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***Research paper***

# Visualization of Carbon Nanotube Aggregates in Dilute Phase of a Fluidized Bed

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## Abstract

**Background/Objectives**: Fluidization characteristics and aggregation behavior of carbon nanotube (CNT) particles have been determined in the freeboard of a bubbling fluidized for the design and scale-up of the process.
**Methods/Statistical analysis**: The aggregation behavior of the CNT particles was observed in a gas solid fluidized bed (0.15 m i.d. X 2.6 m high) using laser sheet technique for their visualization. A high speed camera was installed at the height of 0.67, 1.05 and 1.50 m above the gas distributor to observe the CNT aggregates behavior and determine their size and shape. The Image J was applied to process the obtained images.
**Findings**: Effect of height in the reactor on aggregation of CNT particles have been determined. The axial local bulk density distribution is almost similar with a general bubbling fluidized bed such as Geldart A or Geldar B particles, which shows typically a dense bed at the bottom of the reactor and a decrease of the local bulk density with increasing height. The Feret and Heywood diameters of the aggregates are larger than the average diameter of the CNT particles, indicating that the CNT particles form the aggregates by physical entanglements and van der Waals force in the dilute phase of fluidized bed. A possible mechanism of aggregates formation was proposed based on the variation of size and shape of CNT aggregation with the height. The aggregation process in dilute phase is attributed largely to nanotubes stripping off the surface of CNT particles in addition to the inter-particle aggregation. The aggregation process affects the decrease of aspect ratio and the increase of solidity of aggregates with increasing the height.
**Improvements/Applications**: The obtained results on the CNT properties could be used for the design of cyclone and the modeling of heat transfer in the fluidized bed reactor.

***Keywords:*** *Carbon Nanotube Fluidized Bed, Aggregates, Nanotube Shape, Visualization*.

## 1. Introduction

Carbon nanotubes (CNTs) are very promising materials for use in nanotechnology applications [1]. Recently, researches on the CNTs synthesis by catalytic chemical vapor deposition (CCVD) have focused on mass production in fluidized beds [2]. The strong anisotropy of the nanotube on particle can affect fluidization behavior of the particles in the fluidized bed reactor because the CNT particles fall under the Geldart C classification. It is difficult to handle the CNT particles in a gas-solid fluidized bed reactor because cohesive force between the particles is stronger than fluid mechanical movement. The strong cohesive forces between the particles promote the aggregates fluidization of primary particles [3]. The aggregates have the inherently dynamic and chaotic properties in meso-scale flow structure of gas-solid flow in the fluidized bed. The measurement and characterization of the aggregates are complicated due to the dynamic properties.

Intrusive and non-intrusive methods have been used for acquiring the aggregates properties in the gas-solid fluidized beds [4]. The intrusive methods such as optical fiber probe, capacitance probe and momentum probe are advantageous in cost and installation. However, they made disturbance of the local particle flow. The non-intrusive methods such as digital image analysis methods combined with laser sheet, tomography and nuclear magnetic resonance techniques measure the whole image of the particles flow in a wide range [5]. The imaging based on laser sheet technique has been used to measure aggregation phenomena at different flow regime in fluidized beds with advantages of easy installation and in-situ measurement [4,6-8]. More recently, a few studies [4,6] has used the laser-based image analysis method to measure sizes of multi-walled CNT aggregates. Jeong and Lee [4] measured the sizes of aggregates just above the bed surface for inferring particles behavior in the dense bed. Kim [6] measured the aggregates properties at a point in the dilute phase of reactor. However, the lack of information on variation in the aggregates size and shape along height of the reactor exists for understanding the macro and microscopic structure of the aggregates in the freeboard of the fluidized bed. Further study on the fluidization characteristics of CNT aggregates in the dilute region is required for the design of freeboard part in the CNT reactor such as the heat transfer modeling [9] and the cyclone design [10].

The objective of this study is to determine fluidization characteristics and aggregation behavior of CNT particles in a gas solid fluidized bed based on imaging analysis using laser sheet technique. The aggregates properties such as size, aspect ratio and solidity with height variation were measured and compared to analyze the dynamic behavior of the CNT aggregates in the freeboard region of reactor.

