 8874.
E-mail address: strumendo@iit.edu (M. Strumendo).

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Nomenclature

c_P	specific heat at constant pressure
f	fugacity
H	Henry constant and enthalpy
j	mass flux (radial direction)
K	thermal conductivity
ℓ_2	upper limit of the gas phase domain
PM	molecular weight
q	heat flux (radial direction)
r	radial coordinate
R	droplet radius
R_{gas}	gas constant
RF	reduction factor in the grid definition
t	time
T	temperature
u	gas velocity (radial direction)
v_∞	droplet/gas approach velocity
Y	mass fraction

Greek letters

$\wp$	mass diffusivity
Π	pressure
λ	enthalpy variation between the CO_2 enthalpy in the gas phase and the CO_2 partial enthalpy in the solution
μ	fluid viscosity
ρ	density
τ	stress tensor
ξ	dimensionless radial coordinate

Subscripts/superscripts

C	carbon dioxide
eq	equilibrium value
i	cell index
in	initial value
int	intercept of a linear relationship
mol	molar
N	total number of cells
sl	slope of a linear relationship
trist	tristearin
1	liquid phase (solution)
2	gas phase (environment)
ˆ	value in the mixture
–	partial molar

effect and of the cooling due to the supercritical fluid evaporation.

Further advantages of the PGSS process [5] are: solvent-free products; low consumption of carbon dioxide; the possibility of treating thermo-labile materials; a wide range of potential applications, since the solubility of compressed gases in liquids and solids is often high.

So far, PGSS has been used to produce glycerides [5], pharmaceutical compounds like nifedipine, felodipine, dihydropyridine, fenofibrate [5–7] and polymers [8]. Recently, patents have been proposed (a review is presented in [4]) to obtain microcapsules with polymeric shells by PGSS and/or its variations.

A fairly general experimental knowledge of the effects of the operative parameters on particle properties (size, shape, porosity, morphology) is not available yet, but some correlations have been proposed [5–10]. It seems that an increase of the mixing unit pressure results in smaller particle size, but sometimes [8] particle size showed no dependency on this parameter. Particle size was found to increase monotonically with respect to the spray temperature [5,9], and also with respect to the nozzle diameter [8].

Different kinds of particle morphologies have been recognized, such as porous structures, spheres, sponges, fibres [6,8–10] but explanations on which formation mechanism should be related to each specific structure are still hypothetical. Empirical correlations to determine the particle morphology and bulk density as a function of the process conditions have been obtained for polyethyleneglycol-carbon dioxide systems [9,10].

Theoretical investigation of PGSS has just begun and few papers have been published to date in this area. Nevertheless, it is clear that a rational understanding can be useful in improving the PGSS process. Fundamental modeling of PGSS physics is particularly essential to the design of particles with specific characteristics. However, an exhaustive description of the PGSS process demands the investigation of many different fields and phenomena, including supercritical fluid thermodynamics, jet/spray hydrodynamics, droplet fluid dynamics, crystallization kinetics, bubble formation and droplet coalescence. In a schematic way, the overall investigation can be split into the following parts/steps:

1. thermodynamics;
2. nozzle hydrodynamics and atomization;
3. isolated droplet fluid dynamics, evaporation and solidification;
4. behaviour of the droplets ensemble in the spray, accounting for the droplet interactions and coalescence phenomena.

Thermodynamics modeling is required to calculate the "initial condition", i.e. the mixture composition for a given temperature and pressure in the mixing vessel; it is necessary also in the next steps, for example, to estimate the driving force for the energy and mass transfer. Such thermodynamics information is often provided in terms of melting point temperature curve as a function of the carbon dioxide pressure or in terms of carbon dioxide solubility isotherms. Investigations on the PGSS thermodynamics have been performed by Knez [8] and by Elvassore et al. [11]. Both these authors measured solubility curves and melting point temperature curves, obtaining similar results. Particularly, the melting point temperature was found to decrease when increasing the carbon dioxide pressure, until a minimum in the melting point temperature was reached; afterwards, the melting point temperature was increasing together with the carbon dioxide pressure. Besides, Elvassore et al. [11] reproduced experimental data imposing thermodynamical equilibrium conditions and using the Perturbed Hard-Sphere Chain