

Investigation of a Fluidized Bed Chemical Vapor Deposition (FBCVD) Reactor towards a Large Scale Multi-walled Carbon Nanotubes

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Abstract— In this work, three major investigations were conducted for the development of a large-scale production of multi-walled carbon nanotubes (CNT) using chemical vapor deposition in a fluidized bed reactor. The process involves the use of methane gas as carbon source, NiO/MgO as catalyst carried out at 600°C for 2 hours of reaction. First, the effect of catalyst reduction time to produce carbon nanotubes suggests that at least thirty seconds of reduction time is necessary to produce 14 g CNT/ g catalyst. Second, a 20° angular opening of the fluidized bed reactor design best fits a near perfect uniform distribution of velocity profile (catalyst and carbon nanotubes) using a feed inlet velocity of up to 9.42 m/s of methane gas. Lastly, upon comparison with other production of CNT using the same catalyst of different substrates, the current set-up shows a comparatively higher carbon deposition of 2833% and methane conversion of 27%.

Further characterization of the carbon nanotubes using transmission electron microscopy (TEM) shows a herringbone, multi-walled carbon nanotubes with multi-branched junction morphology. Thermogravimetric analysis (TGA) gives a potential pure quality of 85% of as grown CNT without further purification. Raman spectroscopy indicates both the presence of ordered graphene sheets and the amorphous carbon.

Keywords—multi-walled CNT; Fluidized Bed Reactor; Chemical Vapor Deposition; Large scale synthesis

I. INTRODUCTION

The discovery of carbon nanotubes in the early 90's has made a significant impact in different fields of science and technology today such as biotechnology, electronics, medicine, semiconductors and agriculture. The most obvious reason for this phenomenon is the outstanding properties that carbon nanotubes have been known to have mechanical strength of fifty times greater than that of steel; a current density of approximately 10^9 Amperes/cm²; an elasticity of 1 to 1.2 TPa; a thermal conductivity of more than twice that of a diamond; a density of half of that of aluminum; chemical reactivity that functionalizes like graphite; a thermal stability up to 2,700°C and a chirality for metallic and semiconducting properties [1].

Different routes of producing CNTs have also surfaced through the years. First was the Arc-discharge method of Iijima [2] which is considered to be the easiest and most common. This process involves the growth of CNT on

carbon (graphite) electrodes in the presence of an inert gas such as Helium or Argon. However, tedious purification of the product is required. Another method is the laser ablation technique [3]. In this route, carbon nanotubes were synthesized by laser vaporization of a mixture of carbon graphite and transition metals located on a target. Although this process offers high purity of product and can be carried out at room temperature, it is limited to single walled- carbon nanotubes only. On the other hand, chemical vapor deposition (CVD) synthesis of carbon nanotubes is able to produce multi-walled carbon nanotubes. This technique involves the decomposition of a hydrocarbon in the presence of a catalyst. CVD comes in two types. One is the fixed bed vessel and the other is the fluidized bed reactor. Fluidized bed reactors employ a vertical type of vessel where a gas phase flows through the reactor to maintain a fluidization velocity and thus making the process more efficient [4]. The CVD offers a simple and relatively inexpensive method that can be done in low temperature but with high yields. It can both produce single and multi-walled carbon nanotubes. Of the three methods mentioned, CVD has a promising potential for large-scale synthesis and is considered as a superior method of producing carbon nanotubes, so far, in terms of commercial applications and cost-effectiveness [5,6,7,8,9,10]. Furthermore, fluidized bed reactors were developed to promote a uniform gas-solid phase mixture, avoidance of catalyst particle sintering, and potentially continuous high yield of carbon nanotubes [11] and thus considered to be better than Fixed Bed. However, few studies investigate on practical large-scale synthesis of CNTs using FBCVD.

