

Droplet Dynamics in Supercritical Antisolvent Micronization Process

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Abstract. Supercritical antisolvent process (SAS) is one of the emerging processes for production of micro to nano size range particles. SAS is performed by atomization of a solution to produce droplets in a chamber filled with a gas at supercritical conditions. Solute precipitation occurs due to two-way mass transfer as the atomized droplet falls down in the chamber, producing solid particles. This two-way mass transfer includes diffusion of antisolvent into the droplet and simultaneous evaporation of the solvent into the antisolvent environment. As the antisolvent diffuses into the droplet, the solubility of solute in solvent decreases rapidly resulting in nucleation and then growth on existing nuclei. The aim of this work is to develop a mathematical model of the droplet moving in a supercritical carbon dioxide environment. The solvent chosen in this study is ethanol. The two film theory is used to calculate the mass transfer rates of carbon dioxide and solvent. Due to the mass transfer phenomena, the size of the droplet changes as it moves downwards in a chamber. The density of the droplet is also changing because its composition is changing. The droplet diameter, carbon dioxide mole fraction and moles of carbon dioxide & ethanol are calculated.

Keywords: Supercritical antisolvent process, Micronization, Mass transfer

1. Introduction

The supercritical antisolvent (SAS) process is a semi continuous precipitation technique that can be used to produce micrometric and nanometric sized particles with a better control of their particle size than conventional methods [1]. In SAS process, a supercritical fluid (SCF) and a liquid solution are continuously delivered to a high-pressure precipitator in which the SCF forms a solution with the liquid, inducing the precipitation of the dissolved solid. The most attractive characteristics of SAS are the possibility to control particle size and particle size distribution and to eliminate the solvent residue without post-processing of the produced powders.

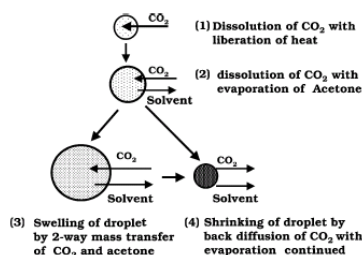


Fig. 1: Mass transfer phenomena in supercritical antisolvent process. Adapted from reference[4]

The supercritical antisolvent (SAS) process is used when a solute produced into fine particles is not soluble in the supercritical fluid. The fine particles are prepared by sudden reduction of the solubility [2] of the solvent when solution containing the issued materials and appropriate solvent is dissolved in supercritical solvent. The core principle (see Fig. 1) of the SAS process is to spray a solution in the antisolvent environment throughout a fine nozzle. Through this action, fine droplets are generated in the precipitator [3]. As soon as the drop comes in contact with surrounding supercritical fluid, the supercritical fluid is rapidly diffused into the drop. The drop is swollen by continuous 2-way mass transfer that is diffusion of

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supercritical fluid into drop and evaporation of solvent from drop surface to flow of supercritical fluid. The two-way mass transfer is very important factor for micronization. Because the SAS is a semi-continuous process, this process can obtain a higher supersaturation than that of the GAS which is batch process. As a result, the particles produced by this process have a very small size and narrow particle distribution.

2. Mathematical Model Formulation

Ethanol solution is sprayed by a nozzle in supercritical CO₂ where atomization occurs and fine droplets are formed. The initial size of the droplet depends upon the nozzle diameter and the initial velocity of the droplet in addition to the physical properties of the solvent, such as, density, surface tension and the viscosity. Four alternative equations are available for prediction of the initial size droplet [3]. The total number of moles of ethanol initially is calculated by the following equation.

$$N_e = \rho_e V$$

Where ρ_e is the molar density of ethanol and V is the volume of the droplet.

As the droplet moves downward in the CO₂ chamber, mass transfer from the droplet and into the droplet takes place. Carbon dioxide diffuses into the droplet and ethanol evaporates into the CO₂ environment. Now the droplet is a mixture of carbon dioxide and ethanol. Let d be the diameter of droplet during its flight, then the total number of moles of CO₂ and ethanol in the droplet is

$$N_t = N_c + N_e = \rho_m V$$

Where ρ_m is the molar density of the mixture and V is the volume of the droplet given by

$$V = \frac{1}{6} \pi d^3$$

The molar density of the mixture (CO₂ + ethanol) is calculated by Peng-Robinson equation of state.

