The Production of Single-Walled Carbon Nanotubes by Chemical Vapor Deposition: Design and Scale Up

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Abstract

Carbon nanotubes are a new form of carbon-based materials that are fabricated using several distinct techniques. Carbon nanotubes exhibit exceptional mechanical properties that are ideal for reinforced composites, nanoelectronic structures, and sensor devices. In the present research, single-walled carbon nanotubes are formed by chemical vapor deposition in a fluidized bed at various temperatures and gas flow rates with transition metal catalysts. Two processes to produce 10,000 tons per year of single-walled carbon nanotubes are proposed. Process simulations and cost analyses are included in the evaluation of each process design.

Acknowledgements

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Background and Research

Carbon nanotubes were first brought to the attention of the scientific community around 20 years ago. Two types of carbon nanotubes exist, single walled tubes which are just a simple rolled sheet of graphite and multi walled which are sheets of graphite wrapped around each other like rings in a tree trunk [1]. The single walled variety will be the focus of this report. Figure 1 shows an example of both.

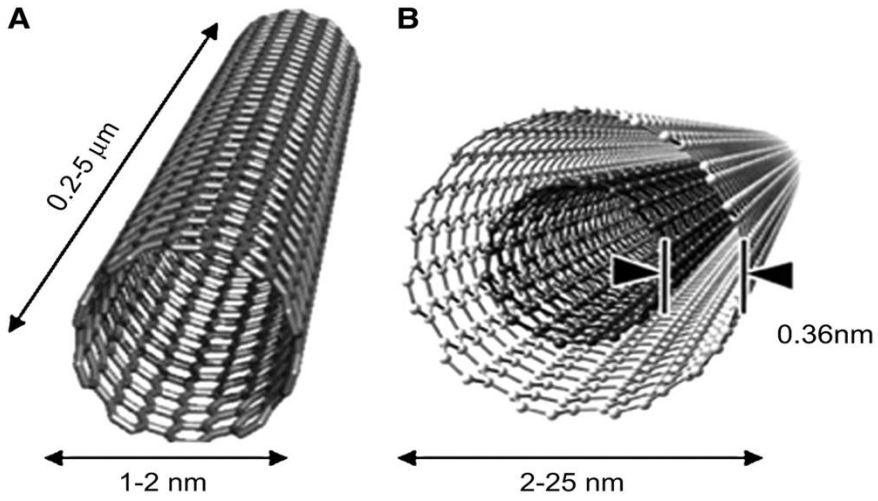

Figure 1: Single and Multi Walled Carbon Nanotube.

Single walled carbon nanotubes (SWNTs) are unique nanostructures that can have either metallic or semi-conductive electronic properties. As well as having very high tensile strength, high current carrying capacity, and high thermal conductivity [2]. These unique properties allow for many uses including: hydrogen storage, electrochemical devices, composites, sensors and probes, nanometer sized electronic devices, field emission devices etc [1].

There are three main ways of creating nanotubes used in the field: Arc Discharge, Laser Ablation and Chemical Vapor Deposition (CVD). Arc Discharge uses a high voltage between two graphite rods form a high energy arc. The anode gets consumed in the process and nanotubes then start to form on the cathode. Laser Ablation uses a laser fired at a graphite target in an inert atmosphere to created nanotubes [3]. Finally chemical

vapor deposition uses gaseous carbon sources to grow nanotubes on metal catalyst at temperatures of around 500-1000°C.

Chemical Vapor Deposition is the most interesting method because of its potential for scale up. It also has the most challenges because of all the variables that go into running the reactor. Researchers in Australia ran experiments using a fluidized bed and used statistical analysis to determine which variables were most important in producing tubes. Their findings were that time, temperature and catalyst were three most important factors in final SWNT yield [4]. Common catalysts that are used are Iron, Cobalt and Nickel. Although some research suggests that Fe/Mo or Fe/Ru mixtures could be better than just using any plain single metal [5]. Early research for the effects of temperature on the process suggested that with increasing temperatures you would increase the SWNT yield as well as increase the diameter of the nanotubes [6]. Further testing will need to be done on both temperature and catalyst in the future.

Base Case Design

Overview and Process Description:

The base case model is centered on a chemical vapor deposition production of carbon nanotubes. The process begins with catalyst preparation of an iron catalyst on a magnesium oxide support, where it is then transferred to a fluidized bed reactor. The reactor is then purged of air using argon, and then methane is added to fluidize the bed and provide a carbon source for reaction. After the reaction has taken place, all the solid particles are then transferred to a froth flotation system, where it is acidified and separated. The outlet slurry of concentrated nanotubes and acidic solution are then sent to an evaporator where the nanotubes are dried and ready for use. A schematic of the process can be seen below in Figure 2.