This study investigates the use of a chemical vapor deposition method in a fluidized bed reactor in producing multi-walled carbon nanotubes to support large-scale production. To carry out this study, three major key factors were conducted to develop a large-scale fluidized bed reaction in the future. Firstly it examines the effect of the catalyst reduction time in relation to CNT productivity and its application to the reactor design. Secondly, it gives a theoretical fluid dynamics analysis of different fluidized bed reactors of different velocity profiles. Different velocity profiles give various radial velocity distributions. Thirdly it then compares the existing productivity profile, carbon

deposition and methane conversion with other existing nickel based production of carbon nanotubes.

The success of building a feasible technology for a large-scale production of carbon nanotubes would definitely answer the growing market demand for carbon nanotubes.

II. MATERIALS AND METHODS

A. Materials

The catalyst in powdered, grayish form used in the experiments was similar to the catalyst used in previous studies of Jin-Mei Zhou et al. [12] and P. Chen et al. [13], where preparation of the said catalyst was done in pure AR (Analytical Reagents) grade reagents of two powders of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ mixed thoroughly at specific amounts, added with citric acid, homogenized into solution, evaporated, dried and calcined. The solid solution type was a catalyst with a specific molecular formula of $\text{Ni}_{0.5}\text{Mg}_{0.5}\text{O}$, a surface area of $34\text{m}^2/\text{g}$ and sieved through standard screen mesh numbers of 40 – 100. Pure methane gas was also used.

B. Methods

A fluidized bed reactor set-up was used in this experiment. It was composed of five main component parts; the vertical quartz tube reactor, the furnace, Gas Chromatography, inlet and outlet pipes, and thermocouples. The quartz tube reactor was inserted in the middle of the furnace. The catalyst was placed in the middle part of the quartz tube reactor, resting on the surface of the steel balls, approximately 17.0 cm above the base of the tube reactor. Both ends of the quartz reactor were aluminum caps used to seal and enclose the inlet and outlet pipes. The inlet and outlet pipes were made of rubber with a diameter of one third of the quartz tube reactor. The inlet pipe was connected from the gas source (N_2 , Ar, H_2 , CH_4) while the outlet pipe was connected to the online GC 950 model instrument for online analysis of product samples. The furnace was 35.0 cm in height and 21.0 cm in diameter with a steel cover around its circumference and asbestos for internal insulation. It was used to raise and maintain the temperature at specific magnitudes. Setting of temperatures and gas velocities (for carrier and reacting gases) were carried out on the calibrated PC logic controller displayed on the monitor board of the reactor set-up. Both control valves and monitors for temperature and gas velocities were all placed in one monitoring board. The temperature thermocouples were directly connected to the temperature control monitor, thus giving convenience during the experimental activities conducted.

Computational fluid dynamics code in FLUENT 6.3 software was utilized in designing different fluidized bed reactor of different velocity profiles. The details of this modeling can be fully available online from Fluent 6.3 user guide of Fluent, Inc., Lebanon, N.H., USA, 2006. However, most of the equations used in this paper were adopted from the study of Britt M. Halvorsen's master thesis on "CFD Study of a Bubbling Fluidized Bed", at the Process Technology Hogskolen i Telemark, 2008.

In this particular case of modeling, an Eulerian multiphase model was used with a Laminar flow system considering the low velocity profiles (50 – 100L/min). The Eulerian multiphase model in FLUENT allows for the modeling of multiple separate, yet interacting phases. The phases can be liquids, gases, or solids in nearly any combination. An Eulerian treatment is used for each phase, in contrast to the Eulerian-Lagrangian treatment that is used for the discrete phase model. The Eulerian multiphase model does not distinguish between fluid-fluid and fluid-solid (granular) multiphase flows. A granular flow is simply one that involves at least one phase that has been designated as a granular phase. The kinetic theory of granular flow describes the interaction between particles and is based on the kinetic theory of gases. The interaction between particles and the continuous gas phase are described by drag model and several models can be used in this software. These include Gidaspow, Syamlal O' Brien and Lun et al.

