



Trends in  
**Applied Sciences  
Research**

ISSN 1819-3579



Academic  
Journals Inc.

[www.academicjournals.com](http://www.academicjournals.com)

## Mass Production of Carbon Nanotubes Using Fluidized Bed Reactor: A Short Review

<sup>1,2</sup>S. Shukrullah, <sup>1</sup>N.M. Mohamed, <sup>1</sup>M.S. Shaharun and <sup>1,2</sup>M.Y. Naz

<sup>1</sup>Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS, 31750 Tronoh, Perak, Malaysia

<sup>2</sup>Department of Physics, University of Agriculture, Faisalabad, Pakistan

*Corresponding Author: S. Shukrullah, Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS, 31750 Tronoh, Perak, Malaysia*

### ABSTRACT

In recent years, the carbon nanotubes (CNTs) have remained the most discussed materials due to their distinctive characteristics and potential industrial applications. These materials have brought revolutionary changes in the field of medical treatment, electronic devices, communication, sensors, energy storage, etc. Among the various practiced techniques, the Fluidized Bed Catalytic Chemical Vapor Deposition (FBCCVD) is the most pronounced technique for mass production of carbon nanotubes. Although, FBCCVD is a scalable and relatively low cost technique for bulk production of CNTs, still some of the dominant process parameters impacting the CNTs nucleation and growth should be more understood. Better control over these parameters would help the researchers to improve CNTs morphology, to optimize productivity and to scale up the process parameters. Therefore, this study includes a general overview of FBCCVD and other key parameters effecting CNTs formation. The main objective of the presented literature review is to discuss and elaborate the scientific phenomena behind this process and to sketch a future roadmap.

**Key words:** Fluidized bed, chemical vapor deposition, transitions metals, nano particles

### INTRODUCTION

CNTs consist of hexagonal  $sp^2$  carbon layers (rolled graphene) which form several millimeters long cylindrical tubes with diameters in the nanometer range. Many unusual properties associated with CNTs are derived from these curved graphene layers while imposing topological constraints and supplementary quantum confinement in circumferential direction (Peigney *et al.*, 2001). CNTs are classified as Single Walled CNTs (SWCNTs), Double Walled CNTs (DWCNTs) and multiwalled CNTs (MWCNTs). The SWCNT structure can be conceptualized by shaping a single atom thick graphene layer into a seamless cylinder as shown in Fig. 1. Similarly, the MWCNTs are formed by a number of concentric SWCNTs. The properties of SWCNTs are mainly influenced by the way of wrapping around the graphene sheets. Depending on their chiral vectors, the SWCNTs can be conducting or semi-conducting (Baddour and Briens, 2005; Paradise and Goswami, 2007). Nevertheless, SWCNTs reveal very unique optical and electrical features when compared with MWCNTs which exhibit high chemical resistance (Hrapovic *et al.*, 2008). It predicts that the CNTs have many potential industrial applications like; nano-electronic devices, electrochemical double layer capacitors, field emitters, functional polymers, hydrogen storage, high strength microwave and electromagnetic absorbing composites, fibers, sensors, radiation sources, energy

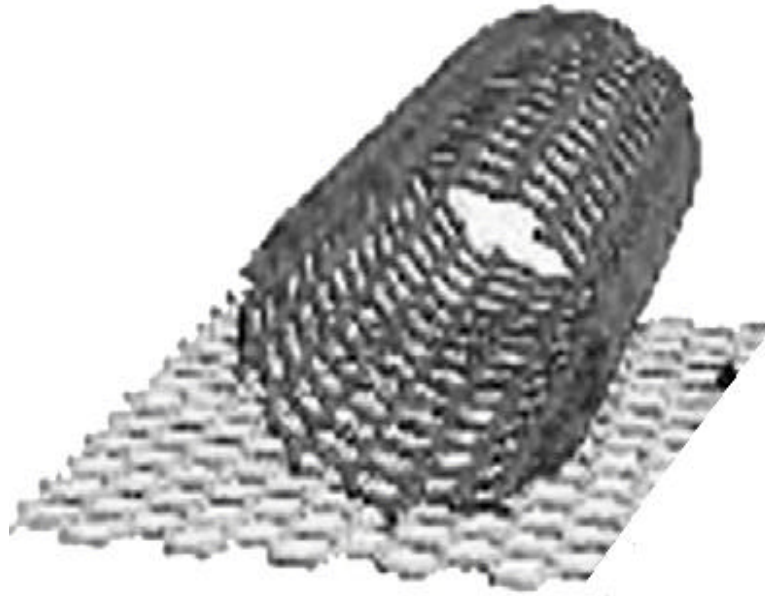


Fig. 1: Structure of SWCNT formed from a graphitic sheet

conversion and energy storage devices, probes, carbon nanotubes interconnector (Tsukagoshi *et al.*, 2002; Dillon *et al.*, 1997; Tans *et al.*, 1997; Baughman *et al.*, 2002; Dalton *et al.*, 2003; Fan *et al.*, 2006) etc.

