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An Investigation of Carbon Nanotube Jet Grinding

Cedric Briens[*] Carole E. Baddour[†] Serge Bordere[‡]
Patrice Gaillard[**] Didier Anglerot[††]

[*]University of Western Ontario, cbriens@eng.uwo.ca
[†]McGill University
[‡]Arkema
[**]Arkema
[††]Arkema

AN INVESTIGATION OF CARBON NANOTUBE JET GRINDING

Cedric L. Briens[a,*], Carole E. Baddour[a,1],
Serge Bordere[b], Patrice Gaillard[b] and Didier Anglerot[b]

[a] Department of Chemical and Biochemical Engineering, The University of Western Ontario, 1151 Richmond St., London, Ontario, Canada N6A 5B9
[b] Arkema, Groupement de Recherches de Lacq, BP 34, 64170 Lacq, France
[1] Present address: Department of Chemical Engineering, McGill University, 3610 University St., Montreal, Quebec, Canada H3A 2B2
*corresponding author: cbriens@uwo.ca

ABSTRACT

The main challenges for the development of an industrial process for carbon nanotubes (CNTs) synthesis are the formation of agglomerates and the control of their size distribution. The project objective was to investigate the feasibility of CNT grinding with two arrangements. Experiments showed that a commercial jet mill can meet product quality requirements. However, in-situ grinding of CNTs, within the fluidized bed reactor, would improve both the productivity and quality of CNTs. A new, two-parameter grinding model shows that the primary grinding mechanism is fragmentation for the jet mill and erosion in the fluidized bed column.

INTRODUCTION

The most popular nano-materials to date are carbon nanotubes (CNTs): tubular carbon molecules with remarkable mechanical, electrical, chemical and thermal properties which make them useful in various applications (1). Of the various methods of CNT synthesis (1), the CVD (chemical vapor deposition) process has the greatest potential: it is simple, inexpensive, easily scaled up and provides CNTs of high yield and purity. With respect to the fixed bed method, different carbon nanotubes (single wall SWCNTs or multiple walls MWCNTs) can be produced with different substrates. It has been found that the substrate/CNT surface interactions govern the alignment and type of CNT produced (2, 3, 4).

The CVD fluidized bed method is ideal for large scale production. It provides a large effective surface area and a large amount of space for CNT growth (5). Additionally, it is well known that fluidized beds provide excellent temperature uniformity due to good mixing.

The main challenge faced in the development of fluidized bed processes is the formation of large CNT agglomerates, which reduces productivity, since it hinders access to the catalyst and may result in the complete de-fluidization of the bed. The formation of large (> 1 mm) grains containing tangled nanotubes is also a product quality issue since they cause problems in post-synthesis applications. For example, these large grains affect the dispersion and electrical conductivities of CNT/polymer mixtures.

Two methods have been proposed in the literature to control the size of CNT grains, using ultrasound power (6, 7, 8), and ball milling (9, 10, 11, 12). Ultrasound power (8) was effective but required suspension of the CNTs in an acid solution and was only tried at the milligram scale. Ball milling (9) used an agate mortar with an agate ball, which was vibrated at 50 Hz, but was only tested at the gram scale and presented the risk of contamination of the CNT product by agate fragments.

This paper, therefore, investigates two possible solutions to the agglomeration problems. First, a standard jet mill, downstream of the reactor, could eliminate the agglomerates and problems encountered in post-synthesis applications. The second solution would be a jet attritor within the fluidized bed reactor, which would provide the best solution since both productivity and product quality would be improved.

EQUIPMENT AND EXPERIMENTAL PROCEDURES

Characteristics of original carbon nanotubes

To make the carbon nanotubes, catalyst was made by deposition on alumina support particles. The catalyst particles had a loose bulk density of about 1100 kg/m^3. The CNTs, which grew on the catalyst particles in the fluidized bed reactor, formed grains with a much lower bulk density of about 100 kg/m^3. Figure 1 shows that the carbon nanotubes formed round grains. A laser diffraction size analysis, with a Malvern particle size analyzer, showed that their Sauter-mean diameter was 202 μm and their volume-based arithmetic mean diameter was 429 μm. Figure 2 shows that the grains were made of tangled nanotubes, with a very open structure which explains their low bulk density.

