A Numerical Study on Particle Growth in Choked Capillary Nozzle Flow*

Hae Young JEONG**, Sang Soo KIM**
and Kang-Ho AHN***

This work presents the results of one- and two-dimensional numerical analysis of a choked capillary flow and the analysis of particle formation and growth in a capillary. The object of this study was to determine conditions of seed particle growth and homogeneous nucleation. The Lagrangian approach was used for the calculation of droplet growth, and vapor depletion and latent heat release were considered in the calculation of the two-dimensional flow field. Several parameters were derived from the analysis of the flow field and the growth rate of the droplet, and their effects are discussed. It was found that the viscous pressure loss during the expansion has a significant effect on both heterogeneous and homogeneous condensation. The difference in the results between one- and two-dimensional calculations is also discussed and conclusions are presented.

Key Words: Particle Growth, Homogeneous Nucleation, Choked Flow, Supersaturation, Nozzle Expansion, Pressure Loss

1. Introduction

The formation and condensational growth of particles through nozzle expansion has been studied for the verification of nucleation theory, the production of ultra-fine particles, and the generation of cluster beams. In order to attain the desired supersaturation, various types of expansion devices have been used. Subsonic and supersonic nozzles have been used for the study of cluster beam generation and homogeneous nucleation⁽¹⁾⁻⁽³⁾. For the effective control of expansion rate, a capillary has been frequently used for the process of rapid expansion of supercritical solutions^{(4),(5)}. The shape and the dimension of the expansion device have been

parameters of the condensation process and particle growth.

There have been many efforts to determine the dependence of particle size distribution on the expansion conditions. Turner and his research team calculated particle formation and growth in a subsonic convergent nozzle⁽³⁾. Kwauk and Debenedetti presented a mathematical model of nucleation and particle growth during the expansion of dilute supercritical solutions in a sub-sonic converging nozzle⁽⁶⁾. In the above two cases, both teams introduced inviscid and one-dimensional assumptions, and controlled the expansion rate by means of changing the exit Mach number. At a narrow expansion device such as a capillary, however, viscous wall friction has a significant effect on the expansion process and can also be helpful in controlling the expansion rate. Lele and Shine calculated the axial flow properties of a supercritical solution expansion device with viscous fluid friction, and examined the effect of capillary dimension on the morphology of produced particles⁽⁴⁾. However, studies on seed particle growth in expanding flow are rare. Mallina

* Recieved April 30, 2000

** Dept. of Mechanical Engineering, Korea Advanced Institute of Science and Technology, 373-1 Kusong-dong, Yusong-gu, Taejon 305-701, Korea,

*** Dept. of Mechanical Engineering, Hanyang University, 1271 Sa-1-dong, Ansan, Kyunggi-do 425-791, Korea

and his team calculated particle growth in high-speed particle beam inlets⁽⁷⁾. They calculated the two-dimensional viscous flow for various types of nozzles and the growth of the particles that flow along the centerline of the nozzle. In their paper, the effect of the radial variation and dimension of the capillary was not clearly understood.

For the analysis of particle growth through narrow nozzle expansion, accurate calculation of flow field in the nozzle is necessary. Thus we treat the capillary expansion as viscous two-dimensional flow and also consider the vapor depletion and latent heat release from the spontaneous homogeneous nucleation and the subsequent growth. The purpose of this study is to control particle formation and growth through capillary expansion. The dimensionless parameters that affect the flow and particle growth in the capillary are derived from the analysis of the flow and the condensational growth rate of seed particle. And the effects of the dimensionless parameters are examined using one- and two-dimensional calculations.

The control of particle growth using capillary expansion is useful in several aerosol fields. It can be used for the measurement of ultrafine particles, the generation of mono-disperse particles, and in the manufacture of metal and ceramic particles. This capillary expansion system can be used as a condenser of the condensation nucleus counter, as opposed to conventional devices that use the conductive cooling of saturated gas, the mixing of saturated hot gas and cold gas, or the volume expansion of saturated vapor. Choked capillary expansion has advantages over conventional methods such as easy control of the flow rate, possible increase of the flow rate, and a simple particle growth system.

