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Motion of carbon nanotubes in a rotating drum: The dynamic angle of repose and a bed behavior diagram

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The granular flow behavior of carbon nanotubes produced by the CCVD method in a laboratory continuous inclined rotary reactor and of a catalyst was experimentally studied using a rotating drum. The dynamic angle of repose of the bulk solid and the standard variation of the solid bed surface were determined as a function of rotational speed of the rotating drum and for several filling percentages of the drum. Whatever the carbon nanotube production conditions, the dynamic angle of repose and the standard variation of the solid bed depended only on the filling percentage of the drum. Results were very interesting for practical application to carbon nanotube production in an industrial continuous inclined rotary reactor, because the granular flow behavior was the same during the reaction throughout the length of the reactor and depended only on the reactor filling. A bed behavior diagram based on the drum rotational speed and on the drum filling percentage was also constructed experimentally. The flow behavior of the solid during carbon nanotube production was on the boundary between the slumping and the rolling modes, leading to a good mixing of gas and solid during the reaction and to an improvement of the mass and heat transfer in the bed.

1. Introduction

Carbon nanotubes represent a very promising new material that has attracted much attention in the past few years and intense research has been carried out to identify their remarkable properties and potential applications. Carbon nanotubes are now expected to bring significant breakthroughs in the technology of electronic and engineering materials [1]. The large-scale synthesis of nanotubes is the key point for their commercial application. Of the different techniques developed to synthesize carbon nanotubes, the CCVD method appears to be the most promising for the processing of carbon nanotubes, due to its relatively low cost and its potential high yield production [2]. Indeed, the CCVD method can be operated continuously and presents an advantage for large-scale production compared to other methods such as electric arc-discharge or laser ablation which are not easily adaptable to industrial production. The CCVD method consists of the decomposition of a hydrocarbon source into solid carbon and gaseous hydrogen over a catalytic surface.

Because a discontinuous reactor leads to a small amount of carbon nanotubes by the CCVD process, a technology based on a continuous reactor is used to produce a large amount of carbon nanotubes. Pilot scale production reactors using the CCVD method to produce carbon nanotubes are already running [3–6], using a fluidized bed process [4,5], or an inclined mobile-bed rotating reactor [7]. The inclined mobile-bed rotating reactor seems to be one of the most appropriate forms of technology because the kinetics of carbon nanotube synthesis by hydrocarbon decomposition is quite slow [8,9], and because the ratio between the volume of the product and of the catalyst is very large (larger than 50). Furthermore, the rotation of the reactor allows the rolling of particles inside the reactor. So complete mixing of particles can be obtained during the reaction, and the flow regime does not correspond to a heterogeneous phase between gas and solid because the best gas–solid contact is achieved by improvement in mass and heat transfer in the solid bed, in comparison with a fixed bed for which concentration gradients can be observed when the thickness of the catalytic bed is sufficiently great [10].

So the granular flow behavior during the reaction is very important to estimate contacts between gas and solid, which influence reaction performance and carbon nanotube production. This paper deals with the behavior of the granular flow in a rotating drum during carbon nanotube production. A rotating drum consists of a cylinder rotating around its central axis, which is either horizontally

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positioned or inclined at a few degrees to the horizontal. Devices based on such a configuration play an important role in the processing of granular materials in the chemical, metallurgical, food, and pharmaceutical industries, in which they are used to perform mixing, drying, heating, and chemical reactions [11,12]. Although the concept is simple, the motion of solids in rotating drums is very complicated. With increasing rotational speed, six modes of solid motion have been observed: slipping, slumping, rolling, cascading, cataracting and centrifuging modes [13].

This paper aims to study granular flow during carbon nanotube production through a rotating drum. Here, the dynamic angle of repose of the bulk solid was determined as a function of rotational speed of the rotating drum, of the filling percentage of the drum, and of the reaction production conditions of carbon nanotubes. The standard variation of the solid bed surface position was also observed. Finally, a bed behavior diagram, which is based on the drum rotational speed and on the drum filling percentage, was constructed.

