PARTICLE GROWTH CHARACTERISTICS IN DRYING OF ORTHOPHOSPHATE SOLUTION IN A FLUIDIZED BED

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The particle growth properties in drying of an aqueous mixture of sodium orthophosphates were studied in a 0.078 m-ID $\times$ 0.84 m-high fluidized bed. Glass beads and sodium tripolyphosphate (STPP) particles were used as the initial seed particles. Particle growth was mainly governed by the agglomeration of product particles in beds of glass beads and STPP particles. Particle growth conversion decreased with increasing gas velocity and bed temperature but increased with an increase in feed solution concentration. The particle size distribution of products can be represented by the lognormal distribution function. A semiempirical correlation is proposed to predict the size distribution of product particles in the bed.

Introduction

From the refining and neutralization of wet phosphates, a mixture of monosodium orthophosphate and disodium orthophosphate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) can be obtained. Through drying and calcination processes, sodium tripolyphosphate (STPP, $\text{Na}_5\text{P}_3\text{O}_{10}$), used as a builder in detergents, can be produced.

In the STPP manufacturing process, the orthophosphate solution is dried in a spray drier to produce powders which are then calcined in a kiln. However, this two-step process has a low thermal energy efficiency. A more efficient single-step process is needed for the production of STPP.

In a fluidized-bed granulator, seed particles are fluidized by hot air in which the solution is spraying either directly into or onto the bed. With this process, the orthophosphate solution can be dried and calcined simultaneously in a single-step process. Stable operation can be maintained in the bed with good temperature control since the bed temperature is kept very uniform by vigorous solid mixing. This process has greater processing capacity with easy control of particle size than that in the spray drier. However, in a fluidized-bed granulator, excess particle growth may result in defluidization, and when the particle size becomes too small, particle entrainment is a serious problem. Thus, particle size control is a major factor in a fluidized-bed granulation operation.

In general, the change of particle size in fluidized-bed granulators is governed by particle growth and degradation.^{1,10,13)} Particle growth is mainly

governed by two mechanisms: surface deposition (layering) and subparticle agglomeration. In layering growth, excess liquid beyond the deposition at the surface of liquid-wetted particles is evaporated and the liquid deposited on the solid particles provides the particle growth. Liquid bridged agglomerates can be produced by successive collision and adhesion between the wet particles in the bed. Thereafter, solidification of liquid bridged agglomerates occurs due to evaporation of the liquid, and then the agglomerates become stabilized. Particle degradation can result from mechanical wear and temperature variation between the core and the surface of particles. Mechanical wear of particles in the bed mainly comes from attrition, fragmentation and collision with the column wall. Therefore, information on particle growth characteristics is needed for the design of a fluidized-bed granulator to produce a specific product size and for prediction of reactor performance.

The size distribution of product particles in fluidized-bed granulators based on material balances^{3,4)} and population balances^{6,15)} has been determined.

Ormos *et al.*¹¹⁾ and Rankell *et al.*¹²⁾ have reported that the particle size distribution of products in a fluidized-bed granulator is well represented by the lognormal distribution function.

The objective of the present study is to determine the effects of gas velocity, feed concentration of orthophosphate and operation time on particle growth conversion and the variation of particle size distribution.

1. Experimental

Experiments were carried out in a 0.078 m-ID and

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0.84 m-high stainless steel column of the main bed, and the freeboard was expanded to 0.13 m ID with a height of 0.4 m for reducing particle entrainment as shown schematically in Fig. 1. The outside of the column wall was heavily insulated by glass-wool. Sodium tripolyphosphate (STPP) particles and glass beads were used as the seed particles in the bed. The physical properties of these particles are listed in Table 1. Solid particles were supported on a perforated distributor plate which contained 19×2 mm-ID orifices with a triangular pitch arrangement. The perforated distributor plate was covered with a 200-mesh stainless steel screen, which was situated between the main column and a 0.1 m-high air box into which preheated air (90°C) was fed to the column through an oil filter, a pressure regulator, a calibrated flowmeter and an electric preheater. The entrained solid particles from the bed were collected by a cyclone. Pressure taps were mounted flush with the column wall at 0.05 m height intervals from the distributor plate, and were connected to water manometers.

