Industrial Scale Synthesis of Carbon Nanotubes via Fluidized Bed Chemical Vapor Deposition: A SENIOR DESIGN PROJECT

York R. Smith,[1] Alan Fuchs,[1] and M. Meyyappan[2]
1 University of Nevada • Reno, NV 89557
2 Center for Nanotechnology, NASA Ames Research Center • Moffett Field, CA 94035

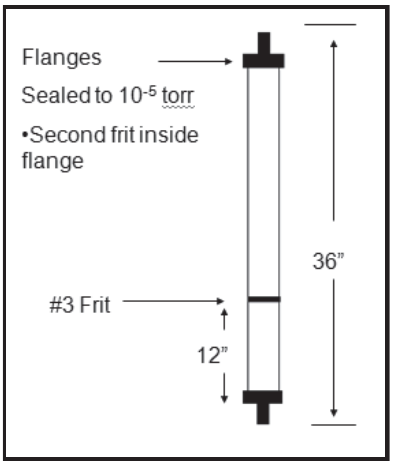
The University of Nevada, Reno, Chemical Engineering, Capstone Senior Design class is a yearlong design experience. The first semester uses a traditional format incorporating the following concepts: process flow diagrams, piping and instrumentation diagrams, process simulation, engineering economics, heuristics, and systems engineering—multiple unit operations, environmental health and safety, engineering ethics, and teaming. During the second half of the first semester the students select design projects that continue for the following one-and-a-half semesters. One of these projects is a collaborative effort with the Center for Nanotechnology at the NASA Ames Research Center in Moffett Field, CA. The objectives for this design project were prepared in close collaboration with Dr. M. Meyyappan at NASA Ames. This particular project and the project approach have been used for two consecutive years with two different senior design teams. During the first attempt, the design effort was primarily aimed at the detailed design and economics of a 10,000 tonne per year single-wall carbon nanotube (SWNT) plant. In the second year this project was offered, the design class, besides the students' own design effort, included building a pilot-scale reactor that was used to synthesize carbon nanotubes as well as to measure selected design parameters.

The group sizes for this particular Senior Design Project ranged from three to four students. The students worked collectively to manage their own groups to meet weekly projected goals with each student acting as the group leader on a rotating basis. The weekly assignments consisted of either a brief written report or a presentation to the class. Weekly reports included updates in the following areas: literature review, experimental instrumentation, experimental results, and full-scale design calculations. At the end of the semester,

Alan Fuchs *is an associate professor of chemical engineering at the University of Nevada, Reno. He teaches the Capstone Senior Design Class, Separations Processes, and Polymer Science and Engineering. His research is in new polymer materials.*

M. Meyyappan *is chief scientist for exploration technology at NASA Ames Research Center. His research interests include carbon nanotubes and inorganic nanowires and their applications. He has published more than 170 articles in peer-reviewed journals. He is a Fellow of MRS, ECS, AVS, and IEEE and a member of AIChE. For his contributions to nanotechnology he has received numerous awards and for his contributions to education he has received awards from IEEE and NASA.*

York R. Smith *recently graduated from the undergraduate chemical engineering program at the University of Nevada, Reno. He is currently a research assistant within the department where his research interests are synthesis of nano-structured metal and mixed metal oxides for photocatalytic and photovoltaic applications along with designing and engineering alternative energy systems.*



Scheme 1. *Dimensions of quartz tube used as a fluidized bed reactor for CNT synthesis.*

the students submitted a final report, PowerPoint presentation, and poster. Students presented their results at a preliminary and final design review at NASA Ames. Success of the overall project was evaluated by the students' ability to stay on task and accomplish their overall objectives of the project.