2. Experimental

The experimental set-up used in this study consists of a short drum rotating around its central axis, which is horizontally positioned. The diameter and the length of the cylinder are respectively 84 and 10 mm. The drum rotational speed ω is precisely controlled by a DC motor and a PID system between 6 and 10 rpm, *i.e.* 0.1 and 0.167 s^{-1}. It should be noted that rotational speed greater than 10 rpm were not tested because the rotational speed for carbon nanotube production in an industrial reactor was smaller than 5 rpm in practice. In the present study, the drum was filled at different percentages with the catalyst (5%, 10% and 20%) or carbon nanotubes (10% and 30%). These filling percentages correspond to those used in practice for carbon nanotube production in an industrial continuous inclined rotary reactor. The experimental set-up is shown in Fig. 1 and is similar to the set-up previously used by Castellanos and co-workers [14]. To perform the measurements, the rotating drum is back-illuminated with a stroboscope and the granular flow is recorded using a CCD camera with a resolution of 1024 × 1024 pixels. For each angular velocity, 50 images of the pile separated by 0.5 s are recorded. Afterwards, a dedicated image-processing algorithm tracks the position of the air/powder interface. The average interface position and the fluctuations around this average position are computed. Fig. 2 shows a typical picture of the pile during an experiment. The grey line corresponds to the average position of the interface calculated over 50 pictures. The two other white lines show the standard deviation of the interface. To obtain an estimation of the fluctuation of the interface, an average of this standard deviation over the interface is computed. The dynamic angle of repose is measured in the linear part of the average interface.

Several types of granular powders were tested: the catalyst [15] and different types of carbon nanotubes previously produced by the CCVD method in a laboratory continuous rotating reactor inclined at a few degrees to the horizontal. In order to study the influence of the nature of carbon nanotubes, some samples synthesized in different experimental conditions were used. The composition of reactional gas, the inclination angle, the rotational speed and the residence time of the solid were modified. A synthesis of the conditions of five samples is presented in Table 1.

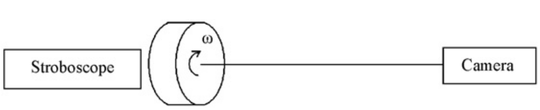

Fig. 1. Experimental set-up.

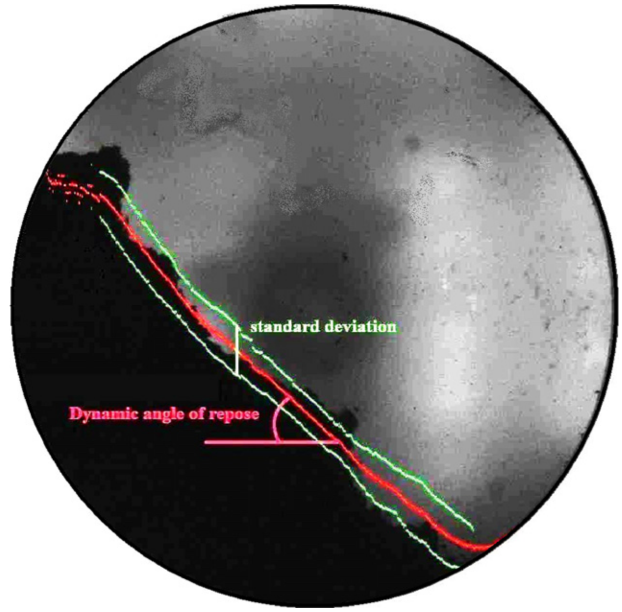

Fig. 2. Dynamic angle of repose and standard deviation of the bed free surface.

Table 1
Experimental conditions of carbon nanotube production in a continuous laboratory reactor and studied in this work.

Sample	Inclination angle (°)	Rotation speed (rpm)	Gas composition C_2H_4–H_2–N_2 (%)	Residence time (min)
1	3	1.5	60–20–20	20
2	1	3.5	60–20–20	20
3	3	0.9	60–20–20	50
4	3	1.2	60–20–20	30
5	3	1.5	60–0–40	20

3. Results

Several operating variables could have an influence on the powder flow behavior in the rotating drum, characterized by the mean dynamic angle of repose of the bulk solid and the standard deviation of the surface around its mean position. Five operating variables were studied: the filling percentage and the rotational speed of the rotating drum, the composition of the reaction gas, the inclination angle of the laboratory reactor and the rotation speed of the laboratory reactor. The two last operating variables determine the residence time of the solid in the reactor.

