Design and Experimental Study of a Tapered Fluidized Bed Reactor without a distributor of Carbon Nanotubes

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Abstract. Fluidized bed reactor is a key component in chemical engineering. The tapered fluidized bed reactor (TFBR) without a distributor was innovatively used for the preparation of carbon nanotubes (CNTs) in this paper. And it was designed and studied experimentally. The tapered angle is an important part in the design of the tapered fluidized bed reactor. The parameterized design (5°, 10°, 11°, 13°, 15°, 18°, 20°) was carried out by using CFD analysis, and the optimal tapered angle was selected as 11°. The fluidization mass and behavior of the tapered reactor, the quality and yield during the growth of CNTs were studied experimentally. Results showed that the pressure drop of the multi-walled CNTs in the bed and the expansion process of the bed are in good agreement with each other in the process of acceleration and deceleration, and the fluidization in the bed is more uniform. Moreover, the yield of multi-walled CNTs reached 94.2 g and the quality of multi-walled CNTs reached 97.96 % in a linear increase within 1 h, which verified the feasibility and reliability of the reactor design.

Keywords: Fluidized bed reactor, carbon nanotubes, cone angle.

1. Introduction
Fluidized bed reactor is a key component in chemical engineering, and it is the place for chemical reactions [1][2]. Because of its good heat and mass transfer performance and easy operation and control characteristics, it is widely used in high exothermic chemical processes, such as coal, biomass, multiple catalytic reactions, adsorption, drying [1]. Carbon nanotubes (CNTs) are widely used in various fields because of their unique properties, including lithium electricity, biology and medicine, as polymer additives and energy devices [3]. There are physical processes such as heat transfer, catalysis, oxidation-reduction, decomposition-combination reaction in the process of preparing CNTs. For different reactions, fluidized bed reactor is an advantage reactor for preparation of CNTs compared with fixed bed, moving bed, rotary cone and carrying bed [1][5]. Extensive research on it have been reported by experts, scholars and engineers [5] [6] [7] [8] [9]. However, the preparation of CNTs belongs to the gas-solid multiphase flow reaction system, there are complex behaviors such as structural inhomoegeneity, basin polymorphism and its nonlinearity. Hence, it is still very difficult to establish a mathematical model to accurately describe the fluidization reaction process.
At present, the preparation of CNTs by fluidized bed reactor has entered the stage of industrialization, which is a leading position compared with the industrialization of other low-dimensional nanomaterials such as graphene. The fluidized bed reactors reported in literature are all tapered fluidized bed reactors (TFBRs) with a distributor [5] [8] [10], which is the nano-agglomerated fluidized bed reactor (NAFBR) described and mentioned by the Weifei team [6]. The distributor is a more important internal component in the fluidized bed reactor. It can limit the bubble growth, make the gas-solid more fully contact, and increase the heat and mass transfer rate. However, the internal component makes the structure of the reactor complex and increases the operation difficulty. At the engineering level, as shown in Figure 1, on the one hand, it is easy to cause the blocking of the distributor and the production of coke on the reactor structure during the growth process due to the multi-stage agglomeration network mode of CNTs; on the other hand, the temperature required for the preparation of CNTs is generally above 600°C, it is easy to cause the sintering and fracture of the distributor, which directly result in the decrease of the quality and yield of CNTs. Therefore, the presence of distributor in the NAFBR is not the optimal design.

In this paper, a tapered fluidized bed reactor without a distributor (NAFBR) is proposed to reduce the unnecessary trouble caused by the distributor above mentioned, as shown in Figure 2. Then, the tapered angle is parameterized, the optimal tapered angle is determined, and the fluidized bed with the optimal tapered angle is simulated and studied experimentally. Finally, the feasibility and reliability of the design of TFBR without a distributor are verified.

![Figure 1. Problems with a distributor](image1)

![Figure 2. Reactor size](image2)

![Figure 3. Mesh model](image3)

2. Basic points of design of TFBR without a distributor

In this paper, the reactor is the most common type of reactor in oil refining process. Its structure is relatively simple, the bottom tapered angle design is beneficial to the contact and mixing of catalyst and carbon source, which can effectively avoid the phenomenon of "dead bed" in the reactor and reduce the fluctuation of bed in the reactor, which is more suitable for the reaction mode of volume increase. Studies have shown that the tapered angel is less than 30° [4], otherwise the catalyst or the growing CNTs will stay on the wall, affecting the mass and momentum transfer of the reaction. In addition, the reactor has simple operation, strong adaptability, internal structure and reduced raw material cost.