The most common methods for CNTs production are laser ablation method, electric arc discharge, solar energy route, flame synthesis, catalytic chemical vapor deposition, etc. (Guo *et al.*, 1995; Journet *et al.*, 1997; Laplaze *et al.*, 1998; Li *et al.*, 2004; Vander Wal, *et al.*, 2000). The laser ablation and arc discharge methods normally require high amount of energy for CNTs formation. This energy is normally provided through laser or plasma arc discharge in order to reorganize the carbon atoms into CNTs. In these processes, the required temperature sometimes even exceed 3000°C which is advantageous for very fine crystallization of the CNTs. Therefore, the final product is always formed with good alignment of graphite. However, the essential needs of these systems are the continuous graphite target replacement and sensitive vacuum conditions. In contrast, the Chemical Vapor Deposition (CVD) has proven itself as a favored method for mass production of CNTs (Andrews *et al.*, 1999; Colomer *et al.*, 2000; Dasgupta *et al.*, 2008). With this technique, the carbon is obtained from hydrocarbon or other carbon bearing precursors and deposited onto a substrate in the presence of a catalyst. In the CVD process, the required temperature is normally kept below 1200°C. In addition, the CNTs structure such as diameter, wall number, length and alignment can also be controlled during this process. Thus, the CVD technique has the advantage of calm operation, controllable process, low cost and most promising way for large scale production of CNTs.

So far, the CVD has been carried out by various scalable processes, for example, Carbon Multiwall Nanotubes (CMWNTs) by Hyperion Company (Hyperion Catalysis International, Inc., 1987), CoMoCAT™ Process at SWeNT by University of Oklahoma (Resasco *et al.*, 2008) and a nano agglomerate fluidized bed of Tsinghua University (Wang *et al.*, 2002). Although, the fluidized bed process is the most promising route for large scale production of CNTs but the fluidization of nano

sized entities is still a great challenge for the researchers. The literature published so far on this issue includes four excellent reviews (Philippe *et al.*, 2007; See and Harris, 2007; Danafar *et al.*, 2009; MacKenzie *et al.*, 2010). The main focus of these reviews was on growth mechanisms and morphology of CNTs. In order to synthesize the CNTs, we also need to understand the present status of fluidized bed reactors. It is noted that characteristic features of conventional fluidized beds are distinguished to that of nano particle fluidization. Therefore, this review has focused on the current challenges regarding the FBCCVD synthesis of CNTs and how these challenges have been met so far. A critical review of the published work on hydrodynamics of FBCCVD, the effect of processing parameters on CNTs yield and morphology, mechanics, design and scale-up procedure of fluidized bed have been presented. An attempt was made to highlight the research gaps and suggestions were made for future work in this area.

### **FBCCVD WORKING MECHANISM**

Schematic of a fluidized bed reactor for growing CNT samples is shown in Fig. 2, where a is the mass flow controller, b is the gas distributor, c is the fluidized bed reactor, d is the temperature controller, e is the cold trap system and f is the furnace. The microscopic scale FBCCVD CNTs growth mechanism composed of three relatively independent phenomena leading to the tubular carbon formation in a  $sp^2$  structure. All these phenomena involve the catalytic dissociation of hydrocarbon molecules, atomic carbon saturation in catalyst nanoparticles and carbon precipitation from catalyst to form CNTs, respectively (Peigney *et al.*, 2001). The resultant CNTs features like chirality, dimensions, wall number, diameter and graphitization are calculated via process conditions and growth mechanism. It emphasizes that parametric factors affecting the FBCCVD should be well understood for the desired clean CNTs synthesis. In CNTs synthesis using fluidized bed, the most critical part is the selection and synthesis of the supporting catalysts.

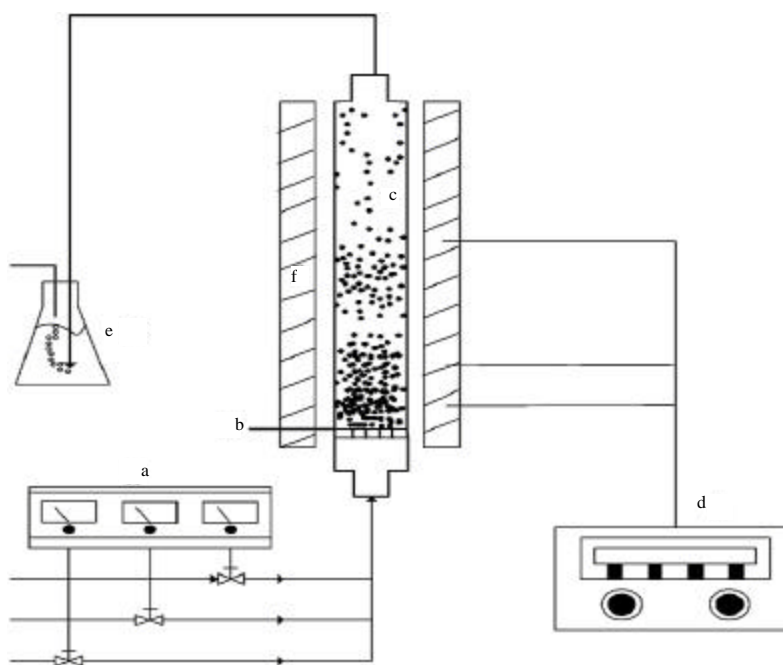


Fig. 2: Schematic diagram of the fluidized bed reactor for growing CNTs

As, catalysts play very important part in the growth of CNTs using FBCCVD, therefore, the good understanding and improvement in the desired features of the catalysts can increase both CNTs quantity and quality. Normally, the materials having the ability of decomposing hydrocarbon for the production of atomic carbon and then CNTs are employed as catalyst in FBCCVD process. However, it is realized that only the decomposing hydrocarbons ability of catalyst may not be sufficient for good CNTs production (Yao *et al.*, 2004).