Nomenclature

a_0 : speed of sound, m s^{-1}
 C_c : slip correction factor, dimensionless
 $c_{p,v}$: specific heat of vapor at constant pressure, $\text{J kg}^{-1} \text{K}^{-1}$
 d_p : diameter of particle, m
 D : diameter of capillary, m
 f : friction coefficient, dimensionless
 G : growth parameter, m^2
 h_{fg} : latent heat of vaporization, J kg^{-1}
 H : heating parameter, dimensionless
 k_g : thermal conductivity, $\text{W m}^{-1} \text{K}^{-1}$
 L : length of capillary, m
 Le : Lewis number, dimensionless
 M : Mach number, dimensionless
 D_{vg} : diffusion coefficient of vapor, $\text{m}^2 \text{s}^{-1}$
 p : pressure of gas, Pa

p_v : vapor pressure, Pa
 R : gas constant, $\text{J kg}^{-1} \text{K}^{-1}$
 Re : Reynolds number, dimensionless
 S : saturation ratio, dimensionless
 T : temperature of gas, K
 M_v : molecular weight of vapor, kg mol^{-1}
 x : axial distance from inlet, m
 $\bar{x}$: normalized axial distance, dimensionless
 Y : flow parameter, dimensionless
 α : thermal diffusivity, $\text{m}^2 \text{s}^{-1}$
 γ : specific heat ratio, dimensionless
 μ : absolute viscosity, $\text{kg s}^{-1} \text{m}^{-1}$
 ν : kinematic viscosity, $\text{m}^2 \text{s}^{-1}$
 ρ : density, kg m^{-3}
 ρ_v : density of vapor, kg m^{-3}
 ω : normalized mass fraction of vapor, dimensionless $=(\rho_v/\rho)/(\rho_{v,01}/\rho_{01})$

Subscripts

0 : stagnation
 1 : inlet of capillary
 2 : exit of capillary
 g : gas
 p : particle
 s : surface of particle
 v : vapor

2. Flow Field

A capillary expansion system can be divided into three sections: a reservoir, a capillary expansion zone, and a free expansion zone. The reservoir contains a mixture of carrier gas, saturated condensable vapor, and seed particles at constant pressure and temperature. The mixture expands through a capillary that is connected to the free expansion zone. The pressure at the free expansion zone is low enough to cause a choked flow at the end of the capillary. The expansion process between the reservoir and the entrance of capillary can be considered nearly isentropic. However, the expansion process in the capillary deviates from isentropic because of wall friction. It is well known that condensable vapor becomes supersaturated in an isentropic expansion process. The reason is that the saturation vapor pressure decreases with temperature more rapidly than does the static pressure. Similarly, the condensable vapor in the capillary also becomes supersaturated, unless the deviation from the isentropic process is severe. Under the supersaturated condition, the vapor condenses on the surface of the seed particles. Large supersaturation may cause not only heterogeneous condensation but also spontaneous homogeneous nucleation. During these phase transition processes, the vapor concentration in the mixture is reduced and

the corresponding latent heat is released. This process has an effect on the thermodynamic properties of the gas and the flow field.

A one-dimensional analysis of the capillary flow is a simple way to obtain the useful information about the flow characteristics. We derive the relationship between the flow conditions and the thermodynamic state in the capillary flow. We assume that the gas mixture is an ideal gas, the expansion process between the reservoir and the inlet of the capillary is isentropic, and the effect of latent heat and the heat transfer through the wall are negligible. The one-dimensional analysis of a viscous compressible adiabatic tubular flow is well established. The Mach number in the capillary can be expressed in Eq. (1). Using a fully developed laminar flow friction coefficient and isentropic relation in entrance region, the distribution of the Mach number in the capillary can be determined by a unique parameter Y as shown in Eq. (2).

$$\frac{4f(L-x)}{D} = \frac{1-M^2}{\gamma M^2} + \frac{\gamma+1}{2\gamma} \ln \left[\frac{(\gamma+1)M^2}{2+(\gamma-1)M^2} \right] \quad (1)$$

$$Y = \frac{M_1}{(1-\bar{x})} \left[1 + \frac{\gamma-1}{2} M_1^2 \right]^{\frac{(\gamma+1)}{2(\gamma-1)}} \times \left\{ \frac{1-M^2}{\gamma M^2} + \frac{\gamma+1}{2\gamma} \ln \left[\frac{(\gamma+1)M^2}{2+(\gamma-1)M^2} \right] \right\} \quad (2)$$

where $Y \equiv \frac{64\mu L}{\rho_{01} D^2 a_0}$, $\bar{x} = \frac{x}{L}$.