III. RESULTS AND DISCUSSION

In this section, results and discussions are divided into four. First it the characterization of the carbon nanotubes produced in this process. This includes TEM, and Raman spectroscopy analysis. Second part discusses the effect of the reduction time during the conversion of the carbon source to carbon nanotubes. An optimum reduction time is suggested at the end of this section. Third section discusses the fluidized bed reactor designer suited for this process based on the inlet angular opening. And lastly, a comparative table is discussed to show the productivity and conversion of the raw carbon source to carbon nanotubes.

A. CNTs produced

To give a vivid picture of the carbon nanotubes produced in the process involved, a High resolution TEM (TECHNAI F30 HRTEM Model) in Figure 1 displays the surface roughness view of the varied forms of carbon allotropes and graphite produced. A combination of closed and end capped carbon nanotubes and crosslinked-junction carbon nanotubes (CNTs) are seen in Figure 1a. These gave similar results with Amendola et al.'s work[14], where herringbone structured CNTs were produced as branches. Carbon nanotubes diameters ranged from 8 to 50 nm. The larger diameters are basically the main tubes while smaller ones become branches. Tube lengths are difficult to measure in this case varying roughly from 100 nm to several microns. Small, circular deep black spots in Figure 1b are suggested to be catalyst or carbonaceous matter. These spots are seen either in the end of the tubes or along with it. Figure 1c shows clear multi-walled carbon nanotubes with the catalyst embedded in the tubes' end. A distinct bamboo shaped CNT is also evident in the figure. Figure 1d shows a catalyst clearly embedded on the end of the carbon nanotube, which suggests a tip grown structure. An inset picture of this figure shows a herringbone structure of multi-walled carbon nanotubes captured in the sample with no deposited carbon. Herringbone structured CNTs have walls arranged in an angular position rather than the straight ones and with not such a smooth morphology.

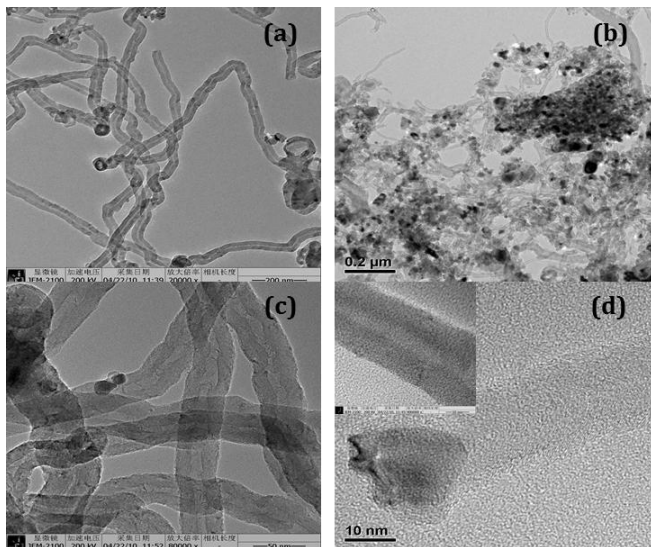


Fig.1 TEM images of carbon nanotubes produced in a fluidized bed chemical vapor deposition reactor. Reaction conditions: methane gas at 400-405 sccm, carrier gas at 400 sccm, NiO/MgO, 600°C, 2 hrs reaction. Units

The Raman spectra (from Renishaw in via Raman Microscope) shown in Figures 2a gives evidence on the presence of the tangential vibrational mode of graphene sheets as the G band (1349.2 cm^{-1}), while D band (1581.4 cm^{-1}) represents the amorphous carbon or defects in the graphene sheets. These results are closely related to early studies [15,16] that have proved to have E2 symmetry of graphene and for (HOPG) highly oriented pyrolytic graphite, while D bands are described to be disordered microcrystalline graphite and glassy carbon, which can also be seen as defects of the sheets or carbonaceous particles in the surface of tubes [9]. G line can also be interpreted as the multi-walled structure of CNT as identified at near 1580.