Generally, the transition metals in pure (e.g., Fe, Mo, Co, Ni) or in compound form are used as a catalyst in CNTs synthesis (Andrews *et al.*, 1999) but iron is supposed to be more active metals for the synthesis of CNTs. The catalyst is dispersed on a supported material with nanosized pores (<50 nm), for example, magnesia (MgO), alumina (Al<sub>2</sub>O<sub>3</sub>), zeolite (ZrO<sub>2</sub>), silica (SiO<sub>2</sub>) and CaO etc. These small sized supporting catalysts are very cohesive in nature. The efficiency of CNTs production can be increased by fluidizing the catalyst particles in the presence of carbon source gas heated to the reaction temperature in the reactor. Thus high quality, aligned and perfect CNTs can be grown by using proper catalyst, sufficient growing space, mass and heat transfer (Hao *et al.*, 2003). Wang *et al.* (2007) examined the fluidization behavior of Degussa Aerosil R974 (silica) powder. They used a glass made fluidized bed reactor having 50 mm internal diameter and 900 mm height and a 3 mm thick sintered bronze porous distributor plate. The density and primary particle size were 2200 kg m<sup>-3</sup> and 12 nm, respectively. Transmission Electron Microscopy (TEM) images confirmed that the primary particles were joined to form the chains and tree like structures. Furthermore, the particles aggregate with size mostly in the range of 1-100 μm. In this study, the minimum fluidization velocity was found around 2.5 mm sec<sup>-1</sup>. When the gas velocity was very low, e.g., below 1 mm sec<sup>-1</sup>, the particle motion was negligible due to low pressure drop. In later stages, the gradual increase in pressure drop was observed with rise in gas velocity, then an optimum point was reached where pressure drop was balanced with particle weight per unit area. With further increase in velocity, the drop in pressure was started to increase until the pressure drop was more or less 15% above the particles weight per unit area. Above this limit, gas velocity started fluidization and bed expansion was also taken place. Overpressure was required to overcome the adhesion between the distributor plate and the particles along with any friction among the particles and the walls. The amount of pressure drop above the weight of the particles per unit area was named as over pressure. It is believed that for nanoparticles the homogeneous fluidization is commonly achieved by aggregation of the primary nanoparticles to form larger particles and to lose aggregates. For some CNTs, very smooth and bubbles free fluidization occurs with continuous bed expansion. Such fluidization of nanoparticle agglomerates is termed as Agglomerate Particulate Fluidization (APF) (Wang *et al.*, 2002). For other nanoparticles, fluidization results in a relatively limited bed expansion and large bubbles rise up very quickly through the bed. This type of fluidization has been termed Agglomerate Bubbling Fluidization (ABF) (Wang *et al.*, 2002). Zhu *et al.* (2005) studied gas fluidization characteristics of 11 different nanoparticle materials. They observed that for both APF and ABF nanoparticle agglomerates, the pressure drop increases with rise in the superficial gas velocity and then reaches a plateau and depends largely on the bulk density and the primary particle size.

In short, fluidization gives high space velocity leading to efficient solid-gas interaction and consequently the high mass and heat transfer. In line with that high process yield, purity, homogeneity and selectivity of the final product are attained (See and Harris, 2008; Hsieh *et al.*, 2009). Moreover, fluidized bed is a flexible process due to varying the operating conditions and parameters (gas mixture and temperature) which can be finely adjusted according to the

requirement of the desired product (Zhu *et al.*, 2005; See and Harris, 2008; Hsieh *et al.*, 2009). In addition, accessible space for CNTs growth and their residence time can also be controlled (Hsieh *et al.*, 2009) which favors the selective mass production of CNTs with uniform properties.