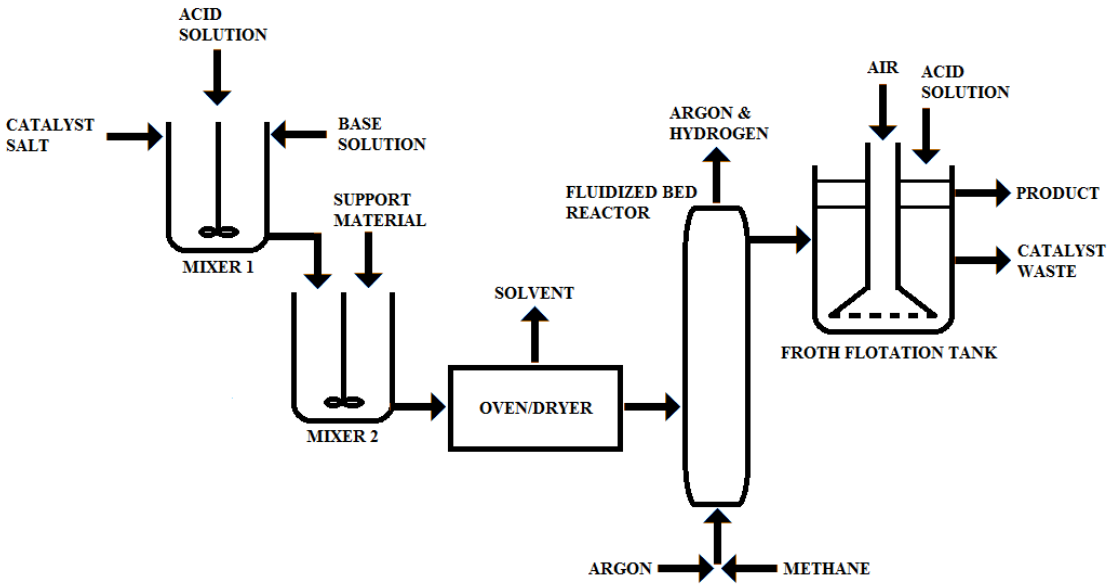

Figure 2: Base Case Block Flow Diagram

Calculations and Scale Up:

CAPCOST was used to calculate the bare module cost of each of the components of the process. CAPCOST uses nonlinear scaling of reactor components to estimate the cost by Equation 1. The constants K_1, K_2, and K_3 can be found on tables for different unit operations of different configurations. These costs are scaled linearly for current cost of materials and demand with the chemical engineering plant cost index (CEPCI).

$$\log_{10}(Cp^{o}) = K_1 + K_2 \log_{10}(A) + K_3[\log_{10}(A)^2] \quad (1)$$

Catalyst Preparation

This scale-up uses the following assumptions and the tested catalyst-support combination of Fe/MgO.

1. 500:1 SWCNT to catalyst weight ratio [7].
2. 5% wt loading of iron on MgO
3. 10,000 metric tons per year of SWCNT produced
4. 90% recycle of catalyst
5. Density of MgO is about 3580 kg/m^3 [8].

Table 1 shows the CAPCOST table for the process. The assumptions are listed below.

- *Mixer*
  - Impregnation will require about 10 times the volume of the catalyst/support to be prepared.
  - The vessel will be made of stainless steel to with a 10 hp mixer.
- *Acid Wash Vessel*
  - Will assume a volume of 30 L/min to be fed continuously with catalyst and acid.
  - Special materials will be used to resist acid corrosion.
  - The smallest possible vessel in CAPCOST will be used.
- *Oven/Dryer*
  - Assume rotary dryer that is gas fired.
  - The area will be 10 m^2 so that for the 130 L produced per day will be at an average thickness of about 1.3 cm
- *Ball Grinder*
  - Will be sized to about 1000 L with much of the volume fill by steel balls.
  - Will be approximated in cost by a blender.
- *Sieve*
  - Will have an area of 1 m^2
  - Vibrating to help mass transfer.
- *Catalyst Surplus Storage*
  - A 10 m^3 surplus storage tank will be incorporated so that the plant can function in case of an interruption of supply.

Table 1: Bare module costs for base case catalyst preparation

Blenders	Type	Volume (cubic meters)	# Spares			Purchased Equipment Cost	Bare Module Cost
B-101	Rotary	2	0			$ 29,900	$ 44,900
Dryers	**Type**	**Area (square meters)**				**Purchased Equipment Cost**	**Bare Module Cost**
Dy-101	Rotary	10				$ 60,900	$ 91,300
Mixers	**Type**	**Power (kilowatts)**	**# Spares**			**Purchased Equipment Cost**	**Bare Module Cost**
M-101	Propeller	7.46	0			$ 43,700	$ 65,500
Screens	**Type**	**Area (square meters)**	**# Spares**			**Purchased Equipment Cost**	**Bare Module Cost**
S-101	Vibrating	1	0			$ 17,200	$ 25,700
Vessels	**Orientation**	**Length/Height (meters)**	**Diameter (meters)**	**MOC**	**Demister MOC**	**Pressure (barg)**	**Purchased Equipment Cost**	**Bare Module Cost**
V-101	Vertical	3	0.5	Stainless Clad		1	$ 3,850	$ 20,900
V-102	Vertical	3	1	Carbon Steel		1	$ 7,330	$ 29,800
						Total Bare Module Cost		$ 233,200

