International Journal of Engineering & Technology, 7 (3.33) (2018) 85-89

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

Application of Particle Imaging Method for Measurement of Solid Volume Fraction in Carbon Nanotube Particles Fluidized Bed

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Abstract

Solid volume fraction in the carbon nanotube (CNT) fluidized bed reactors is an important parameter which is responsible of fluidization quality and the design of reactor. The solid volume fraction can be obtained from the pressure drop across the bed with the information of gas and particle densities. However, previous method such as the Hg-porosimetry for the measurement of the particle density did not adequately draw the solid volume fraction of the CNT aggregates with entangled nanotubes network. A new method to measure the apparent particle density of the CNT aggregates was proposed to calculate the solid volume fraction in the CNT fluidized bed. The density of the vertically aligned CNT particle was measured based on the apparent volume by shape analysis using two dimensional imaging. The solid fraction based on imaging method showed a significant value of 0.69 for the fixed bed, which describes well the entangled structure of the CNT aggregates. The distribution of solid volume fraction in the CNT fluidized bed with variation of gas velocity was determined based on the imaging method. The method was verified by applying the obtained values to the Richardson-Zaki equation on the bed expansion in the fluidized bed.

Keywords: *Carbon nanotube, Fluidized bed, Solid volume fraction, Particle density, Imaging, Shape analysis.*

1. Introduction

These Carbon nanotubes (CNTs) have received much attention as promising materials in various engineering applications [1]. Recently, studies have been conducted to synthesize carbon nanotubes in a mass production by using catalytic chemical vapor deposition (CCVD) in a fluidized bed [2]. Two forms of multi-walled CNTs, such as vertically aligned carbon nanotubes (VACNT) and entangled carbon nanotubes (ENCNT), can be produced by the CCVD method. The VACNTs are bundles of carbon nanotubes that grow perpendicular to a substrate and are dense and orderly arranged. The VACNT possess many advantages for multifunctional applications [3]. Solid volume fraction in the CNT fluidized bed reactors is an important parameter which is responsible of fluidization quality, homogeneous mixing, and process efficiency [4]. To obtain the solid volume fraction (ε_s) in the fluidized bed, pressure drops (ΔP) are measured across the bed height (ΔL). The measured pressure drop is related directly to the densities of gas and particles in the bed, assuming negligible acceleration and wall friction as.

$$\Delta P/\Delta L = (\rho_p \varepsilon_s + \rho_g \varepsilon_g) \quad (1)$$

,where gas volume fraction, ε_g = 1- ε_s, and g is gravitational constant.

In equation (1), gas density (ρ_g) can be easily obtained from thermodynamic data. However, the information for particle density (ρ_p) should be experimentally determined.

For particle density, there are several particle density definitions available. A definition may be more suitable than the others depending on the application. The definition of particle density for nonporous particles is straight forward: the mass of the particle is divided by the volume of the particles. However, the particle volume should be replaced with the envelop volume (apparent volume) for the particles with meso- or micro-pores such as the CNT and catalyst particles. This would be more correct from a hydrodynamic point of view if the particle behavior in the flow filed is of interest as the hydrodynamics in the fluidized bed [5]. For porous particle, the enveloped or pore volume is usually measured through mercury porosimetry, which involves the intrusion of the mercury at high pressure into a material.

In recent years, a few studies [6 - 8] reported limited data on the bulk density and solid volume fraction in the CNT fluidized bed. They reported the bulk densities of the CNT particles show relatively low values because the multi-aggregates structure has significant voidage inside of the CNT particles. Although the structure of the CNT particles, they calculated the solid volume fraction based on the mercury porosimetry method. However, the mercury porosimetry method is not adequate for obtaining the apparent volume of the VACNT particles, because the method has limitations in measuring pore volume of the VACNT with the entangled nanotube network structure by the interactions and entanglement between nanotubes on the particles [3]. Therefore, a study for better measurement method on the apparent volume of the VACNT is required to calculate accurately the solid volume fraction.

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In this study, a new method to measure the particle density was proposed for the calculation of solid volume fraction in the VACNT fluidized bed. The VACNT particle density was measured based on apparent volume using two dimensional imaging of the particles. The distribution of solid volume fraction in the CNT fluidized bed with variation of gas velocity was determined. The observed results were verified based on the Richardson and Zaki equation [9].