## **FLUIDIZED BED REACTOR DESIGN AND OPERATION**

Despite of all the stated advantageous, improper design and operation of the fluidized bed reactor can cause conversions which might be well below the perfectly mixed flow in theoretical studies. Xu and Zhu (2004) studied the fluidized bed reactor due to many advantage of these kinds of reactors for large scale production of CNTs. They demonstrated a brand new methodology of fluidizing bed Metal-Organic Chemical Vapor Deposition (MOCVD). It also acted as one-step preparation, with supported catalysts of highly dispersed metal followed by FBCCVD to synthesize CNTs. This process is highly useful compared with other conventional methods (such as ion exchange, impregnation, co-crystallization and co-precipitation) because it reduces the crystalline size growth of the supported metal particles and it also reduces the use of operations just like calcination, reduction and drying. Effect of supported-catalyst in CNTs growth by using FBCCVD method was also investigated. Acetylene was used as a carbon precursor. Results indicated that the deposited metals were highly dispersed on the surface of the support particles in case of all the metal-supported catalysts. Concerning to a related challenge of the mass production of CNTs and development of FBCCVD, See and Harris (2008) investigated the growth of CNTs by using the scientific feasibility of  $\text{CaCO}_3$  as a soluble support material via., FBCCVD. They obtained MWCNTs having comparable quality to those produced by traditional CVD techniques. These models also showed the flexibility of FBCCVD which fulfill the main concern of this method for large scale production. All the parameters which manipulate the reaction and fluidization quality are also very important and should be considered. The factors affecting the efficiency of CVD reactor have been discussed in earlier research works (Wang *et al.*, 2007; Yao *et al.*, 2002; Zhu *et al.*, 2005; See and Harris, 2008; Hsieh *et al.*, 2009; Xu and Zhu, 2004). The CVD renovation into a fluidized reactor depends on the fundamental features called fluidization quality. The term 'fluidization quality' depicts the various fluid-dynamic conditions which were appeared during the fluidization process itself. Most important quantities which determine the fluidization mode and characteristics include reactor geometry, intrinsic properties of particles, fluidizing velocity, superficial and minimum fluidization velocity.

Morancais *et al.* (2007) studied the large scale production of MWCNTs by fluidized bed catalytic chemical vapor deposition. Mesoporous alumina ( $\text{Al}_2\text{O}_3$ ) as a supporting catalyst of mass 50 g was introduced into reactor. Ethylene was used as carbon feedstock while Hydrogen and nitrogen gases were acting as carrier gases and introduced in fluidized bed with constant flow rate. When the thermal regime was reached, the flow rate of nitrogen was lowered to a pre-calculated value. Then at the same time, ethylene was feed into bed to retain the constant total flow rate. In order to completely dissolve the alumina and iron catalyst, whole bed composite particles were chemically treated in a sulfuric acid bath. Thermo Gravimetric Analyses (TGA) were carried out in order to evaluate the amount of carbon. SEM and TEM techniques were also used to detect the undesired products (soot). MWCNTs growth induced an explosion of the catalytic grains, MWCNTs growth also promoted the fixed bed height and reductions in minimum fluidization velocity. It had been proved that the temperature influenced significantly the morphology of the CNTs hank growth as well as the porosimetry properties of the MWCNTs. The other parameters had less manifest effect on MWCNTs morphology for instance pressure etc. Partial bed agglomeration occurs if the forces

exerted by the gas on particles became lower than the inter-particles forces. A limiting step in this process was the internal diffusion into mesopores of alumina or the MWCNTs jumbles. At ambient pressure, the kinetic law of MWCNTs formation was seemed to have positive order dependant on ethylene partial pressure.

Venegoni *et al.* (2002) also used FBCCVD for the growth of carbon nanotubes. Reactor was composed of a quartz tube (2.8 cm diameter) with sealed porous quartz distributor. An ASM flow controller was used to regulate the flow rate of the gases. Silica (supporting catalyst) of mass 10 g was introduced into reactor having the quartz distributor. Catalyst was calcinated at 450°C for 60 min by flowing air at 150 sccm. Iron was taken as catalyst, for example  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Fe}(\text{CO})_5$ . Catalyst was also activated at 650°C for 2 h by flowing a mixture of  $\text{H}_2$  (50 sccm) and He (100sccm) which was a carbon feed stock. After this  $\text{H}_2$  flow was stopped then the furnace was shifted relatively to the fluidized bed until reactor reached the operating temperature for the deposition of CNTs. Then furnace was repositioned to heat the fluidized bed and reactive gas phase was set. At the end of run,  $\text{C}_2\text{H}_4$  and  $\text{H}_2$  were allowed to flow and heating was switched off. Furnace was shifted to the FB and Catalyst activation was kept same for all experiments. The resultant MWCNTs were homogeneously distributed on the support and small amounts of encapsulated iron particles were also found. These particles were depended on the processing condition. The nanotubes remained anchored to the silica support, because neither elutriation, nor rough effect of the support was noticed. 10-20 nm yields of MWCNTs were obtained when process operated between 550 and 750°C. At high temperatures, catalyst particles started sintering and thus yield also decreased. Some SWCNTs bundles were also observed. The presence of hydrogen gas was necessary for both high production and improvement of MWCNTs.