## 2. Materials and Methods

### 2.1. Experimental Method

To investigate the fluidization behavior of CNTs, the particles used in the study were FT-9000 (C-Nano) multi-walled CNTs. The CNT with average diameter of 0.25mm is a type of the entangled CNT. The CNT particle is macroscopically seen as a black powder whereas microscopically the nanotubes on the particle surface are randomly oriented in an entangled spaghetti-like configuration [6]. Experiments were carried out in a fluidized bed unit made of transparent Plexiglas column as shown in figure 1. It consisted of a main column (0.15 m-ID X 2.0 m high) and a cyclone. The column was expanded to 0.30 m to reduce elutriation of particles. A tuyere type distributor was used to inject air for fluidization. A mass flow meter was used to measure the gas flow rate in the column. Pressure taps were mounted flush with the column wall to measure pressure drops from which the local bed densities were deduced. Bed materials of 0.92 kg were loaded and the fixed bed height was 0.50 m. The superficial gas velocity was 0.051 and 0.065 m/s considering operating condition of the CNT reactor.

A high speed camera (RX100M4, Sony, Japan) was installed at the height of 0.65, 1.05 and 1.50 m above the gas distributor to visualize the CNT aggregates behavior and determine their size and shape at different height. The light emitted from a He-Ne laser (Model 1145, Lumentum, US) passed through a grass rod lens and illuminated the center region of column. The sampling rate and exposure time of the camera were 480 frames/s with the resolution of 350 dpi and 1000 μs.

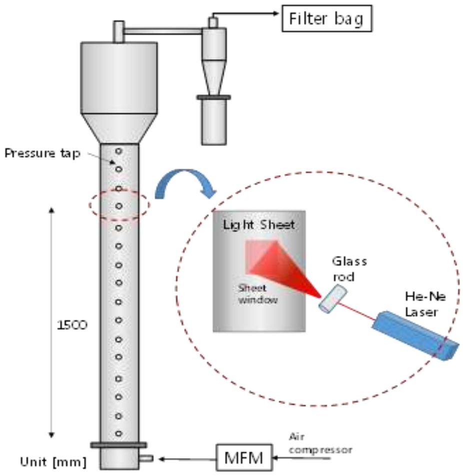


**Figure 1**: Experimental apparatus and schematic diagram of laser light sheet method

### 2.2. Image Analysis

To minimize the uncertainties from dynamic flow state in the fluidized bed, about 30 images were obtained with a time interval of approximately 3 minutes after ensuring the steady state operation by pressure measurement. The Image J [11], developed by National Institute of Standards and Technology US, was applied to process the image obtained as in figure 2(a). The obtained images were first converted to threshold ones as in figure 2(c) to identify the aggregates after removing some background light noise as shown in figure 2(b). This process is called thresholding [7]. After the thresholding as in figure 2(c), function of 'Analyze Particle' in the Image J provides measured values of the aggregates properties such as shape, size and area as in figure 2(d). In addition, particle number in the aggregated were counted from the original image (figure 2(a)) based on light spots on the aggregate because the catalysts for the CNT synthesis is composed of metal components.

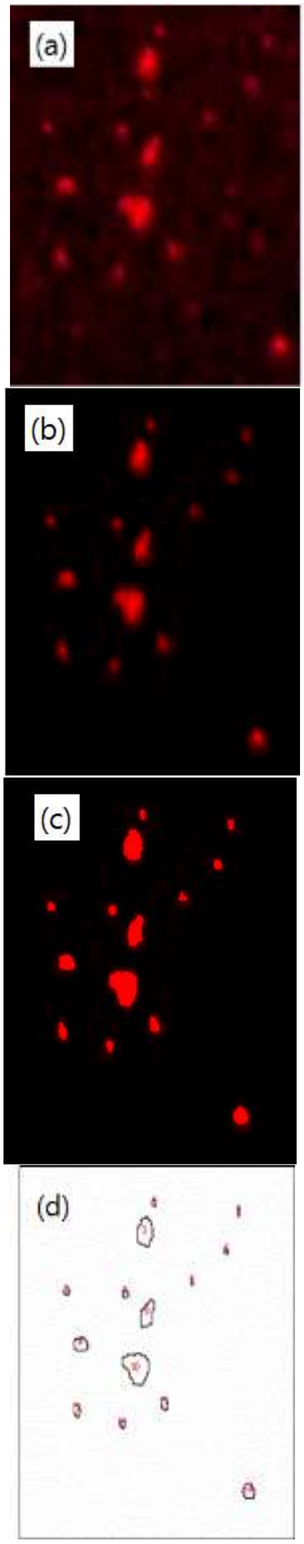


**Figure 2**: Image processing (a) Original image, (b)Removal of noise, (c) Thresholding, (d) Analyzed particle image

## 3. Results and Discussion

Axial distributions of the local bulk density across bed with axial height at different gas velocity is shown in figure 3. The local bulk density ($\square_{bulk}$) of particles is an indicator to show how many CNT particles are distributed along the reactor height in fluidization state. It can be obtained from Eq. (1) as following.

