

# Solidification of Precirol<sup>®</sup> by the expansion of a supercritical fluid saturated melt: From the thermodynamic balance towards the crystallization aspect

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## Abstract

The following article presents the thermodynamic and crystallization aspects of the solidification through expansion of a melted fat, Precirol<sup>®</sup>, previously saturated with supercritical CO<sub>2</sub>. A simplified macroscopic energy balance is used to understand the mixture behaviour during expansion. It allows the quantification of the CO<sub>2</sub> to be added to the mixture in order to control the state and the temperature of the compound at the outlet of the expansion device. The required physico-chemical parameters were determined experimentally. The variation of the operating parameters appearing in the energy balance revealed three regions/areas of possible states for the expanded lipid: solid, molten or solid–liquid equilibrium. This, together with the outlet temperature could be tuned by varying not just the inlet or saturation conditions, but also the ratio of supercritical CO<sub>2</sub> to be expanded with the saturated fat. As for the crystallization aspect, the variation of chemical potential, which is the driving force, was calculated; the critical radius of nuclei and the nucleation rates were estimated according to the classic melt media theory. The main assumptions were that solidification occurred mainly at atmospheric pressure and that only homogeneous nucleation took place. The orders of magnitude obtained put in light the necessity to determine precisely the viscosity of the melt saturated fat and the solid/melt interfacial tension.

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**Keywords:** Supercritical fluids; Thermodynamics process; Crystallization; Particle formation; Nucleation rate; Fats

## 1. Introduction

Supercritical fluids and especially supercritical CO<sub>2</sub> are an attractive substitute of an organic solvent for the generation of micro or nanoparticles with controlled size and morphology [1–2]. Compared to classical powder generation processes they include an additional varying parameter, the pressure, which greatly influences the density of the supercritical fluid. So, the supercritical technology uses the variation of both pressure and temperature to design particle size and morphology.

Among the main principles involved in supercritical processes, one is based on the use of the supercritical fluid as a solute. For instance, the process known as PGSS<sup>TM</sup>, for Particles from Gas Saturated Solutions, is based on this principle [3]. It involves the dissolution of a dense gas into a liquid or a molten solid until its saturation. This saturated compound is then

expanded through a nozzle where the cooling due to the pressure drop generates dry powder. In a varying process both the saturated solution and the supercritical fluid are expanded [4]. These processes are easy to perform and can be applied to a large number of compounds since dense gases are quite soluble in liquids or melted solids. It has been shown to be effective for the generation of particles from various compounds such as polymers, fats, and pharmaceuticals, in addition to composite particles [5–6]. In such processes, the Joule Thomson effect caused by the expansion induces a drastic undercooling, which induces solidification of the melted compound. As the undercooling amplitude is a key-factor for crystallization mechanisms, it is necessary to model it in order to control the process. So far, the literature has not yet dug deep enough into the understanding of these particle formation processes. Elvassore et al., considered the thermodynamic aspect of PGSS<sup>TM</sup> applied to pure tristearin or a 50:50 mixture of phosphatidylcholin and tristearin [7]. From the calculation of the enthalpy variation upon the expansion step, the authors determined the final temperatures that were reached. They chose to consider the expansion of a saturated solution without any excess

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**Nomenclature**

|                   |                                                                                                       |
|-------------------|-------------------------------------------------------------------------------------------------------|
| $a$               | attraction parameter in Peng–Robinson equation of state ( $\text{Pa m}^6/\text{mol}^2$ )              |
| $A$               | cross section area ( $\text{m}^2$ )                                                                   |
| $b$               | van der Waals co volume ( $\text{m}^3/\text{mol}$ )                                                   |
| $C_p$             | isobaric mass heat capacity ( $\text{J}/(\text{kg K})$ )                                              |
| $d_0$             | molecular diameter ( $\text{m}$ )                                                                     |
| $E_v$             | activation energy ( $\text{J}$ )                                                                      |
| $f_L$             | lipid–liquid fraction after expansion, quantity of liquid on the total lipid expanded                 |
| $G$               | growth rate ( $\text{m/s}$ )                                                                          |
| $h$               | mass enthalpy ( $\text{J/kg}$ )                                                                       |
| $H$               | molar enthalpy ( $\text{J/mol}$ )                                                                     |
| $J$               | nucleation rate ( $\text{nuclei}/\text{m}^3/\text{sec}$ ) or ( $\text{nuclei}/\text{cm}^3/\text{s}$ ) |
| $k$               | Boltzmann's constant, $1.38 \times 10^{-23}$ ( $\text{J/K}$ )                                         |
| $K$               | constant of the Stephan–Shapski–Turnbull's law                                                        |
| $m$               | weight ( $\text{kg}$ )                                                                                |
| $\dot{m}$         | mass flow rate ( $\text{kg/s}$ )                                                                      |
| $P$               | pressure ( $\text{Pa}$ )                                                                              |
| $r$               | solubility ratio ( $\text{kg}_{\text{CO}_2}/\text{kg}_{\text{Precirol}}$ )                            |
| $r_c$             | critical radius of nuclei ( $\text{m}$ )                                                              |
| $R$               | perfect constant gas $8.314 \text{ J}/(\text{kg mol})$                                                |
| $s_k$             | mass entropy of the state $k$ , $\text{J}/(\text{mol K})$                                             |
| $S$               | mass ratio of dissolved $\text{CO}_2$ compared to the total $\text{CO}_2$ ( $\text{kg}/\text{kg}$ )   |
| $S_k$             | molar entropy of the state $k$ ( $\text{J}/(\text{kg K})$ )                                           |
| $T$               | temperature ( $\text{K}$ )                                                                            |
| $T_F$             | final temperature reached by the system at the nozzle outlet ( $\text{K}$ )                           |
| $T_{\text{melt}}$ | normal melting point ( $\text{K}$ )                                                                   |
| $u$               | velocity ( $\text{m/s}$ )                                                                             |
| $v_L$             | specific volume ( $\text{m}^3/\text{kg}$ )                                                            |
| $v_o$             | molecular volume ( $\text{m}^3/\text{mol}$ )                                                          |
| $V$               | volume ( $\text{m}^3$ )                                                                               |
| $w_{\text{CO}_2}$ | mass ratio of $\text{CO}_2$ into the mixture before expansion                                         |