Zhang *et al.* (2010) used FBCCVD for mass production of vertically aligned CNT (VACNT) arrays. Fe/Mo/vermiculite were used as a catalyst and vermiculite powder of size of 100-250  $\mu\text{m}$  acted as carrier catalyst. The solution of iron nitrate  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  were also used to compose final catalyst. Before reaction, 5 g of catalyst was introduced into the reactor. In argon atmosphere the fluidized bed reactor was heated to reaction temperature. Carbon source  $\text{C}_2\text{H}_4$  was fed into the reactor due to reduction of  $\text{H}_2$ . The reaction happened within the vermiculite particles because catalyst was efficiently fluidized in the reactor. Ar and  $\text{N}_2$  gases were used to cool down the reactor to room temperature and the  $\text{H}_2$  gaseous mixture as reducing gas to start TPR observation. Thus FBR was cooled under argon atmosphere. Finally VACNT arrays were obtained. Morphology of the VACNT arrays was characterized by using SEM and TEM techniques. TGA was used to check the purity of grown CNTs. It was noted that with an increase of temperature the alignment of CNTs among the lamellar catalyst become poorer. Thus the structural and agglomerated properties of the CNTs were affected significantly with the growth of temperature. The influence of the other parameters was less prominent on CNTs morphology. With the growth of the space velocity the  $I_p/I_G$  ratio also increased gradually. In order to get high conversion of carbon sources, the reduction of catalyst and medium value of the space velocity are necessary. The size of the grown products were found large in case of particulate fluidization and bubbling fluidization while in the case of turbulent fluidization the size of the grown products was observed small due to the violent collisions. The 3.0  $\text{kg h}^{-1}$  VACNT arrays was first produced in pilot plant fluidized reactor. It was primary approach to produce high output of CNTs. Pilot plant fluidized bed reactor provided an access to obtain large amount of CNT arrays for further applications in future.

Corrias *et al.* (2003) studied CNTs produced by FBCCVD (first approach of the process). In this technique, controlled amount of  $\text{Fe}/(\text{Al}_2\text{O}_3)$  used as catalyst particles while Mesoporous alumina

(Al<sub>2</sub>O<sub>3</sub>) particles introduced as initial fluidized powder. These catalysts and initial fluidized powder were fed into the reactor. Introduction of pure nitrogen and hydrogen in bed with constant flow rate fluidized the bed. Then it was heated up to thermal regime. Once the thermal regime was reached, the flow rate of nitrogen was decreased to a pre-calculated value of deposition and at the same time ethylene C<sub>2</sub>H<sub>4</sub> (Carbon source) was also loaded into bed. In order to completely dissolve the alumina and most of the iron catalyst whole bed particles were chemically treated in acid bath after each run. The CNTs were analyzed by using the techniques SEM, TEM, TGA and nitrogen adsorption desorption analysis. The carbon yield often exceeded 95% and the nanotubes selectively were closed to 100%. Under the tested conditions, no decrease of the fluidization quality had been detected.

Li *et al.* (2004) have effectively produced SWCNTs by using FBCCVD technique that fluidized the catalyst at high temperatures by a hydrocarbon flow. When nickel-nitrate or nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) catalyst was coated with silica gel particles which acted as the catalyst support and methane was used as a carbon feed stock, on the entire surface of the support particles SiO<sub>2</sub>, SWCNTs were found to grow densely at 760°C which were characterized by Raman spectrometry and SEM analysis. These results have shown several advantages over the common fixed bed process, such as avoidance of catalyst particle sintering, uniform gas-solid mixture, secure for the large-scale production and unbroken SWCNTs at high rate. The SEM investigated that images of the manufactured CNTs were randomly dispersed and in the form of curve. Raman spectroscopy and transmission electronic microscopy observed that these SWCNTs were formed in bundles having diameter of 20 nm. Similarly the MWCNTs had been found with same diameter and carbon encapsulated with nickel particles was also found. In the products total carbon content of 12.5 wt.% was calculated by using TGA analysis. The typical Raman spectra indicated that SWCNT structure has strong G band around 1580 cm<sup>-1</sup> (Rols *et al.*, 2000) while D band at around 1335 cm<sup>-1</sup> in the presence of the sharp radial breath modes (RBM) with lower wave number region (100-300 cm<sup>-1</sup>) (Rao *et al.*, 1997). Ten positions were randomly recorded by Spectra. Low intensity ratio (I<sub>D</sub>/I<sub>G</sub> = 0.14) indicated a low amount of amorphous (Lefrant *et al.*, 2002). This showed that the Ni (60 wt.%) was used as a catalysts to produce SWCNTs at relatively low temperature (760°C) while MWCNTs at a higher temperature (860°C). These results indicated that at higher temperatures nickel particles were found larger and the surface of the support was not fully utilized with this lower catalyst loading. Further it gave the information of how to control the growth of SWCNTs and their associated mechanisms.

Danafar *et al.* (2011) studied the particle size catalytic by using fluidized bed chemical vapor deposition synthesis to produce CNTs. Catalytic particles contained iron (2.5%) and cobalt (2.5%) and alumina (95%) as a support. Six different particles were chosen with size fractions such as (10-20, 20-53, 53-75, 75-100, 100-200 and 200-300 μm). It was experimentally proved that greater carbon deposition efficiency and CNTs production occur with use of smaller diameter of catalytic particle diameter. It was observed that mass and heat transport of CNTs were affected by changing the catalytic fine particles diameter range. It should also be ensured high interstitial velocity. So, the quality and synthesis rate of the CNTs were found inversely proportional to the size of the catalytic particles. The 10-20 μm catalytic particles indicated 30% higher deposit carbon efficiency than the 200-300 μm catalytic. Thus it led to high reaction rate and also large CNTs productivity.