Figure 2b gives a typical TGA of the CNTs produced in this process. TG on the left side of the graph gives the percentage weight loss at different temperatures (the x axis of the graph) during the oxidation process analysis. DTG on the right hand side of the graph gives the derivative percentage weight loss. Weight loss at greater than 550°C is attributed to carbon nanotubes, while less than 550°C is attributed to amorphous carbon and carbon nanofibers [12] produced. In this case, the as-grown purity was at least 85%, thus implying that almost 5% (4.83%) is attributed to the metal catalyst. The solid green curve corresponds to the weight loss of the sample. In this graph, 589.0°C corresponds to the immediate high decomposition point. This may correspond to the decomposition of the multi-walled carbon nanotubes. The highest point of the derivative weight loss curve (dotted green curve) was 633.1°C . Oxidation reaction ceased at 660°C , where a stable weight loss was at 4.83%.

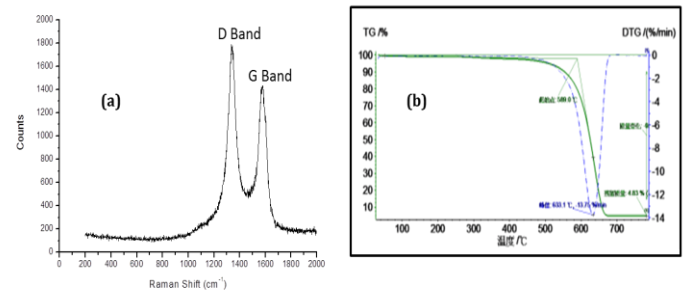


Fig. 2 a) Raman spectra analysis of carbon nanotubes using a uniform #80 mesh of catalyst particle, b) Thermogravimetric analysis of multi-walled carbon nanotubes produced.

B. Effect of Reduction Time

Reaction productivity is compared as seen in Figure 3. There are no significant differences in the productivity of carbon nanotubes from 30 seconds to one hour reduction time using different concentrations of reducing agents in either Nitrogen (in squares and diamond shaped points) and Argon (in triangular shaped points) as carrier gas environment. Productivity ranges from 13-15 g/g catalyst. Furthermore, the use of pure and 5% Hydrogen as the reducing agent also gives no effect on productivity. This indicates that the reduction of catalyst inside the FBCVD reactor would only consume at least 30 seconds enough to produce a stable production of CNTs. A provision for internal pipe in the reactor can be installed as the catalyst is being reduced at the same time fed to the reactor; ready to aid in the decomposition reaction that proceeds. Having known the optimum catalyst reduction time of at least 30 seconds in Hydrogen gas would definitely lead to a continuous fluidized bed reactor. Catalyst reduction and CNT formation can be done in one single reactor rather than in two separate reactors. A continuous production of CNTs can be developed in this type of reactor, thus developing a uniquely structured reactor.

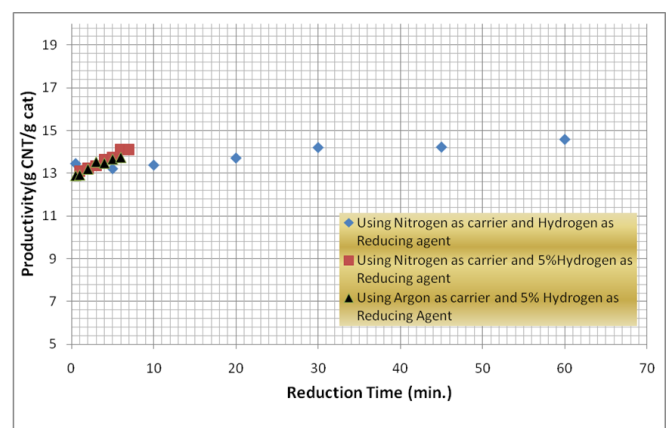


Fig. 3 Productivity comparison at different reduction time using different reducing agents and carrier gases.