**Greek letters**

|          |                                                        |
|----------|--------------------------------------------------------|
| $\alpha$ | shape factor                                           |
| $\beta$  | shape factor                                           |
| $\gamma$ | interfacial tensile strength ( $\text{J}/\text{m}^2$ ) |
| $\eta$   | dynamic viscosity ( $\text{kg}/(\text{m s})$ )         |
| $\mu$    | driving force ( $\text{J/kg}$ )                        |
| $\rho$   | density ( $\text{kg}/\text{m}^3$ )                     |
| $\omega$ | acentric factor                                        |
| $\Delta$ | properties variation                                   |

**Subscripts**

|       |                                                 |
|-------|-------------------------------------------------|
| atm   | atmospheric pressure and temperature properties |
| $c$   | critical                                        |
| crist | crystallization                                 |
| $d$   | divergent diss, dissolution                     |
| $F$   | final state at the nozzle outlet                |
| in    | inlet conditions                                |
| $L$   | liquid phase                                    |

|      |                                       |
|------|---------------------------------------|
| melt | melting properties                    |
| out  | outlet conditions                     |
| $S$  | solid phase                           |
| SC   | supercritical conditions              |
| SL   | refer to solid–liquid surface tension |
| $V$  | gaseous state                         |

**Superscripts**

|    |            |
|----|------------|
| ®  | Registered |
| TM | Trade mark |

$\text{CO}_2$  in the vessel. The macroscopic energy balance was solved, based on both experimental methods, using apparatus like differential scanning calorimetry (DSC), to measure the calorimetric parameters of the lipids, and a theoretical approach, using the perturbed hard sphere chain theory model (PHSCT) to estimate the solubility of  $\text{CO}_2$  in the lipid. On the pressure–temperature phase diagram of the binary fat/ $\text{CO}_2$ , three different areas were distinguished, corresponding to three different final states of the fat: solid, solid/liquid equilibrium or liquid. The authors noticed that the area that led to solid nanoparticles was directly linked to the heat of solidification of the fat. In addition, the authors reported some variations between the heat of fusion and the heat of formation (or crystallization) for the pure compound processed by PGSS<sup>TM</sup> or not. The very fast crystallization of PGSS<sup>TM</sup> from a melt is responsible for the observed variations, due to the modification of the structure of the lipid. Li and Matos, did the most complete model for particle formation by PGSS<sup>TM</sup>, on the hydrogenated palm oil/ $\text{CO}_2$  system [8]. The authors considered the influence of the nozzle hydrodynamic on particle size as well as the thermodynamic and crystallization aspects. Most of the parameters required for the modelling were estimated by calculation, except calorimetric parameters that were measured via a DSC apparatus. They considered the expansion in steady state conditions of the mixture: saturated melt phase and the supercritical  $\text{CO}_2$ . The model aimed to determine the profiles of pressure, temperature, densities, volume fraction of  $\text{CO}_2$  in the melt phase or in the whole system, as well as the mean particle diameter along the nozzle. The volume fraction of excess  $\text{CO}_2$  that was expanded was calculated along the nozzle, and was initialized to 0.95 at the inlet, based on a their previous experiments [9]. The crystallization was considered, taking into account nucleation, condensation and coagulation of the solute and assuming a homogeneous nucleation, rather than the classical heterogeneous one, since crystallization processes using supercritical fluids are very fast, and therefore far from equilibrium conditions. The authors reached typical values for critical nucleus, particle average size and nucleation rates on the basis of assumptions from molten metal crystallization. These authors showed that the mean particle diameter depends directly on both the critical nucleus volume and nucleation rates that are drastically affected by the undercooling. From a hydrodynamic point of view, the results show that the nozzle diameter has a moderate influence on the size of the particles obtained; because coagu-

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