CENTER FOR NANOTECHNOLOGY AT NASA AMES RESEARCH CENTER

Started in 1996, the Center for Nanotechnology has several scientists and engineers working on various aspects of nanotechnology. The early focus was on carbon nanotubes (CNTs) because of their potential in a broad array of applications. Right from the beginning the Center has had a strong educational component through an active undergraduate student research program (USRP) and a high school student research program (HSRP) both of which are paid internship programs during the summer. Each program has had more than a hundred students in the last 10 years and a high percentage of the students have been coauthors in publications. Several of them have returned for more than one summer. NASA tracking indicates nearly 100% of the undergraduates going on to graduate school and the high school students moving on to elite universities across the United States for science and engineering. During the semester, the students are typically from the local universities. In addition, the NASA team created an "Introduction to Nanotechnology" course for engineering majors at the senior undergraduate and first-year graduate level, first taught at Santa Clara University.[1] This senior ChE design course participation is an extension of this long-standing education focus at NASA Ames.

DESIGN PROJECT

Carbon nanotubes have attracted much attention due to their extraordinary mechanical properties and unique electronic properties, and been considered for applications in electronics, sensors, instrumentation, field emission devices, flat panel displays, nanoelectromechanical systems, composites, and several others.[2] Major challenges to commercialization currently include control of diameter and hence the properties

Scheme 2. *Depiction of experimental setup. Quartz tube reactor within vertically mounted tube furnace.*

and the cost. The latter is an issue because production of even 1 kg/day of SWNTs is not common. At present SWNTs cost $500/g. Unless the production volume goes up, thus bringing the price down to a few hundred dollars per kg, their great potential will not be realized. Production of SWNTs by chemical vapor deposition covers all the "bread and butter" subjects taught in chemical engineering education: catalysis, reaction kinetics, heat transfer, fluid flow, adsorption, diffusion, and others. Future commercial production plants will be designed, built, and operated by chemical engineers.

The objective of the senior design project in collaboration with NASA was to design a process that would have the capability to synthesize 10,000 tonnes of SWNTs per year. Further, the students were also asked to design and conduct experiments to verify predictions made in their proposed design. For this design, the students chose to synthesize SWNTs using a fluidized bed chemical vapor deposition technique (FBCVD). This technique was chosen due to its ease of scalability[3] along with its practicality and costs for their experiments as opposed to other CNT synthesis techniques such as arc discharge[4-6] and laser ablation.[7] In the case of arc discharge, the scale up procedure is not evident because of the elaborate design of the system and also because the SWNT product purity is not attractive. Laser ablation is simply not scalable and practical.

EXPERIMENTAL WORK

The work of Mauron, et al.[3] along with See and Harris[8] served as an excellent review of the literature. A fluidized bed was designed and constructed consisting of a vertically mounted quartz tube (OD 40mm, ID 36mm) within a tube furnace (Thermo Scientific 21100). The tube was 36" in length and contained a porosity #3 quartz frit (14-40μm) welded 12" from one side, and a second frit of the same porosity located underneath the top sealed flange (Swagelok). A depiction of the reactor can be seen in Schemes 1 and 2.

All chemicals, magnesium oxide (MgO, Fischer Chemical, powder), ferric nitrate ($Fe(NO_3)_3.9H_2O$, Acros Organics, 99+%), ethyl alcohol (C_2H_5OH, Acros Organics, 95%), and hydrochloric acid (HCl, Fischer Chemical, technical grade) were received and used without any further treatment.

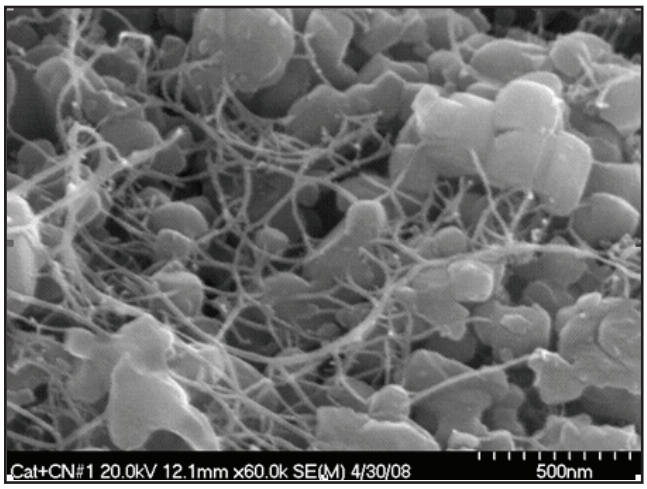


Figure 1. *SEM images of bundles of web-like CNT structures formed on iron particles through fluidized bed chemical vapor deposition at 900 ˚C for 30 minutes.*

