

MODELING OF PARTICLE FORMATION FROM A GAS-SATURATED SOLUTION PROCESS

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Assuming a steady, one-dimensional, inviscid and non-equilibrium two-phase flow with an annular pattern, Hydrogenated Palm Oil (HPO) particle formation from a gas-saturated solution (PGSS) process using supercritical carbon dioxide in a capillary nozzle is modeled using mass, momentum and energy conservation equations for the two phases – a (virtually pure) CO₂ supercritical fluid phase and a HPO-rich liquid phase. The model gives the profiles along the nozzle for the temperature, pressure, density and velocity of each phase. Also, the mean particle diameters are calculated under different pre-expansion conditions and compared with experimental results. Because the temperature of the HPO-rich phase changes little, from the simulated data the atomization mechanism for PGSS at the exit of the nozzle is proposed instead of crystallization.

INTRODUCTION

The PGSS process is a promising technique for the production of fine powder under mild conditions. It has wide applications because the solubilities of compressed gases in liquids or solids (such as polymers) are usually high, even much higher than the solubilities of the same liquids or solids in the compressed gas phase. Jung [1] gave a very complete review about this topic including patents and publications. Yet, the mechanism followed for the particle production in the nozzle whether by crystallization or atomization is still uncertain. Therefore, it is much useful the implementation of a physically sound and fluid-mechanical based model for the PGSS process.

In this work we develop such a model considering hydrodynamic equations of two phases for a PGSS process and resolve them under some simplified conditions to simulate the profiles for pressure, densities, temperatures and velocities along the nozzle. Considering the profiles for the temperatures and velocities of both phases, we deduce the mechanism for the drop formation in the PGSS process. With this mechanism we calculate the particle diameters of HPO produced under different process conditions.

MATHEMATICAL MODEL

Figure 1 shows schematically a typical nozzle used in a PGSS process. The device consists of a converging inlet followed by a straight capillary with diameter d_{nozzle} . The mixed flow of CO₂ and HPO in the nozzle is assumed as a one-dimensional, inviscid and non-equilibrium two-phase flow - supercritical CO₂ phase (phase 1) and mixed CO₂ and HPO phase (phase 2), as shown in the enlarged section of Figure 1. Generally, temperatures (T_1 and T_2), velocities (u_1 and u_2) and densities (ρ_1 and ρ_2) of the two phases are different while pressure P is the same, as required by the mechanical equilibrium condition.

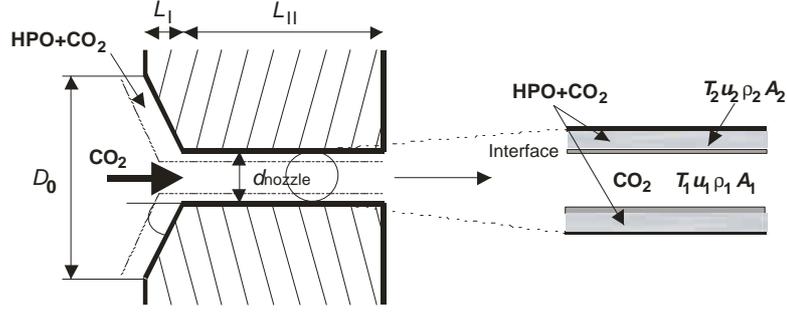


Figure 1 : Typical nozzle used in PGSS processes.

Neglecting the precipitation phase of HPO, the governing equations for mass, momentum and energy conservation equations for the two phases for a steady state PGSS process are:

$$\frac{d(\rho_1 M_1 u_1 A_1)}{dz} + \frac{d(\rho_2 M_2 u_2 A_2 w_c)}{dz} = 0 \quad (1)$$

$$\frac{d(\rho_1 M_1 u_1 A_1)}{dz} + \frac{A_1 dP_1}{dz} + \tau_{w1} S_1 + \tau_{12} S_{12} - \rho_1 M_1 g A_1 + S_{12} u_{12} \left(\epsilon_0 + \frac{m_{12}}{2} \right) = 0 \quad (2)$$

$$\frac{d[\rho_1 M_1 u_1 (h_1 / M_1 + u_1^2 / 2) A_1]}{dz} + \frac{d(q_{w1})}{dz} + \frac{d(q_{12})}{dz} + \frac{d(q_c)}{dz} - \rho_1 M_1 u_1 g A_1 = 0 \quad (3)$$

$$\frac{d(\rho_2 M_2 u_2 A_2)}{dz} - \frac{d(\rho_2 M_2 u_2 A_2 w_c)}{dz} = 0 \quad (4)$$

$$\frac{d(\rho_2 M_2 u_2 A_2)}{dz} + \frac{A_2 dP_2}{dz} + \tau_{w2} S_2 - \tau_{12} S_{12} - \rho_2 M_2 g A_2 - S_{12} u_{12} \left(\epsilon_0 - \frac{m_{12}}{2} \right) = 0 \quad (5)$$

$$\frac{d[\rho_2 M_2 u_2 (h_2 / M_2 + u_2^2 / 2) A_2]}{dz} + \frac{d(q_{w2})}{dz} + \frac{d(q_L)}{dz} - \frac{d(q_{12})}{dz} - \frac{d(q_c)}{dz} - \rho_2 M_2 u_2 g A_2 = 0 \quad (6)$$