2.1. Determination of diameter of TFBR without a distributor

The diameter of the reactor is the most important process size of the reactor design. The diameter of the bed can be calculated according to the material balance of the reaction using Eq. (1) [2] [4]:

\[
Q = 3600\pi D^2U/4
\]

Where, \(Q\) — volumetric flow of gas, \(m^3/s\); \(D\) — diameter of fluidized bed reactor, \(m\); \(U\) — operating gas velocity, \(m/s\).
Before selecting the operating gas velocity, the minimum fluidization velocity $U_{mf}$ and the terminal extraction velocity $U_t$ should be calculated according to the physical parameters in the reactor, and various factors should be considered synthetically. Because there are surface diffusion and surface adsorption processes in the synthesis of CNTs, although the steps to control the growth rate of CNTs are controversial so far, the whole process of carbon source conversion to CNTs is relatively slow and belongs to a slower reaction, so the operating gas velocity should not be too high.

2.2. Determination of TFBR height

The total height of the reactor is composed of the taper, the expansion section and the straight section, and the straight section can be divided into concentrated and thin sections according to the actual fluidized state. In the design of this reactor, we mainly use the empirical method to estimate the catalyst loading according to the "contact time" or "airspeed" during the experiment, and then calculate the bed height by the calculated bed diameter. The formulas for airspeed and contact time (2) and (3) are as follows:

$$U_v = \frac{Q}{V_v} \quad (2)$$

$$t = \frac{1}{U_t} \quad (3)$$

Where, $V_r$ — the amount of catalyst," storage ", g. $U_v$ — volume airspeed, h-1. $t$ — contact time, h.

The amount of catalyst stored is calculated using Eq. (4):

$$V_r = Qt \quad (4)$$

Catalyst filling is calculated using Eq. (5):

$$W_s = V_r \rho_1 \quad (5)$$

Where, $\rho_1$ — packing density of catalyst, Kg/m³.

Therefore, when the diameter of the bed has been fixed, the static height of the bed, as shown in formulas (6) and (7):

$$H_0 = V_r / A = Qt / A \quad (6)$$

$$H = RH_{mf} \approx RH_0 \quad (7)$$

Where, $H_{mf}$ — height in minimum fluidization, m. R — radius of straight pipe section, m. $H_0$ — initial height of bed, m. The final determined TFBR structure is shown in Figure 2.

3. Parameterization design of tapered angle and analysis

In order to achieve or better fluidization performance with a distributor, the tapered angle of the proposed reactor structure is parameterized. The model of each angle ($5^\circ$, $10^\circ$, $11^\circ$, $13^\circ$, $15^\circ$, $18^\circ$, $20^\circ$) was analyzed by CFD to compare the tapered angle with better fluidization performance.

The numerical model adopts polyhedral mesh, and the number of mesh of the model of each tapered angle is determined to be 100000 or 110000 after mesh independent verification. The finite volume method is used to simulate the flow field of one-phase (air) and two-phase flow simulation of gas-solid flow at room temperature and atmospheric pressure. The viscous equation adopts the RNG k-e turbulent flow model derived from the renormalization group RNG method, the pressure velocity coupling adopts the simple algorithm, and the momentum discrete equation adopts the second-order welcome style [1]. The mesh model is shown in Figure 3.

The structure design in the CFD software is used to parameterize the tapered angle less than $30^\circ$, and the single gas flow field is analyzed. In this paper, the parameterized design mode of nozzle and tapered angle is used to simulate and analyze the velocity field distribution of different tapered angles, especially the velocity field distribution of the tapered angle part. By intercepting the cross section upward from the bottom of TFBR, the positions are: 1.44, 1.43, 1.42, 1.4, 1.35, 1.32, 1.3, 1.2, 1.15, 1.1, 1.0, 0.6, 0.3, 0.1 (m), as shown in Figure 4(h). Figure 4(a) - 4(g) is the gas phase velocity field.
distribution of tapered angle 5°, 10°, 11°, 13°, 15°, 18°, 20°, respectively. In the Figure 4, it can be seen that the flow field of the inner tapered angle part of the reactor with different taper is different, and the velocity is obviously decreasing in the transition from the taper part to the straight pipe section. The velocity field distribution is similar at the upper half part and the expanded section of the straight pipe section, showing a more uniform distribution form. The main reaction zone of CNTs is at the bottom of the taper, so the focus of the reactor is the distribution of the flow field at the bottom of the cone.