Fluidized Bed

In the analysis on the scale-up design of the fluidized bed reactor, the following calculations are based on obtaining vigorous agitation of the Fe catalyst and MgO support in contact with the fluidizing medium of CH_4. Prior to any flow of the carbon source (CH_4) into the reactor, the pressure drop begins at zero and can theoretically be measured with variations in the bed height as well as the particle diameter. When speaking of the bed height, this is the height within the reactor at which the particles rest. It should be noted that all calculations were conducted in SI units. The following correlation is used to find the pressure drop within the bed and is the Carmen-Kozeny given in Equation 2:

$$-\frac{\Delta P}{H} = \frac{180(1-\varepsilon)}{\varepsilon^3}\frac{\mu U}{x_p} \tag{2}$$

The pressure drop is symbolized as ΔP, H is the bed height in meters, ε is the void fraction, μ is the viscosity of the fluidizing medium CH_4, U is the superficial fluid velocity, and x_p is the diameter of the particle. This equation applies to a bed of particles

with a diameter of less than 0.1 mm and the Reynolds number is less than 10. It applies to the viscous flow regime, and reveals the point at which the bed will start to fluidize. The point at which the superficial velocity is equal to the minimum fluidization velocity, which will be expanded upon later, the state of the bed has reached incipient fluidization. The void fraction is assumed to be 0.4, based on the assumption that the particles are nearly spherical.

The superficial velocity is determined using Equation 3.

$$U = \frac{Q}{A} \tag{3}$$

The Q in the above equation is the volumetric flow of the CH_4 and the A is the cross sectional area of the bed. The superficial velocity is significant in the calculations because it is the point at which the upward force exerted by the CH_4 gas on the catalyst and support is sufficient enough to balance out the net weight of the bed. Essentially, the particles start to separate from each other and the bed starts to expand at this point while the pressure drop stays constant. This is when the fluidization occurs, and the solid particulates behave as a "fluid."

In looking at the graph of the pressure drop as a function of the superficial velocity (Figure 3) in correlation with the graph of the bed height as a function of the superficial velocity (Figure 4), it should be noted that the point at which the pressure drop ceases to increase is the point at which the minimum fluidization velocity is reached.

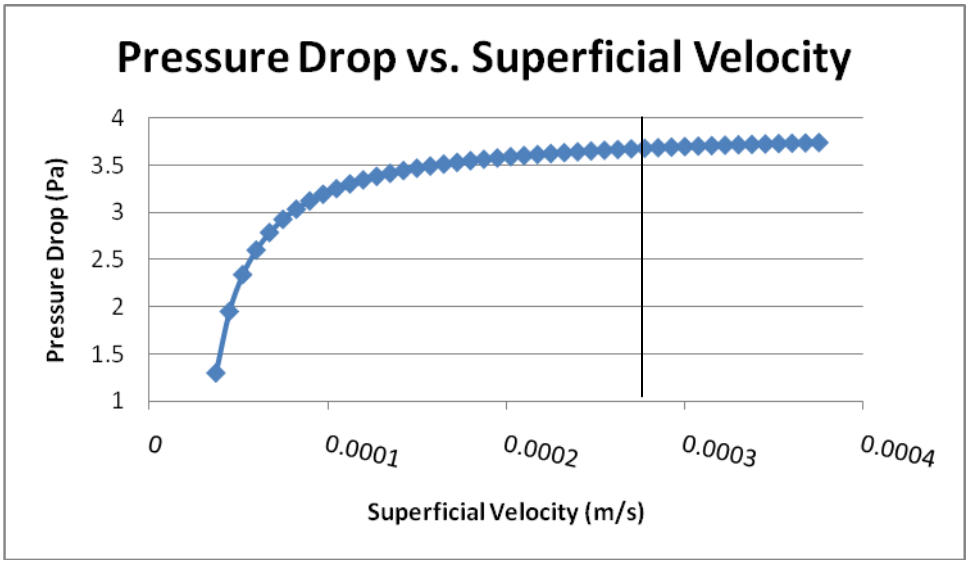

Figure 3: Pressure drop as a function of superficial velocity

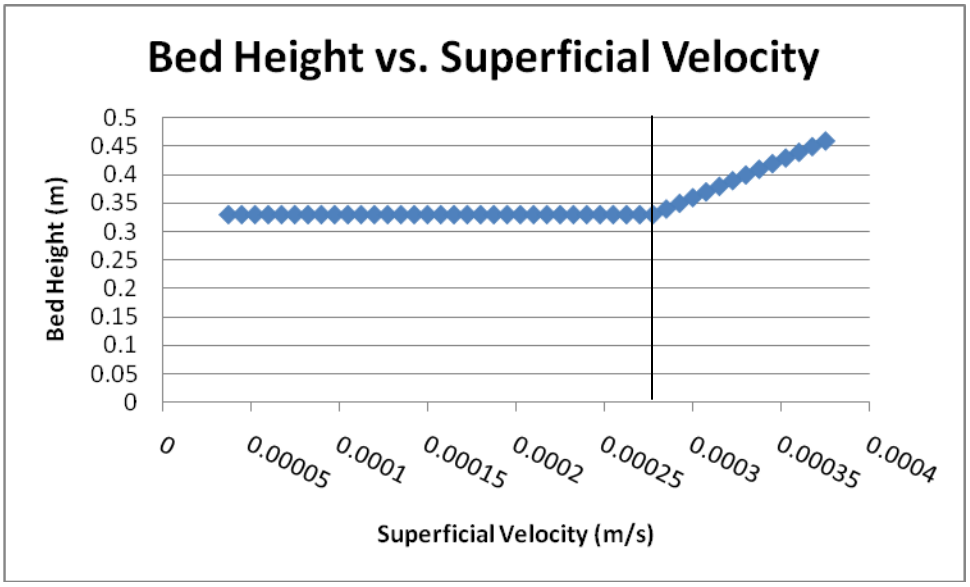

Figure 4: Bed height as a function of superficial velocity

As shown in the previous graphs, this point is at approximately 0.0003 m/s, which is thus the minimum fluidization velocity required to fluidize the bed at the given bed height at