In the equations above, M_i is the molar mass of phase i and w_c is the mass fraction of CO_2 in phase 2. S_i is the perimeter of phase i and S_{12} is the perimeter of the interface. In addition, t_{wi} is the friction force produced by the nozzle wall, q_{wi} is the heat transfer rate from nozzle surface, q_{12} is the heat transfer rate between the two phases, q_c is the heat transfer rate due to the CO_2 mass transfer, and q_L is the heat rate for particle production. In Equations (2) and (5), ϵ_0 is the irreversible Reynolds flux per unit area of the interface, and m_{12} is the rate of vaporization per unit area of the interface, determined according to Wallis [2]. The Peng-Robinson equation of state (PR-EOS) with conventional mixing rules is chosen to describe the mixture's nonideality and also to calculate the required thermodynamic properties of supercritical CO_2 .

The two-phase flow pattern through the nozzle is assumed as an annular flow, where a mixed phase layer, that contacts the nozzle wall, and a core, that essentially is supercritical CO_2 , have, respectively, cross-sectional areas A_2 and A_1 . They are related to the nozzle cross-sectional area A by β , the cross-sectional area fraction of phase 1.

NUMERICAL RESOLVING

To solve the conservation equations further simplifications are required. For example, we take $\beta = 0.52$ because it matches the experimental CO_2 flow rate [3]; the precipitation of HPO in the nozzle is omitted; the irreversible Reynolds flux is neglected; in the converging region of the nozzle, the mixture of CO_2 and HPO is taken as adiabatic and non-frictional; the two velocities are equal initially; the PR-EOS binary interaction parameter for CO_2 and HPO is taken as that of the pseudobinary system $\text{CO}_2 + \text{PDDO}$ [4]. With the assumptions above and for $d_{\text{nozzle}} = 25 \mu\text{m}$, nozzle length $L_{\text{II}} = 250 \mu\text{m}$, pre-expansion temperature 353 K, pre-expansion pressure 180 bar, temperature of nozzle wall 353 K, HPO melting point 333 K, and Fanning friction coefficient 0.0125 for short capillary nozzle, we used the Runge-Kutta-Fehlberg algorithm to obtain the total pressure, the solubility of CO_2 in HPO, temperatures, densities and velocities of the two phases by adjusting the initial velocity to satisfy the choked flow condition of the CO_2 phase. Figures 2 and 3 give the profiles along the nozzle for, respectively, total pressure and temperature, and velocities for each phase. These figures indicate that the temperature of phase 2 changes very little and that there is a remarkable difference in the velocities of the two phases in the nozzle.

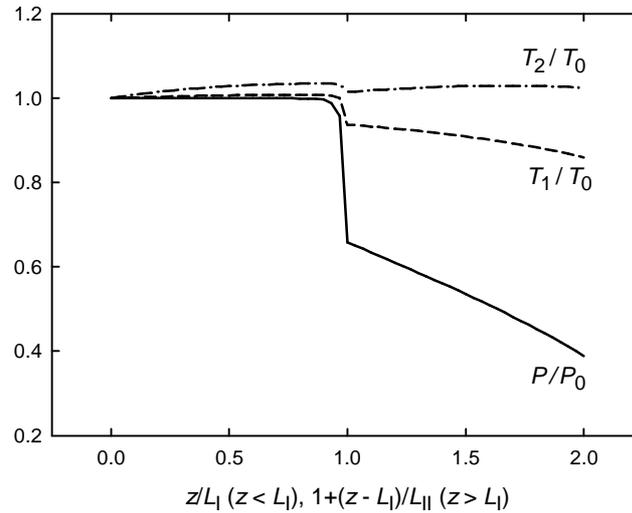


Figure 2 : Profiles for the total pressure and temperatures of each phase. Subscript 0 indicates pre-expansion conditions; L_{II} is the nozzle length.