Yen *et al.* (2008) synthesized CNTs from solid-stated polyethylene and polymers-polycarbosilane (PCS) by using (FBCCVD) method. Fe(NO<sub>3</sub>)<sub>3</sub> and MgO acted as the



catalysts, where as polyethylene and PCS used as carbon feed source. The experimental results showed that by using PCS the diameters of CNTs was changed from 15-90 nm and similarly the lengths also varied several micrometer. This happened only when reaction temperatures were kept at 850-950°C. But on the other way by using of polyethylene as carbon source, the diameter of CNTs was changed from 25-90 nm and the length can reached to 1 µm while reaction temperatures kept at 750-850°C. From comparison of these two different carbon sources, the CNTs synthesized from polyethylene had improved quality and features. CNTs also revealed and possessed high degree of graphitization as compared to the others. Thus, better yield and quality of CNTs was obtained.

Rashidi *et al.* (2011) studied the performance of both fixed and fluidized bed reactors. The production of (SWCNTs) had been found by using both reactors in which methane was used as carbon source over Co-Mo/MgO nano-catalyst under two different operating conditions. At the end CNTs were characterized by TGA, TEM and Raman spectroscopy. Results indicated that the performance of a fluidized bed in the production of CNTs is much better than that of a fixed bed because FBCCVD offered more space for the development of CNTs. At the same temperature, results were better in FBCCVD as compared to fixed reactor due to more control of heat and mass transfer. Therefore, the  $I_D/I_G$  ratio was 0.11 in case of FBCCVD while the  $I_D/I_G$  ratio obtained from fixed reactor was 0.71 which also showed that the production of SWCNTs in the FBCCVD was 92 wt.% while it was 78 wt.% in the fixed bed. Considering the presented discussion, it would be reasonable to declare that the important features of FBCCVD for CNTs synthesis are still blurred. The thermodynamic and hydrodynamic behaviors of CNTs growth in fluidized beds have not been understood yet. This short review would be helpful to understand the basics of some of the research achievements and problems regarding the mass production of CNTs using FBCCVD.

Maghsoodi *et al.* (2010) produced continuous production of CNTs by using (FBCCVD) of methane (carbon source) on iron floating catalyst with supporting catalyst MgO in a reactor. At high temperature, ferrocene vapors were contacted with MgO powder and then started to fluidized by carbon feed stock to produce Fe/MgO catalyst. The efficiency of ferrocene and MgO was increased by using annular tube. MgO powder was continuously introduced into reactor via star valve. That's why both SWCNTs and MWCNTs were continuously synthesized on the Fe/MgO catalyst. The SEM and TEM investigated that the CNTs are mostly entangled bundles with diameters of about 10-20 nm. Raman spectra indicated that the CNTs showed low defects.  $I_G/I_D$  ratio = 10.2 were high at 900°C. The RBM Raman peaks showed that diameter of (SWNTs) were 1.0-1.2 nm diameter. So, high quality and quantity of CNTs was produced by this method.

## CONCLUSION

Up till now, the bulk production of CNTs has been a major challenge for their future applications. Over the last few years, significant advances in development of new CVD methods made possible the commercial production of CNTs. It is understandable that the fluidized bed catalytic chemical vapor deposition method has the potential to deliver large scale CNTs products at affordable rates. But for process scale up, we must understand the kinetics, hydrodynamics and mass transfer of the bed during the process because all these aspects have not been previously addressed in a proper way in the literature. This study also emphasizes on the use of cheap precursors with minimized total number of steps involved in CNTs production. However, the FBCCVD is in its infancy and further research will improve the yield, purity and selectivity of CNTs

growth. Many of the challenges and ambiguity associated with CVD and FBCCVD synthesis of CNTs have been highlighted in this study. It has been demonstrated that further investigations, both theoretical and experimental, are required to study the effective parameters on FBCCVD process.

### **FUTURE DIRECTIONS**

The large scale production of CNTs by using a fluidized bed reactor, comprehensive experimental programmes should be started in order to develop a relationship between rate controlling steps and system design and operation parameters. Furthermore, the CNTs production mechanisms should also be investigated experimentally as well as theoretically. In this connection, the modeling of process parameters and equipments by using Computational Fluid Dynamics (CFD) has already gained attention of the scientists and practitioners. The substantial additional research is needed to meet the challenges set by CFD study of the fluidized bed reactors. The future simulations should also focused on Discrete Elemental Method (DEM) for fluidized bed studies.

### **ACKNOWLEDGMENTS**

This study is partially funded by NanoMalaysia Center of Excellence Grant Scheme (NanoCOE) No. 0153C1-003 and Tuition Fee Assistantship Scheme of Universiti Teknologi PETRONAS, Malaysia.