2. Materials and Methods

The CNTs particles (FT-7000) were obtained from C-Nano as the bed materials to investigate the fluidization behavior of the VACNTs. The FT-7000 (d_p = 0.41mm) is a type of the vertically aligned CNT as in Figure 1. The aggregated CNT particles in the reactor were sampled after the test including the axial pressure drop measurement in the fluidized bed.

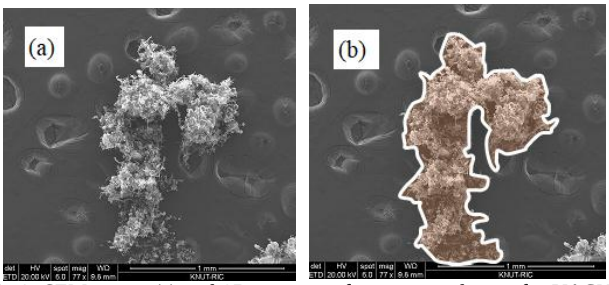


Fig.1: SEM image (a) and 2D imaging of apparent volume of a VACNT aggregate.

The fluidization test was carried out in a cold flow reactor made of transparent Plexiglas column with a tuyere type distributor for injecting air as shown in Figure 2. It consisted of a main column (0.15 m-ID X 2.0 m high) and an expanded upper column (0.30 m-ID) at the top to reduce the entrainment of particles. Air as fluidizing medium was introduced into the column through a mass flow controller.

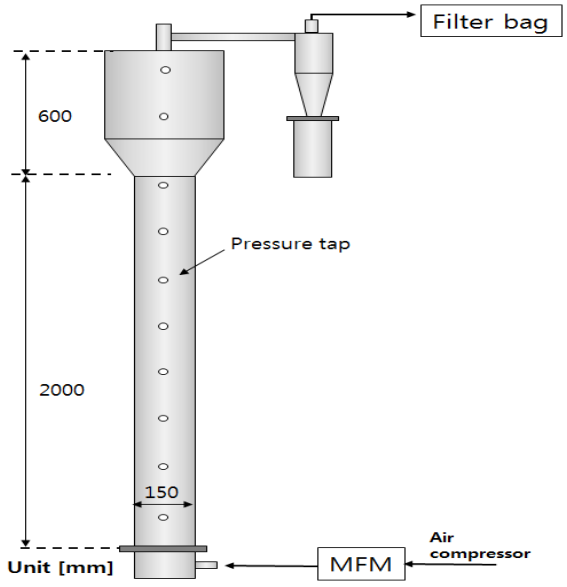


Fig. 2: Experimental apparatus.

Pressure taps were installed vertically along the column wall to measure pressure drop. Bed materials of 0.51 kg were loaded and the static bed height was 0.50 m. The gas velocity was varied 0.07 – 0.09 m/s for the experiment on the axial distribution of the solid volume fraction. After preparation of samples, two dimensional images of the CNT particles were obtained with a high resolution camera (RX100M4, Sony, Japan) for scanning the particles. The images were processed to enhance them and to distinguish individual particles [10, 11], and analyzed to obtain the apparent volume based on the imaging of the particles. The Image J software [12] was applied to process the image obtained as shown Figure 3.

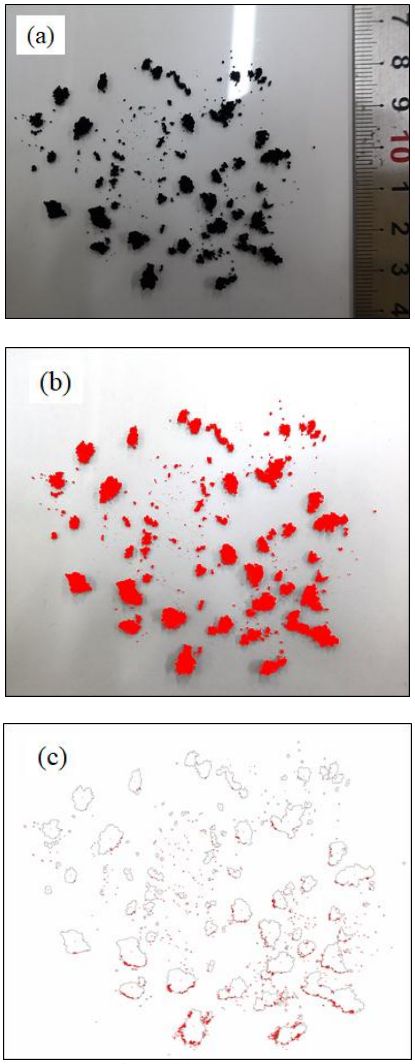


Fig. 3: Images processing for calculating apparent volume of CNT aggregates: (a) original image; (b) threshold and contrast processed image; (c) outlined processing image.