In a first time, the influence of the filling percentage of the rotating drum on the mean dynamic angle of repose of the bulk solid and the standard deviation of the bed surface around its mean position was studied. Several filling percentages were tested: 10% and 30% for carbon nanotubes and 5%, 10% and 20% for the catalyst. Results using sample 1 (Table 1) are presented in Fig. 3 and are representative of the tendency corresponding to the four other carbon nanotube samples. Fig. 3a highlights the fact that the dynamic angle of repose was found to increase with the filling percentage of the rotating drum. It can also be observed that the dynamic angle of repose did not vary with increasing drum rotating speed. It can be noted that the dynamic angle of repose for granular powders generally increased with increasing rotational speed, except in the case of rheofluidizing granular flow. Rheofluidization represents an improvement in the flowability when the shear rate increases. So it seems that carbon nanotubes are a rheofluidizing granular powder. As for the standard deviation of the bed surface around its mean position, this stayed constant with the drum rotation speed but

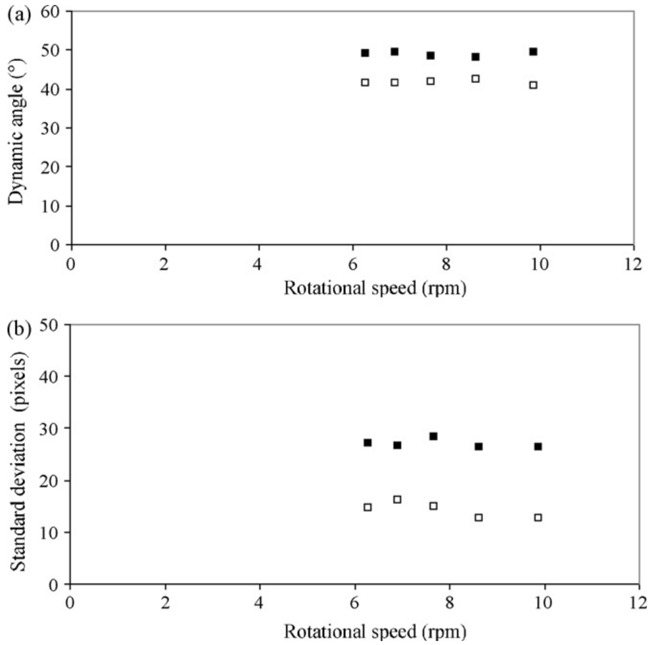

Fig. 3. (a) Dynamic angle of repose and (b) standard deviation of the bed surface around its mean position as a function of drum rotational speed for (□) 10% of filling and (■) 30% of filling of carbon nanotubes using sample 1.

increased with the filling percentage of the rotating drum (Fig. 3b), because the number of degrees of freedom was greater at a high percentage of filling.

The composition of the reaction gas for carbon nanotube production by the CCVD method influences the specific production, *i.e.* the mass of produced carbon nanotubes per unit of mass of catalyst, and the quality of produced carbon nanotubes, *i.e.* the percentage of carbon in produced nanotubes. So it is important to determine whether the behavior of the granular flow through the rotating drum is influenced by the nature of the carbon nanotubes. Samples 1 and 5 are compared in Fig. 4. They correspond to a residence time equal to 20 min and differ by the presence of hydrogen in the reaction gas. The carbon percentage of the two samples was respectively equal to 94% and 90%. Nevertheless, TEM images of samples 1 and 5, which were produced in extremely different experimental conditions exhibit no morphology differences. The average size of the nanotube agglomerates [16] was around 500 μm for all the powder types. Fig. 4 highlights that the dynamic angle of repose is not influenced by the drum rotational speed or the nature of the carbon nanotubes. So whatever the gas composition for a given residence time, the dynamic angle does not change.

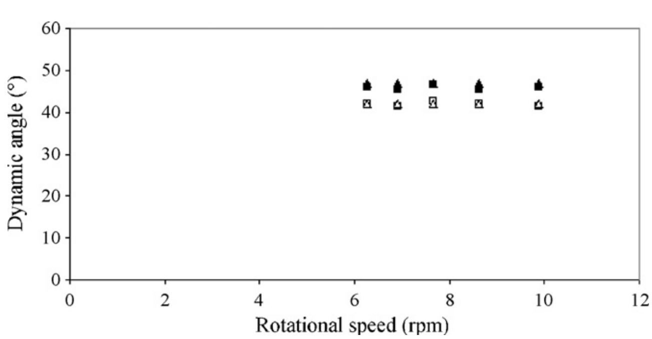

Fig. 4. Dynamic angle of repose as a function of drum rotational speed for (□) 10% of filling of nanotubes corresponding to sample 1; (■) 30% of filling of nanotubes corresponding to sample 1; (△) 10% of filling of nanotubes corresponding to sample 5; (▲) 30% of filling of nanotubes corresponding to sample 5.