various particle sizes. To know what particle size is appropriate for fluidization, the Geldart Graph was analyzed. The Geldart Graph shows a correlation between the difference in particle density to that of the fluid density (ρ_p - ρ_f) versus the diameter of the particles being fluidized. This is shown in Figure 5.

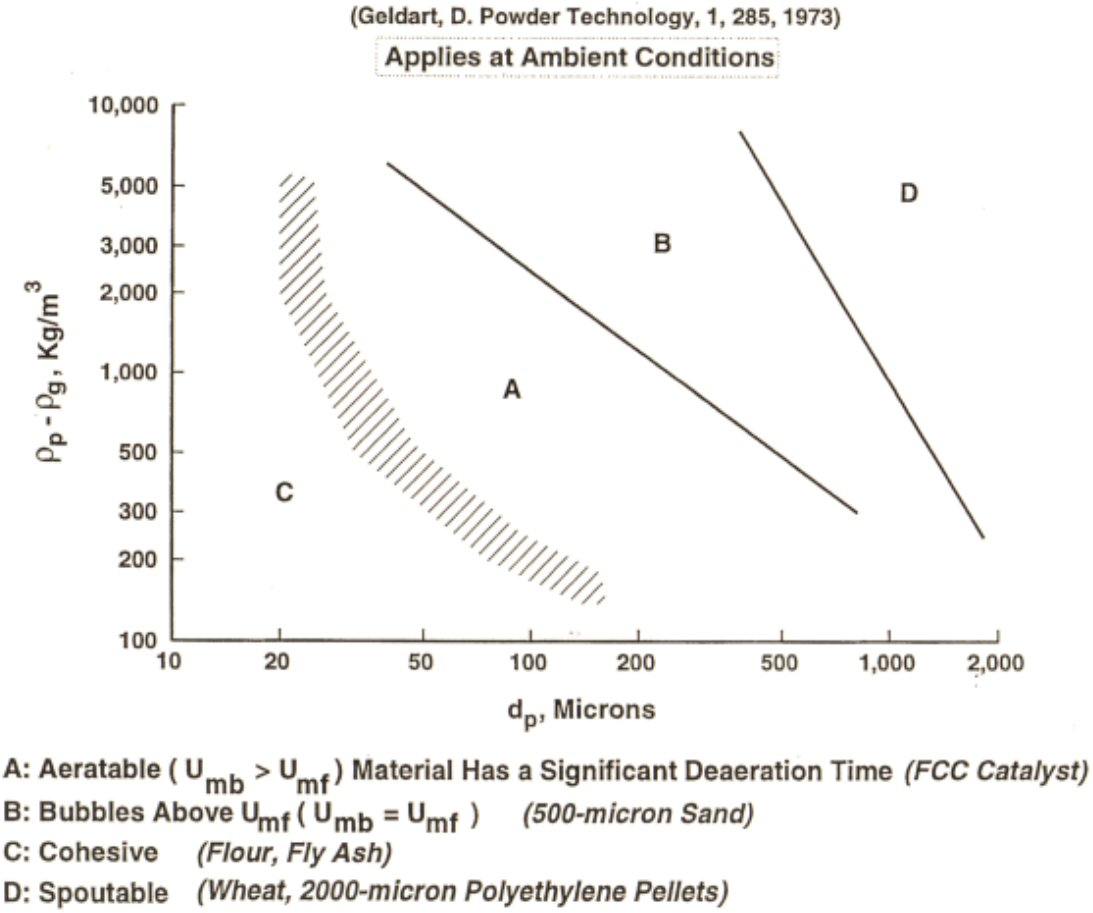

Figure 5: Geldart Graph

As shown in Figure 5, we wish to achieve Geldart A particles. Since the difference in particle density to that of the fluid density for this particular scale-up example is 5726.28 kg/m^3, it can be seen how the particles must be between approximately 30 – 470 microns in diameter to be able to fluidize (this realm is highlighted in the diagram). With this knowledge, all calculations were conducted with this range of particles to deduce ideal parameters for the fluidized bed reactor.

Below the Geldart Graph, there are notes that refer to a "U_{mf}," which is the minimum fluidization velocity. The minimum fluidization velocity is the velocity at which bubbling starts to occur within the fluidized bed and is calculated for Geldart B particles. The minimum fluidization velocity is calculated with the following equation:

$$U_{mf} = \frac{(\rho_p - \rho_f)^{0.934} g^{0.934} x_p^{1.8}}{1110\mu^{0.87}\rho_f^{0.066}} \quad (4)$$

In analyzing the best bed height and cross sectional area for a 100 ton/year production of SWNTs, it was found that an area of 1.3 m^2 is ideal along with a bed height of 0.33 m. The base cost was found to be $67,342 with a bare module cost of $94,601. These results were calculated using CAPCOST.