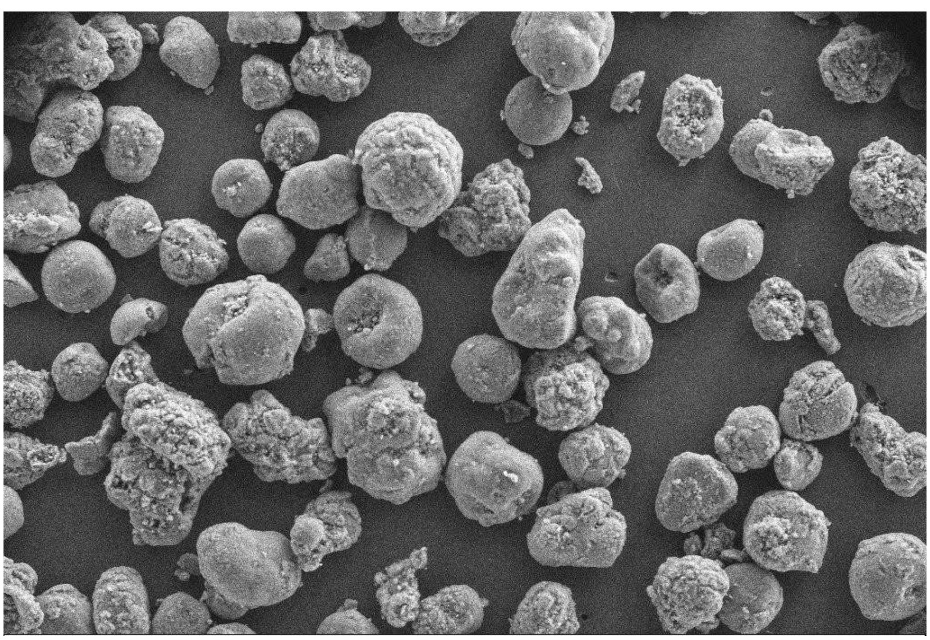

Figure 1 – Carbon nanotubes before grinding (22X magnification)

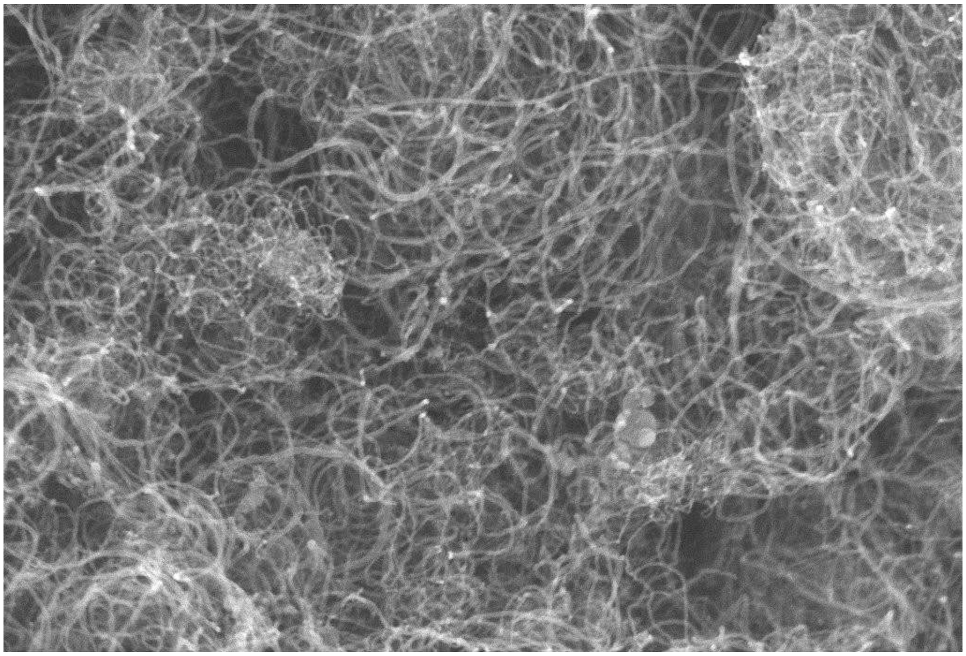

Figure 2 - Tangled nanotubes in a CNT grain before grinding (30000X magnification)