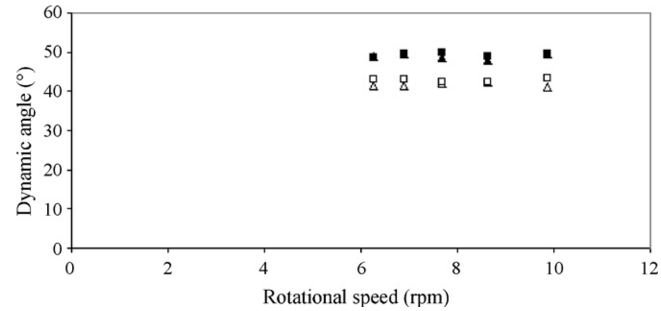

Fig. 5. Dynamic angle of repose as a function of drum rotational speed for (□) 10% of filling of nanotubes corresponding to sample 1; (■) 30% of filling of nanotubes corresponding to sample 1; (△) 10% of filling of nanotubes corresponding to sample 2; (▲) 30% of filling of nanotubes corresponding to sample 2.

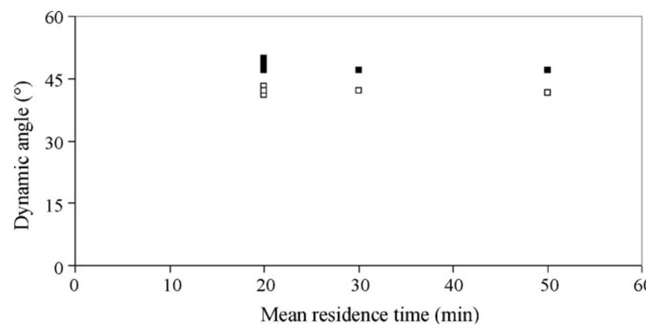

Fig. 6. Dynamic angle of repose as a function of mean residence time of carbon nanotubes in the reactor for (□) 10% of filling and (■) 30% of filling.

A given mean residence time in a rotating reactor can be obtained by varying the inclination angle and/or the rotational speed. Fig. 5 shows that nanotubes produced with a rotational speed of 3.5 rpm and an inclination angle of 1° (sample 1) and nanotubes produced with a rotational speed of 1.5 rpm and an inclination angle of 3° (sample 2) flowed with the same dynamic angle of repose for a given filling percentage, whatever the rotational speed of the drum. So the way the residence time was shown not to influence the granular flow.

The influence of the residence time of the solid in the reactor was also studied by comparing the five samples corresponding to three different residence times. Fig. 6 highlights the fact that the mean residence time of carbon nanotubes did not influence the dynamic angle of repose for a given drum filling percentage, whichever the way the residence time was reached.

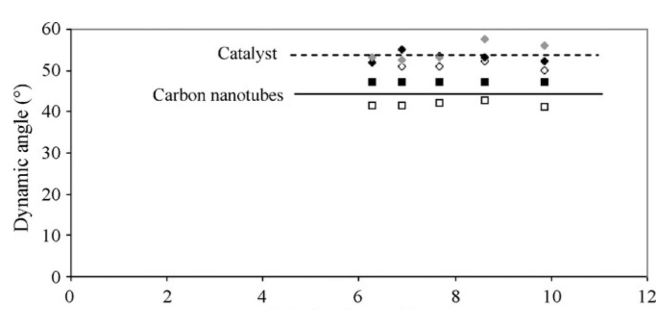

Fig. 7. Dynamic angle of repose as a function of drum rotational speed for (□) 10% of carbon nanotube filling corresponding to sample 1; (■) 30% of carbon nanotube filling corresponding to sample 1; (○) 5% of catalyst filling; (◆) 10% of catalyst filling; and (●) 20% of catalyst filling.

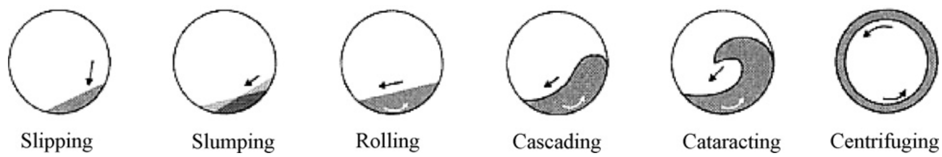

Fig. 8. Mode of granular motion in a rotating drum [14].