### **REFERENCES**

- Andrews, R., D. Jacques, A.M. Rao, F. Derbyshire and D. Qian *et al.*, 1999. Continuous production of aligned carbon nanotubes: A step closer to commercial realization. *Chem. Phys. Lett.*, 303: 467-474.
- Baddour, C.E. and C. Briens, 2005. Carbon nanotube synthesis: A review. *Int. J. Chem. Reactor Eng.*, Vol. 3. 10.2202/1542-6580.1176
- Baughman, R.H., A.A. Zakhidov and W.A. de Heer, 2002. Carbon nanotubes--the route toward applications. *Science*, 297: 787-792.
- Colomer, J.F., C. Stephan, S. Lefrant, G. van Tendeloo and I. Willems *et al.*, 2000. Large-scale synthesis of single-wall carbon nanotubes by Catalytic Chemical Vapor Deposition (CCVD) method. *Chem. Phys. Lett.*, 317: 83-89.
- Corrias, M., B. Caussat, A. Ayrat, J. Durand, Y. Kihn, P. Kalck and P. Serp, 2003. Carbon nanotubes produced by fluidized bed catalytic CVD: First approach of the process. *Chem. Eng. Sci.*, 58: 4475-4482.
- Dalton, A.B., S. Collins, E. Munoz, J.M. Razal and V.H. Ebron *et al.*, 2003. Super-tough Carbon-nanotube fibres. *Nature*, 423: 703-703.
- Danafar, F., A. Fakhru'l-Razi, M.A.M. Salleh and D.R.A. Biak, 2009. Fluidized bed catalytic chemical vapor deposition synthesis of carbon nanotubes-a review. *Chem. Eng. J.*, 155: 37-48.
- Danafar, F., A. Fakhru'l-Razi, M.A.M. Salleh and D.R.A. Biak, 2011. Influence of catalytic particle size on the performance of fluidized-bed chemical vapor deposition synthesis of carbon nanotubes. *Chem. Eng. Res. Des.*, 89: 214-223.
- Dasgupta, K., R. Venugopalan, G.K. Dey and D. Sathiyamoorthy, 2008. Novel catalytic route to bulk production of high purity carbon nanotube. *J. Nanoparticle Res.*, 10: 69-76.
- Dillon, A.C., K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune and M.J. Heben, 1997. Storage of hydrogen in Single-walled carbon nanotubes. *Nature*, 386: 377-379.

- Fan, J.P., D.M. Zhuang, D.Q. Zhao, G. Zhang, M.S. Wu, F. Wei and Z.J. Fan, 2006. Toughening and reinforcing alumina matrix composite with Single-wall carbon nanotubes. *Applied Phys. Lett.*, 89: 121910-121913.
- Guo, T., P. Nikolaev, A. Thess, D.T. Colbert and R.E. Smalley, 1995. Catalytic growth of Single-walled nanotubes by laser vaporization. *Chem. Phys. Lett.*, 243: 49-54.
- Hao, Y., Z. Qunfeng, W. Fei, Q. Weizhong and L. Guohua, 2003. Agglomerated CNTs synthesized in a fluidized bed reactor: Agglomerate structure and formation mechanism. *Carbon*, 41: 2855-2863.
- Hrapovic, S., K.B. Male, Y. Liu and J.H. Luong, 2008. Preparation of Polymer-carbon nanotube composite materials and their applications for enzyme entrapment. *Anal. Lett.*, 41: 278-288.
- Hsieh, C.T., Y.T. Lin, W.Y. Chen and J.L. Wei, 2009. Parameter setting on growth of carbon nanotubes over transition metal/alumina catalysts in a fluidized bed reactor. *Powder Technol.*, 192: 16-22.
- Hyperion Catalysis International, Inc., 1987. Carbon fibrils, method for producing same and compositions containing same. U.S. Patent US4663230. <http://www.google.sc/patents/US4663230>
- Journet, C., W.K. Maser, P. Bernier, A. Loiseau and M.L. de la Chapelle *et al.*, 1997. Large-scale production of Single-walled carbon nanotubes by the Electric-arc technique. *Nature*, 388: 756-758.
- Laplaze, D., P. Bernier, W.K. Maser, G. Flamant, T. Guillard, A. Loiseau, 1998. Carbon nanotubes: The solar approach. *Carbon*, 36: 685-688.
- Lefrant, S., I. Baltog, M. Baibarac, J. Schreiber and O. Chauvet, 2002. Modification of surface-enhanced Raman scattering spectra of single-walled carbon nanotubes as a function of nanotube film thickness. *Phys. Rev. B*, Vol. 65 10.1103/PhysRevB.65.235401
- Li, Y.L., I.A. Kinloch, M.S. Shaffer, J. Geng, B. Johnson and A.H. Windle, 2004. Synthesis of single-walled carbon nanotubes by a fluidized-bed method. *Chem. Phys. Lett.*, 384: 98-102.
- MacKenzie, K.J., O.M. Dunens and A.T. Harris, 2010. An updated review of synthesis parameters and growth mechanisms for carbon nanotubes in fluidized beds. *Ind. Eng. Chem. Res.*, 49: 5323-5338.
- Maghsoodi, S., A. Khodadadi and Y. Mortazavi, 2010. A novel continuous process for synthesis of carbon nanotubes using iron floating catalyst and MgO particles for CVD of methane in a fluidized bed reactor. *Applied Surface Sci.*, 256: 2769-2774.
- Morancais, A., B. Caussat, Y. Kihn, P. Kalk and D. Plee *et al.*, 2007. A parametric study of the large scale production of multi-walled carbon nanotubes by fluidized bed catalytic chemical vapor deposition. *Carbon*, 45: 624-635.
- Paradise, M. and T. Goswami, 2007. Carbon Nanotubes-production and industrial applications. *Mater. Des.*, 28: 1477-1489.
- Peigney, A., P. Coquay, E. Flahaut, R.E. Vandenberghe, E. de Grave and C. Laurent, 2001. A study of the formation of Single-and Double-walled carbon nanotubes by a CVD method. *J. Phys. Chem. B*, 105: 9699-9710.
- Philippe, R., A. Morancais, M. Corrias, B. Caussat and Y. Kihn *et al.*, 2007. Catalytic production of carbon nanotubes by fluidized-bed CVD. *Chem. Vapour Deposit.*, 13: 447-457.
- Rao, A.M., E. Richter, S. Bandow, B. Chase and P.C. Eklund *et al.*, 1997. Diameter-selective raman scattering from vibrational modes in carbon nanotubes. *Science*, 275: 187-191.