Jet mill

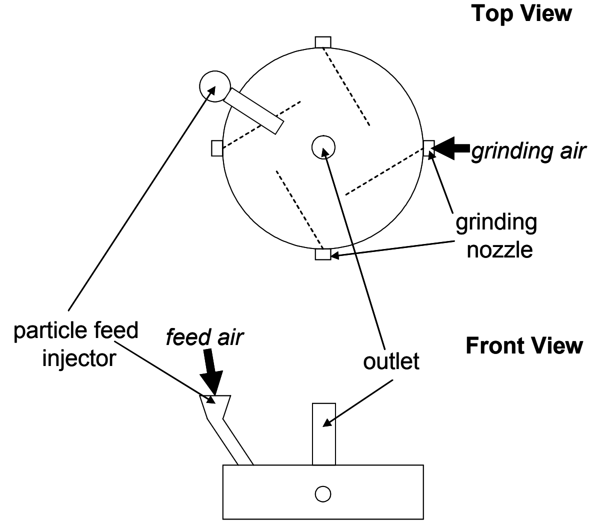

Figure 3 - Schematic of the Alpine Spiral Jet Mill

Hosokawa Micron Limited manufactures many of the jet mills used in industry worldwide. Upon consultation with Hosokawa representatives, the Alpine Spiral Jet Mill 50 AS was selected for this study since it was a lab-scale unit frequently used by industry to determine whether powders could be ground by air jets. A schematic diagram is shown in Figure 3. Particles are injected into the mill with the addition feed air by means of a particle feed injector (diameter = 0.0008 m). The high velocity grinding air jets originate from 4 nozzles, each with an inner diameter of 0.0008 m. Ground particles are carried into the exiting the gas flow, which is forced into a vortex by the geometry of the outlet. Large particles are not able to follow the vortex and centrifugal forces keep them in the grinding chamber until they are small enough to be entrained out by the gas.

Most experiments were conducted with a mass flowrate of 1.14 g/s through each nozzle, which gave sonic conditions with an upstream pressure of 300 kPa. A few experiments used lower flowrates, including subsonic conditions. The solids feedrate was varied from 0.4 to 25.9 g/min.

Fluidized bed attritor

For this study, a non-reacting, batch system was used. The fluidized bed column was 5.4 cm in diameter. In all experiments, 12 g of CNTs were used, for a bed height to diameter ratio of about 1. A vertical grinding jet was used, with a 0.2 mm diameter nozzle that formed a vertical gas jet that picked up the fluidized grains, accelerated them to a high speed and smashed them on a conical steel target (Figure 4). The conical shape prevented solids from defluidizing on top of the target, which was located well below the fluidized bed surface. It should be noted that there was no noticeable erosion of the target. In large units, many such nozzles would be used in parallel. The total superficial gas velocity was kept constant at 30 mm/s, or about 3.9 times the measured minimum fluidization velocity, by adjusting the flowrate of air through the porous distributor to compensate for changes in the attrition nozzle flowrate (the porous distributor flowrate was always well above the minimum flowrate required for fluidization).

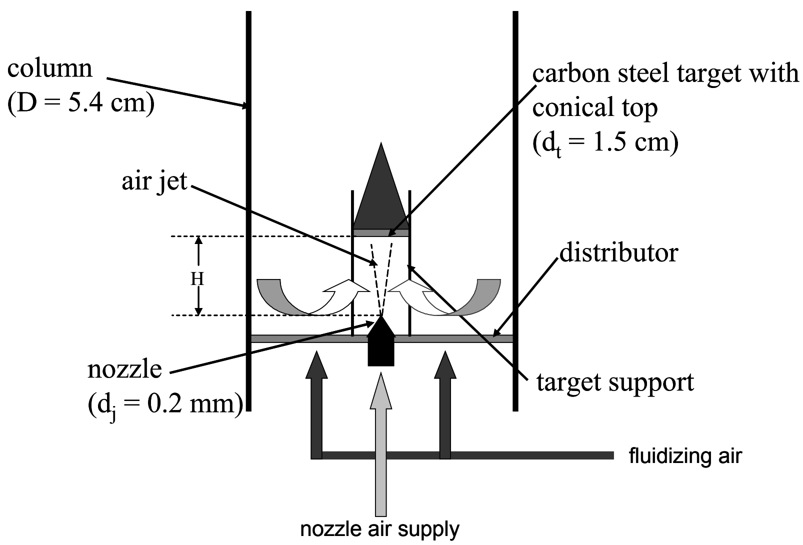

Figure 4 – Schematic diagram of the fluidized bed

MODEL

The proposed model assumes that one mother particle will break into two daughter particles of different size, as shown in Figure 5.

