Generation of Fine Solid Particles by Desublimation in a Subsonic Nozzle Expansion

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Abstract

The generation of fine solid particles by heterogeneous desublimation of succinic acid vapor is investigated experimentally and theoretically. In the experimental investigations, a gas mixture consisting of air and succinic acid vapor is cooled by means of subsonic nozzle expansion and is directly cooled by mixing. As a result of the cooling process, the gas mixture is supersaturated and the succinic acid vapor desublimes to fine particles. The number concentrations and particle size distribution of the powders generated are measured with an optical particle counter. The particle growth by desublimation is calculated with an Eulerian-Eulerian approach in a two-dimensional flow field. The population balance for the particle size distribution is solved and the mass and energy balance equations for each particle class are implemented in a CFD program (CFX 4.2).

Introduction

Gas-to-particle conversion processes can be used to produce very fine solid particles with narrow size distributions and of high purity. In the process, the particle formation is driven by the cooling of a supersaturated vapor or by the generation of atoms or molecules by chemical reactions of gaseous precursors. The use of gas-phase reactions is well established, for example, in flame synthesis processes used to produce submicron particles of titanium dioxide, silica or carbon black [1].

One method of gas-to-particle conversion is the desublimation process, which is the direct conversion from the vapor state to the solid state without passing through the liquid state. Desublimation can be used to separate a single desublimable component from a mixture of gaseous components. On account of the high purity and the good appearance (morphology) of the solid product, desublimation is widely employed to purify chemicals such as salicylic acid, naphthalene, anthracene or anthraquinone [2].

To desublime a single component from a mixture of gaseous components, the vapor phase must be supersaturated with the component that is to desublimate. This can be achieved by cooling a saturated gas mixture. In this case, the cooling method and the process conditions determine whether nucleation, particle growth or coagulation will be the dominant mechanism in the process of particle formation. Thus, within limits, it is possible to control the number concentration, the particle size distribution and the surface structure of the desublimed particles. Direct cooling by mixing with an inert cooling gas leads to the formation of very small particles [3], [4]. Monodisperse particles are obtained if the gas mixture is cooled by a subsonic nozzle expansion [5]. Though desublimation by direct cooling and cooling due to expansion can be used to produce fine solid particles in a continuous process, little is found in the literature regarding these processes.

In the present experimental and theoretical work, the particle growth by desublimation due to expansion and direct cooling by mixing is investigated.

Experimental set-up

The experimental set-up to investigate the particle growth by desublimation due to expansion and direct cooling is shown schematically in Fig. 1. A filtered flow of pressurized ambient air is divided into a flow of carrier gas and a flow of cooling gas. One part of the carrier gas flows through a heated sublimer, in which solid succinic acid is sublimed into the carrier gas. One part of the carrier gas flows through a heated sublimer, in which solid succinic acid is sublimed into the carrier gas. The second gas flow is transported to an aerosol generator.

In the aerosol generator, sodium chloride nuclei are formed by means of an electrically heated platinum wire, which is coated with sodium chloride. The sodium chloride is vaporized into the gas flow, where the formation of solid nuclei subsequently takes place.

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The nuclei formed are to a large extent smaller than 100 nm, and number concentrations of $10^6$ nuclei per cm$^3$ of air are achievable [6]. After heating the gas flow containing the sodium chloride nuclei, it is mixed with the gas flow containing the desublimable vapor.

The resultant gas mixture containing air, succinic acid vapor and nuclei is then expanded in a nozzle and a capillary tube. Due to the expansion, the gas mixture is cooled. Therefore, the gas mixture is supersaturated and the heterogeneous particle growth on the nuclei is initiated in the nozzle and the capillary tube. The residence time in this section of the set-up depends on the length of the capillary tube. The design of this section was calculated with a one-dimensional model of the particle growth in the nozzle and the capillary tube [7], [8]. In the experimental investigation, the length of the capillary tube is 0.5 m. The diameter is 1 mm and the diameter of the nozzle inlet is 6 mm.

After entering the mixing chamber, the remaining succinic acid vapor is desublimed due to direct cooling by mixing with the flow of cooling gas. The walls are heated in order to avoid desublimation of succinic acid vapor at the walls of the chamber. The diameter of the mixing chamber is 40 mm and it has a length of 0.6 m. At the bottom of the mixing chamber, a sample is taken from the gas flow and the number concentration and the particle size distribution of the particles are measured by means of an optical particle counter.