Separation Process

Froth Flotation System

Froth flotation is a process for selectively separating hydrophobic materials from hydrophilic. This is used in several processing industries, and will be used as our base case separation system. The used catalyst and carbon nanotube powder will be mixed along with 0.1M HCl in the flotation device, where the hydrophobic carbon nanotubes (CNTs) will float to the top and the dissolved hydrophilic catalyst and support will stay in the flotation cell and sent out with the pulp. A schematic of the froth flotation system can be seen below in Figure 6.

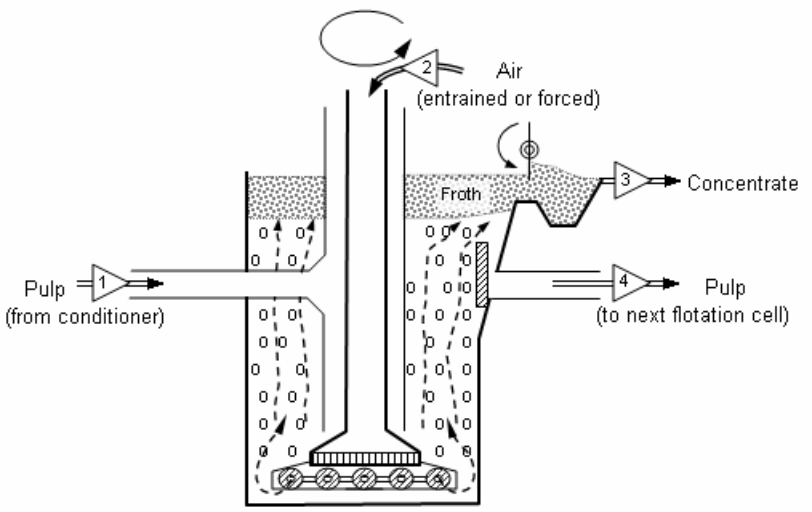

Figure 6: Froth Flotation Schematic

The mean residence time will be given as 1 hour from the inlet at the bottom of the flotation vessel until the enriched stream exits the top of the vessel. As far as pricing goes, it will be assumed to be a "specialized CSTR" with the outlet at the top of the reactor of two streams as given in the figure above [9]. In order to properly price the flotation system, the specialized CSTR will have an additional cost of $200,000 to make the proper additions of the opening at the top, the entrained air system, and the two exit streams.

Using the calculated total flow rate to produce 10,000 tons/year of CNTs, the volume of the reactor can be figured out using Equation 5.

$$\tau = \frac{V}{v} \tag{5}$$

Where τ is the residence time, V is the volume and v is the volumetric flow rate.

It was found that the needed froth flotation volume is 10.18 m^3 in order to complete the residence time needed. From here multiple CSTRs were priced using CAPCOST and can

be seen below in Table 2. It was found that the most economical system is two 5.09 m^3 Froth Flotation systems for total cost of $1,044,444.

Table 2: CAPCOST CSTR Pricing

No. Reactors	size of each(m^3)	Purchase Price (10^3)	BM Cost (10^3)	Total Cost (10^3)
1	10.18	n/a	n/a	n/a
2	5.09	144	261	522
3	3.393	120	180	540
4	2.545	106	158	632
5	2.036	95.6	143	715
6	1.697	88.1	132	792
7	1.454	82.2	123	861
8	1.273	77.4	116	928
9	1.131	73.4	110	990
10	1.018	70.1	105	1050

Evaporator

An evaporator will be put in place to evaporate any excess acidic solution coming out of the froth flotation system. The evaporator area can be calculated using Equation 6 below

$$m = \theta A(x_s - x) \tag{6}$$

where m is the amount of evaporated water (kg/h), θ = (25 + 19 v) and is the evaporation coefficient (kg/m^2h), v is the velocity of air above the water surface (m/s), A is the water surface area (m^2), x_s is thehumidity ratio in saturated air at the same temperature as the water surface (kg/kg), x is the humidity ratio in the air (kg/kg).

It will be assumed that the amount of waste water that exits with the CNTs is 10% of the total wastewater, which is equal to $3.19 \cdot 10^7$ mol/h. This problem yields an evaporator surface area of 3886.78 m^2 with no convective evaporation and a Δx of 0.09.

The heat supply required to maintain the evaporator can be found using Equation 7 below

$$Q = \Delta H * m \tag{7}$$

where Q is the heat supplied (kW) and ΔH is the evaporation heat of water (kJ/kg).

This equation yields a heat requirement of 551.4 KW. The sizing of the evaporators was done for a number of evaporators and it was found that the most efficient evaporator system was one 3887 m^2 evaporator with a total cost of $3,930,00. A comparison of prices can be found below in a CAPCOST comparison below in Table 3.

Table 3: CAPCOST Pricing of Evaporators

CAPCOST, CEPCI=536

Type	Number of reactors	Size (m^2)	Purchase Price (10^3)	BM Cost (10^3)	Total Cost (10^3)
Forced Circulation	4	1000	675	19600	$78400
Forced Circulation	8	485.8	3940	11400	$91200
Falling Film	8	485.8	1980	4450	$35600
Falling Film	16	242.9	1120	2530	$40480
Short-Tube	40	100	284	822	$32880
Long Tube	1	3890	1360	3930	$3930
Long Tube	2	1940	1040	3010	$6020
Long Tube	4	486	608	1760	$7040

A concluding table of the separation size and pricings for the CNT base case model is illustrated below in Table 4.