As shown in Figure 5, according to the distribution of the surface uniformity of velocity, the velocity surface uniformity of the cross sections with different tapered angles from the bottom of the taper up to different positions is different. The cross section of the bottom part of the taper is mainly located in the first four sections. For the overall distribution, the three tapered angles of 10°, 11°, and 13° are better than the velocity uniformity calculated by other tapered angles. According to the distribution of the surface of the cross section standard deviation of velocity, the lower the value, the smaller the maximum and minimum value of the section velocity is compared with the difference of the standard velocity, and the more uniform the temperature distribution during the growth of the CNTs. The comparison shows that the 11° and 13° are better than the tapered angle of 10° in Figure 6. In order to contrast the optimal tapered angle, the surface velocity standard deviation is further calculated for the middle section of the reactor. As shown in Figure 7, it can be seen that the velocity standard deviation of the middle section at 11° tapered angle is 0.62 m/s and that of the middle section at 13° tapered angle is 0.78 m/s. Obviously, 11° is better than the 13° tapered angle. Therefore, in the parameterized design of different tapered angles in this paper, tapered angle of 11° is the most suitable.
4. Experimental study on TFBR without a distributor

4.1. Experimental apparatus and materials

The apparatus mainly includes straight pipe, expansion section, tapered section and heating furnace, as shown in Figure 8, the cold and hot experiments are carried out respectively. It is made of quartz glass, the top is connected with bag filter, the inner diameter is 50 mm and height is 1430 mm. The extended part and the filter screen mesh are used to reduce the entrainment of fine CNTs at the top of the device. The bottom adopts the side wall surface 1-type air intake mode, the inlet distance is 2 mm from the
bottom of the taper. The tapered angle is the most suitable angle (11°) mentioned above. The measuring instrument is pressure sensor and meter ruler. The pressure sensor is used to measure the transient pressure in the reactor, and the meter ruler is used to measure the expansion height of the bed. The material is multi-walled CNTs with a bulk density of 132 Kg/m³, a particle density of 150.22 Kg/m³, an average diameter of 480 um and a weight of 39.49 g.

4.2. Results analysis

As shown in Figure 9, the experimental process of the whole bed covers four stages of fixed bed, particle fluidization, bubbling fluidization, stable fluidization and correspond to the minimum fluidization velocity $U_{mf} = 0.0041$ m/s, the bubbling fluidization velocity $U_{mb} = 0.0124$ m/s, the stable fluidization velocity $U_{fc} = 0.0287$ m/s, and the terminal velocity $U_t = 0.052$ m/s, respectively. In the stable fluidization, the bed height increases obviously with the increase of operating gas velocity. At the terminal velocity, the bed height reaches three times the static bed height. In Figure 10, as the gas velocity increases, the void rate of the whole bed decreases first and then increases, and the solid fraction of CNTs particles decreases along the axial direction, which is due to the high pore structure between the CNTs and the weak interaction force between the agglomerated particles. Moreover, the pressure drop in the bed of the multi-walled CNTs and the expansion process of the bed layer are in good agreement with each other in the process of acceleration and deceleration, so the CNTs fluidization in the bed is more uniform.

The relationship between yield and time of CNTs during growth shown in Figure 11. The yield of CNTs increases gradually over time in 1 h. And the yield of CNTs reaches 94.2 g from 12.3 g in a linear manner from 5 min to 1 h [11]. Figure 12 shows the relationship between ash and time during the CNTs growth, and the ash of CNTs decreases gradually with the increase of time in 1h, indicating that the quality of CNTs increases gradually with the increase of time in 1h, and finally reaches 97.96 % [11]. Therefore, the feasibility and reliability of the reactor design are verified by the production and quality of CNTs.
5. Conclusion
This paper presents a CNTs TFBR without a distributor and designs its diameter and height. The tapered angle was parameterized using the CFD simulation method and the optimal tapered angle (11°) was determined by analyzing the surface uniformity and surface standard deviation of velocity in the cross section, as well as the surface standard deviation of velocity in the middle section. Then the cold and hot experimental equipment was built, and the design was studied in terms of the fluidization quality and behavior of the reactor. It was proved that the CNTs could get more uniform flow in the bed. According to the quality and yield of CNTs, it is verified that the bed can achieve higher quality and yield growth of CNTs. Therefore, the TFBR proposed in this paper is feasible in the field of CNTs preparation and has the prospect of easy engineering scale-up.

Acknowledgements
This work is supported by the National Natural Science Foundation of China (No. 51676103) and Taishan Scholar Project of Shandong Province (No. ts20190937).

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