The non-dimensional flow parameter Y is proportional to the ratio of the characteristic time for propagation of the pressure wave in the capillary (L/a_0) and the characteristic time for momentum transfer between the capillary wall and the flow ($D^2/4\nu_{01}$). Therefore its physical meaning is how much the viscous friction affects the flow during the passage through the capillary. It is easy to estimate the effect of friction from the experimental conditions, because the parameter consists of the gas properties at the reservoir and the dimension of the capillary.

3. Particle Growth

The theory of growth rate in the continuum region has been recently developed. Clement and Barrett developed more accurate expressions of growth rate in the continuum region⁽⁸⁾. Ignoring thermal diffusion and Dufour effect, continuum mass flux to the surface of droplet is expressed as Eq. (3). This is the same expression as Eq. (13b) of Barrett and Clement⁽⁸⁾ for dilute condensable vapor. The temperature at the surface of the droplet can be expressed as Eq. (4).

Considering the dependence of diffusion coefficients on the temperature and the pressure, and introducing the linear approximation of the Clapeyron-Clausius vapor pressure equation with temperature, the equation can be transformed into Eq. (5). The heating parameter H represents the effect of the temperature rise at the particle surface caused by the latent heat. Neglecting the effect of vapor depletion of the flow, the growth of the droplet can be determined by values of the flow parameter Y , the heating parameter H , the growth parameter G , and the material properties of condensable vapor.

$$\frac{\rho_p d_p}{4} \frac{dd_p}{dt} = \frac{M_v D_{vg}}{RT(1-p_v/p)} (p_v - p_{v,s}) \quad (3)$$

$$T_s - T = \frac{\rho_p d_p h_{fg}}{4k_g} \frac{dd_p}{dt} \quad (4)$$

$$\frac{dd_p^2}{dx} = \frac{G}{M} \left(1 + \frac{(\gamma-1)}{2} M^2 \right)^{1/2} \frac{1-\delta/S}{1+H(\delta/S)} \quad (5)$$

where $\delta = \exp \left(\frac{4\sigma v_m}{d_p k T_s} \right)$.

$$H \equiv \frac{Le_{01}}{(1-p_{v,01}/p)} \frac{\rho_{v,01} h_{fg}^2}{\rho_{01} c_{p,v} R T_0^2} \quad (6)$$

$$G \equiv \frac{8L\rho_{v,01}D_{vg,01}}{\rho_p a_0 (1-p_{v,01}/p)} \quad (7)$$

4. Numerical Method

For the analysis of particle growth, accurate calculation of the capillary flow is required. In this study, we calculate the two-dimensional flow field; in addition, the vapor depletion and the release of latent heat from nucleation and subsequent growth are considered. For the modeling of the flow and the growth process, the following assumptions are used: the flow is laminar and compressible, the capillary wall is adiabatic, and the concentration of the vapor is so dilute that the change of vapor concentration does not affect the flow directly.

For the calculation of the flow field, Navier-Stokes equations and the energy equation for compressible flow are used with the SIMPLER algorithm. In order to handle both incompressible and compressible flows, the pressure is selected as a primitive variable and the density is corrected according to the pressure change⁽⁹⁾.

Droplet growth is calculated with respect to two condensable vapors, water and n-Butanol. For an accurate calculation, rigorous expressions of growth rate, Eqs. (3) and (4) are used. The non-continuum effect was considered using Fuchs and Sutugin

correction factors. In this study, the values of accommodation coefficients for heat and mass transfer are assumed to be one. The Lagrangian approach is used for the calculation of the particle motion and the Brownian diffusion of particle is neglected. The seed particles starting at every grid point of inlet are selected for the calculation. We perform the calculations with different values of the flow parameter Y , heating parameter H and the growth parameter G .

In order to account for the effect of the vapor depletion and the latent heat release, we calculate the spontaneous nucleation and the subsequent growth. A general theory of homogeneous nucleation does not exist yet. Volmer and Flood showed that the critical supersaturations of water and n-Butanol agree with classical nucleation theory⁽¹⁰⁾. Therefore, Becker-Döring classical nucleation theory⁽¹¹⁾ is used. The growth of nuclei is calculated using the moment method⁽¹²⁾ and the concentration and the latent heat source are calculated using the particle-source-in cell method⁽¹³⁾.