CNT Synthesis

An iron catalyst (5 wt%) supported by magnesium oxide was homogenized in ethanol through ultrasonication. The solution was dried overnight in an air oven and ground into a fine power. A 0.5-1.0 g sample of the prepared catalyst-precursor was used to promote SWNT growth and the required gas velocity for fluidization was determined. The system was then allowed to reach the synthesis temperature of 900 ˚C - 950 ˚C while being purged with nitrogen. Once the reactor reached a temperature of 850 ˚C, methane was introduced as the carbon source and mixed with the nitrogen stream at a rate well under the explosive limit of the exit gas stream.[9, 10] The reactor was operated at 900 ˚C for one hour unless otherwise specified.

Separation of the nanotubes from the catalyst-precursor was performed in 0.1M HCl bath while stirred for 15 hours at 75 ˚C.[11] The cleaved nanotubes were decanted from solution and allowed to dry in air. The products were then analyzed through energy dispersion spectroscopy (EDS) and scanning electron microscopy (SEM) techniques.

Health and Safety

A major pedagogical issue for the students to understand was that health and safety issues are paramount. Because it

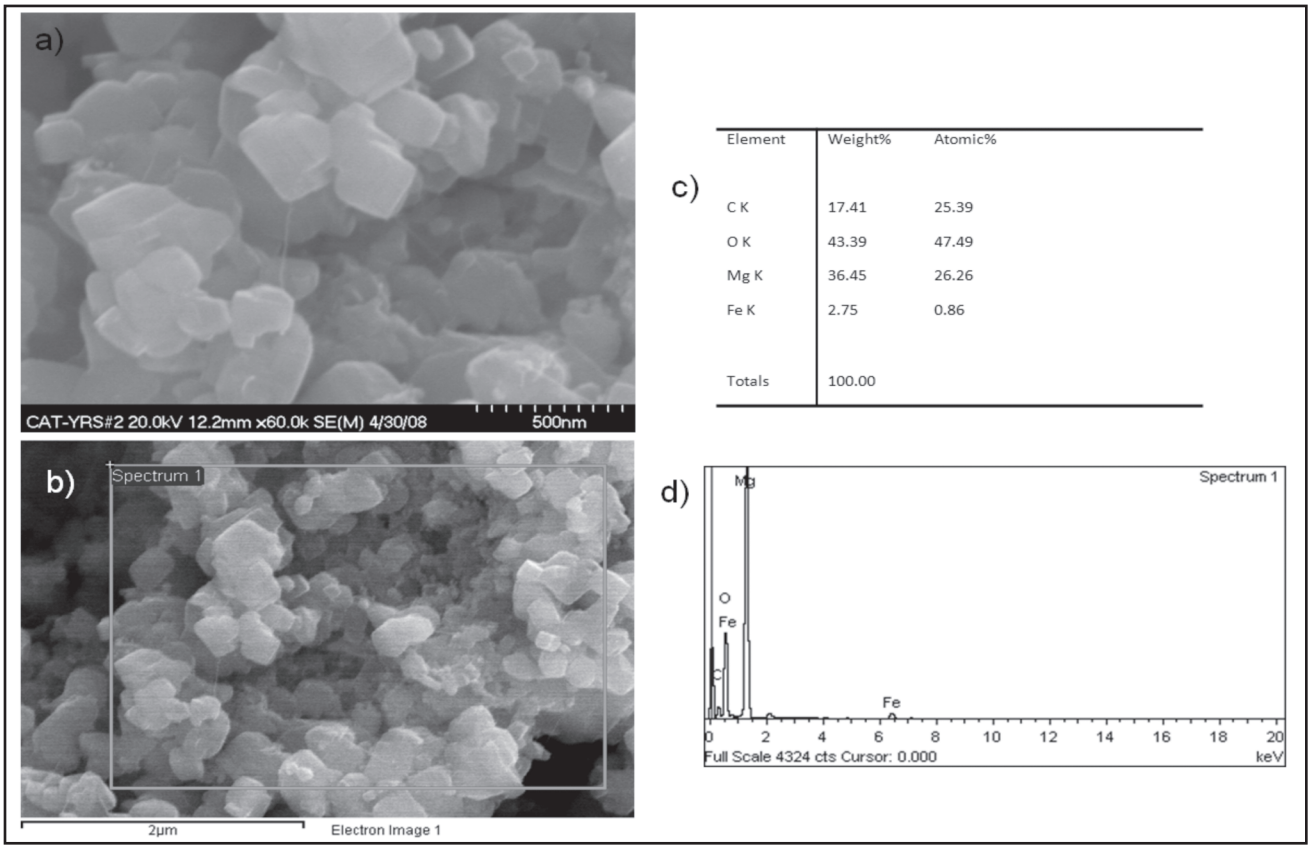


Figure 2. *SEM and EDS of CNT formed on iron particles through fluidized bed chemical vapor deposition at 900 ˚C. (a) SEM image of CNT bundle ~10 nm in diameter, (b) EDS spectrum zone, (c) and (d) EDS results.*

was necessary to deal with explosive gases at high temperatures, many safety precautions were taken. The students were required to have their experimental design approved by the Environmental Health & Safety Department (EH&S). In addition, a hazard and operability (HAZOP) analysis was done by the students and approved by EH&S before any experiments were conducted. These operating conditions and procedures were also incorporated into their full-scale design.