**Experimental results**

In the experimental investigations, the change of state of the gas mixture in the nozzle and capillary tube is adiabatic. In Fig. 2, experimental results are given for the measured mean particle diameter of the volume distribution of the powder generated depending on the partial pressure of the succinic acid at the inlet of the nozzle. The number concentration of the particles varies. The gas flow through the nozzle is 3 l/min and the cooling gas flow amounts to 6 l/min. The total pressure at the inlet of the nozzle is 145 kPa. An increase of the mean particle diameter is achieved by increasing the partial pressure. For a constant number concentration of particles, the measured points are represented by the continuous lines. These curves describe the expected relationship between the particle diameter and the partial pressure. For a constant partial pressure and an increasing number concentration, the mean particle diameter decreases.

Fig. 3 shows the measured sum of the number distribution of the powder generated. The partial pressures of succinic acid $p_{Sa}$ are 162 Pa, 233 Pa, 253 Pa, 293 Pa, and 314 Pa. The gas temperatures $T_0$ are 432 K, 462 K, and 492 K. The cooling gas flow rates $V_c$ are 3 l/min and 6 l/min. The particle diameter $d_p$ is measured for constant number concentration $n_p$.

![Fig. 1 Experimental set-up](image1)

![Fig. 2 Measured mean particle diameter of the generated powder](image2)

![Fig. 3 Measured sum of the number distribution of the powder for constant number concentration](image3)
The number concentration of particles is kept constant. The temperature at the nozzle inlet is 432 K. For an increasing partial pressure, the curve for the number distribution is shifted to the right and to greater particle diameters. This can be explained by the increasing amount of vapor available for the growth of every single particle. Additionally, the number distribution becomes wider for an increasing partial pressure. The duration of particle growth increases and therefore there is a greater influence on the particle growth of inhomogeneities of the flow field in the mixing chamber.

In Fig. 4, the sum of the number distribution is shown for a varied number concentration of the particles. The initial partial pressure of succinic acid is kept constant. For greater number concentrations, smaller particles are generated. An increasing number concentration has the same effect as a decreasing partial pressure. Accordingly, the number distribution of the particles becomes narrower for an increasing number concentration.

The influence of the expansion on the particle size distribution of the particles generated cannot be investigated using the experimental results described. At the end of the capillary tube the particle growth is not finished and the particles are not in thermodynamic equilibrium. Therefore, no sample can be taken at the outlet of the capillary tube to measure the particle size distribution. To investigate the influence of the expansion, two different operating points of the experimental set-up are compared. On the one hand, the experiments are performed with an adiabatic nozzle and capillary tube, and on the other hand, the capillary tube is overheated. The latter has the consequence that there is no supersaturation in the capillary tube and, accordingly, no particle growth takes place. In Fig. 5, the sum of the number distribution of the particles generated are shown for both cases, the adiabatic and the overheated capillary tube.

In the case of the adiabatic capillary tube, the standard deviation of the particle size distribution is approximately 10% smaller than in the case of the overheated tube. The reason for the reduction in the case of an adiabatic tube can be explained by the particle growth in the homogeneous flow field of the capillary tube. The particles are enlarged by about one decade in the homogeneous flow field of the capillary tube [7], [8], before entering the inhomogeneous flow field of the mixing chamber.

Theoretical results

On the basis of the calculated two or three-dimensional flow field, the particle growth by desublimation is evaluated by solving a population balance for the particle size distribution. It is presumed that the particles are small enough to travel at the same velocity as the local gas mixture at any point. Furthermore, the density of the solid phase is presumed to be much greater than that of the gas. Thus, the presence of the solid particles makes no contribution to the specific volume of the mixture. If there is no particle diffusion at any point, the balance equations for mass and energy of a particle class can be written as:

$$\frac{\partial r_i}{\partial t} + \nabla (r_i \bar{v}) = S_{r,i}$$

(1)

$$\frac{\partial r_{hi}}{\partial t} + \nabla (r_{hi} \bar{v}) = S_{h,i}$$

(2)

Here, $r_i$ is the volume fraction and $h_i$ is the total specific enthalpy of the particle class. $S_{r,i}$ and $S_{h,i}$ are source terms for mass and energy, respectively. In order to determine these terms, the following population balance for the particle size distribution $n=f(s,t)$

$$\frac{\partial n}{\partial t} + \nabla (n \bar{v}) = \frac{\partial}{\partial s}(n \tau_s)$$

(3)
has to be evaluated [9]:

$$\dot{n} = \frac{\partial n}{\partial t} + s \frac{\partial n}{\partial s} + n \frac{\partial s}{\partial s}$$  \hspace{1cm} (3)$$