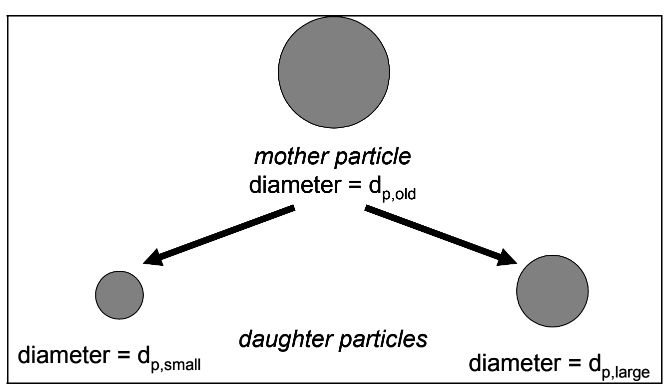

Figure 5 - Breakage mechanism considered for model

The two model parameters are F, the fraction of particles broken per second, and γ, the symmetry coefficient (ratio of the volume of the small daughter particle to the volume of the large daughter particle). As shown in (13), these parameters can easily be obtained from experimental size distributions.

RESULTS

Results obtained with the jet mill

The arithmetic mean diameter of the ground particles clearly decreases with increasing grinding air mass flux (Figure 6). Figure 6 also shows that the arithmetic mean diameter of the ground particles increases with the solids feed rate. As the solids mass feed rate increased, the grinding of the particles was less efficient since the residence time of the particles in the chamber decreased. The grinding chamber could hold approximately 1 g of particles, thus the residence time varied from 0.04 seconds (at 25.9 g/min) to 0.67 seconds (at 1.5 g/min).

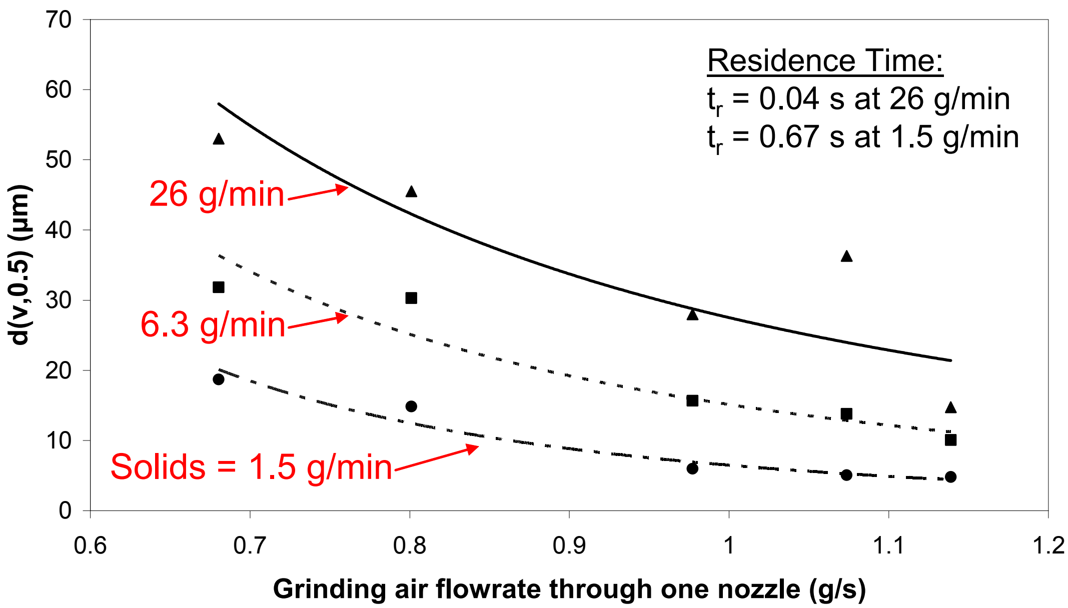

Figure 6 - Effects of solids and grinding air flowrates on volume-based arithmetic mean diameter of product

Figure 7 shows that the particle size distributions are shifted towards smaller diameters with increasing grinding air flowrate. The grinding process is more efficient at high grinding air flowrates since the distributions become progressively narrower. In Figure 7, there are clearly two groups: the first group, for 0.68 g/s and a slightly larger grinding air flowrate, corresponds to subsonic grinding jets, while the second group, for grinding air flowrates of 0.98 g/s and higher, corresponds to sonic jets.

