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Modeling of Droplet Composition in Supercritical Antisolvent Process: Part A

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***Abstract*—Supercritical fluids (SCF) are the fluids at the temperature and pressure above the critical temperature and critical pressure respectively. One of the important applications of these fluids is the precipitation of micro to nano range of particles. 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 rate 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.**

***Index Terms*—Supercritical, antisolvent, carbon dioxide, ethanol, droplet.**

I. INTRODUCTION

The supercritical antisolvent (SAS) process is a semicontinuous 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.

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 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 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.

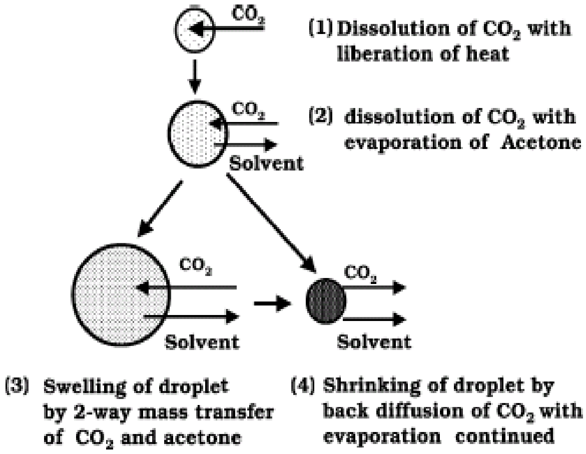

Fig. 1. "Mass transfer phenomenon in supercritical antisolvent process" [4].

II. MATHEMATICAL MODELLING

In this work, a model is developed to predict the composition of ethanol and carbon dioxide and size of droplet in SAS process. The droplet is moving through CO_2 continuum and mass transfer take place to and from the droplet which led to the supersaturation and then fine particle of solute.

Supercritical antisolvent (SAS) crystallization process involves atomization of the solution in an antisolvent CO_2 environment. As the atomized droplet comes in the contact with the antisolvent CO_2, the latter diffuses into the droplet and the solvent evaporates from the droplet surface. This two-way mass transfer process results in extremely high, very rapid and uniform supersaturation which leads to the formation of very small size particles with narrow size distribution. The simultaneous diffusion of CO_2 and the evaporation of solvent from the droplet cause swelling of the droplet which may be followed by shrinking, as illustrated in Fig. 1. The performance of SAS is characterized by the rate of attainment of supersaturation, which is decided by the increase in the mole fraction of CO_2 in atomized droplet. The solute to be crystallized is insoluble in SC CO_2 and soluble in the organic solvent. At supercritical condition carbon dioxide has high solubility in organic solvent. Therefore when SC CO_2 dissolves into the droplet, the solvent power of the organic solvent reduces drastically which results in the

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precipitation of the particle. The time for complete evaporation of the solvent is of the order of seconds. Therefore nuclei do not have the much time to grow and particle of nano to micrometer range are produced.

A. Assumptions in the Model

The precipitation of solid in SAS process is governed by two general phenomena: phase equilibrium and kinetics. The knowledge of the phase equilibrium helps to calculate mass transfer flux to and from droplet. The crystallization kinetics help to predict the supersaturation with precipitation and final average particle size with particle size distribution. In this work, two film theory of mass transfer is applied to a single droplet moving in SC CO_2. The system considered in this work is CO_2 (1)-ethanol (2). The assumptions made in this work are given below.

1) Solution is generally very dilute and the equilibrium compositions (at the interface) of the binary and ternary mixtures are not significantly different
2) The solid present in the solution does not affect the relative concentrations of CO_2 and solvent, and hence the rates of their mass transfer, to and from the droplet, respectively, are also not affected. The solution is therefore considered to be a binary mixture of CO_2 and solvent for the analysis of mass and heat transfer.
3) It is assumed that the initial velocity of the droplet is same as the exit velocity of the solution through the nozzle.
4) It is also assumed that the droplet is internally well mixed and the film theory is applicable to the transfer of SC CO_2 across the liquid film at the interface, as well as to the transfer of solvent vapor across the fluid film at the interface.
5) The driving force for the CO_2 transfer is due to its concentration difference across the liquid film, whereas the driving force for the solvent transfer is due to its concentration difference across the fluid film.
6) The transfer of solvent vapor is assumed to be controlled by the resistance in the fluid (SC CO_2) film, because the driving force would be very high across the liquid film, x_2^i being very small.
7) The liquid and vapor phase mole fraction, x_1^i and y_2^i, at the interface are constrained by the thermodynamic criterion of phase equilibrium, namely the chemical potentials (or fugacities) of each species are individually equal in the equilibrium phases.
8) The concentration at the interface is assumed to be given by the product of the corresponding phase equilibrium composition and molar density at the pressure and temperature of the binary (solvent–CO_2) mixture, as $\rho_L^i x_1^i$ and $\rho_V^i y_2^i$.

