Journal of Industrial and Engineering Chemistry 35 (2016) 217–223

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Fluidization behaviors of different types of multi-walled carbon nanotubes in gas–solid fluidized beds

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ARTICLE INFO

Article history:
Received 23 September 2015
Received in revised form 24 December 2015
Accepted 26 December 2015
Available online 31 December 2015

Keywords:
Fluidization behavior
MWCNTs
Agglomerate
Hydrodynamics
Flow regime

ABSTRACT

The fluidization behaviors of different types of multi-walled carbon nanotubes (MWCNTs) were investigated in a fluidized bed with a 0.14 m-ID × 2.4 m-height Plexiglas column. Four types of MWCNTs were used as the bed materials: (i) N refers to the NC7000™ prepared by Nanocyl®, (ii) S_f refers to the agglomerate by which fine entangled MWCNTs were agglomerated by strong cohesive force such as van der Waals force, (iii) S_c refers to the coarse entangled MWCNTs with a shape such as a single particle, (iv) S_{mix} refers to the binary mixture of S_f and S_c physically mixed in a 1:1 volumetric ratio. For N and S_f, the fluidization behavior with superficial gas velocity is similar to that of Geldart's group A particles. In the bubbling fluidization of N and S_f, no bubbles were observed. The minimum fluidizing gas velocity and bed expansion ratio of S_f was higher than those of N. The fluidization behavior of S_c was similar to that shown by the results from Geldart's group B with a wide size distribution. For the binary mixture, S_f and S_c are the flotsam and jetsam, respectively. The fluidization behavior of S_{mix} was divided into four regions with decreasing superficial gas velocity. S_c and S_f were not mixed sufficiently at high velocity due to the high bed expansion ratio of S_f. As the superficial gas velocity was decreased, S_c gradually became defluidized. When S_c had a fixed bed at the bottom, S_f showed particulate fluidization at the top. At this point, S_c and S_f were completely segregated. The variation in the pressure drop across the beds at the superficial gas velocity was similar to that for the S_c; however, the bed expansion was similar to that for the S_f.

Introduction

According to Geldart's classification, nanoparticles classified into group C particles are difficult to fluidize due to their very small size and strong cohesive force [1]. However, some studies have reported that nanoparticles can fluidize into agglomerate forms [2–4]. Agglomerates have two types of fluidization behaviors, agglomerate particulate fluidization (APF) and agglomerate bubbling fluidization (ABF), in gas–solid fluidized beds [3]. The fluidization characteristics of agglomerates are affected by the size and density of the multi-agglomerate structure [3]. The APF as a homogeneous fluidization has been classified into two fluidization states: solid-like fluidization in which agglomerates fluidize in the same position and liquid-like fluidization in which agglomerates move freely throughout the bed [5].

In recent years, researches on the synthesis of carbon nanotubes (CNTs) with superior physical and chemical properties by catalytic chemical vapor deposition (CCVD) in fluidized beds have focused on mass production [6–12]. However, the effects of factors such as catalyst, type of carbon source, and reaction temperature on the synthesis of CNTs have been mainly studied. In terms of the process, the interpretation and discussion of the hydrodynamics of CNTs are insufficient. A better understanding of the fluidization characteristics of CNTs is required for the design and scale-up process. However, studies on the fluidization characteristics of nanomaterials have been carried out using nanoparticles such as SiO_2 or TiO_2 with spherical shapes [3–5,13–16]. Yu et al. [17] reported results on the hydrodynamics of CNT. While meaningful, their study was limited to only one type of CNT.

CNTs prepared by CCVD in fluidized beds have a wide particle size distribution because of the difference in the residence time of catalyst. Moreover, the fine CNTs generated by the attrition are agglomerated, and then agglomerates can fluidize in a freeboard and carry over from the reactor. The operating conditions such as

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http://dx.doi.org/10.1016/j.jiec.2015.12.035
1226-086X/

Nomenclature

A_t	cross-sectional area of reactor [m^2]
$d_{pi,max}$	maximum particle size in interval [μm]
d_t	diameter of main column of experimental apparatus [m]
H	height at the positon measured pressure drop [m]
H_b	bed height [m]
H_t	total height of experimental apparatus from distributor [m]
H_0	static bed height [m]
N	NC7000™ prepared by Nanocyl®
S_c	agglomerate that fine entangled MWCNTs were agglomerated by strong cohesive force
S_f	coarse entangled MWCNTs that have a shape such as a single particle
S_{mix}	binary mixture in which S_f and S_c. are physically mixed at the volumetric ratio of 1:1
U_{cf}	complete fluidization velocity [m/s]
U_{mb}	minimum bubbling velocity [m/s]
U_{mf}	minimum fluidizing velocity [m/s]
U_0	superficial gas velocity [m/s]
W	bed weight [kg]
W_0	initial bed weight [kg]
x_i	weight percentage of solids in interval [%]
$-\Delta p$	measured pressure drop [Pa]
$-\Delta p_{bed}$	pressure drop across the fluidized bed [–]
ρ_b	bulk density of MWCNTs [kg/m^3]

gas velocity can hinder the safe and efficient operation without proper understanding of the phenomenon occurring in the synthesis process of CNTs.