C. Fluidized Bed Reactor Design

The reactor fabricated from the Geometry And Mesh Building Intelligence Toolkit (GAMBIT 2.3.16) is shown on Figure 4. It has total height of 1.2 m, a top diameter of 13.0 cm, while having a bottom diameter of 15mm, and a total volume of approximately 0.01426 m³. The inlet portion of the reactor is where the small diameter is located. It has basically three parts. Fluids 1 and 2 are located on the base conical structure. Fluid 1 is where the solids (catalyst and CNT) are formed or fed, while fluid 2 is an extension of the conical volume. The whole upper portion of the reactor is fluid 3, where formed carbon nanotubes can be observed during a reaction. The reactor is composed of hexahedral cells and mixed faces on different zones.

The fluidized bed model was set as a 3dimensional (3d), double precision (dp), pressure based, laminar, multiphase Eulerian model settings. Examination of the velocity distribution profile is of interest in the study. The 2 Phase system is composed of methane (Phase1) as the carbon source and the catalyst-CNT (Phase 2). Phase 1 enters the inlet portion of the reactor with phase 2 being patched as volume fraction on the bottom portion (fluid 1) of the reactor. Three different kinds of reactors were considered in the simulation of the fluidized bed. The three reactors have the same features (diameters, volume and length) except the conical angular values located on the bottom part. Three angles are considered in the study, namely 30, 20 and 10°. With each angle, three different velocities are tried based on a laminar flow value model. The three velocities are at 4.71, 6.59 and 9.42 m/s, which correspond to 50, 70 and 100 L/min of methane gas feed respectively. The main purpose of running a fluidized bed simulation is to create a fluidized bed system reactor in support of the actual realization towards the development of the large-scale size production in the future.

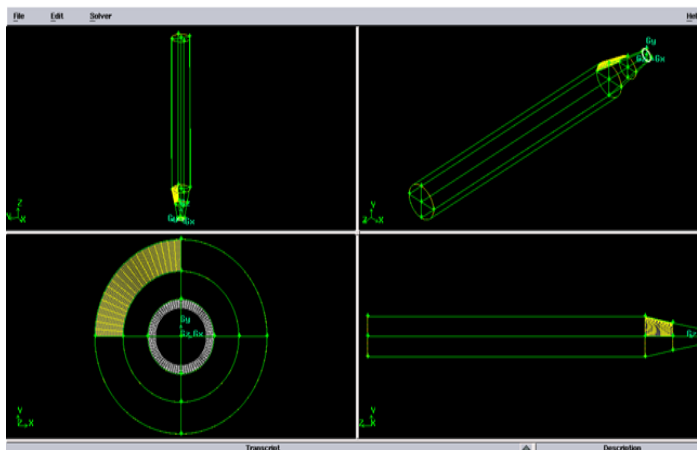


Fig. 4 Fluidized bed reactor layout for chemical vapor deposition.

Figure 5 shows the results of the simulation run using the 20° angle opening of a 15 mm diameter inlet fluidized bed reactor. Among the three types of reactors, 10°, 20° and 30° angle openings, the 20° angle opening best fits a uniform velocity profile within the reactor of up to 9.42 m/s of inlet feed velocity.

It can be observed that each reactor gives a multi-colored two-dimensional view of the velocity profile of the phase 2 (catalyst-CNT) in the system. The color ranges from dark blue to dark red (as seen in the rectangular velocity description on the left side of each reactor). This color range gives an increasing velocity magnitude from dark blue to dark red respectively. The middle velocity is the light green shade profile. Each reactor has two sets of velocity profiles-one for the whole reactor and another within the inlet conical volume. Thus the more color present in the velocity profile of the reactor, the more different velocities are present in the system. Different velocities result in the non-uniform distribution of fluids within the system which can suffer in the accumulation or sticking of catalyst or product within the reactor. Non-uniform velocities affect the fluidization of the reagents and the product thereof.