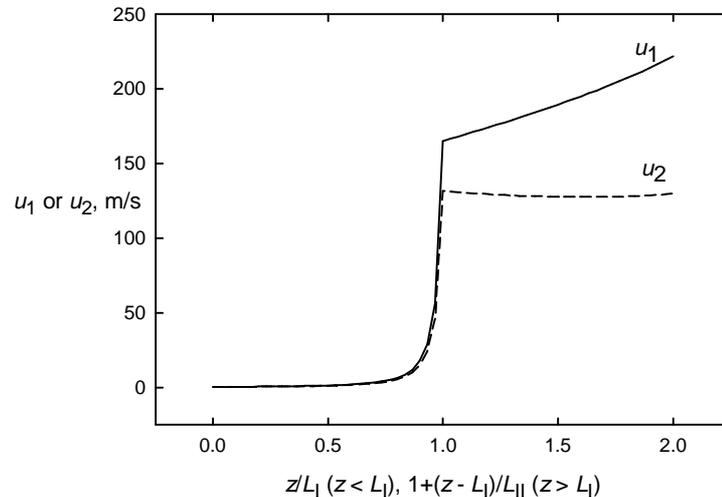


Figure 3 : Profiles for the velocity of each phase.

ATOMIZATION AND MEAN DIAMETER

Atomization processes, particularly for air and burning fuels such as diesel oil, are widely studied. For mean droplet diameter, the classical formulae include the Hinze relation and the Nukiyama-Tanasawa formula. For an atomization process, formulae developed later such as by Jasuja describe well the Sauter mean diameter [5].

For the case presented here, simulation shows that the temperature of the HPO-rich phase changes very little. This means that solidification plays a little role in the particle formation. Yet, the relative velocities of the two phases change along the nozzle, and the difference becomes more obvious along the flow direction. Therefore, for the process studied here, we consider atomization as the mechanism for particle formation. The mean particle diameters can therefore be calculated from Jasuja's formula,

$$d_{32} = 0.17 \left(\frac{\sigma}{\rho_1} \right)^{0.45} \left(\frac{1}{u_{12}} \right)^{0.9} \left(1 + \frac{L}{G} \right)^{0.5} d_{\text{nozzle}}^{0.55} + 0.015 \left(\frac{\eta_m^2}{\sigma \rho_2} \right)^{0.5} \left(1 + \frac{L}{G} \right) d_{\text{nozzle}}^{0.5} \quad (7)$$

In Equation (7), the interfacial tension s is calculated from data for the supercritical CO₂/stearic acid system [5]. The relative velocity, $u_{12} = u_1 - u_2$, and the mass ratio of phase 2 to phase 1, L/G , are obtained from the conservation equations. In Equation (7) η_m is the viscosity of the HPO-rich phase, estimated from the viscosity of supercritical CO₂ at the mixture's temperature and pressure and from the viscosity of liquid HPO.

Table 1 and Figures 4 to 6 show the results calculated from Equation (7). For comparison, Table 1 presents also experimental results obtained under similar conditions.

We see from Table 1 that experimental results are much larger than the mean diameters obtained from the simulation. Coagulation is likely to occur in the free-jet region of the nozzle because our simulated results are available only at the exit of the nozzle.

The dependence of the mean diameters with the pre-expansion pressure shown in Table 1 and Figure 4 is in qualitative agreement with the experimental results [3] where a slight decrease of the diameters is observed. Figure 5 gives the effect of the pre-expansion temperature on the mean diameter. It shows that a decrease on the pre-expansion temperature reduces the particle diameter, in the temperature range reported here. Figure 6 shows the effect of the nozzle dimension on the mean diameter. The particle diameter first decreases with nozzle length but, at about 600 micron, it begins to slightly increase with the nozzle length for a given nozzle diameter. Figures 5 and 6 also reveal that the pre-expansion temperature and the nozzle length influence little the particle diameter for the ranges studied here.

Table 1 : Atomization diameters for HPO produced with supercritical CO₂ with a pre-expansion temperature $T_0 = 353$ K.

| Pre-expansion Pressure P_0 , MPa | HPO Particle Diameter | |
|--|--------------------------|----------------|
| | d_{32} , μm | |
| | Jasuja's formula | Experiment [3] |
| 12 | 0.17 | 17.6 |
| 14 | 0.14 | 21.8 |
| 16 | 0.13 | 9.7 |
| 18 | 0.11 | 16.8 |