Here, \( s \) is the squared radius of the particles and \( n \) is the number of particles per unit volume having sizes between \( s \) and \( s + ds \). Multiplying the population balance with the volume of the particles, \( V_p \), and introducing the volume fraction of the particles in this range, \( \nu \), gives:

$$\nu = V_p n,$$  \hspace{1cm} (4)$$

Eq. (3) can be transformed into the following differential equation:

$$\dot{V}_p n = \frac{\partial V}{\partial t} + s \frac{\partial V}{\partial s} - \nu V_p \frac{\partial V}{\partial s} + \nu s V_p \frac{\partial s}{\partial s}.$$  \hspace{1cm} (5)$$

Assuming that the particles are spherical and that the growth rate is limited by the mass transfer in the gas phase, a mass balance at the surface of the particles leads to the equation for the change of the particle surface, \( \dot{s} \), [4]:

$$\dot{s} = 2 s_p \frac{\partial s}{\partial t} = \frac{\partial s}{\partial t} = \frac{\partial s}{\partial t} - \frac{\partial}{\partial t} - \frac{\partial}{\partial t},$$  \hspace{1cm} (6)$$

Here, \( s_p \) is a function of the Knudsen number and takes into account the conditions in the entire range of continuum, transition and free molecules regimes [10], [11]. \( S_k \) is the Sherwood number, \( D \) is the diffusion coefficient, \( s_p \) is the particle density, \( M_v \) is the molecular weight of the vapor and \( R \) is the universal gas constant. \( p_v \) and \( p_v^* \) are the vapor pressures at the particle surface and in the gas mixture, respectively. \( T \) is the temperature.

If the temperature of the particles is independent of their size, then so is the change of particle size, \( \dot{s} \). Taking also into account the fact that the volume of the particles, \( V_p \), is independent of time, Eq. (5) can be simplified:

$$\dot{V}_p n = \frac{\partial V}{\partial t} + s \frac{\partial V}{\partial s} - \nu V_p \frac{\partial V}{\partial s} + \nu s V_p \frac{\partial s}{\partial s}.$$  \hspace{1cm} (7)$$

Also

$$\nu = \frac{\nu}{\nu - \nu_{j-1}},$$  \hspace{1cm} (8)$$

Integration with respect to \( s \) and with some rearrangement, the source term for the mass balance of a particle class can be derived:

$$S_{s,j} = -\dot{s} \left( \nu_j - \nu_{j-1} \right) + \frac{3}{2} \int_{s_{j-1}}^{s_j} \nu \, ds + \int_{s_{j-1}}^{s_j} V_p \, ds$$  \hspace{1cm} (9)$$

For the integration, spherical particles are presumed. \( s_j \) and \( s_{j-1} \) are the upper and lower boundaries of the particle class \( j \). If there is no agglomeration of the particles in the flow field, the last integral on the right-hand side of Eq. (9) describes the change of the volume fraction \( \nu_j \) of the particle class due to homogeneous nucleation. At a certain point in the flow field, the rate of nucleation, \( I \), is calculated for one critical radius of the particles, \( r_{p,\text{crit}} \). Therefore, the integral can be replaced by:

$$\int_{s_{j-1}}^{s_j} V_p \, ds = \frac{\pi}{6} I \left( \frac{\sqrt[3]{s_j}}{2} + \frac{\sqrt[3]{s_{j-1}}}{2} \right)^3$$  \hspace{1cm} (10)$$

The source term for mass can be written as:

$$S_{s,j} = -\dot{s} \left( \nu_j - \nu_{j-1} \right) + \frac{3}{2} \int_{s_{j-1}}^{s_j} \nu \, ds + \frac{\pi}{6} I \left( \frac{\sqrt[3]{s_j}}{2} + \frac{\sqrt[3]{s_{j-1}}}{2} \right)^3$$  \hspace{1cm} (11)$$

The remaining integral on the right-hand side can only be solved if the dependency of the volume fraction, \( \nu \), on the particle size, \( s \), is known. Therefore, a step function for the volume fraction is assumed as shown in Fig. 6. This means that the volume fraction is constant between the upper and lower boundary of a particle class. With

$$\nu_j = \frac{\nu_j}{\nu_s - \nu_{j-1}},$$  \hspace{1cm} (12)$$

the source term reads:

$$S_{s,j} = -\dot{s} \left( \nu_j - \nu_{j-1} \right) + \frac{3}{2} \int_{s_{j-1}}^{s_j} \nu \, ds + \frac{\pi}{6} I \left( \frac{\sqrt[3]{s_j}}{2} + \frac{\sqrt[3]{s_{j-1}}}{2} \right)^3$$  \hspace{1cm} (13)$$

The last two terms in Eq. (13) stand for the mass transfer between the gas phase and the specific particle class. The mass transfer into the particle class containing bigger particles is described by the first
The second describes the mass transfer into the class containing smaller particles. The source term of the energy can be derived in the same way.