Table 4: Separation System Overview

	Number of Unit Ops	Area or Volume	Price (10^3)
Froth Flotation	2	$5.09m^3$	$1,044.44
Evaporator	1	3887 m^2	$3,930
Total			$4,974

Alternate Case Design

Overview:

Out of the three common methods for the production of carbon nanotubes, chemical vapor deposition (CVD) is the most promising candidate for scale up. In our base case, we examined a process involving the scale up of a Fluidized Bed Chemical Vapor Deposition (FBCVD) process. In this alternative case, we propose another design based on a simple CVD process and a vastly different separation operation that takes advantage of the growth method. The reactor design is based largely on a paper which determines a method of continuously renewing the catalyst as the reaction is running, causing very rapid growth of single-walled carbon nanotubes dubbed "super-growth".

Process Description:

This growth method uses simple alkanes as a carbon source under an inert argon atmosphere with a small amount of water (200 ppm) acting as the catalyst renewing agent. Natural Gas can be used as the carbon source for this process, making the chemical cost for the process amazingly low. As carbon nanotubes consist entirely of carbon, the byproduct of the reaction is hydrogen gas. This hydrogen gas has a potentially detrimental effect on the reaction, so it has to be separated before any unused carbon source or inert can be recycled back into the process. We propose using proton exchange membranes (PEMs) to separate hydrogen gas from the process stream and generate electricity as a byproduct. The downside to this method is that PEMs are made of polymers that are not very tolerant to high temperatures, so the process stream would require substantial cooling before undergoing this separation and then reheating before being re-introduced to the reactor. While natural gas is not expensive, the savings from not having to continuously purchase argon would make this viable. It is also possible to incorporate a great deal of heat integration by warming the fresh carbon source with the spent product from the reactor.

In addition to the separation of the undesired byproduct of this reaction, this process uses a unique method of separation for the nanotubes as well. The catalyst for this process is iron on a floating quartz support. The iron has a greater affinity for the quartz support

than the nanotubes, making it possible to shear the nanotubes on of the flat catalyst surface with a blade. The nanotubes can then be simply separated via a filter from the gas stream after being sheared off. This process is made continuous by fixing the catalyst to a conveyer in which the conveyer direction runs counter-current to the gas stream and at the end of the conveyer the nanotubes are being sheared off by a fixed blade.

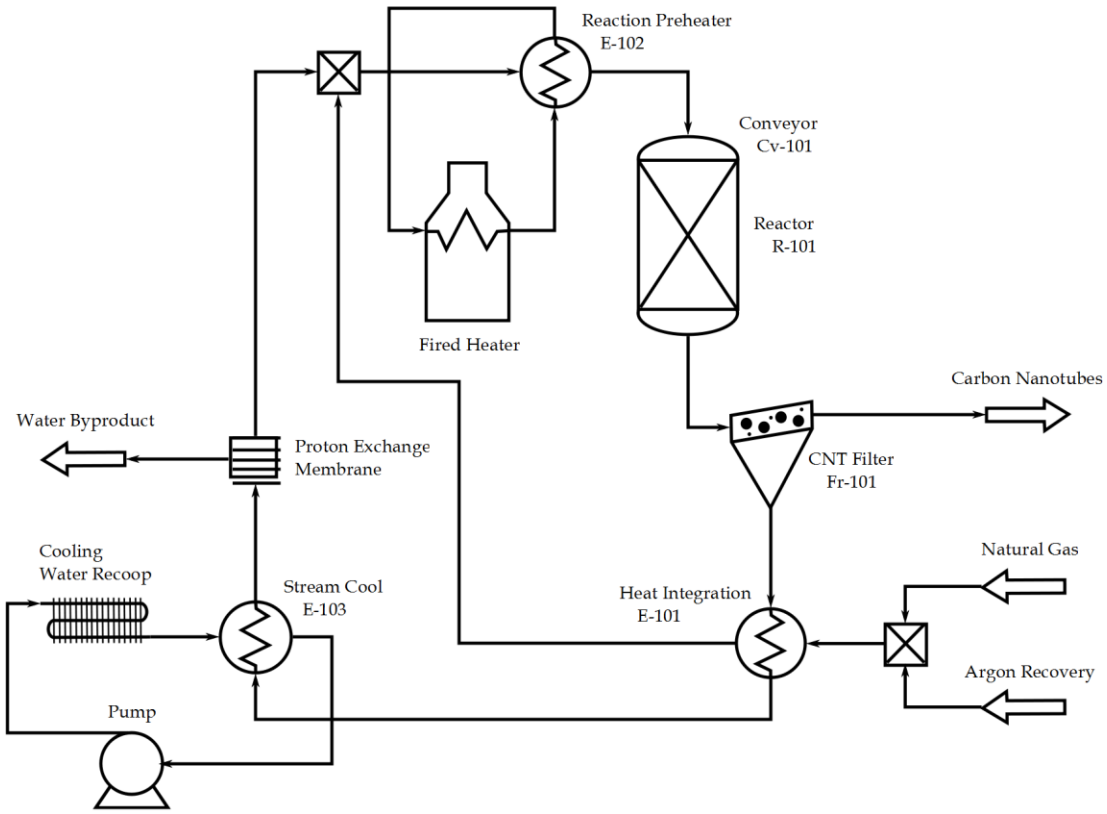

Figure 7: PFD for Alternative Case

Calculations and Scale-Up

Catalyst preparation

The following assumptions will be used for scale-up of the catalyst preparation. Table 5 shows the bare module cost for the alternative case catalyst preparation.