3. Results and Discussion

In this study, particle density was measured by estimating the apparent volume of the VACNT aggregates including nanotube entanglement of the VACNT particles through the particle shape analysis. First, the weight of the sampled particles was measured, and then evenly spread them on the plate for imaging as in Figure 3(a). After obtaining the diameters from the two-dimensional surface area of the photographed particles (Figure 3(c)), the volume of the particles was estimated assuming a spherical shape. Finally, the particle density is calculated by dividing the weight by the estimated volume. Figure 4 compares the particle density measured by the particle imaging with the method by the Hg-prosimetry. The particle density by the shape analysis was much lower than that by the Hg-porosimetry. In order to verify the correctness of the proposed method, the measured bulk density and the density from each method were compared in Figure 4(a).

The bulk density is defined as the mass of many particles of the material divided by the total volume (entire bed volume) they occupy. The bulk density represents the density in the fixed bed state, which can be expressed by the following equation for the particle density and the solid volume fraction.

$$\rho_{bulk} = \rho_p \rho_s \quad (2)$$

Generally, for particles greater than 0.02 mm, the solid holdup has a value of 0.28 or greater [13]. Assuming that the fixed bed has a measured bulk density, the solid volume fraction of the fixed bed calculated on the basis of the Hg-porosimetry is a very low value of 0.16, which does not match the reported solid fraction for the various particles. The solid volume fraction based on the imaging method showed a significant value of 0.69 for the fixed bed, which describes well the entangled structure of the CNT aggregates with high internal porosity and large apparent diameter compared to initial particle. Additionally, Figure 4(b) compares the apparent particle volume for both methods. It can be seen that the apparent volume of the CNT particles based on the imaging method represent well the VACNT shape in which the voidage(ε) of a considerably large fraction are contained in the VACNT aggregates.

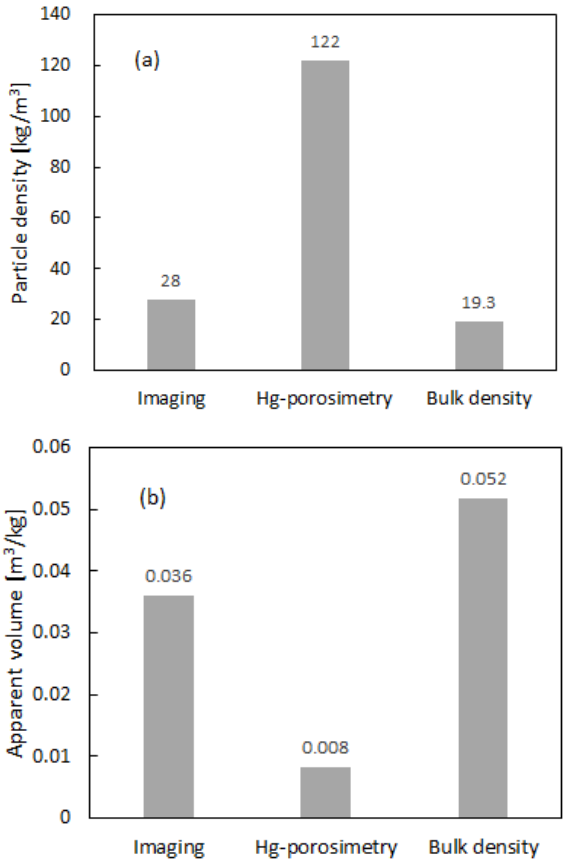
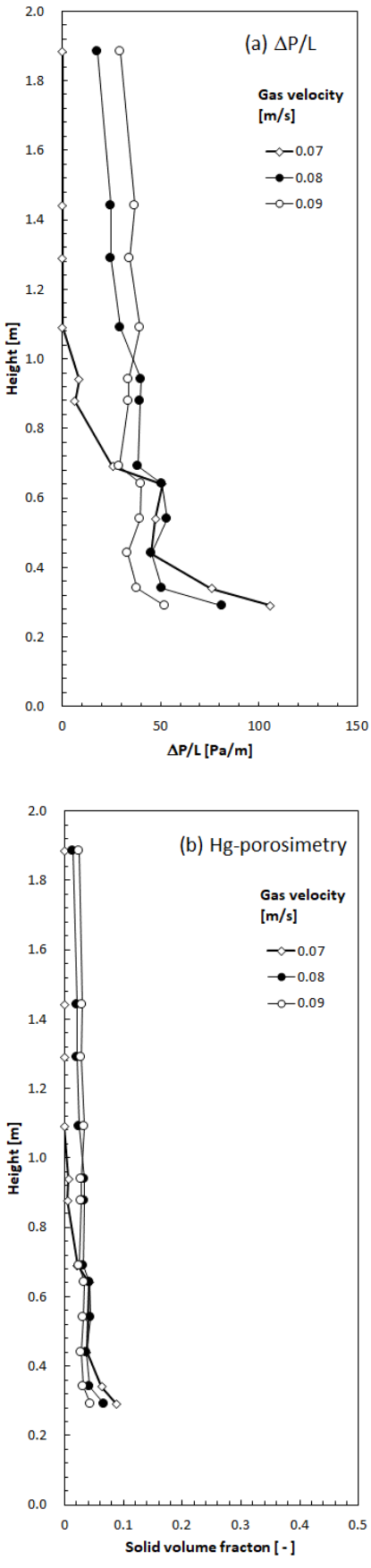