$$\rho_{bulk} = \frac{\Delta P}{\Delta L g} \qquad (1)$$

where ΔL is distance between two taps for the pressure drop measurement. The local bulk density distribution is seemingly similar to that of the bubbling fluidized bed of Geldart A [5] particles, where the pressure drop 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 0.6 m from the distributor. The local bulk density distribution is almost similar with a general bubbling fluidized bed such as Geldart A or Geldar B particles, which shows typically a dense bed at the bottom of the reactor and a decrease of the local bulk density with increasing height. However, the CNT fluidized bed shows an entrainment of the big particles by burst of large bubbles at the bed surface as in case of Ug = 0.065 m/s because the CNT aggregates, which have multi-aggregation structure with high internal voidage, easily lead to the formation and growth of large bubbles in the dense bed [2].

The sizes and shape properties of the CNT aggregates were visualized and measured in the freeboard of the fluidized bed. Figure 4 shows the images of the CNT aggregates at heights of 0.65, 1.05 and 1.50 m at superficial gas velocity of 0.065 m/s. The bright spots represent particle aggregates. The solid volume fraction of large aggregates was decreased as increasing of height. The aggregates have different size and shape depending on the height. The aggregates at the height of 1.0 and 1.5m are relatively small and the shape is close to a circle. However, it was observed that a few particles are stuck together, and accordingly big particles with irregular shape occurred at the height 0.65 m.

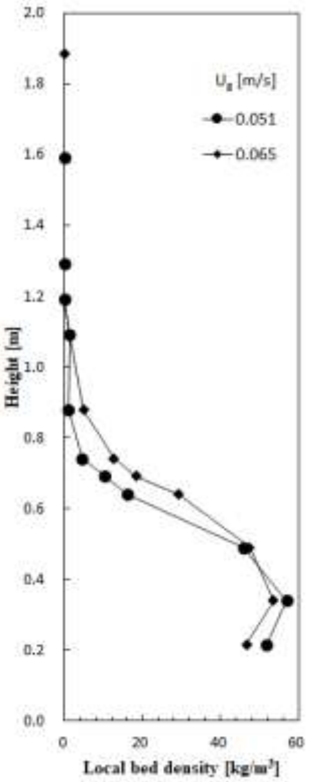


**Figure 3:** Axial solid bulk density distribution of CNT particles

The effect of reactor height on (a) Feret diameter, (b) Heywood diameter and (c) particle number in the aggregates is shown in figure 5. The Feret diameter is a statistical diameter representing the mean value of the distances between pairs of parallel tangents to a projected outline of the particle [5]. The Heywood diameter is the equivalent diameter of the circle having the same area as the projected area. At all the measured locations in operating gas velocity range, the Feret and Heywood diameters are larger than the average particle diameter of 0.25 mm, indicating that the CNT particles form the aggregates in the dilute phase of fluidized bed. The CNT particles usually have bundles of hundreds of microns formed by thousands of individual nanotubes held together by physical entanglements and van der Waals force [12]. The phenomena affect inter-particle aggregation, which leads to enlargement of solids diameter in the freeboard region. The diameters of the aggregates decrease with increasing height in the freeboard region. The Feret and Heywood diameters show high values at the 0.65 m, because enhanced inter-particle force by high solid volume fraction in the dense bed makes the aggregates bigger and the aggregates emit from the bed surface. However, large aggregates are able to easily fall back to the bed due to a decrease of the local gas velocity by the bubble breakage just above dense bed region [7]. Only smaller aggregates reach the higher location above 1.05 m. The CNT particle number (bright spot number per an aggregate) in aggregates is about 1.3 on average at the height of 0.65 m as in figure 5(c). The number decreases with increasing the height in the freeboard region. This result supports that higher value of the aggregate diameter at 0.65 m is attributed to aggregation of the CNT particles. However, it cannot describe the aggregation phenomena at high location of 1.05 and 1.5 m.