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)}, \text{ where}$$

$$a_{T_c} = 0.45724 \frac{R^2 T_c^2}{P_c}, \quad b = 0.0778 \frac{RT_c}{P_c}, \quad a = a_{T_c} \alpha(T_R, \omega), \quad \alpha = \left[1 + \beta \left(1 - T_R^{1/2} \right) \right]^2,$$

$$\beta = 0.37464 + 1.54226\omega - 0.2699\omega^2$$

The droplet is a mixture of carbon dioxide and ethanol. Therefore, a mixing rule is applied to calculate the parameters in Peng-Robinson equation. According to the mixing rule,

$$a_m = \sum_{i=1}^n \sum_{j=1}^n x_i x_j a_{ij}, \quad b_m = \sum_{i=1}^n \sum_{j=1}^n x_i x_j b_{ij}$$

$$a_{ij} = (1 - k_{ij}) (a_i a_j)^{0.5}, \quad b_{ij} = (1 - l_{ij}) (b_i + b_j) / 2$$

Therefore, the diameter of the droplet at any time during its flight is calculated by

$$N_t = \rho_m \left(\frac{1}{6} \right) \pi d^3$$

$$d = \left(\frac{6N_t}{\pi \rho_m} \right)^{1/3}$$

d can be calculated if the total number of moles in the droplet at any time is known. To calculate the total number of moles in droplet at any time, number of moles of CO₂ diffused in droplet and number of moles of ethanol evaporated in to CO₂ environment should be known. Two film theory is used to calculate moles transferred into the droplet (CO₂ mole) and from droplet (ethanol mole) by the following equations.

$$dN_c = k_L (C_{L,c}^i - C_{L,c}) A \Delta t$$

$$dN_e = k_G (C_{G,e}^i - C_{G,e}) A \Delta t$$

Where dN_c is the number of moles of carbon dioxide diffusing into the droplet and dN_e is the number of mole of ethanol evaporated from the droplet in a time interval Δt . A is surface area of the droplet. Liquid phase and gas phase mass transfer coefficient are k_L and k_G respectively.

Liquid-phase mass transfer coefficient is calculated by penetration theory and gas phase mass transfer coefficient is calculated from the correlation of Hughmark [4].

$$k_L = \sqrt{\frac{4D_L}{\pi t_c}} = \sqrt{\frac{4D_L u}{\pi d}}$$

$$k_G = \frac{D_G}{d} \left(2 + 0.00187 N_{Re}^{0.779} N_{Sc}^{0.546} (dg^{0.333} D_G^{-0.667})^{0.116} \right)$$

The driving force for carbon dioxide diffusion is $(C_{L,c}^i - C_{L,c})$, where $C_{L,c}^i$ is the interfacial concentration of carbon dioxide at the liquid film and $C_{L,c}$ is the concentration of carbon dioxide in the droplet. Similarly the driving force for ethanol evaporation is $(C_{G,e}^i - C_{G,e})$. The concentration can be written as product of molar density and mole fraction. The mole fraction in the droplet can be calculated in each interval as mole of carbon dioxide and ethanol in the droplet in every interval is known. At $t = 0$, mole fraction of carbon dioxide is zero and mole fraction of ethanol is one. These values of mole fraction are used to calculate the mole of carbon dioxide diffused and mole of ethanol evaporated in first time interval, Δt . Therefore the composition of droplet is known after Δt and the droplet size can be calculated by the equation discussed earlier. For second time interval, the mole fraction of first interval is used to calculate the mole of CO₂ diffused and mole of ethanol evaporated and so on.

The liquid phase mass transfer coefficient depends on the velocity of the droplet. To calculate it, velocity of the droplet in each interval should be known. The velocity of the droplet is calculated by balancing three forces. These three forces are the weight of the droplet, buoyancy on the droplet and viscous friction. The following relation is obtained from the momentum equation for a single droplet:

$$\frac{dv}{dh} = \left(\frac{\rho_L - \rho_G}{\rho_L} \right) \left(\frac{g}{v} \right) - \frac{18\mu_G}{\rho_L d^2}$$

$$dh = v dt$$

$$\frac{dv}{dt} = \left(\frac{\rho_L - \rho_G}{\rho_L} \right) g - \frac{18\mu_G v}{\rho_L d^2}$$

Where ρ_L and ρ_G are the densities of the liquid (droplet) and gas phase (CO₂). The density of the gas phase is constant in all time intervals because the evaporation of the ethanol from the droplet into carbon dioxide environment will not change the gas density much. But the density of the droplet is changing in every interval as the droplet composition is changing. Therefore the density of the droplet (mixture of CO₂ and ethanol) is updated at each interval in all equations.

3. Results

The equations in the mathematical model outlined above are solved numerically by Runge-Kutta 4th order method and Newton-Raphson method in MATLAB version 7.1. The values of all parameters are calculated in each time interval. The total time of evaporation of droplet is taken as the time at which the 99 % of the ethanol is evaporated from the droplet to avoid computational error. The composition of the droplet and therefore, diameter of the droplet changes in the CO₂ chamber are calculated. The variation in the droplet diameter, carbon dioxide mole fraction, moles of carbon dioxide and moles of ethanol are shown below.