5. Results and Discussion

According to the one-dimensional consideration of the capillary flow, it is found that the flow configuration without condensation depends on the flow parameter only. This is found to be true even in two-dimensional calculations. For example, while the length to diameter ratio of a capillary varies 4 times with the same flow parameter, the variation of dimensionless flow rate and inlet Mach number is within 1 percent. Figure 1 represents total pressure at exit and the Mach number at inlet as a function of the flow parameter. The difference of the inlet Mach number between one- and two-dimensional results can be explained by the additional pressure loss in the boundary layer developing region. For small values of

Fig. 1 Comparison of total pressure ratios and inlet Mach numbers from one- and two-dimensional calculation.

Fig. 2 Comparison of dimensionless flow rates from the calculation and experiment.

Fig. 3 The saturation ratio S and the normalized mass fraction of vapor ω in the capillary. ($Y=1$, $H=0.5$, $G=1 \mu\text{m}^2$, aspect ratio=100:1)

the flow parameter, the difference increases because the portion of the developing region in the whole length of capillary becomes large. As the flow parameter increases, the total pressure at the exit decreases. The decrease of the total pressure indicates the pressure loss caused by viscous wall friction. From the viewpoint of particle growth, the pressure loss is important because this pressure loss affects the supersaturation in the flow.

In order to examine the validity of the laminar flow assumption, we measure the flow rate and compare calculated flow rates with the experimental results. Figure 2 shows that the numerical results with the laminar assumption slightly overestimate the flow rates. We believe that occurs near the entrance of the flow. Although the Reynolds number of the flow ranges from 2000 to 40000, the laminar assumption is valid. The two-dimensional calculation better predicts the flow rates than does the one-dimensional. The difference between the one- and two-dimensional calculation results can be explained by the additional pressure loss in the boundary layer developing region.

The release of the latent heat of vapor increases

Fig. 4 The volumetric size distributions of the droplet formed through homogeneous nucleation and growth process. ($H=0.5$, $G=1 \mu\text{m}^2$)

the temperature and the pressure in the capillary and also changes the flow conditions. The differences of the flow rates between the flows with and without condensable vapor are within 2 percent. This indicates that the effect of the latent heat on the flow rate is small. The saturation ratio near the wall shown in Fig. 3 is lower than at the core of the flow. This is because the viscous dissipation of the flow near the wall prevents the temperature from decreasing during the expansion. As the flow approaches the exit, the saturation ratio increases. The normalized mass fraction of vapor decreases near the centerline of the exit, which shows the depletion of the vapor. There is a region near the exit where the saturation ratio is lower than that of the neighborhood. This is the effect of the latent heat release and the vapor depletion. Therefore the effect of the latent heat and the depletion of vapor on droplet growth can be important.

As shown in Fig. 3, nucleation and subsequent growth take place near the centerline of the exit. The size distributions of the droplets formed through nucleation and the growth process are represented as the mixing-cup-averaged volumetric size distribution in Fig. 4. As the flow parameter decreases, the size of the droplet and the total volume of the droplet increase. This is because the saturation ratio increases with the decrease of the flow parameter. When the growth of the seed particle is used for the measurement of condensation nuclei, the formation of droplets must be suppressed and thus a low value of the flow parameter must be avoided. When producing a fine particle by means of capillary expansion, changing the flow parameter can control the size of the particle and the yield.

Seed particles starting at different positions have different growth histories. The residence time of a particle starting near the wall is longer than that of

one starting from the centerline. However, the size of a seed particle starting near the centerline is larger than that of one near the wall. This is because the saturation ratio near the centerline is higher than that of one near wall, as shown in Fig. 3. In the high supersaturation region where the depletion of vapor is dominant, however, particle growth rate depresses. The particle lag motion and its effect on the transport process are considered. The results show that the enhancement of growth rate by this lag motion is so small as to be negligible.

The mass averaged seed particle size at the exit is shown in Figs. 5 and 6. As the flow parameter increases up to 1, the size decreases slowly. As the flow parameter exceeds 1, the size decreases rapidly. This can be explained from the fact that increasing the flow parameter decreases the saturation ratio. The result of the one-dimensional calculation shows more rapid decrease of the size near 1. This is because there is a region near the centerline where the flow still remains supersaturated and this radial nonuniformity is not considered in the one-dimensional calculation. As the heating parameter increases, the size of the

Fig. 5 The mass averaged seed particle size at the exit with different heating parameters from two-dimensional calculation. ($G=1 \mu\text{m}^2$)

Fig. 6 The mass averaged seed particle size at the exit with different heating parameters from one-dimensional calculation ($G=1 \mu\text{m}^2$)

particle decreases. This indicates that the heating of the particle surface reduces the growth rate. The results of the calculation with different growth parameters show that the size at exit is proportional to the square root of the growth parameter and the growth parameter becomes approximately the square of the particle size at exit without particle heating. Therefore the control of seed particle growth and homogeneous nucleation can be controlled by the selection of the flow parameter, the heating parameter, and the growth parameter.