An electric heater (3.5 kW) was installed around the external wall of the main column. The desired temperature in the bed was maintained by using a variable transformer and on-off controllers. Bed temperatures were measured by chromel-alumel thermocouples at four vertical positions along the center of the column (0.04, 0.13, 0.54 and 0.84 m above the distributor plate) and were recorded by a multipoint recorder (Molytek, 2700).

An aqueous mixture of mono- and disodium orthophosphates was used as the feed solution. It was sprayed downward from the top to the bed surface by a vertically movable air atomizing nozzle (Spraying System Co., 1/4 JBC 2A). A cooling jacket was installed to prevent the evaporation of feed solution in the feed line inside the bed.

Preliminary tests were carried out to determine the degree of overspray onto the column wall. The optimum nozzle height was found to be in the range 0.15–0.20 m above the static bed height.

The feed solution was completely mixed in a thermostated feed tank at 40°C and the solution was fed to the column. The feed rate of the solution into the nozzle was controlled by a flowmeter. Atomizing air was simultaneously injected into the nozzle through an oil filter and a flow meter. The feed solution was heated to 90°C by an external heating band (0.5 kW) around the feed line. Before spraying, compressed air was injected into the nozzle to prevent the attachment to the nozzle tip of particles from the bed.

Seed particles were initially charged into the bed to give a static bed height of 0.15 m and were gradually heated by an external heater at the given fluidizing condition. After the system reached steady state, the feed solution was sprayed through the nozzle. The

Fig. 1. Schematic diagram of experimental apparatus

1: feed tank	2: feed pump
3: pressure gauge	4: 3-way valve
5: air-atomizing nozzle	6: air filter
7: pressure regulator	8: rotameter
9: liquid flowmeter	10: air preheater
11: fluidized granulator	12: external heater
13: transformer	14: cyclone
15: sampling line	P: pressure tap
	T: thermocouple

Table 1. Physical properties of seed particles

Seed particle Properties	Glass beads	Sodium tripolyphosphate $\text{Na}_5\text{P}_3\text{O}_{10}$ (P_2O_5 min. 57%)			
Real density (kg/m^3)	2500	2570			
Bulk density (kg/m^3)	1350	600			
Minimum fluidizing gas velocity (m/s)	0.14	0.038			
	size (mm)	wt. %	size (mm)	wt. %	
Particle size distribution	> 1.410	0.00	> 1.410	0.26	
	0.410–0.707	1.13	1.410–0.841	1.17	
	0.707–0.500	13.65	0.841–0.500	3.34	
	0.500–0.420	45.38	0.500–0.297	12.26	
	0.420–0.297	36.26	0.297–0.210	26.45	
	0.297–0.149	3.59	0.210–0.149	34.76	
			0.149–0.105	15.41	
			0.105–0.074	6.35	
Volume-surface mean diameter (mm)	0.418		0.190		

granulation products were sampled through the sampling tube at 10-minute intervals at a constant fluidizing-bed height. The product particle size distribution in each operation was determined by sieve analysis. In the present study, complete defluidization due to the excess particle growth of products was observed after 50 minutes operation. In addition, it has been found that the optimum calcination conditions for obtaining 90% conversion to STPP

with the present sample in a kiln are about 30 minutes operation time at a reaction temperature of 350–450°C.¹⁶⁾ Therefore, the operation time in the bed was set at 40 minutes at a reaction temperature of 250–380°C since the reaction temperature in a fluidized-bed operation should be lower, due to the temperature uniformity, than that in a kiln reactor.

Particle growth conversion of products can be expressed as:

$$X = \frac{d_p - d_{pi}}{d_{pi}} \quad (1)$$

where d_p and d_{pi} are the measured volume-surface mean diameter of the product and initial seed particles respectively.

2. Results and Discussion

The probability density function as a lognormal particle number distribution can be expressed as:

$$N(x) = \frac{1}{x\beta\sqrt{2\pi}} \exp\left[-\frac{(\ln x - \ln \alpha)^2}{2\beta^2}\right] \quad (2)$$

where $\ln \alpha$ is a mean of $\ln x$ and β is a standard deviation of $\ln x$. The particle volume distribution can be derived from Eq. (2) as:

$$W(x) = \frac{x^2}{\alpha^3 \beta \exp\left(\frac{9}{2}\beta^2\right)\sqrt{2\pi}} \exp\left[-\frac{(\ln x - \ln \alpha)^2}{2\beta^2}\right] \quad (3)$$

The mean particle size can be expressed from Eq. (3) as:

$$\bar{d}_p = \alpha \exp\left(\frac{7}{2}\beta^2\right) \quad (4)$$

The porosity of the granules is assumed to be independent of particle size. Then Eq. (3) can describe the particle weight distribution. The optimum α and β parameters were determined by the measured $W(x)$ and Eq. (3) by an optimizing technique.