With the model, F = 0.08 to 0.107 Hz and γ = 0.74 were generally suitable for most conditions. However, γ values ranging from 0.42 to 0.74 were needed to model the effect of solids mass feedrate and γ values ranging from 0.52 to 0.74 were necessary to model the effect of grinding air flowrate (13). This shows that the main attrition

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mechanism, with the jet mill, was splitting or fragmentation. This was confirmed by electronic microscope photographs: catalyst particles were broken by the jet mill.

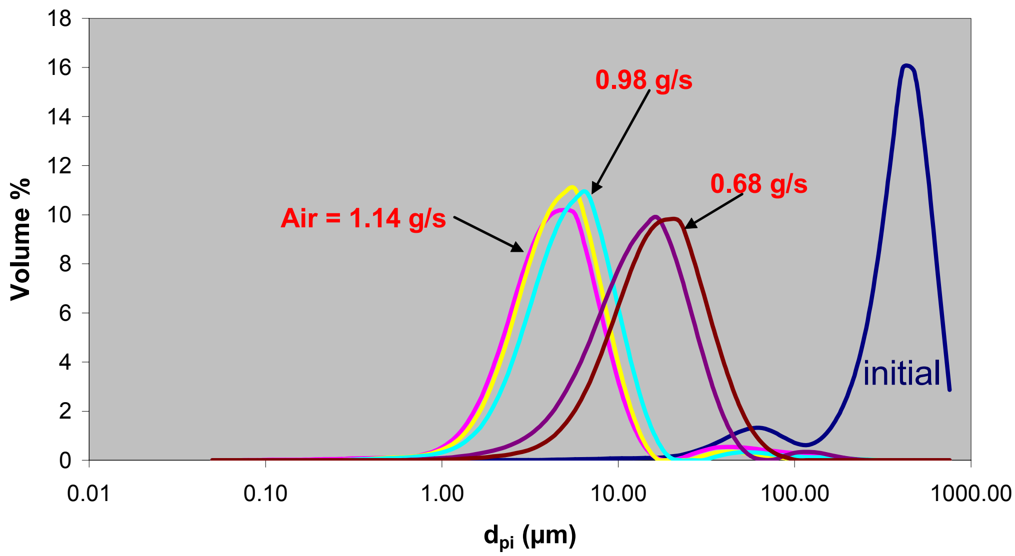

Figure 7 - Effects of grinding air flowrate on size distribution (solids feedrate of 1.5 g/min)