Fig. 4: Apparent particle densities (a) and apparent particle volume (b) from different measurement methods.

The axial distributions of pressure drop and the solid volume fraction with gas velocity are shown in Figure 5. The axial pressure drop and the solid volume fraction distributions are seemingly similar to that of the bubbling fluidized bed of Geldart A particles, where the fraction around the bottom or the dense region of reactor is high due to high solids concentration and it decreased with increasing height. The dense bed is formed up to 0.7 m over 0.5 m of initial bed height. The significant bed expansion of the CNT particles with gas velocity is generally observed, which is due to the unlocked entangled nanotube network between CNT aggregates [3, 6, 8]. The solid volume fraction in the freeboard region of the bubbling fluidized bed significantly increases by increasing drag force on the particles with gas velocity [13]. In the comparison of the solid volume fraction distributions according to the particle density measurement method, the solid volume fraction calculated by the Hg-porosimetry method showed values less than 5% in the entire region of the reactor. These are typically appeared in the lean-phase region of the turbulent and fast fluidized beds [14, 15]. On the other hand, it is judged that the solid volume fractions by the imaging method represents the actual phenomenon well with showing much more than 15% in the dense bed within the experimental range.



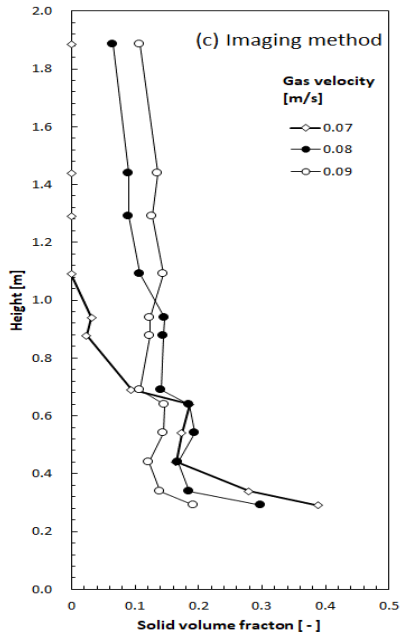


Fig. 5: Axial distributions of pressure drop across bed (a) and solid volume fraction based on particle densities by Hg-porosimetry (b) and by imaging method (c) with axial height.

The validity of measured solid volume fraction can be ascertained from variation of the bed expansion behaviour with gas velocity. The bed expansion is directly related to voidage or solid volume fraction in the fluidized bed, which is very well represented by the Richardon and Zaki equation [8, 16, 17].

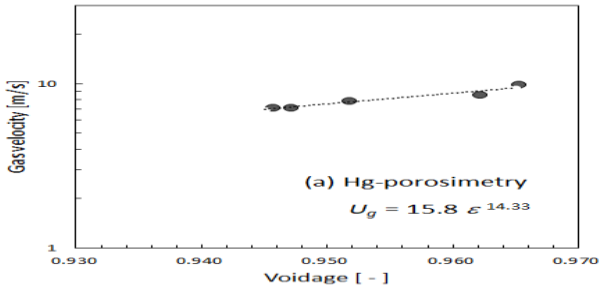
Richardson and Zaki [9] observed that a straight line is resulted when gas velocity was plotted against the expanded bed voidage. Such a straight line can be described by the following equation.