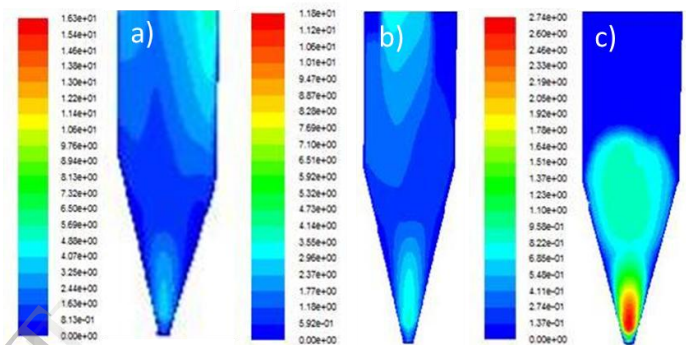


Fig. 5 Velocity distribution profile of phase 2 using 20° angle on 15 mm diameter inlet fluidized bed reactor. a) using 4.71 m/s, b) 6.59 m/s, and c) 9.42 m/s of methane gas inlet feed.

To take a closer look at the velocity profile inside the conical volume, Figure 6 displays such picture. Three different velocities were run at 4.71, 6.59, 9.42 m/s of methane gas on the same reactor. For all the three velocities, the velocity profiles of phase 2 can be observed from the bottom of the reactor up to a certain height. The height of the phase 2 velocities differs significantly in the 9.42 m/s. However the 4.71 and 6.59 m/s are relatively the same in height and of little range of velocities. When the feed rate is increased to 9.42 m/s, higher range of velocity is seen. The highest velocity is found near the bottom part of the reactor and the velocity distribution spreads through the side walls of the reactor. Thus, at higher velocity, phase 2 profile is higher too. However in terms of uniformity of the velocity profile, the first two velocities, 4.71 and 6.59 gives a better advantage of fluidization. Although at 9.42 m/s feed rate creates a high velocity of the resulting phase 2 fluids, it becomes more uniform as it goes up through the length of the reactor. Thus fluidization is recovered.

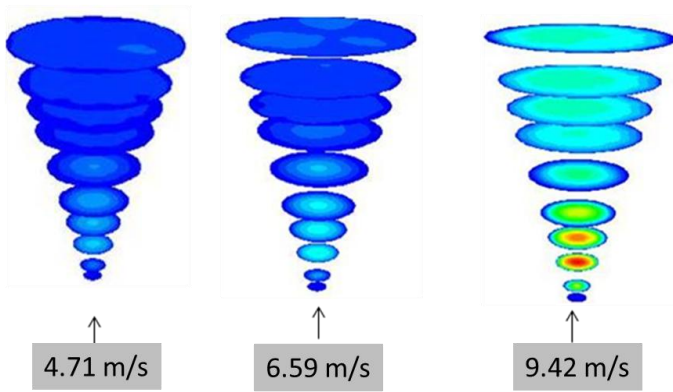


Fig. 6 Inside conical volume velocity profile distribution profile of phase 2 using 20° angle on 15 mm diameter inlet fluidized bed reactor.

D. Production of CNTs

Table 1 shows the productivity comparison based on CCVD processes from different references of different parameters. The productivity ranges from 0.065 to 18.56 g / g catalyst. This study shows a highly efficient productivity of 14.46. This may not be the highest in the table, however, this has shown that at a low temperature of 600°C a relatively high production can be obtained even higher than at 700 and 1000°C reaction temperatures.