In order to produce carbon nanotubes by the CCVD method in a continuous inclined rotary reactor, the catalyst is introduced into the reactor with the reaction gas which flows co-currently. So in the inlet of the reactor, the powder alone is the catalyst. This explains the interest in studying catalyst behavior in a rotating drum. However, the carbon nanotube production is rapid, so that the catalyst is rapidly covered by nanotubes which grow over the catalytic surface. Indeed, in the present study, for a residence time of 20 min, a specific production equal to 1 $kg_{carbon}\ kg_{catalyst}^{-1}$ was already reached after less than 4% of the length of the reactor, which corresponds to a volume increase by a factor equal to more than 50. This means that studying of the catalyst flow is only useful for less than the first percent of the length of the reactor. The mean size of the catalytic particle was around 350 μm. Fig. 7 shows that the dynamic angle of repose of the catalyst was higher for the catalyst than for the carbon nanotubes and that it was equal to 53°. The angle was not influenced by the rotational speed of the drum, which means that the catalyst was also a rheofluidizing solid, and that the drum filling percentage did not have a significant influence. The smaller dynamic angle of repose of carbon nanotubes indicates that the carbon nanotubes flowed more easily than the catalyst powder, which is a very cohesive powder [14]. In addition, carbon nanotube powder consists of a very cohesive powder, but the mechanism through which carbon nanotube agglomerates are formed leads to the production of very little cohesive granular powder.

4. Discussion

A bed behavior diagram, based on the drum rotational speed and on the drum filling percentage, was constructed in order to determine the mode of solid motion of the carbon nanotubes and of the catalyst in the rotating drum. The six modes of solid are presented in Fig. 8 [17]. The bed behavior diagram highlights the boundaries between the different modes of granular motion for increasing the solid filling percentage and for the increasing dimensionless Froude number *Fr*, *i.e.* for increasing rotational speed:

$$Fr = \frac{\omega^2 R}{g} \quad (1)$$

where ω is the drum rotational speed (s^{-1}), R is the drum radius (m) and g is the acceleration due to gravity (9.81 $m\,s^{-2}$).

Fig. 9 presents the bed behavior diagram of the carbon nanotubes, obtained by observing the flow of carbon nanotubes during each experiment in the rotating drum. It can be observed that the rolling–cascading boundary depends only on the filling percentage of the drum, and does not depend on the rotational speed. This observation is in agreement with the dynamic angle of repose measured for the carbon nanotubes, which was found to depend only on the filling percentage and not on rotational speed or on the nature of the carbon nanotubes (Figs. 3–6). As far as the slumping mode is concerned, this exists for rotational speeds smaller than those studied in this paper. For carbon nanotube production, the Froude number is generally smaller than 5×10^{-5} and often around 2.5×10^{-5}, while the filling percentage varies between around 5% at the reactor inlet and 30–40% at the reactor outlet. So the mode of carbon nanotube motion in the production reactor is on the bound-

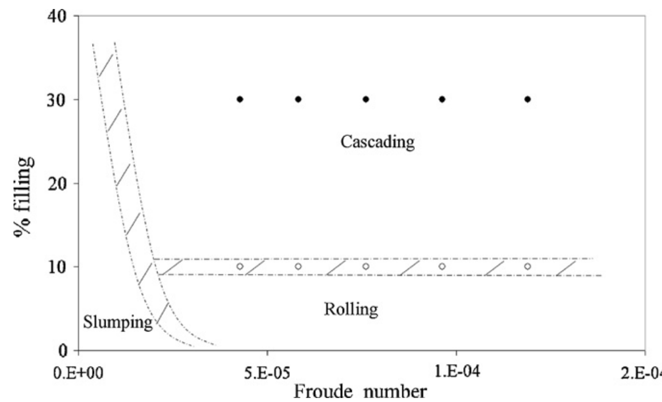

Fig. 9. Bed behavior diagram for carbon nanotubes: (○) experimental rolling–cascading boundary; (●) cascading mode.

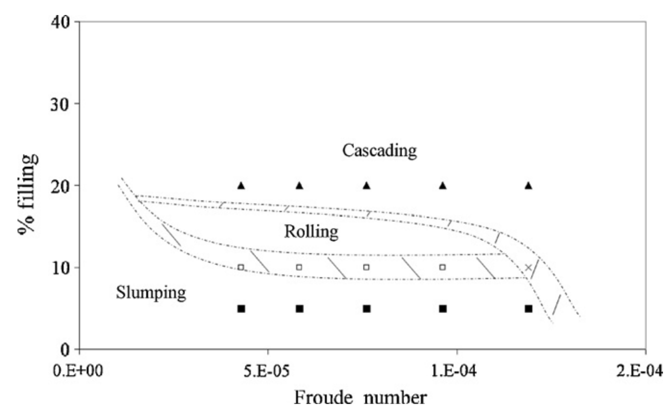

Fig. 10. Bed behavior diagram for catalyst: (■) slumping mode; (□) experimental slumping–rolling boundary; (×) experimental rolling–cascading boundary; (▲) cascading mode.

