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Crystallization kinetics of barium carbonate crystals in a lab-scale bubble-column scrubber

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ABSTRACT

The crystallization kinetics of barium carbonate crystals in the absorption of CO_2 gas and reactive crystallization with barium chloride solution within pH range 12–13 was explored in a continuous lab-scale bubble-column scrubber under a constant pH environment. In considering the agglomeration of crystals, a population balance model with well mixed scrubber was proposed to determine the crystallization kinetic data by simultaneously including nucleation rate, agglomeration kernel and growth rate, using the first three moments. Investigation parameters focused on the pH of the solution, liquid concentration, liquid flow rate, gas concentration and gas flow rate. The effect of these parameters on the crystallization kinetics was explored. Herein, liquid concentration and liquid flow rate were found to be the dominant factors significantly influencing both nucleation rate and agglomeration kernel, while the pH of the solution had a moderate influence. Correlation expressions of the kinetic data were also discovered and analyzed further. Evidence indicated that particle size was limited by the nucleation rate, agglomeration kernel and mean residence time.

1. Introduction

Absorption of carbon dioxide in an alkaline solution with reactive crystallization has also been adopted in exploring the removal of carbon dioxide from waste gas [1–6]. This approach, with the production of carbonate by means of reactive crystallization, has been found to be effective. However, some of these operations could only be performed in batch mode [3,4,6,7]. Some investigators [8,9] have studied the dynamics, mass transfer, and control of the crystal size and shape of products for industrial purposes.

In these processes, a continuous bubble-column scrubber was more effective in the removal of carbon dioxide in comparison to other scrubbers [1,10–12]. For this reason, bubble-column reactors are widely used in the chemical, petrochemical, biochemical, and metallurgical industries [13] since they are more simply constructed, have higher heat and mass transfer coefficients, higher removal efficiency, and effective control of the liquid residence time. However, the hydrodynamics in bubble-column reactors significantly affects absorption, reaction and even crystallization. In a bubble flow regime, the gas flow controls the fluid dynamics of the individual phases of these systems. This in turn controls liquid mixing and inter-phase mass transfer, which subsequently influence conversion and selectivity [14]. From RTD experiments the flow pattern of the bubble column was found to be close to that of a two-mixed tank of different volumes operating in series. At a superficial velocity of 5.64 mm/s and a solid fraction of 0.047, the volume ratio was found to be 18.6 and the ratio of the larger volume to total volume was 0.949. This indicated that the smaller one (0.949) is much less than the larger one (18.6). Therefore, the flow pattern in bubble-column can be assumed to be a single stirred tank. In order to better understand the flow pattern of solids in a bubble-column crystallizer, suspension of solids in a bubble-column should be explored further.

First of all, for a stirred-tank the process can be described by the Kolmogoroff microscale and characteristic velocity:

$$\lambda = \left(\frac{\nu_L^3}{P/m}\right)^{1/4} \tag{1}$$

and

$$\varpi = (\nu_L(P/m))^{1/4} \tag{2}$$

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Nomenclature

B	birth function (no./s-m^6)
B^0	nucleation rate (no./s-m^3)
B_1	ionic contributions constant in Eq. (16)
C_g	concentration of feeding gas (M)
C_L	concentration of feeding liquid (M)
$\bar{C}_s$	concentration of suspension solids in column (kg/m^3)
D	death function (no./s-m^6)
D_a	diameter of impeller (cm)
D_T	diameter of column (cm)
G	linear growth rate (m/s)
G_v	volume growth rate (m^3/s)
H	height of column (cm)
I	ionic strength (M)
K_i	stability constant in Table 1
K_w	water equilibrium constant in Table 1
K_{sp}	solubility product in Table 1
L	crystal size (m)
m	mass of fluid (kg)
M_T	suspension density (kg/m^3)
N	stirring speed (rpm)
n	population density in volume coordinate (no./m^6)
P	power input (W)
Q_g	gas flow rate (L/min)
Q_L	liquid flow rate (mL/min)
R_p	production rate of slurry (mol/L/s)
TBa	total barium concentration (M)
TCO	total carbonate concentration (M)
t_c	time constant (s)
u	superficial velocity (cm/s)
v	volume of crystal (m^3)
W_i	weight fraction of ith channel (−)
y_1	input gas concentration in volume fraction (−)
z_i	charge number of ith component