TABLE 1 PRODUCTIVITY COMPARISON of CNT PRODUCED FROM CCVD

Catalyst Type	Substrate Type	Carbon Source	Carrier Gas	Reaction Temp. (°C)	Deposition Time (min)	CNT Type	Yield (g/gcatalyst)	Ref.
Fe:Co	CaCO ₃	C ₂ H ₂	N ₂	700	60	MWCNTs	3.59	[16]
	MgO		N ₂	700	60		2.29	[16]
Ni:Cu:Al	N/A	CH ₄	H ₂	750	60	MWCNTs	1.78	[6]
			N ₂	750	60		6.64	[6]
			None				18.56	[6]
Fe:Co	CaCO ₃	C ₂ H ₂	N ₂	720	10	MWCNTs	0.3	[17]
Fe:Co	MgO	CH ₄	H ₂	1000	10	SWCNT/	0.076	[18]
Fe	Al ₂ O ₃	C ₂ H ₂	H ₂ , N ₂	650	60	MWCNTs	0.132	[19]
Fe						MWCNTs	0.06	[18]
Co							0.065	[18]
Ni	MgO	CH ₄	N ₂ /Ar	600	120	MWCNTs	14.46	This paper

The catalyst used in this research was found to be of higher carbon deposition ability compared to the ones that used Al₂O₃ and CeO₂ as substrate on both reaction temperatures of 550 and 700 °C, which was lower than 2000%. Comparing it with SiO₂ and HZSM-5 substrate in Table 3.2, it exceeded both the 700°C results. However, at 550°C, these two catalysts are of quite higher of values, but used a higher reaction duration of 3 hours. The current study was based on the optimum time productivity of 2 hours and was competent enough with both SiO₂ and HZSM-5 substrate catalysts at 2833.11%.

TABLE 2 CARBON DEPOSITION COMPARISON USING DIFFERENT SUBSTRATE FOR NiO CATALYST

Catalyst	Carbon Deposition (%)	Reaction Temperature (°C)	Reaction Time (h)	Reference
NiO/SiO ₂	3451	550	3	[11]
	1032	700	1	
NiO/HZSM-5	3130	550	3	[11]
	981	770	1	
NiO/Al ₂ O ₃	599	550	3	[11]
	69	770	1	
NiO/CeO ₂	1824	550	3	[11]
	649	550	1	
NiO/MgO	2833.11	600	2	This paper

IV. CONCLUSIONS

In aiming towards the development of a large-scale fluidized bed reactor for a high production of multi-walled carbon nanotubes, three main factors can be concluded in relevance to its objectives:

That a minimum catalyst reduction time of 30 seconds is sufficient enough to maintain a stable productivity range of 13 to 15 g CNT/ g-catalyst using pure or non- pure Hydrogen as a reducing agent; where either Nitrogen or Argon can be used as a carrier gas and as a reducing agent as well. This important parameter can be used in giving provision of the reduction process inside the reactor.

Based on a Fluidized Bed modeling of a Laminar-Eulerian- Granular multiphase system ran in a 3- Dimensional Fluent, Inc. software, a 15mm inlet diameter reactor would best fit in maintaining the fluidization velocity of up to 9.42m/s of methane gas inlet, which corresponds to 100L/min of gas velocity, using a 20° Angular opening of the inlet conical volume. From this reactor and simulation, it showed the best uniform velocity distribution of the catalyst; and the carbon nanotubes produced specifically the maximized use of the conical volume on the bottom part of the reactor. Lesser voids and thus lesser sticking of the catalyst and products were also observed in the simulated profile having a good convergence characteristic. Also, this reactor is believed to be cost effective compared to other reactors produced. Thus CFD simulation in this study revealed how it can affect the future design of the fluidized bed reactor.

The product characteristics based on Raman Spectra, TEM and TGA revealed that multibranch, herringbone multi-walled carbon nanotubes were produced in this Chemical Vapor Deposition process using methane as the carbon source and in a Ni based catalyst system. The as-grown nanotubes have a purity of almost 85% at a high production rate of 14.46g/g catalyst based on its optimum reaction time. Carbon deposition was quite competitive compared to the other Ni

based catalyst and non- Ni based CVD process, with 2833.11% deposition rate at a relatively low reaction temperature of 600°C.

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