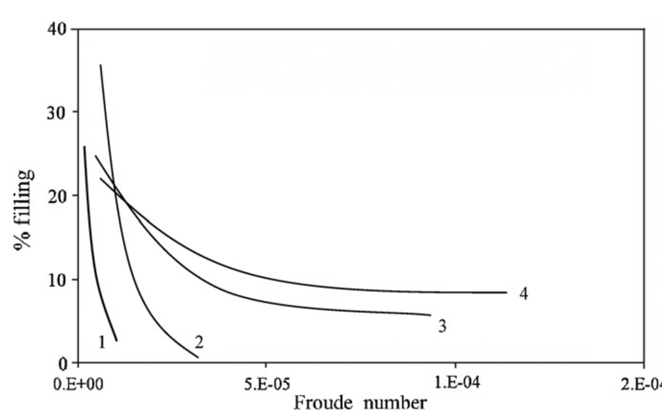

Fig. 11. Slumping–rolling boundary for (1) sand [14]; (2) carbon nanotubes [this work]; (3) limestone [14]; and (4) catalyst [this work].

ary between two or three behaviors, which are the slumping, the rolling and the cascading modes.

The bed behavior diagram of the catalyst is presented in Fig. 10. It is quite different from the nanotube behavior diagram. Indeed, the slumping mode is observed for small filling percentages and does not significantly depend on rotational speed. As was the case for the carbon nanotubes, the rolling–cascading boundary of the catalyst appears for greater filling percentages and does not depend on rotational speed. For carbon nanotube production, the Froude number is often around 2.5×10^{-5} and the filling percentage of the catalyst is smaller than 5%. So it can be said that the catalyst flows in the slumping mode for the conditions of carbon nanotube production.

Fig. 11 highlights the comparison of the slumping–rolling boundary for different types of granular powders. It can be said that carbon nanotubes exhibit a behavior similar to sand, while the catalyst is more similar to limestone.

5. Conclusions

The present paper has presented a study of the granular flow during carbon nanotube production through a rotating drum. The dynamic angle of repose of the bulk solid was determined as a function of the rotational speed of the rotating drum and for two carbon nanotube filling percentages (10% and 30%). It was shown that whatever the conditions for which carbon nanotubes are produced (inclination angle of the reactor, residence time in the reactor, gas composition), the dynamic angle of repose did not vary with the rotational speed of the drum. This characteristic is representative of a rheofluidizing powder. It was shown that the dynamic angle of repose was only influenced by the filling percentage of the drum. It was found to be equal to around 42° and 48° for a filling percentage of 10% and 30%, respectively. In the same way, the dynamic angle of repose of the catalyst did not vary with the rotational speed of the drum. Furthermore, it did not change significantly with the filling percentage of the drum. It was found that to be greater than for the carbon nanotubes and was shown to be equal to around 53°, which means than the catalyst is a more cohesive powder than carbon nanotubes, which tend to form agglomerates. So the catalyst powder flows less easily than the carbon nanotubes. It has to be noted that the catalyst was found to be only present in a very few length percentages at the reactor inlet because the reaction was sufficiently rapid enough and carbon nanotubes grow quickly on the catalytic surface. These results are very important for practical application because, for carbon nanotube production in an industrial inclined rotary reactor, the fact that the dynamic angle of repose does not change during the reaction is very interesting. It means that the granular behavior is the same during the reaction throughout the length of the reactor and that it depends only on the reactor filling.

A bed behavior diagram based on the drum rotational speed and on the drum filling percentage was constructed experimentally for carbon nanotubes and for the catalyst. It can be concluded that during carbon nanotube production, the catalyst flows in the slumping mode in the first stage of the reaction, then carbon nanotubes flow into the boundary between the slumping, the rolling and the cascading modes. The greater the importance of the growth of carbon nanotubes, the greater the filling percentage of the drum, and the greater the contribution of the rolling mode. Thus the mixing of the solid during the reaction is good, with the consequence of the improvement in mass and heat transfer inside the granular bed.

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