EXPERIMENTAL RESULTS

Fluidized Bed Reactor Experiments

Figures 1 and 2 show from SEM images that carbon nanotubes formed web-like structures across the surface of the iron catalyst. The diameters of these nanotubes have a large variation, which indicates that MWNTs along with bundles of SWNTs could have been formed. Energy dispersion spectroscopy (EDS) indicates that the web-like formations are indeed carbon deposits. SWNTs have diameters within the range of a few nanometers, which is beyond the resolution of the SEM. Further characterization techniques such as Raman spectroscopy and/or high-resolution tunneling electron microscopy (HRTEM) would confirm the nanotube morphology.

DESIGN METHODOLOGY

The sizing and fluidized bed characteristics for the industrial scale reactor were determined following the texts of Kunii and Levenspiel and Geldart.[12, 13]

Reaction Kinetics and Bed Sizing

Methane (CH_4) as carbon source and an iron catalyst supported by magnesium oxide (MgO) were chosen in this project. For a low carbon-to-hydrogen ratio, methane is ideal for SWNT production. A kinetic model was adapted from the work of Pinilla, et al.,[14] which provided a reaction rate as a function of partial pressure of methane for carbon formation of different carbonaceous catalysts at 800-900 °C. This study also provided a pseudo steady-state activation energy of 230 kJ/mol.

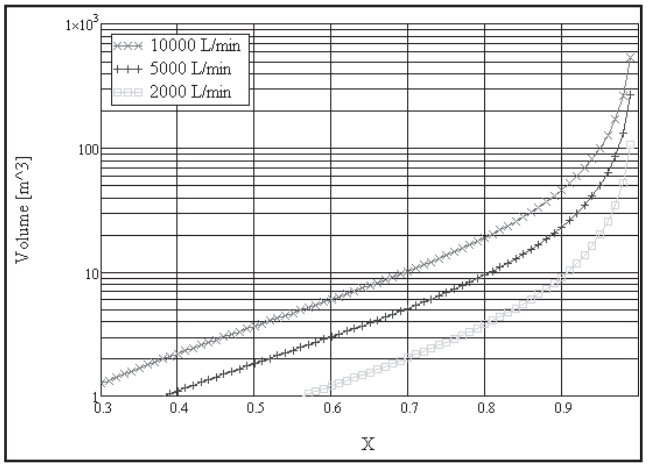


Figure 3. *Volume of fluidized bed reactor (m^3) as a function of reaction conversion (X) for various volumetric flow rates of gas.*