Therefore, in this study, the fluidization behaviors of different types of multi-walled carbon nanotubes (MWCNTs) were investigated and compared to those of the particles belonging to the Geldart classification. Moreover, the fluidization behavior of a binary mixture system containing physically mixed low- and high-density MWCNTs was investigated, and the fluidization regime was divided with decreasing superficial gas velocity. The results of this study provide useful information to understand the fluidization characteristics of the MWCNTs in the synthesis process.

Experimental

Bed material

To investigate the fluidization behavior of MWCNTs, in this study, four types of MWCNTs were used as the bed material. The morphologies of MWCNTs are shown in Fig. 1. N is the NC7000™ prepared by Nanocyl® (Fig. 1a). S_f is the agglomerate by which the fine entangled MWCNTs were agglomerated by strong cohesive force such as van der Waals force (Fig. 1b). Because MWCNTs have a nanoscale diameter and microscale length, primary entangled MWCNTs are formed when MWCNT strands become entangled during the growth of MWCNTs [18]. As shown in Fig. 1b, S_f has an irregular morphology, and S_c is the coarsly entangled MWCNTs with a shape such as a single particle (Fig. 1c). S_{mix} is the binary mixture of S_f and S_c physically mixed at a 1:1 volumetric ratio (Fig. 1d). As shown in Fig. 1d, the light and dark spots correspond to the S_c and S_f, respectively.

Fig. 2 shows the cumulative size distribution of N and S_c analyzed using the sieving method. The Sauter mean diameters of N and S_c were 242 and 1203 μm, respectively. The maximum size of N was 710 μm. S_c has the sizes in the range of 500–2800 μm. The size distribution of S_c is wider than that of N. Size analysis of S_f and S_{mix} is not possible by sieving because of the strong cohesive force of S_f.

Compared to normal particles such as sand, the density of CNTs is very low, because CNT is a hollow tube and inner pores are formed, while CNT strands are entangled. The bulk densities of N, S_f, S_c, and S_{mix} used in this study were 57, 20, 81, and 53 kg/m^3, respectively.

Experimental setup

Fig. 3 shows the schematic diagram of a fluidized bed system used to investigate the fluidization behavior of different types of MWCNTs. The column was made of Plexiglas with a total height and diameter of 2.4 and 0.14 m, respectively. At the top of the column, an expanding part of 0.3 m inner diameter was used to reduce the entrainment of the fine MWCNTs. A cyclone and a standpipe were used to collect the entrained fine particles and return them to the column. A porous distributor was also used. The MWCNTs were fluidized with the air at room temperature and ambient pressure. Fluidizing gas was injected into the column using a mass flow controller. To measure the pressure drop, the first port was 0.05 m above the distributor. Ports were positioned at intervals of 0.05 m up to 0.55 m. From the height above 0.55 m, the ports were positioned at intervals of 0.10 m. After the steady state at a constant superficial gas velocity, the pressure drop was measured at each port. The data sampling rate was 60 Hz and the measured data were stored on a computer using an analog to digital (A/D) converter.

Results and discussion

Fluidization of Nanocyl® NC7000™ (N) and fine MWCNTs agglomerate (S_f)

To investigate the fluidization behavior of N, the pressure drop was measured with decreasing superficial gas velocity. Fig. 4 shows the pressure drop across the bed and bed expansion ratio of N with superficial gas velocity. When the superficial gas velocity was above 0.004 m/s, the pressure drop across the beds was maintained at a constant level. In contrast, channeling was observed at a lower superficial gas velocity of 0.004 m/s. Because channeling showed an unstable bed condition, reproducible data from the pressure drop measurement could not be obtained. Therefore, the minimum fluidizing velocity (U_{mf}) was determined as 0.004 m/s based on the experimental results, because a constant pressure drop was maintained at the onset with a stable bed condition. The bed height gradually increased with increasing superficial gas velocity from 0.004 to 0.047 m/s. The gas fluidization type had uniformly dispersed particles in a fluidizing medium with no bubbles, and the bed height was increased with increasing superficial gas velocity in the case of particulate fluidization. The particulate fluidization called 'homogeneous fluidization' appears mainly in the liquid–solid fluidization [19]. In a gas–solid fluidization, particulate fluidization appears under specific conditions. Geldart's group A particles have a particulate fluidization regime. At a superficial gas velocity of 0.047 m/s, the bed height is the maximum value corresponding to 2.59 times the static bed height. With further increase in the superficial gas velocity, the fluctuation of the bed surface occurred as the bed surface collapsed. At this time, the bed height slightly decreased. A similar bed expansion curve was observed for the Geldart group A