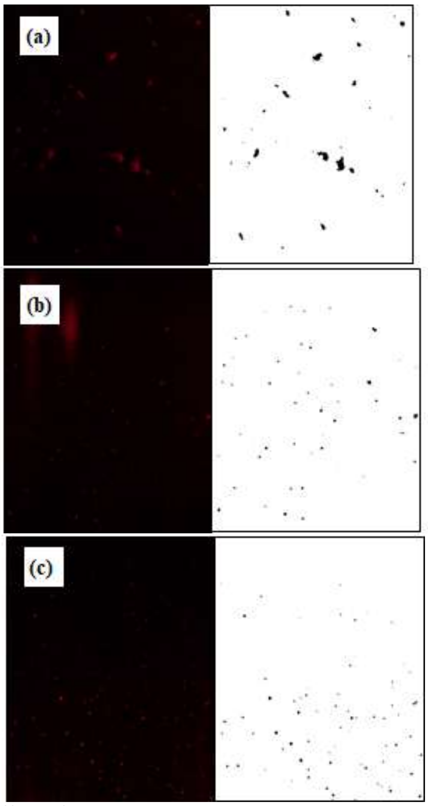


**Figure 4:** Effect of height on aggregates size and shape in original and processed images at $U_g$ = 0.065 m/s; (a) height=0.65 m, (b) height=1.05 m, (c) height=1.50 m.

To explain the aggregation at high location of the reactor, the Heywood diameter distribution of the aggregates is shown in figure 6. When compared to the diameter distribution at 0.65 m, particles larger than 0.80 mm hardly appear at 1.05 and 1.5 m, indicating the large particles or aggregates have no rising up to 1.0 m. Interestingly, the fraction of particles smaller than 0.20 mm decreases, whereas the fraction of particles between 0.30 and 0.40 mm relatively increases despite no noteworthy increase of particle number in aggregates. The aggregation process in dilute phase is attributed largely to nanotubes stripping off the surface of CNT particles [6]. The nanotubes stripped by mechanical force in fluidization process combine easily with CNTs to form larger aggregates due to van der Waals force.

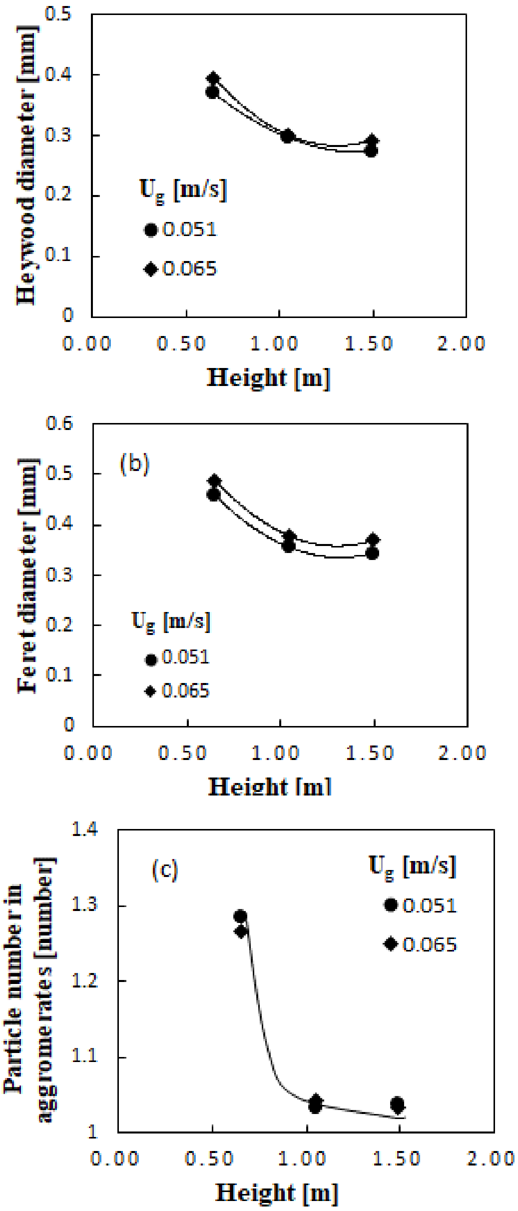
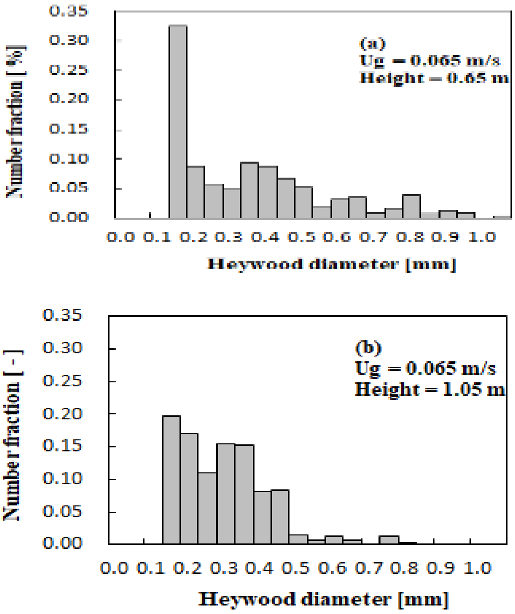