When sizing a fluidized bed reactor, application of a CSTR design equation can be implied. This type of model is a good estimate since it can account for distribution of particles as well as the residence time. The design equation for a CSTR is given by:[15]

$$V\frac{dC_{CH_4}}{dt} = F\left(C_{A0} - C_A\right) + r_A V \tag{1}$$

where V is the reactor volume, F is the volumetric flow rate, r_A is the reaction rate and C_{A0} and C_A are the initial and exit concentrations of the methane, respectively. To solve for the reactor volume, Eq. (1) was solved for steady-state operation and the reaction rate was solved by Eq. (3),

$$V = \frac{FC_{A0}X}{-r_A} \tag{2}$$

$$r_A = -k_0 e^{\left(\frac{-E}{RT}\right)} p_A \tag{3}$$

where X is the conversion factor, E is the activation energy, R is the gas constant, p_A is the partial pressure of methane, T is temperature, and k_0 is the reaction rate constant that was back-calculated by linearization of the Arrhenius equation[15] and use of the pseudo steady-state Arrhenius plot for carbon formation over carbonaceous catalyst with methane gas[14] on the basis of 1.5 g of catalyst/0.5 g of CNT.[3]

As prescribed by Fogler,[15] the design equation for the volume of a CSTR is determined from the following parameters: reaction rate equation, stoichiometric constants, gas concentration, and pressure. Eq. (2) was used to solve for the reactor volume as a function of conversion for various volumetric flowrates since the reaction is also a function of partial pressure, which is given in Figure 3. The minimum fluidization volumetric flowrate of gas was found to be 7,000 L/min. With a conversion of 90% this correlates to a ~50 m^3 reactor volume. These values were determined through iterating a system of nonlinear equations derived from the Ergun equation to determine the bed characteristics (discussed later). Convergence of the system of equations was achieved via a Levenberg-Marquardt algorithm implemented in a program written in Mathcad 13.

Although a CSTR model is a fair approximation, this model is normally used for a homogeneous system. This is not the case for a fluidized bed reactor that is a heterogeneous system consisting of solid and gas phases. For a first-order, solid-catalyzed, gas-phase reaction, a model presented by Kunii and Levenspiel[12] expresses the rate per unit volume of catalyst,

$$\frac{-1}{V_s}\frac{dN_A}{dt} = K_r C_A \tag{4}$$

$$K_r \left[=\right] \frac{m^3 gas}{m^3 solid \cdot s}$$

where K_r is the reaction rate constant and V_s considers the solid as nonporous. Given a feed rate v of reactant gas C_{A0} to a catalyst bed containing solids of volume V_s, integration gives Eq. (5) in terms of the outlet concentration C_{Ai} or the outlet fractional conversion X, and the reactor ability is given in Eq. (6).

$$1 - X = \frac{C_{A0}}{C_{Ai}} = \frac{1}{1 + K_r \tau} \tag{5}$$

$$\tau = \left(\frac{volume\_of\_catalyst}{volumetric\_flow\_of\_gas} \right) = \frac{V_s}{v} \tag{6}$$

This leads to the dimensionless reaction rate group of,

$$K_r \tau = K_r \frac{L_i \left(1 - \varepsilon_i\right)}{u_o} \tag{7}$$

where L is height of bed, ε is void fraction of the bed, u_o is the superficial gas velocity (actual operation) and the subscript i can be the values of fluidization or minimum fluidization. From the dimensionless rate group of Eq. (7), the height of the bed can be determined and from choosing a cross-sectional area, the volume can be approximated.

TABLE 1
Summary of Results for Minimum Fluidization Properties of Industrial-Size Fluidized Bed Reactor

A_r	Archenemies number [dimensionless]	295
Re_{mf}	Reynolds Number of minimum fluidization [dimensionless]	0.331
u_{mf}	Gas velocity of minimum fluidization [m/s]	0.025
u_o	Superficial gas velocity [m/s]	0.125
BE	Bed expansion [m]	1.06
L_{mf}	Bed height of minimum fluidization [m]	10.5
ε_{mf}	Void fraction of minimum fluidization [dimensionless]	0.45
Δp	Pressure drop [psi]	30

TABLE 2
Summary of Single Particle Calculations for Our Catalyst and Feed Gas

u_t	Terminal particle velocity [m/s]	0.62
C_D	Coefficient of drag [dimensionless]	5.82
Re_p	Particle Reynolds Number [dimensionless]	8.22

This method has been shown to correlate very well with experiment.[12] Furthermore, this correlation can be adjusted to incorporate deactivation of the catalyst. Through both these models an appropriate volume can be determined for optimal operation and cost.