- Two vessels
  - Keep chemicals necessary to sputter on support plates

  - Minimum size available in CAPCOST
- Mixer
  - Mix constituents
- Sputtering
  - Approximate with autoclave reactor
- Conveyor
  - To move plates through sputtering reactor

Table 5: Bare module costs for alternative case catalyst preparation

Conveyors	Type	Area (square meters)	Purchased Equipment Cost	Bare Module Cost
Cv-101	Belt	1	$ 17,800	$ 35,500

Mixers	Type	Power (kilowatts)	# Spares	Purchased Equipment Cost	Bare Module Cost
M-101	Propeller	5.97	0	$ 41,200	$ 61,900

Reactors	Type	Volume (cubic meters)	Purchased Equipment Cost	Bare Module Cost
R-101	Autoclave	1	$ 55,500	$ 83,300

Vessels	Orientation	Length/Height (meters)	Diameter (meters)	MOC	Demister MOC	Pressure (barg)	Purchased Equipment Cost	Bare Module Cost
V-101	Vertical	3	0.5	Carbon Steel		1	$ 3,850	$ 15,700
V-102	Vertical	3	0.5	Carbon Steel		1	$ 3,850	$ 15,700
						Total Bare Module Cost		$ 212,100

Continuous Reactor

- Conveyor
  - Move catalyst plates through reactor
  - Size is dependent on desired residence time of catalyst.
- Heat Exchangers
  - Heat and cool entering and exiting gases
- Plate and Frame filter
  - Used to pull separate nanotubes from effluent gas by filtration
- Jacketed Reactor
  - Approximates the body of the conveyor oven

Table 6: Bare module costs for alternative case continuous reactor

Conveyors	Type	Area (square meters)	Purchased Equipment Cost	Bare Module Cost
Cv-101	Belt	30	$ 107,100	$ 214,000

Exchangers	Exchanger Type	Shell Pressure (barg)	Tube Pressure (barg)	MOC	Area (square meters)	Purchased Equipment Cost	Bare Module Cost
E-101	Floating Head	0	1	Carbon Steel / Carbon Steel	100	$ 44,700	$ 147,000
E-102	Floating Head	0	1	Carbon Steel / Carbon Steel	75	$ 40,000	$ 131,600
E-103	Floating Head	0	1	Carbon Steel / Carbon Steel	50	$ 35,600	$ 117,100

Filters	Type	Area (square meters)	Purchased Equipment Cost	Bare Module Cost
Fr-101	Plate And Frame	5	$ 63,500	$ 95,300

Reactors	Type	Volume (cubic meters)	Purchased Equipment Cost	Bare Module Cost
R-101	Jacketed Non-Agitated	30	$ 46,800	$ 70,200

Total Bare Module Cost		$ 775,200

Operating Costs:

The "super-growth" paper reports that the nanotubes produced using their method had a density of 0.037 g/cm^3 and grew thickly on the surface as to be 5.2×10^{11} tubes/cm^3 and 2.5 mm in height. A simple calculation yields:

$$\frac{cm^2}{5.2 * 10^{11}\ tubes} * 0.037\ \frac{g}{cm^3} * 0.25\ cm = 1.78 * 10^{-14}\ \frac{g}{nanotube} \tag{8}$$

Since a nanotube is a single molecule, multiplying it by Avogadro's number will yield the molecular weight of these carbon nanotubes (an important assumption for later ChemCAD simulations) of 10712,211,538 g/mol. Since the objective of this scale up is to produce 100 tons/yr of nanotubes (or 90718.5 kg/yr) it is possible to calculate the amount of carbon source necessary to run this operation and use a ChemCAD simulation to determine the necessary amount of heating and cooling for this process.

$$90718.5\ \frac{kg\ nanotubes}{year} = 10.336\ \frac{kg\ nanotubes}{hour} \tag{9}$$

$$10.336\frac{kg\ nanotubes}{hour} * \frac{16g\ CH_4}{12g\ C} = 13.8\frac{kg\ methane}{hour} \quad (10)$$

This number turns out to be insignificant next to the amount of natural gas required for the heating costs. The reaction process requires a temperature of 760 ºC and the PEMs cannot get hotter than about 100 ºC. Putting this into a ChemCAD simulation that incorporates heat integration reveals that the process requires 39.5 MJ/hr of heating and 37.8 MJ/hr of cooling. Natural gas has an energy content of approximately 1000 BTUs/cubic foot and is sold in Nevada at about $11/thousand cubic feet. Since these are very high temperature processes, we can assume that the cooling can be done via cooling water and ambient cooling, so that the cooling does not factor in. These costs translate in the end to $517/hr for this process or $0.05/g of nanotubes.