In order to calculate the particle growth in a two or three-dimensional flow field, the equations 1, 2 and 6 are implemented in a CFD program (CFX 4.2).

Fig. 7 shows the rotationally symmetrical rescaled geometry of the calculated flow field. The inlet of the saturated gas mixture consisting of gas, vapor and nuclei is at the top, and the cooling gas flows through an annular nozzle. The nozzle and capillary tube are insulated, which means there is no heat flux through the walls. The walls in the upper part of the mixing chamber are heated in order to avoid desublimation at the walls.

Fig. 8 shows the calculated flow field in the upper part of the mixing chamber. The gas mixture containing the particles flows downward out of the capillary tube into the mixing chamber. The gas mixture is directly cooled by mixing with the inert flow of cooling gas. The cooling gas flow enters the chamber through an annular nozzle. Due to the free jet in the center of the mixing chamber, a vortex develops.

Fig. 9 shows the calculated number distribution density for different axial positions in the capillary tube and the mixing chamber. The calculation predicts a growth rate in the capillary tube which allows an enlargement of the nuclei by about a decade. The flow enters the mixing chamber at 0.5 m. At this point the gas flow is mixed with the cooling gas and the particles therefore grow rapidly. Because of the inhomogeneous concentration and the temperature fields in the mixing chamber, the standard deviation of the number distribution becomes wider.

The calculated particle size distribution is compared with the measured size distribution at the outlet.
of the mixing chamber in Fig. 10. For the calculation, it is presumed that the temperature of the particles equals the local gas temperature at any time. Homogeneous nucleation is neglected at any point of the flow field. The calculations are performed with 50 particle classes, which are shown by the dots in the diagram. The measured number distribution is shown by the continuous line. The mean particle diameter of the measured and calculated particle size distribution is in good agreement, although the measured distribution is wider than that calculated.

Conclusion

Desublimation by direct cooling of a mixture of gaseous components is a suitable process to produce fine solid particles in a continuous process. The number concentration and the particle size distribution of the desublimed particles can be influenced by various process parameters. On the one hand, increasing vapor concentration leads to increased mean diameters of the particles. And on the other hand, an increasing number concentration of the desublimed particles results in a decrease to the mean diameters of the particles. For inhomogeneous concentration and temperature fields, the standard deviation of the particle size distribution is wide. The standard deviation of the particle size distribution can be reduced by 10% if the gas mixture is first expanded in a subsonic nozzle expansion. Theoretical simulation of the particle growth in the subsonic nozzle expansion predicts a growth rate which allows an enlargement of the particles by about a decade in the capillary tube. The calculated number distribution of the particles generated is in agreement with the measured distribution.

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Nomenclature

- $D$: m$^2$/s, diffusion coefficient
- $d_{p,3}$: m, mean particle diameter of the volume distribution of the particles
- $h$: J/kg, total specific enthalpy
- $I$: 1/m$^3$s, nucleation rate
- $j$: counter
- $Kn$: Knudsen number
- $M$: kg/kmol, molecular weight
- $n$: 1/m$^3$, number concentration
- $n$: 1/m$^3$, number concentration related to the particle surface
- $p$: Pa, pressure
- $Q_o$: cumulative number distribution of particles
- $q_o$: 1/m, number density distribution of particles
- $r$: volume fraction
- $R$: J/kmolK, universal gas constant
- $r$: m, radius of particle
- $s$: m$^2$, surface of particles
- $Sh$: Sherwood number
- $S_{rh}$: J/kg$s$, source term for the energy of a particle class
- $S_{\eta}$: 1/s, source term for the mass of a particle class
- $T$: K, temperature
- $t$: s, time
- $V$: m$^3$, volume
- $\dot{V}$: m$^3$/s, volume flow
- $\dot{v}$: m/s, local velocity of the fluid
- $x$: m, axial coordinate
- $\beta_m$: =f($Kn$)
- $\rho$: kg/m$^3$, density
- $\sigma$: m, standard deviation

Subscripts

- $\infty$: infinity
- $0$: initial state
- $crit$: critical
- $C$: capillary tube
- $j$: number of particle class
- $N$: nozzle
- $p$: particle
- $SA$: succinic acid
- $v$: vapor
References


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