Greek symbols

β	agglomeration kernel (m^3/no. s)
γ_i	activity coefficient of component i (−)
ε_s	fraction of solids in column (−)
ρ_L	density of liquid (kg/m^3)
ρ_s	density of solids (kg/m^3)
ρ_{sus}	density of suspension (kg/m^3)
σ	relative supersaturation (−)
η_L	viscosity of liquid (pa s)
η_{sus}	viscosity of suspension (pa s)
ν_L	kinetic viscosity of liquid (m^2/s)
ν_{sus}	kinetic viscosity of suspension (m^2/s)
λ	microscale (μm)
ω	characteristic velocity (m/s)
μ_i	ith moments, i = 0,1,2
τ	mean residence time (min)
τ_s	mean residence time in second (s)

where ν_L is the kinetic viscosity of the fluid and P/m represents the specific power input. For a bubble-column, the specific power can be estimated by the following equation [9]:

$$\frac{P}{m} = gu \tag{3}$$

where g is the gravitational acceleration velocity and u is the linear velocity. Here, we face a three phase system. Therefore, ν_L should be replaced by suspension kinetic viscosity, ν_{sus}, if Eqs. (2) and (3) are available for a three-phase system. The suspension kinetic viscosity could be estimated by the definition:

$$\nu_{sus} = \frac{\eta_{sus}}{\rho_{sus}} \tag{4}$$

where suspension density (ρ_{sus}) and suspension viscosity (η_{sus}) can be determined by the following correlations:

$$\rho_{sus} = \varepsilon_s \rho_s + (1 - \varepsilon_s)\rho_L \tag{5}$$

and

$$\eta_{sus} = \eta_L\left(1 + 2.5\varepsilon_s + 10.05\varepsilon_s^2 + 2.73 \times 10^{-3}\exp(16.6\varepsilon_s)\right) \tag{6}$$

For a bubble-column scrubber (D_T = 5 cm; H = 45 cm), $\rho_{sus} \approx 1.16\rho_L$ and $\eta_{sus} \approx 1.25\eta_L$ if $\varepsilon_s = 0.05$, $\rho_s = 4200$ kg/m^3 (barium carbonate) and $\rho_L = 1000$ kg/m^3 (water) are available. For a superficial velocity of 0.02 m/s, the specific power input for the bubbling scrubber is 0.196 m^2/s^3. From a micro scale and characteristic velocity, the values for the bubble column were λ(=47.5 μm) and ω(=0.021 m/s), respectively, as compared with λ(=50 μm) and ω(=0.018 m/s) for the mixed-tank crystallizer with an axial-flow impeller (N = 400 rpm, D_a = 5 cm, D_T = 12 cm). This indicates that at this micro scale, eddies can easily suspend solids when particle size is less than several microns. Alternatively, uniform suspension of solids could be estimated from the literature [9]; for barium carbonate (ρ_s = 4200 kg/m^3) in a bubble-column crystallizer (D_T = 5 cm; H = 45 cm) at a superficial velocity of 0.02 m/s, the Bodenstein number is found to be 4.87×10^{-6} which was used to evaluate $\bar{C}_s/C_{so} \approx 1$. This means that a homogeneous suspension exists in the liquid phase through the bubble column, especially in a smaller column. Recently, Lau et al. [15] assumed that the liquid was perfectly mixed in a bubble column in exploring the effects of operating conditions on the liquid-side mass-transfer coefficient. The assumption of a well-mixed liquid phase within the bubble column when studying the liquid side mass-transfer coefficient was also reported in related literature [16,17].

In this study, a continuous bubble-column crystallizer under a constant pH value was adopted to study the effects of the gas-flow rate, the concentration of gas, the pH of the solution, the liquid-flow rate and the concentration of absorbent on the crystallization kinetics of barium carbonate. From a measured crystal size, distributions with population balance equation, nucleation rate, growth rate, and agglomeration kernel were simultaneously determined by the method of moment analysis according to a well mixed assumption. The effect of process variables on the crystallization kinetics of precipitates was studied and kinetic expressions were also investigated.

2. Determination of kinetic data

For a perfectly mixed continuous crystallizer, the population balance equation was used to obtain the crystallization kinetics data reported in the literature [18–20]. Here, for a continuous perfectly mixed bubble-column crystallizer, it was most convenient to shift the population balance equation into volume coordinates:

$$G_v\frac{dn}{dv} + \frac{n}{\tau} = B - D \tag{7}$$

where G_v is the crystal-volume-independent overall growth rate (m^3/s), and n is the population density (no./m^6). B and D represent