In the present study, it was found that the product particles in the beds of glass beads and STPP seed particles are well approximated by the lognormal distribution function (Fig. 2).

2.1 Effect of operation time

General models for particle growth have been developed to explain the growth process due to the layering deposition and agglomeration of particles in fluidized-bed granulators,^{10,14)} in which particle growth rates in the layering deposition and particle agglomeration have been derived as:

$$\frac{d(d_p)}{dt} = \frac{\Omega}{\left(\frac{3}{d_{pi}} + \frac{12a}{d_{pi}^2} + \frac{12a^2}{d_{pi}^3}\right)} \quad (5)$$

Fig. 2. Comparison of particle size distribution between measured and calculated values from the lognormal distribution function

Seed particles

○: glass, △: STPP, ---: calculated value

Products ($C=40$ wt.%, $U_g/U_{mf}=3.2$, $t=40$ min)

●: glass, ▲: STPP, —: calculated value

Fig. 3. Comparison of particle growth conversion between measured and calculated values ($C=40$ wt.%, $T=300^\circ\text{C}$)

A: STPP ($U_g/U_{mf}=2.4$) B: glass ($U_g/U_{mf}=3.2$) ○: measured, —: agglomeration growth from Eq. (5), ---: layering growth from Eq. (4)

$$\text{where } a = \frac{d_p - d_{pi}}{2}, \quad \Omega = \frac{m_b \rho_s}{M_0 \rho_b}$$

$$\frac{d(d_p)}{dt} = \frac{6\delta}{f} d_{pi} \Omega \quad (6)$$

where f and δ are the solid volume fraction and the dimensionless binder withdrawal from the granule surface, which are obtained from the experimental data.

Combining Eqs. (1), (5) and (6) by integration, the particle growth conversions can be expressed as:

$$X_i = (\Omega t + 1)^{1/3} - 1 \quad \text{in the layering process} \quad (7)$$

$$X_a = \frac{6\delta}{f} \Omega t \quad \text{in the agglomeration process} \quad (8)$$

Comparison of particle growth conversion between the measured and calculated values from Eqs. (7) and (8) is shown in Fig. 3. As can be seen, particle growth

in the present system is mainly governed by the agglomeration process.

The agglomerated product particles from the beds of glass beads and STPP seed particles were photographed by SEM as shown in Fig. 4. At the operation time of 10 minutes (Fig. 4-B), it can be

Fig. 4. SEM photographs of seed and product particles in beds of (1) glass beads and (2) STPP particles
A: seed particles, B: after 10 min, C: after 40 min

observed that the particles grow due to agglomeration with distinct solidified bridges between the sub-particles. After 40 minutes operation time (Fig. 4-C), the particles grow remarkably from the severe agglomeration in a densely packed state. Also, it can be seen that the extent of agglomeration is more pronounced in the bed of STPP than in the bed of glass beads.

2.2 Effect of gas velocity

The effect of gas velocity in terms of fluidization number (U_g/U_{mf}) on particle growth conversion is shown in Fig. 5. As can be seen, the particle growth conversion in the beds of STPP and glass bead particles decrease with increase in gas velocity since the formation of bridges in agglomerates depends on the relative magnitude of the binding strength and break-up forces.¹³⁾ As can be expected, the solid bridges formed in the agglomerates are disintegrated more easily at higher gas velocities due to the increase in inter-particle impacts and in frequency of collision between particles and column wall. Therefore, the particle growth conversion of products may decrease with increase in gas velocity. Consequently, rapid particle growth can be retarded by higher gas velocities so that the present system can operate longer without defluidization.