4. Conclusions

The diameter, mole fraction of carbon dioxide, moles of carbon dioxide and moles of ethanol are calculated with time. The diameter of the droplet first increases and then decreases. The increase in the diameter of the droplet is due to the diffusion of carbon dioxide into the droplet. The diameter of the droplet

decreases due to the back-diffusion of carbon dioxide and evaporation of ethanol. The mole fraction of carbon dioxide increases very rapidly and then becomes constant. The moles of carbon dioxide first increases and then decreases which implies that constant mole fraction of carbon dioxide means decrease in the total moles of the droplet. Moles of Ethanol are also plotted against time. Ethanol moles in the droplet are decreasing continuously due to the continuous evaporation of solvent.

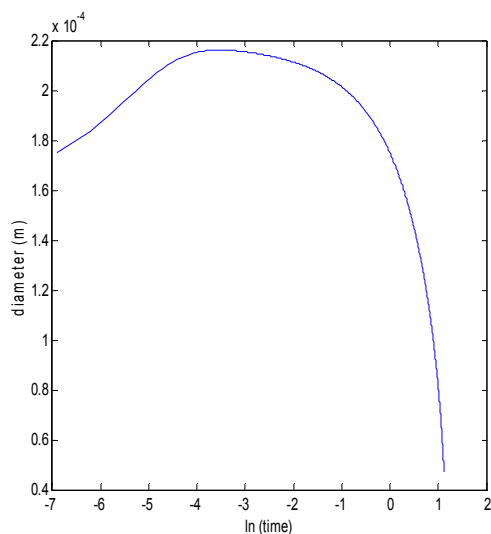


Fig. 2: Diameter vs time at 333.15 K and 100.7 bar.

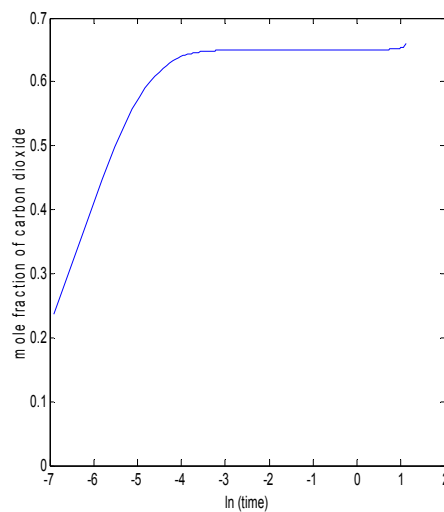


Fig. 3: Carbon dioxide mole fraction versus time at 333.15 K and 100.7 bar.

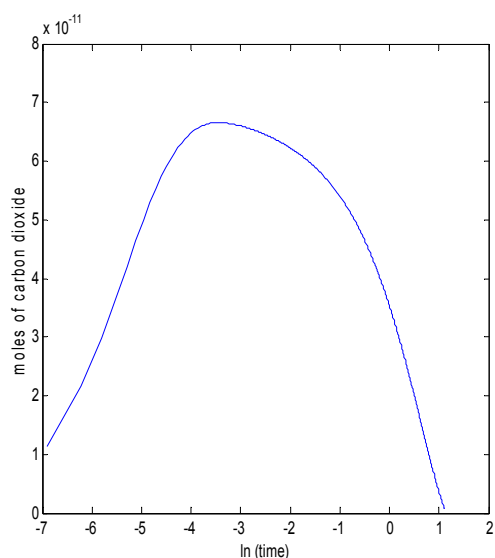


Fig. 4: Moles of Carbon dioxide versus time at 333.15 K and 100.7 bar.

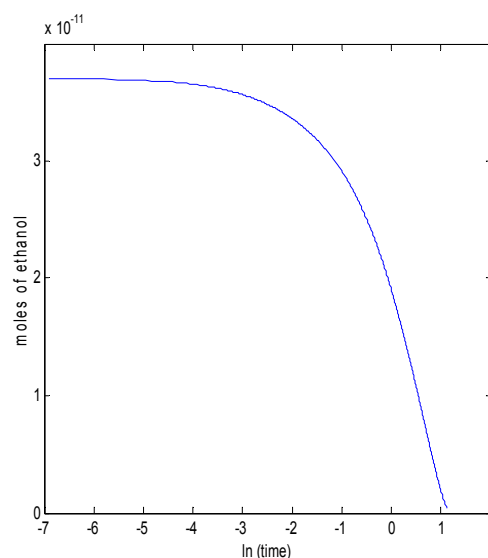


Fig. 5: Moles of Ethanol versus time at 333.15 K and 100.7 bar.

5. References

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