6. Conclusions

The main aim of this work is to control seed particle growth and homogeneous nucleation in capillary expansion. The major parameters that affect particle growth in the capillary are derived from the analysis of capillary flow and growth rate. And the effect of these parameters on the flow fields, the particle growth, and the homogeneous nucleation are examined numerically.

Although the Reynolds number of the flow in this study exceeds the critical Reynolds number, the experimental results show that the laminar assumption is still valid. A low value of the flow parameter causes homogeneous nucleation and a high value of the flow parameter depresses seed particle growth. Although the flow parameter exceeds 1, the growth of seed particles still occurs near the centerline of the capillary. As the heating parameter increases, the growth rate decreases. The particle size at exit is proportional to the square root of the growth parameter. It is found that the proper selection of the flow parameter, the heating parameter, and the growth parameter can control seed particle growth and homogeneous nucleation, independently.

Acknowledgements

This work was supported by a grant from the National Research Laboratory program of the Ministry of Science & Technology and the Brain Korea 21 program of the Ministry of Education.

References

- (1) Abraham, O., Kim, S. S. and Stein, G. D., "Homogeneous Nucleation of Surfactant Hexafluoride Clusters on Laval Nozzle Molecular Beams", *J. Chem. Phys.*, Vol.57 (1981), p.402-411
- (2) Hill, P. J., "Condensation of Water Vapor during Supersonic Expansion in Nozzles", *J. Fluid Mech.*, Vol.25 (1966), p.593-620.
- (3) Turner, J. R., Kodas, T. T. and Friedlander, S. K., "Monodisperse Particle Production by Vapor Condensation in Nozzle", *J. Chem. Phys.*, Vol.88 (1988), p.457-465.
- (4) Lele, A. K. and Shine, A. D., "Morphology of Polymers Precipitated from a Supercritical Solvent", *AIChE J.*, Vol.38 (1992), p.742-752.
- (5) Matson, D. W., Fulton, J. L., Petersen, R. C., and Smith, R. D., PESS, "Rapid Expansion of Supercritical Fluid Solutions: Solute Formation of Powders, Thin Films, and Fibers", *Ind. Eng. Chem. Res.*, Vol.26 (1987), p.2298-2306.
- (6) Kwauk, X. and Debenetti, P. G., "Mathematical Modeling of Aerosol Formation by Rapid Expansion of Supercritical Solutions in a Converging Nozzle", *J. Aerosol Sci.*, Vol.24 (1993), p.445-469.
- (7) Mallina, R. V., Wexler, A. S. and Johnston, M. V., "Particle Growth in High Speed Particle Beam Inlet", *J. Aerosol Sci.*, Vol.28 (1997), p.223-238.
- (8) Barrett, J. C. and Clement, C. F., "Growth Rates of Liquid Drops", *J. Aerosol Sci.*, Vol.19 (1988), p.223-242.
- (9) Karki, K. C. and Patankar, S. V., "Pressure Based Calculation Procedure for Viscous Flows at All Speeds in Arbitrary Configurations", *AIAA J.*, Vol.27 (1989), p.1167-1249.
- (10) Volmer, M. and Flood, H., "Tröpfchenbildung in Dämpfen", *Z. Phys. Chem.*, A170 (1934), p.273-285.
- (11) Beker, Von R. and Döring, W., "Kinetische Behandlung der Keimbildung in übersättigten Dämpfen", *Ann. Physik*, Vol.24 (1935), p.719-752.
- (12) Kim, Y. K. and Kim, S. S., "Transport of a Condensable Species in Nonisothermal Tube Flow", *Int. J. Num. Meth. Heat & Fluid Flow*, Vol.5 (1995), p.797-812.
- (13) Crowe, C. T., Sharma, M. P. and Stock, D. E., "The Particle-Source-In Cell Model for Gas-Droplet Flows", *ASME J. Fluids Eng.*, Vol.99 (1977), p.325-332.