Bed Characteristics

In fluidized bed calculations, different classifications of fluidized powders have different correlations. These powders are classified in terms of their particle size and the density difference of the fluidizing media. Given the density difference of the fluidized catalyst precursor and the fluidizing gas that is a mixture of methane and nitrogen, and estimating the mean particle size to be 120μm, it was found from the Geldart chart to fall within the regime of a Geldart Group B powder.[13] Sand typifies this type of powder classification that contains most solids in the mean size and density range of 60 μm < d_p < 500 μm when ρ_p = 4 g/cm^3 which has been widely investigated. An advantage to this classification of powders is that in contrast to Group A (smaller and finer particles), interparticle forces are negligible and bubbles begin to form at or near the minimum fluidization velocity.[13] It is also assumed that this material has a sphericity of ~0.8. From this calculation a sphere of equivalent volume is calculated and a new particle diameter of 108 μm is used in calculations.

To determine the fluidization characteristics, a series of nonlinear equations derived from the Ergun equation must be solved simultaneously. A summary of the minimum fluidization constants is given in Table 1 for a reactor of diameter of 2.5m, height of 10m which yields a volume of ~50m^3.

Since the desired reactor temperature is 800 – 900 °C, the density of the methane-nitrogen mixture was calculated using the Peng-Robinson equation of state for a binary system, along with other thermodynamic values such as enthalpy, entropy, compressibility, and fugacity.

An important calculation in designing fluidized bed reactors is to ensure that particle entrainment occurs. This determination is used to design the freeboard space required along with the gas distributor. These calculations are first determined by examining single-particle calculations. A summary of these is given in Table 2. Once the gas velocity exceeds the terminal velocity of a single particle, entrainment is likely to occur. Since one cannot physically account for every particle, determination of the suspension bed expansion

TABLE 3
Summary of Results for Determining Bed Suspension

ε_{max}	Maximum void fraction [dimensionless]	0.785
u_f	Actual superficial velocity of gas [m/s]	0.07
u_{ps}	Actual superficial velocity of particles [m/s]	0.055
Q_f	Superficial gas volumetric flowrate [m^3/min]	16.23

is required. The single particle calculations can be used to determine the relationship between settling flux and suspension concentration. If $u_f > u_{ps}$ entrainment is likely to occur and the bed will operate in a stable condition. This relation is shown in Table 3.

When designing the gas distributor, minimal pressure drop across the distributor is required while still maintaining fluidization. Through design criteria based on reactor dimensions, the data obtained indicate that the process would require very high natural gas demand.

Further characterization and design would include more detailed mass and energy balances on the reactor and eventually computational fluid dynamic (CFD) calculations should be used to determine the overall feasibility of this process. An economic analysis was conducted using the aid of the program CAPCOST®[16] for equipment and operating costs. By implementing a rudimentary balance sheet of income vs. expenses it is estimated that the break-even cost for SWNT by implementing this design is ~$300/kg for a production of 10,000 tonne per annum. To account for annual inflation and to achieve a profit margin of 15-20% before tax, a market selling price was estimated around $350-$400/kg. Further economic and market analysis is required, however, to determine how readily the current market would be captured, thus diluting the current market price. This analysis would yield whether or not the process would be profitable. In addition to the results presented, the designs of the catalyst synthesis and separation processes were included, but are not presented in this paper.

CONCLUSIONS

Senior-year chemical engineering students designed a process that would produce 10,000 tonnes of SWNTs per year and also conducted bench-top experiments to synthesize SWNTs. This was an excellent pedagogical experience for the students because it related to real-world design issues. The success of the students' project was evaluated on the basis of completion of weekly assignments and project milestones. The experiments resulted in carbon nanotubes, which were characterized using SEM. Detailed design of the reactor was presented, and the break-even cost of the nanotubes is estimated to be approximately $400/kg.

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