- Rashidi, A., R. Lotfi, E. Fakhrmosavi and M. Zare, 2011. Production of single-walled carbon nanotubes from methane over Co-Mo/MgO nanocatalyst: A comparative study of fixed and fluidized bed reactors. *J. Nat. Gas Chem.*, 20: 372-376.
- Resasco, D.E., B. Kitiyanan, W.E. Alvarez, L. Balzano, 2008. Process and apparatus for producing Single-walled carbon nanotubes. US Patent, 6919064.
- Rols, S., A. Righi, L. Alvarez, E. Anglaret and R. Almairac *et al.*, 2000. Diameter distribution of single wall carbon nanotubes in nanobundles. *Eur. Phys. J. B*, 18: 201-205.
- See, C. and A. Harris, 2007. A review of carbon nanotube synthesis via fluidized-bed chemical vapor deposition. *Ind. Eng. Chem. Res.*, 46: 997-1012.
- See, C.H. and A.T. Harris, 2008. CaCo<sub>3</sub> supported Co-Fe catalysts for carbon nanotube synthesis in fluidized bed reactors. *AIChE J.*, 54: 657-664.
- Tans, S.J., M.H. Devoret, H. Dai, A. Thess, R.E. Smalley, L.J. Geerligs and C. Dekker, 1997. Individual Single-wall carbon nanotubes as quantum wires. *Nature*, 386: 474-477.
- Tsukagoshi, K., N. Yoneya, S. Uryu, Y. Aoyagi, A. Kanda, Y. Ootuka and B.W. Alphenaar, 2002. Carbon nanotube devices for nanoelectronics. *Phys. B: Condensed Matter*, 323: 107-114.
- Vander Wal, R.L., T.M. Ticich and V.E. Curtis, 2000. Diffusion flame synthesis of Single-walled carbon nanotubes. *Chem. Phys. Lett.*, 323: 217-223.
- Venegoni, D., P. Serp, R. Feurer, Y. Kihn, C. Vahlas and P. Kalck, 2002. Parametric study for the growth of carbon nanotubes by catalytic chemical vapor deposition in a fluidized bed reactor. *Carbon*, 40: 1799-1807.
- Wang, Y., F. Wei, G. Luo, H. Yu and G. Gu, 2002. The Large-scale production of carbon nanotubes in a Nano-agglomerate Fluidized-bed reactor. *Chem. Phys. Lett.*, 364: 568-572.
- Wang, X.S., F. Rahman and M.J. Rhodes, 2007. Nanoparticle fluidization and Geldart's classification. *Chem. Eng. Sci.*, 62: 3455-3461.
- Xu, C. and J. Zhu, 2004. One-step preparation of highly dispersed metal-supported catalysts by fluidized-bed MOCVD for carbon nanotube synthesis. *Nanotechnology*, Vol. 15 10.1088/0957-4484/15/11/052
- Yao, W., G. Guangsheng, W. Fei and W. Jun, 2002. Fluidization and agglomerate structure of SiO<sub>2</sub> nanoparticles. *Powder Technol.*, 124: 152-159.
- Yao, Y., L.K. Falk, R.E. Morjan, O.A. Nerushev and E.E. Campbell, 2004. Synthesis of carbon nanotube films by thermal CVD in the presence of supported catalyst particles. Part II: The nanotube film. *J. Mater. Sci.: Mater. Electron.*, 15: 583-594.
- Yen, Y.W., M.D. Huang and F.J. Lin, 2008. Synthesize carbon nanotubes by a novel method using chemical vapor deposition-fluidized bed reactor from solid-stated polymers. *Diamond Related Mater.*, 17: 567-570.
- Zhang, Q., M.Q. Zhao, J.Q. Huang, J.Q. Nie and F. Wei, 2010. Mass production of aligned carbon nanotube arrays by fluidized bed catalytic chemical vapor deposition. *Carbon*, 48: 1196-1209.
- Zhu, C., Q. Yu, R.N. Dave and R. Pfeffer, 2005. Gas fluidization characteristics of nanoparticle agglomerates. *AIChE J.*, 51: 426-439.