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Modeling of fluorinated tetraphenylporphyrin nanoparticles size design via rapid expansion of supercritical solution

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ABSTRACT

Modeling of rapid expansion of supercritical solution (RESS) for an organic fluorinated tetraphenylporphyrin (TBTPP) was carried out applying mass, energy, momentum analogies and appropriate numerical technique. The results of RESS validated model demonstrated that increasing the pre-expansion temperature from 373 to 450 K produced 67% larger particles diameter due to the effect of higher growth mechanisms on materials agglomeration. On the contrary, higher pre-expansion pressure (from 187 to 280 bar) led to 14% smaller particles diameter. The numerical data indicated reducing nozzle diameter from 200 to 25 μm resulted in 67% decreased particle diameter. Furthermore, 70% smaller particle sizes were obtained applying 98% lower expansion chamber pressure. Numerical results showed that operation of nozzle with addition of a capillary decreased the average particle diameter by 32%.

1. Introduction

Supercritical fluids (SCFs) have been shown to be effective solvents for applications in chemical, petrochemical, pharmaceutical and environmental processes. SCFs have superior mass transfer characteristics due to their liquid-like densities, gas-like viscosities and diffusivities at least an order of magnitude higher than liquid solvents at subcritical operating conditions. Further, the solvent density, and hence the solvent effectiveness, can be controlled by small changes in temperature and pressure [1,2]. SCFs have been proposed as media to produce nanomaterials. Particularly, the mix of gas-like and liquid-like properties can be useful in many applications related to nanotechnology such as nanocatalyst synthesis [3]. Carbon dioxide is usually preferred as a supercritical fluid, because it is non-toxic and non-flammable has a low critical temperature of 304.4 K and a moderate critical pressure of 72.8 bar. However, ammonia, alcohols, light hydrocarbons and water have been proposed, among the others, for nanomaterials production at supercritical conditions. A possible general classification of SCF based nanoparticles generation techniques can be proposed according to the role played by the SCF in the process. Indeed, SCFs have been proposed as solvents, solutes, anti-solvents and reaction media [4].

One of the applications of SCFs as solvent is in the RESS process. RESS is one of the novel, attractive, and relatively simple developing techniques for nanoparticles synthesis. This process has different and unique advantages; producing very fine particles with the same and narrow size distribution, controllability of particle size, high purity of particles without solvent residual.

1.1. RESS technology

The density of a supercritical fluid, which contains a dissolved solute, decreases dramatically upon expansion across a nozzle. As a result, the equilibrium mole fraction of a dissolved low-vapor pressure compound drops from values around 1 mol% by several orders of magnitude [5–7]. The rapid expansion of supercritical solutions (RESS) consists of the saturation of the supercritical fluid with a solid substrate; then, the depressurization of the solution through a heated nozzle into a low pressure chamber produces a rapid nucleation of the substrate in form of very small particles that are collected from the gaseous stream. The morphology of the resulting solid material, crystalline or amorphous, depends on the chemical structure of the material and on the RESS parameters (temperature, pressure drop, impact distance of the jet against a surface, nozzle geometry, etc.) [8]. The very fast release of the solute in the gaseous medium should assure the production of very small particles. This process is particularly attractive due to the absence of organic solvents.

For almost 20 years now, this pressure-induced phase separation technique (typically referred to as rapid expansion of supercritical solutions, i.e. RESS) has been investigated for producing very small (from micron- to nanosized) particles. Researchers have evaluated RESS for its ability to control particle size, particle size distribution,