Ethanol solution is sprayed by a nozzle in supercritical CO_2 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.

$$N_e = \rho_e V \tag{1}$$

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

As the droplet moves downward in the CO_2 chamber, mass transfer from the droplet and into the droplet takes place. Carbon dioxide diffuses into the droplet and ethanol evaporates into the CO_2 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 CO_2 and ethanol in the droplet is

$$N_t = N_c + N_e = \rho_m V \tag{2}$$

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

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

The molar density of the mixture (CO_2 + ethanol) is calculated by Peng-Robinson equation of state [5].

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \tag{4}$$

$$a_{T_c} = 0.45724\frac{R^2T_c^2}{P_c} \qquad b = 0.0778\frac{RT_c}{P_c}$$

$$a = a_{T_c}\alpha(T_R,\omega) \qquad \alpha = \left[1+\beta\left(1-T_R^{1/2}\right)\right]^2$$

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

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,

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

$$b_{ij} = \left(1-l_{ij}\right)\left(b_i + b_j\right)/2$$

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

$$N_t = \rho_m\left(\frac{1}{6}\right)\pi d^3 \tag{5}$$

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

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 CO_2 diffused in droplet and number of moles of ethanol evaporated in to CO_2 environment should be known. Two film theory is used to calculate moles transferred into the droplet (CO_2 mole) and from droplet (ethanol mole) by the following equations.

$$dN_c = k_L\left(C_{L,c}^i - C_{L,c}\right)A\Delta t \tag{7}$$

$$dN_e = k_G\left(C_{G,e}^i - C_{G,e}\right)A\Delta t \tag{8}$$

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.

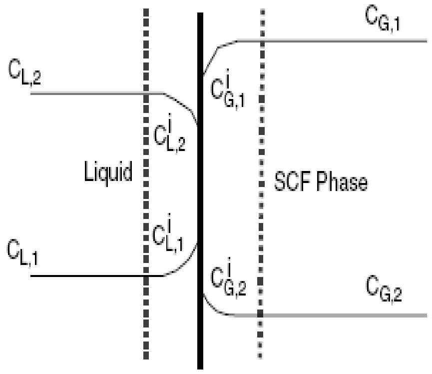

Fig. 2. "Mass Flux of CO2 (1) and Solvent (2)" [6] Liquid-phase mass transfer coefficient is calculated by penetration theory and gas phase mass transfer coefficient is calculated from the correlation of Hughmark [4].

$$k_L = \sqrt{\frac{4D_L}{\pi t_c}} = \sqrt{\frac{4D_L u}{\pi d}} \tag{9}$$

$$k_G = \frac{D_G}{d}\left(2 + 0.00187 N_{\mathrm{Re}}^{0.779} N_{Sc}^{0.546}\left(dg^{0.333} D_G^{-0.667}\right)^{0.116}\right) \tag{10}$$

The driving force for carbon dioxide diffusion is $\left(C_{L,c}^i - C_{L,c}\right)$, 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 $\left(C_{G,e}^i - C_{G,e}\right)$. 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 CO_2 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:

$$\frac{dv}{dh} = \left(\frac{\rho_L - \rho_G}{\rho_L}\right)\left(\frac{g}{v}\right) - \frac{18\mu_G}{\rho_L d^2} \tag{11}$$

$$dh = vdt \tag{12}$$

$$\frac{dv}{dt} = \left(\frac{\rho_L - \rho_G}{\rho_L}\right)g - \frac{18\mu_G v}{\rho_L d^2} \tag{13}$$

where ρ_L and ρ_G are the densities of the liquid (droplet) and gas phase (CO_2). 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 CO_2 and ethanol) is updated at each interval in all equations.

III. RESULTS AND DISCUSSION

The equations are solved in MATLAB software. The values of all varaibles such as moles of carbon dioxide, moles of ethanol, molar flux of carbon dioxide into droplet, molar flux of ethanol from droplet to supercritical carbon dioxide environment, velocity and diameter 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 CO_2 chamber are calculated. The variation in the droplet diameter, carbon dioxide mole fraction, moles of carbon dioxide and moles of ethanol are shown in Fig.1, 2, 3 and 4 respectively.

As the droplet of ethanol comes in the CO_2 environment, mass transfer takes place. Carbon dioxide dissolves in the droplet and ethanol evaporate from the droplet. Initial number of carbon dioxide mole is zero in the droplet and it increases with time. The number of ethanol moles is decreasing with time due to the evaporation of ethanol. When the concentration of the CO_2 becomes more in the droplet than outside concentration, back diffusion take place and CO_2 moles decrease in the droplet.

A. *Droplet Diameter*

The droplet size depends on the total number of mole present in it. Total numbers of moles inside droplet are calculated at each interval and then size of droplet is calculated assuming spherical shape of the droplet. Density of the droplet is calculated using Peng-Robinson equation of state. This equation of state is cubic in term of volume which is solved by Newton-Raphson method. Fig. 3 shows that size of the droplet first increases and then decreases. The decrease in the size of the droplet is due to the evaporation of the ethanol and back diffusion of the carbon dioxide. The size of the droplet changing with respect to time is shown in Fig 3.