Results obtained with the fluidized bed attritor

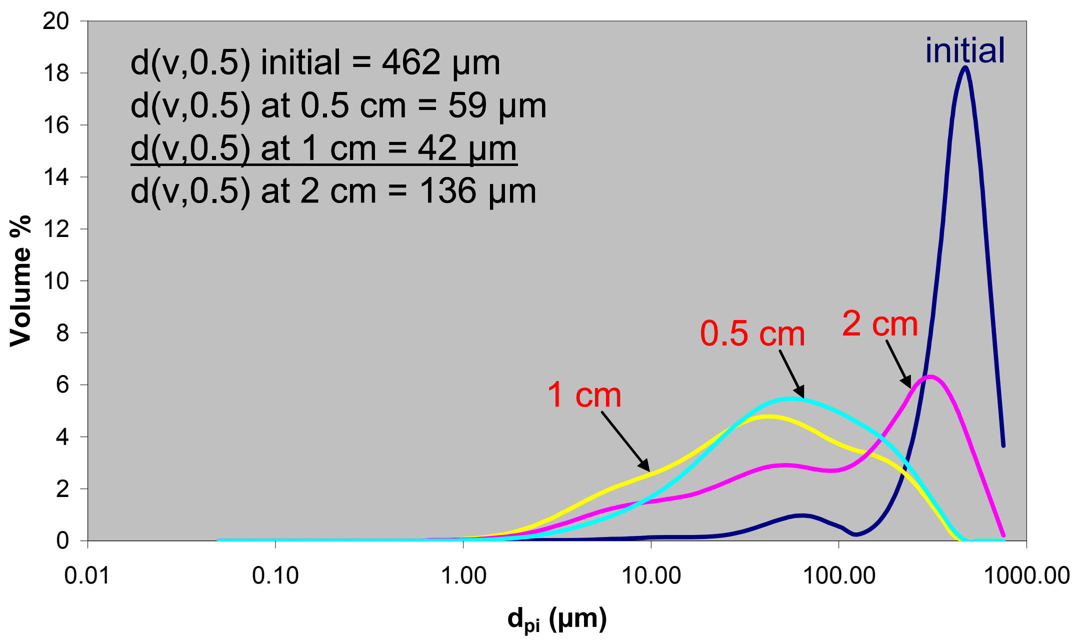

Figure 8 – Effect of distance between nozzle and target on size distribution of product (grinding time of 30 min, attrition gas flowrate of 60.6 g/h)

(the distance H is indicated in red for each curve)

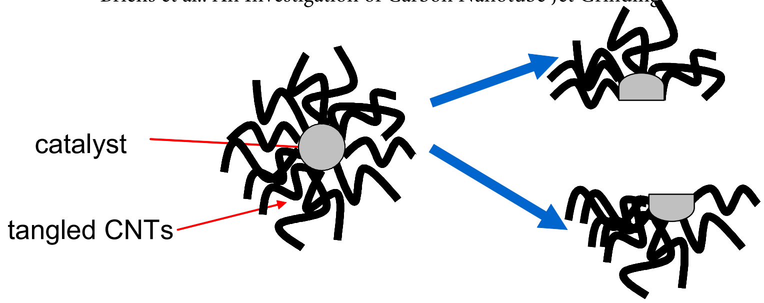

Figure 9 – Diagram of CNT attrition with the jet mill

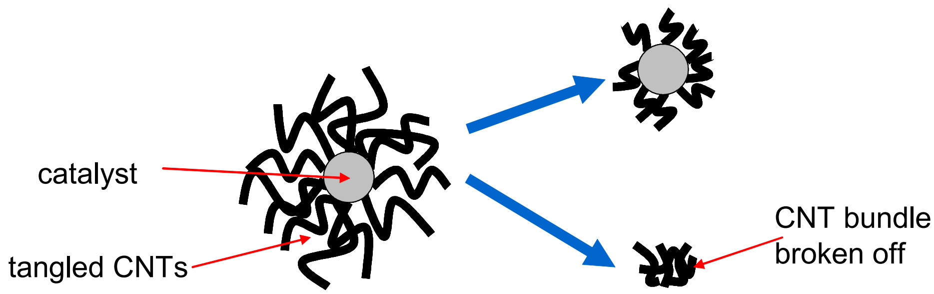

Figure 10 – Diagram of CNT attrition with the fluidized bed jet attritor

A comparison of Figure 7 and Figure 8 clearly shows that the fluidized bed attritor does not grind the particles as fine as the jet mill, and produces particles with a wider size distribution. Figure 8 also shows that the distance between the nozzle and the target (H on Figure 4) has a major effect on the grinding, with the intermediate distance of 1 cm being the best. Two opposing effects combined: as this distance increases, the flowrate of particles entrained into the jet increases while the particle velocity decreases (the gas velocity decreases because of the gas jet conical expansion). Going to subsonic jet conditions greatly reduced the attrition rate.

Attrition is much milder than with the jet mill. Longer experiments showed that, with the fluidized bed attritor, the volumetric, arithmetic mean diameter of the product could not be decreased below about 40 μm. The model showed that the particle splitting frequency (F) was more than one order of magnitude lower than with the jet mill (13). The coefficient γ was only 0.14, showing that the fluidized bed attritor eroded the particles (13), as confirmed by electron microscope photographs. In sharp contrast to the jet mill (Figure 9), the fluidized bed attritor did not break the original catalyst particles but simply eroded away the external layer of tangled CNTs, as shown in Figure 10. This makes it very attractive for use within the fluidized bed of the CNT synthesis reactor since it would not only prevent the formation of excessively large grains, but would also increase the productivity by keeping the catalyst surface easily accessible without damaging the catalyst particles.

CONCLUSIONS

Experiments show that a commercial jet mill can grind CNTs and meet product quality requirements. However, in-situ grinding of CNTs, within the fluidized bed reactor, would provide the best solution since both the productivity and quality of CNTs would be simultaneously improved.

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