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Nomenclature

A	cross-section area of nozzle (m^2)
A_M	coefficient (–)
AAE	average absolute error (m)
ARE	average relative error (–)
a	Peng–Robinson coefficient (bar m^6/mol^2)
b	Peng–Robinson coefficient (m^3/mol)
C_v	specific heat capacity at constant volume (J/mol K)
d_1	outlet nozzle diameter (m)
d_p	particle diameter (m)
D_{AB}	diffusivity coefficient (m^2/s)
E	coefficient in solubility equation (–)
F	coefficient in solubility equation (m^3/mol)
f_{fric}	friction factor (–)
J	rate of crystallization mechanisms (#/s m^3)
j	number of data (–)
k	Boltzmann's constant (1.38×10^{-23}) (J/K)
Ma	Mach number (–)
M_W	molecular mass (g/mol)
N_A	Avogadro number (6.02×10^{23}) (#/mol)
n_{crit}	number of molecules in a critical nucleus (#/m^3)
N_P	number density related to particles (#/m^3)
P	pressure (bar)
PE	probable error (m)
$\dot{q}$	heat flux (W/m^2)
R	gas constant (J/mol K)
r	radius (nozzle or particle) (m)
r_1	nozzle outlet radius (m)
S	supersaturation (–)
T	temperature (K)
t	time (s)
u	bulk fluid velocity (m/s)
V	molar volume (m^3/mol)
Y	dimensionless mole fraction (–)
y	mole fraction (–)
z	distance from nozzle inlet (m)
z_{M0}	coefficient (–)

Greek symbols

α	Peng–Robinson coefficient (–)
β	coefficient (–)
μ	viscosity (kg/m s)
θ	cone angle (rad)
σ	solid–fluid interfacial tension (N/m)
π	constant (3.14) (–)
ρ	molar density (mol/m^3)
φ_p	volume fraction (–)
γ	ratio of heat capacities (c_p/c_v) (–)
υ	molecular volume (m^3/mol)
ω	reference grow rate (s^{-1})
ξ	coefficient of effectiveness (–)

Subscripts

o	initial and/or stagnant condition
1	nozzle outlet condition
2	solute
3	before shock wave
4	after shock wave
crit	critical condition
cond	condensation mechanism
coll	collision
exp	experimental
exp-ch	expansion chamber
nucl	nucleation mechanism
m	molecular/of one molecule
mod	model data
2*SM*	related to the 2-step model
ref	reference
tot	total
M	Mach disk

Superscripts

B	Brownian motion
*	equilibrium condition

and product morphology through changes in operating conditions and nozzle geometry [9–20].

Clearly, the controllability of particle size and morphology is a key factor for the commercialization of a comminution process such as RESS. In this regard, some of the early publications have focused on the relationship between nozzle geometry and processing variables, and the particle size and morphology via applied numerical calculations and computer modeling [21–23]. While most authors were working on qualitative agreement (i.e. trends) between results from their numerical work and those found in experiments, only a few attempted to achieve quantitative agreement between numerical and experiments [10,11,18,24], which proved to be a demanding task for many years to come. The results from a dozen of different authors have been published in numerous papers with convincing and well-founded conclusions, as long as they were understood independently from the results in other papers [20,25].

Recently, RESS was also used to consistently produce nanoparticles (58 ± 16 nm) of a fluorinated tetraphenylporphyrin such as TBTPP (5,10,15,20-tetrakis(3,5-bis (trifluoromethyl)phenyl)porphyrin) from solutions in CO_2 [26]. Beside the aforementioned organic compound, no other group has yet to report the use of RESS for producing organic nanoparticles. Still unanswered is the question as to why RESS can be used to produce nanoparticles from TBTPP, but not from many other organic compounds that have been investigated. For organic particles produced via RESS, there is lack of fundamental knowledge on how the physical and chemical properties of the solute affect the particle growth. RESS modeling work from several groups [11,19,27] all predict that only nanoparticles are formed up to the Mach disk, but that the particles grow by coagulation into submicrometer and micrometer sizes downstream of the Mach disk in the transonic and subsonic free-jet regions.

However, once the conclusions of different authors are surveyed, some puzzling contradictions and incompatibilities start to emerge. It is believed that the weaknesses and systematic errors, even in some of the most intricate models, can be identified rather efficiently via a comparison of advanced and quantitative modeling work using a generalized model that is introduced in this study. Therefore, simulation of RESS for the production of TBTPP nanoparticles was the main objective of this research utilizing a mathematical model in order to investigate the effective parameters on the nanosized particle synthesis and design. Optimization of important variables affecting the particle size, with the application of the validated model, eliminates any further time consuming and costly experiments.

2. Model formulation

RESS process has three main units: (1) extraction, (2) pre-expansion, and (3) precipitation shown in Fig. 1. RESS equipment is composed of the following items: (1) carbon dioxide cylinder, (2)