2.3 Effect of seed particle property

As can be seen in Fig. 5, the decreasing rate of particle growth conversion in the bed of STPP is higher than that in the bed of glass beads. This can be attributed to the difference in physical properties of the particles. The STPP seed particles have intra-particle pores, but glass beads have no pores. With further increase in gas velocity, STPP seed particles may provide more abrasive action to the liquid bridges before solidification since some time gap is needed for filling the liquid droplets into the pores.

The particle growth conversion in the beds of STPP and glass bead particles at $U_g/U_{mf}=3.2$ is shown in Fig. 6. The particle growth conversion in the bed of STPP is higher than that in the bed of glass beads. This may indicate that porous particles have a larger agglomeration tendency, which is in agreement with the data of Dencs and Ormos.²⁾

Smith and Nienow¹³⁾ reported that the break-up force is proportional to the product of the mass and diameter of agglomerates. Consequently, smaller particles more easily form permanent bridges and defluidize in the bed. Therefore, in the present study, the granulation process in the bed of glass beads would take more time than that in the bed of STPP. Also, the higher particle growth conversion in the bed of STPP seed particles can be explained by a higher probability of aggregate formation between the clusters. These phenomena can be seen in Fig. 4, in which the STPP granules are formed by agglomeration

Fig. 5. Effect of gas velocity on particle growth conversion ($T=300^{\circ}\text{C}$, $t=40$ min)
 $C=30$ wt.% ($\circ$: glass, $\triangle$: STPP), $C=40$ wt.% ($\bullet$: glass, $\blacktriangle$: STPP)

Fig. 6. Particle growth conversion in beds of glass beads and STPP particles ($T=300^{\circ}\text{C}$, $U_g/U_{mf}=3.2$)
 $C=30$ wt.% ($\circ$: glass, $\triangle$: STPP), $C=40$ wt.% ($\bullet$: glass, $\blacktriangle$: STPP)

of clusters but the products in the bed of glass beads are formed by the aggregation of the particles themselves.

2.4 Effect of feed concentration

Particle growth conversion with 40 wt% feed concentration is larger than that with 30 wt% feed

concentration (Fig. 6). Particle growth conversion with the variation of feed concentration can be related to the drying rate of droplets coated on the particle surface. The driving force of particle growth is the difference between supersaturated and equilibrium concentrations.²⁾ Since supersaturation is caused by evaporation of the feed solution, increasing feed concentration leads to a higher degree of supersaturation and a higher driving force of particle growth, and to a consequent increase in particle growth conversion. Therefore, the probability of agglomeration due to the solidification of liquid bridges increases with increase in feed concentration. On the other hand, increase in water content of the feed solution leads to weak formation of liquid bridges between the agglomerates. Therefore, the agglomerates are more easily disintegrated by particle mixing and consequent reduction in particle growth conversion.

2.5 Effect of temperature

The Effect of bed temperature on particle growth conversion is shown in Fig. 7. As can be seen particle growth conversion decreases slightly with increased in bed temperature, which is in agreement with the data of Jonke *et al.*⁵⁾ and Nalimov *et al.*⁹⁾ The thermal gradient between the spray zone around the nozzle and the surroundings increases with increase in bed temperature. The increase of thermal gradient may result in thermal shock on the surface of product particles which may cause the cracking of the product particles.⁹⁾ Therefore, particle growth conversion decreases with increase in bed temperature. Moreover, in the present study, product particle size decrease with increase in bed temperature in the beds of STPP and glass beads.

2.6 Effect of size of droplet from the nozzle

The size of droplet from the nozzle can be predicted as a function of the properties of feed solution and the ratio of air-to-liquid volume flow rate (NAR) as⁷⁾

$$d_s = 5.44 \times 10^4 \left(\frac{\sigma}{\rho_l V_a^2} \right)^{0.5} + 5.335 \times 10^7 \left(\frac{\mu}{\sqrt{\sigma \rho_l}} \right)^{0.45} (\text{NAR})^{-1.5} \quad (9)$$

where d_s is droplet size (μm), V_a is the relative velocity between air and liquid (m/s), μ is liquid viscosity (Pa·s), ρ_l is liquid density (kg/m^3) and σ is surface tension of the feed solution (N/m). In the present study, the droplet sizes were in the range 22.4–50.1 μm from Eq. (9) with NAR values of 526–900. The liquid droplet size decreases with increase in the NAR value.⁸⁾