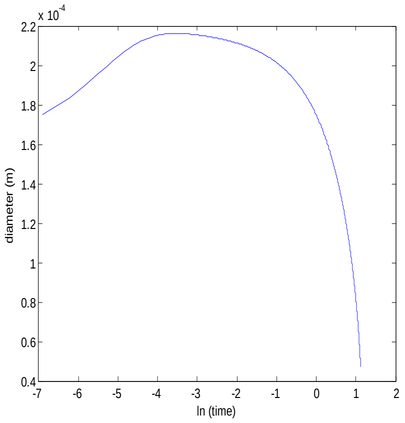

Fig. 3. Diameter vs time at 333.15 K and 100.7 bar.

B. Carbon Dioxide Mole Fraction

Mole fraction of carbon dioxide increases rapidly in the droplet and then becomes constant. This is shown in Fig. 4. Mole fraction of carbon dioxide is calculated by dividing moles of carbon dioxide present in the droplet to total number of moles in the droplet. total number of moles in the droplet is sum of moles of carbon dioxide and ethanol.

Initially droplet contains only solvent, ethanol. As it moves downward, in SC CO_2 environment, carbon dioxide diffuses into it. Thus droplet becomes a binary mixture. The molar flux, moles per unit area per unit time, of carbon dioxide is calculated using two film theory of mass transfer. This molar flux is multiplied with area of the droplet and time interval which then gives net moles of carbon dioxide into droplet. Similarly moles of ethanol are calculated which have diffused from droplet to SC CO_2 environment. Thus total number of moles in the droplet and then mole fraction of carbon dioxide in the droplet is calculated. Mole fraction of carbon dioxide is increasing first which reflects that CO_2 is moving at faster rate initially. After a time, mole fraction of CO_2 becomes approximate constant. This occurs due to the evaporation of ethanol. As ethanol evaporates, the total number of moles in the droplet decreases which yields constant mole fraction of carbon dioxide.

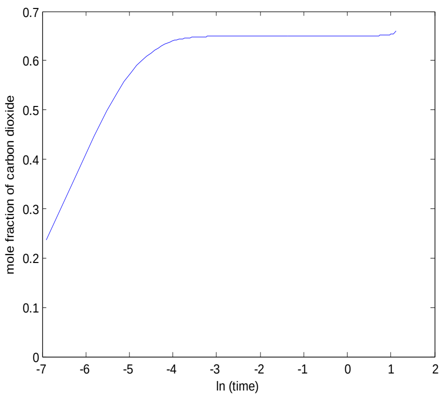

Fig. 4. Carbon dioxide mole fraction versus time at 333.15 K and 100.7 bar.

C. Moles of Carbon Dioxide

Fig. 5 shows variation of moles of carbon dioxide with respect to time. This is evident from the Fig that moles of CO2 first increases, reaches maxima and then decreases. This occurs due to back diffusion of carbon dioxide.

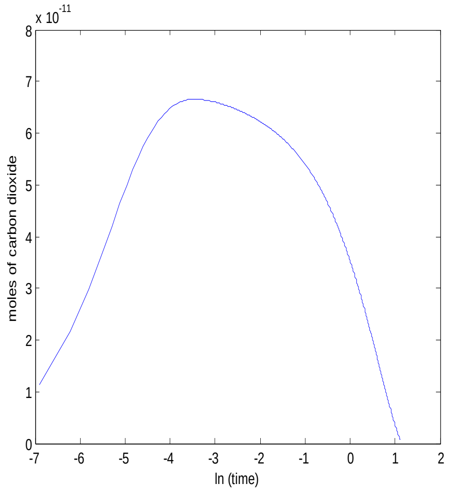

Fig. 5. Moles of Carbon dioxide versus time at 333.15 K and 100.7 bar.

D. Moles of Ethanol

Fig. 6 shows the variation of moles of ethanol in the droplet with respect to time. It is apparent from this Fig that highest numbers of moles of ethanol occur initially. As droplet moves downward in the precipitation chamber of supercritical Antisolvent micronization process, ethanol is evaporated continuously.

The moles of ethanol evaporated are calculated by two film theory of mass transfer. The residence time of the droplet is time when 99 % of the ethanol is evaporated. The evaporation of the ethanol is slower in initial period but becomes very fast at later period. This occurs due to high driving force for evaporation of ethanol.

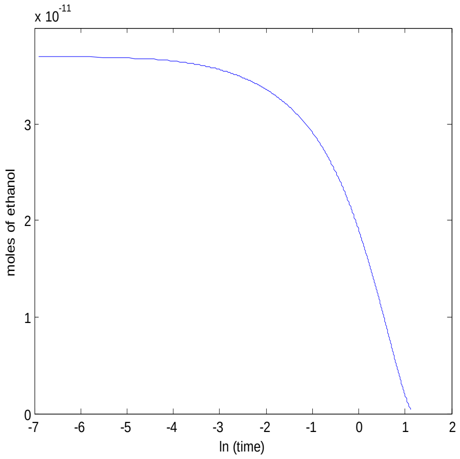

Fig. 6. Moles of Ethanol versus time at 333.15 K and 100.7 bar.

IV. 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.

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