$$U_g/U_g = \square\square^n \quad (3)$$

,where terminal velocity (U_t) of the CNT aggregates can determined with given voidage values at different gas velocity. Several studies [6, 8, 16, 17] showed the nano powder fluidized bed including the CNT particles followed the Richardson-Zaki equation well, and the CNT particle size could be calculated by the Allen equation [18] of equation (4) based on the obtained terminal velocity from equation (3) [8].

$$d_p = 1.23 \frac{U_t^{0.875} \rho_g^{0.25} \mu_g^{0.375}}{(\rho_p - \rho_g)^{0.625}} \quad (4)$$

The calculated diameter of the CNT particles should match the measured particle size if the measured particle volume fractions properly reflect the voidages between particles in the expanded fluidized bed. The Richardson-Zaki equation was applied to the results based on the existing Hg-porosimetry and the results based on the imaging method, in order to confirm the appropriateness of the proposed density measurement method for the CNT particle. The application results are shown in Figure 6 and in equations (5) and (6).



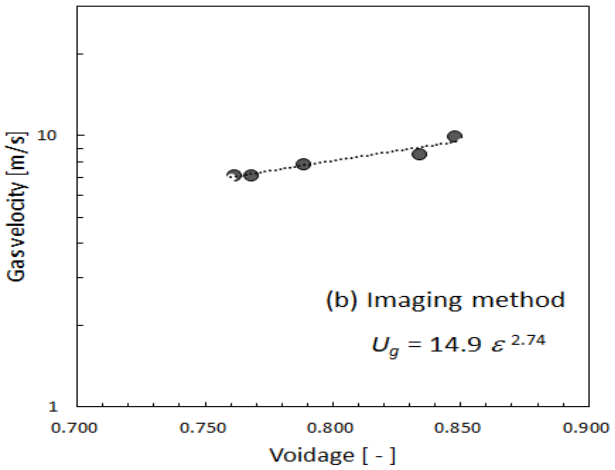


Fig. 6: Semi-logarithmic plot for application of the Richardson-Zaki equation [9] on the bed voidage vs. the superficial gas velocity.

$$U_g = 15.8\ \square^{14.33} \text{ :based on Hg-porosimetry} \quad (5)$$

$$U_g = 14.9\ \square^{2.74} \text{ :based on imaging method} \quad (6)$$

In the comparison of the obtained equations, the terminal velocities showed similar values in both methods, but the Hg-porosimetry method showed a relatively high n value. The average CNT particle size calculated from equations (3) and (4) and the Heywood diameter, which is the equivalent diameter of the circle having the same area as the projected area, measured by the imaging method are compared in Table 1 for both methods.

Table 1: Comparison of CNT particle diameters calculated by different particle density measurements.

Method	Hg-porosimetry	Imaging method
$\square_p$ [kg/m^3]	122	28
U_t [m/s]	0.16	0.15
Air viscosity, $\square_g$ [kg/m s]	1.81 X 10^{-5}	1.81 X 10^{-5}
Air density, $\square_q$ [kg/m^3]	1.182	1.182
Calculated d_p [$\square$m][a]	212	520
Measured d_p [$\square$m][b]		481

a) calculated by Allen equation based on the Richardson and Zaki equation [9]; b) Heywood diameter based on imaging method.

As shown in the table 1, the particle size calculated by the solid volume fraction or voidage obtained from the imaging method is closer to the actual size of the particles compared to Hg-porosimetry, indicating that the particle density measurement by the imaging method is more suitable for the calculation of the solid volume fraction in the fluidized bed of the VACNT.

4. Conclusion

A new method to measure the apparent particle density of the CNT aggregates was proposed to calculate much accurately the solid volume fraction in the CNT fluidized bed. The density of the vertically aligned CNT particle was measured based on the apparent volume by shape analysis using two dimensional imaging of the CNT particles. The solid fraction based on imaging method showed a significant value of 0.69 for the fixed bed, which describes well the entangled structure of the CNT aggregates with high internal porosity and large apparent diameter compared to initial particle. The distribution of solid volume fraction in the CNT fluidized bed with variation of gas velocity was determined based on the imaging method. The proposed method was verified based on the Richardson-Zaki equation. The imaging method pro-

posed in this study is shown to be much suitable compared with the existing Hg-porosimetry method.

Acknowledgement

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2017R1D1A3B030299 17).

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