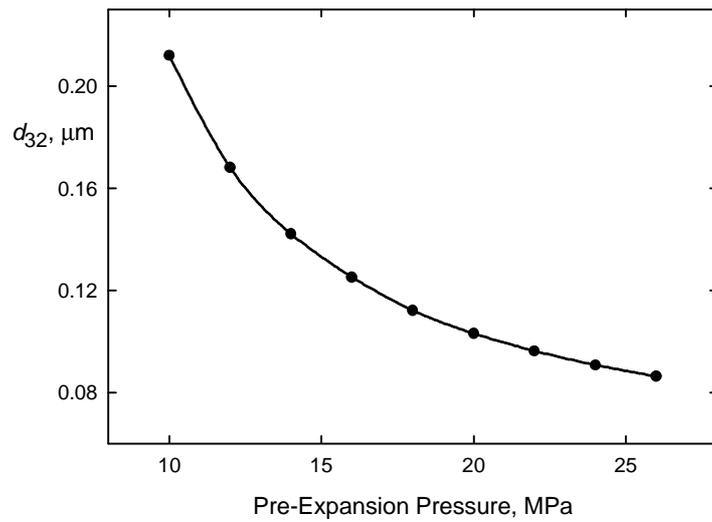


Figure 4 : Effect of pre-expansion pressure on the mean diameter of HPO particles at the nozzle exit.

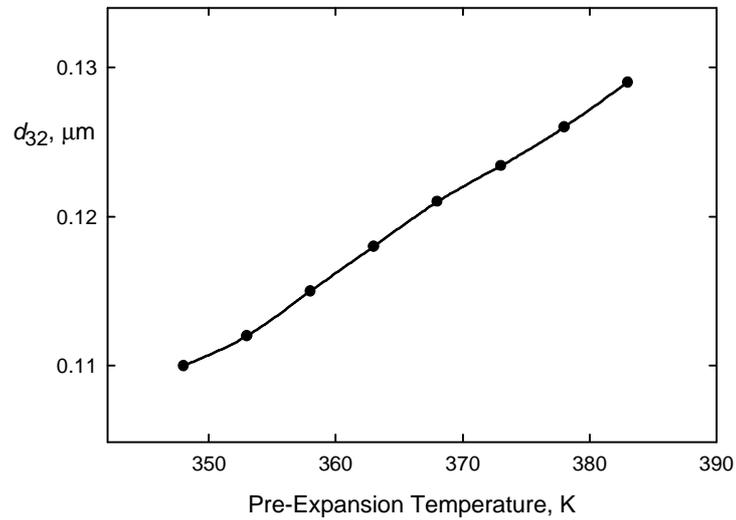


Figure 5 : Effect of pre-expansion temperature on the mean diameter of HPO particles at the nozzle exit.

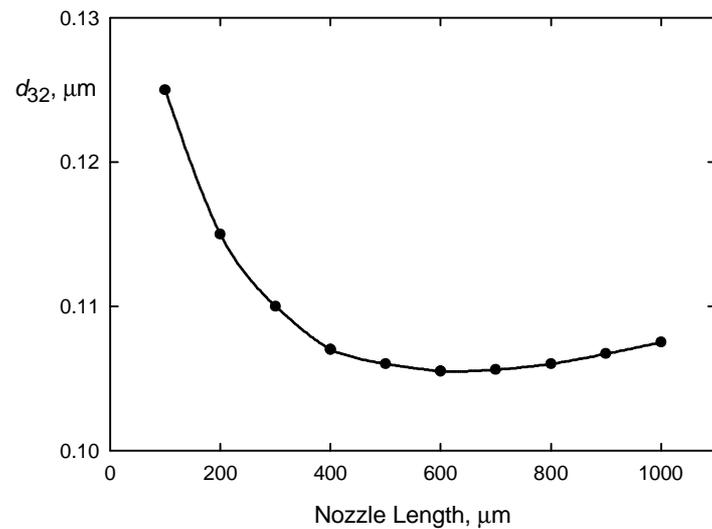


Figure 6 : Effect of the nozzle dimension (for $d_{\text{nozzle}} = 25 \mu\text{m}$) on the mean diameter of HPO particles at the nozzle exit.

CONCLUSIONS

In this paper we present a general mathematical model to study a PGSS process by assuming a one-dimensional, inviscid and non-equilibrium two-phase flow and an annular flow pattern. Under some simplified assumptions, such as considering constant the ratio of the sectional-area of any phase to the total sectional-area, the general model can be solved numerically. The simulation results provide the temperatures, densities, velocities of the two phases and total pressure changes along the nozzle. Our results show that, at the exit of the nozzle, the supercooling of the HPO-rich phase is low while the relative velocity of the two phases is high. Accordingly, the atomization mechanism is proposed for the system studied here and the mean diameters are calculated in terms of existing formulae for the atomization process.

The calculated Sauter mean diameters have a similar trend with the pre-expansion pressure as the available experimental data. However, calculated results are about 100 orders of magnitude smaller than the experimental data. In further studies we shall consider the occurrence of coagulation at the post-expansion region. In the pre-expansion temperature range tested here, higher temperatures generate larger particles. There exists a nozzle length (about 600 micron), below which the particle diameter decreases and above which the particle diameter increases with the nozzle length. Our results show that both the pre-expansion temperature and the nozzle length influence little the particle diameter by the atomization mechanism.

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