**Figure 5**: Effect of height on the (a) Heywood diameter, (b) Feret diameter and (c) particle number in aggregates



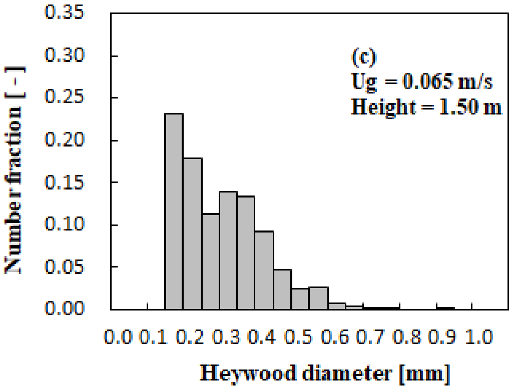


**Figure 6**: Histogram of number fraction with Heywood diameter

The effect of height in the reactor on (a) aspect ratio and (b) solidity is shown in figure 7. The aspect ratio of aggregates decreases with increasing the height as shown in figure 7(a). The aspect ratio of the aggregates is higher than 1.4 in all cases, indicating that main contribution in the CNT aggregates formation is mainly by inter-particle aggregation in the dilute phase of fluidized bed. The solidity, which describes surface roughness [6,11], of the CNT shows an increase with increasing the height as shown in figure 7(b). The increase of solidity describes decrease of concave region even though aggregation of the CNT particles. It supports the contribution of stripped nanotube in forming the aggregates as mentioned in figure 6.

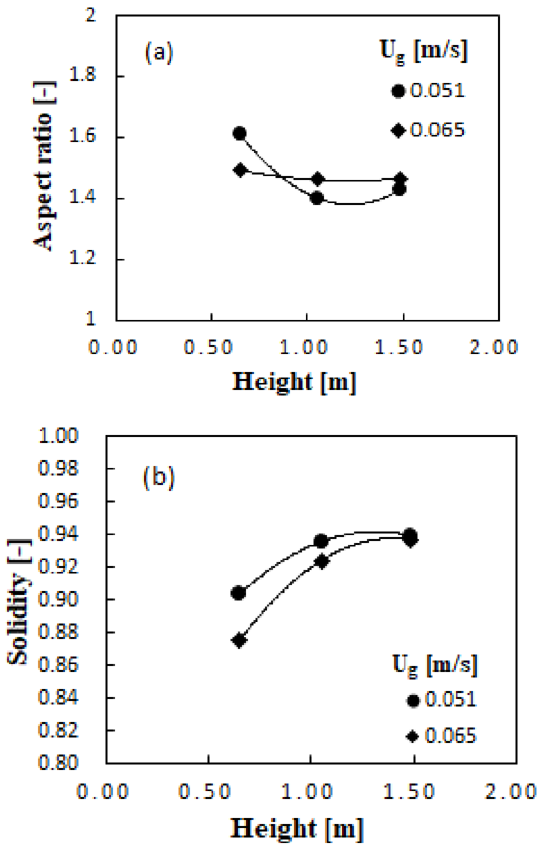


**Figure 7**: Effect of height on (a) aspect ratio and (b) solidity of CNT aggregates

## 4. Conclusion

Effect of height in the reactor on aggregation of CNT particles have been determined observed in a gas solid fluidized bed using laser sheet technique for their visualization. The aggregates have different size and shape depending on the height. The Feret and Heywood diameters of the aggregates are larger than the average diameter of the CNT particles, indicating that the CNT particles form the aggregates in the dilute phase of fluidized bed. A possible mechanism of aggregates formation was proposed based on the variation of size and shape of CNT aggregation with the height. The aggregation process in dilute phase is attributed largely to nanotubes stripping off the surface of CNT particles in addition to the inter-particle aggregation. The aggregation process affects the decrease of aspect ratio and the increase of solidity of aggregates with increasing the height.

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