The effect of droplet size on particle growth conversion in the bed of glass beads is shown in Fig. 8. As can be seen, particle growth conversion increases

Fig. 7. Effect of bed temperature on particle growth conversion in bed of glass beads
t (min); ○: 10, △: 20, ▽: 30, □: 40

Fig. 8. Effect of droplet size on particle growth conversion in bed of glass beads ($C = 30 \text{ wt.}\%$, $T = 300^\circ\text{C}$, $U_g/U_{mf} = 3.2$)
t (min); ○: 10, △: 20, ▽: 30, □: 40

with increase in droplet size. This may be attributed to the higher elutriation of smaller droplets from the bed due to rapid drying or crystallization before liquid coating on the surface of product particles. Moreover, increasing NAR value gives an increase in fluidizing gas velocity through the bed, which may result in smaller particle growth conversion.

2.7 Correlation

In the present study, it was observed that parameter

α in Eq. (3) increases with increase in operation time, so that the following relation can be derived:

$$\alpha = \alpha_1 + \alpha_2 t \quad (10)$$

Substituting Eq. (10) into Eqs. (3) and (4) gives:

$$W(x, t) = \frac{x^2}{(\alpha_1 + \alpha_2 t)^3 \beta \exp\left(\frac{9}{2} \beta^2\right) \sqrt{2\pi}} \times \exp\left\{-\frac{[\ln x - \ln(\alpha_1 + \alpha_2 t)]^2}{2\beta^2}\right\} \quad (11)$$

$$\bar{d}_p = (\alpha_1 + \alpha_2 t) \exp\left(\frac{7}{2} \beta^2\right) \quad (12)$$

Therefore, semi empirical correlations of the particle size distribution and the corresponding mean size of products can be obtained by substituting the values of α_1 , α_2 and β at the given operating conditions into Eqs. (11) and (12). In the present study, goodness of fit in the mean size of product particles between measured values and calculated values from Eq. (12) was obtained with a correlation coefficient of 0.98 (Fig. 9).

Conclusions

Particle growth in beds of glass beads and STPP seed particles with orthophosphate solution is found to be governed by particle agglomeration.

Particle growth conversion decreases with increase in gas velocity and bed temperature, but it increases with increasing feed concentration and liquid droplet size.

The rate of decrease in particle growth conversion in the bed of STPP is larger than that in the bed of glass beads with increase in gas velocity. However, particle growth due to agglomeration is more pronounced in the bed of STPP than in the bed of glass beads.

The particle size distribution of the present products was well represented by the lognormal distribution function. Semiempirical correlations for predicting the size distribution and the mean size of product particles have been developed.

Nomenclature

a	= thickness of layer	[m]
C	= feed concentration	[wt%]
d_p	= size of product particles	[m]
$\bar{d}_p$	= mean particle size	[m]
d_{pi}	= size of seed particles	[m]
d_s	= droplet size	[m]
f	= solid volume fraction of binder	[-]
$N(x)$	= particle number distribution function	[-]
m_b	= mass feed rate of solid leading to growth	[kg/s]
M_0	= mass of particles in bed	[kg]
t	= operation time	[s]
T	= bed temperature	[K]

Fig. 9. Comparison of experimental and calculated values of mean particle size
○: STPP, □: glass

U_g	= superficial gas velocity	[m/s]
U_{mf}	= minimum fluidizing gas velocity	[m/s]
V_a	= relative velocity between air and liquid in nozzle	[m/s]
$W(x)$	= particle volume size distribution function	[-]
x	= particle size	[m]
X	= particle growth conversion	[-]
X_l	= particle growth conversion in layering process	[-]
X_a	= particle growth conversion in agglomeration process	[-]
α	= distribution parameter	[m]
α_1, α_2	= numerical constants	[-]
β	= distribution parameter	[-]
δ	= dimensionless measure of withdrawal of binder from granule surface	[-]
μ	= viscosity of feed solution	[Pa · s]
Ω	= $\frac{M_b \rho_s}{M_0 \rho_b}$	[-]
ρ_b	= binder density	[kg/m ³]
ρ_l	= liquid density	[kg/m ³]
ρ_s	= particle density	[kg/m ³]
σ	= surface tension of feed solution	[N/m]
<Subscripts>		
cal	= calculated value	
exp	= experimental value	

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