Fixed Costs:

The first step for calculating the fixed costs was to determine the size of the heat exchangers. Emphasis was placed on heat integration, so we sized that to be larger than the other two required heat exchangers. The method used to size this heat exchanger was to take to take a general guess at the size of the exchangers based on the temperature differences of the streams involved and an estimated look at the resistances to heat transfer, then ran a simulation with the heat exchangers running in conjunction and attempted to minimize the amount of surface area required. It was found that the area required for the heat integration heat exchanger was 100 m^2. The cooling water heat exchanger was found to be roughly 75 m^2 and the reaction pre-heater was 50 m^2.

The next step was to size the proton exchange membrane. Taking numbers from M. J. Khan [10]:

$$0.065\frac{mol}{s\ atm} * 3atm * \frac{0.25\eta}{232\ cm^2} = 0.00021\frac{mol}{s * cm^2} \quad (11)$$

$$0.00021\frac{mol}{s * cm^2} * \frac{100^2 cm^2}{m^2} * \frac{3600\ s}{hour} = 7564.7\frac{mol}{hour * m^2} \quad (12)$$

$$7564.7\frac{mol}{hr\cdot m^2}\cdot 2\frac{g}{mol}\cdot\frac{kg}{1000g} = 15\frac{kg}{hr\cdot m^2} \tag{13}$$

The amount of hydrogen gas that needs to be separated by these membranes can be found by the difference between the flow rates of nanotubes and methane gas entering and exiting the process.

$$13.8\frac{kg\cdot methane}{hr} - 10.336\frac{kg\cdot nanotubes}{hr} = 3.5\frac{kg\cdot hydrogen\cdot gas}{hr} \tag{14}$$

This yields a total membrane area of:

$$3.5\frac{kg\cdot hydrogen\cdot gas}{hr}\cdot\frac{hr\cdot m^2}{15\cdot kg} = 0.233 m^2 \tag{15}$$

The final thing to size is the reactor. The reactor is a conveyor encased within what amounts to a PFR, so both the reactor volume and conveyor surface area need to be calculated. From the "super-growth" paper, the surface area of the catalyst to the number of nanotubes is given. The mass of an average nanotube has been previously calculated allowing for the following calculation of the conveyor area.

$$\frac{nanotube}{1.78\,10^{-14} g}\cdot\frac{cm^2}{5.2\,10^{11} tubes}\cdot 10.336\frac{kg\cdot nanotubes}{hr}\cdot\frac{m^2}{100^2 cm^2} = 30 m^2 \tag{16}$$

Taking the conveyor width to be 0.3 m and the length to be 100 m the following calculation for reactor volume can be used.

$$\pi\cdot r^2 L = V = 30 m^3 \tag{17}$$

All of these specifications can be priced in CAPCOST save for the PEM. The cost of Nafion membrane of the area require costs about $1000 [11], but that is just for a membrane. It is difficult to price an installed cost for the PEM but an estimation of $10000 is probably reasonable. So the bare module cost including the proton exchange membrane would be $785,200.

Experimental Design and Results

Using the methods by Kitiyananm et al [12], cobalt-molybdenum catalysts supported by silica gel were prepared by impregnation. Experiments to produce carbon nanotubes were performed using Co-Mo catalyst in a quartz tube reactor in which the catalyst was fluidized with a carrier gas (argon) and the carbon source (methane) while being heated by the tube furnace to temperatures of up to 950 °C. Detailed procedures in preparing the catalyst and performing the experiments are found in Appendix A.

The experiments were designed according to a factorial analysis of control variables. Eight experiments were performed by varying the temperature, methane flow rate, and the ratio between the methane and argon flow rates. The mass of the catalyst and the amount of time the methane flowed into the fluidized bed reactor were kept constant over each experiment. A summary of the varying control variables are tabulated in Table 7 in Appendix A. After each experiment, SEM images of the post-reaction catalyst sample were taken in search for carbon nanotubes.

For all of the designed experiments, no carbon nanotubes were reported in the SEM images of the post-reaction samples. Several factors were considered in evaluating the results. First, the methane flow rate may not have been high enough for the catalyst to form carbon nanotubes, and the carbon source may have been diluted too great for small ratios between methane and argon flow. Second, in conjunction with methane flow rate, the amount of time for the methane to flow may not have been enough for methane molecules to find catalyst reaction sites. Third, the catalyst size may have been too big whereas the metal particles were clumped together on the surface and inside the pores of the support particle instead of being spread out homogeneously, and the large support

size may have not been optimum for maximizing the surface area of reaction sites. Fourth, the carbon nanotubes may not have been able to form at the temperatures investigated for the specific catalyst. Fifth, the argon gas molecules, compared to methane molecules, may have been large enough to block methane molecules from entering the catalyst reaction sites. Further studies would be required to investigate these potential factors.

One experiment was performed under the same conditions with the exception that the methane flow rate was greatly increased. After taking SEM images of the post-reaction catalyst samples, a few multi-walled carbon nanotubes were present in the sample. Two sets of SEM images of the multi-walled carbon nanotubes are displayed in Figure 8. The presence of carbon nanotubes in this sample gives evidence that the methane flow rate may not have been high enough in the previous experiments.

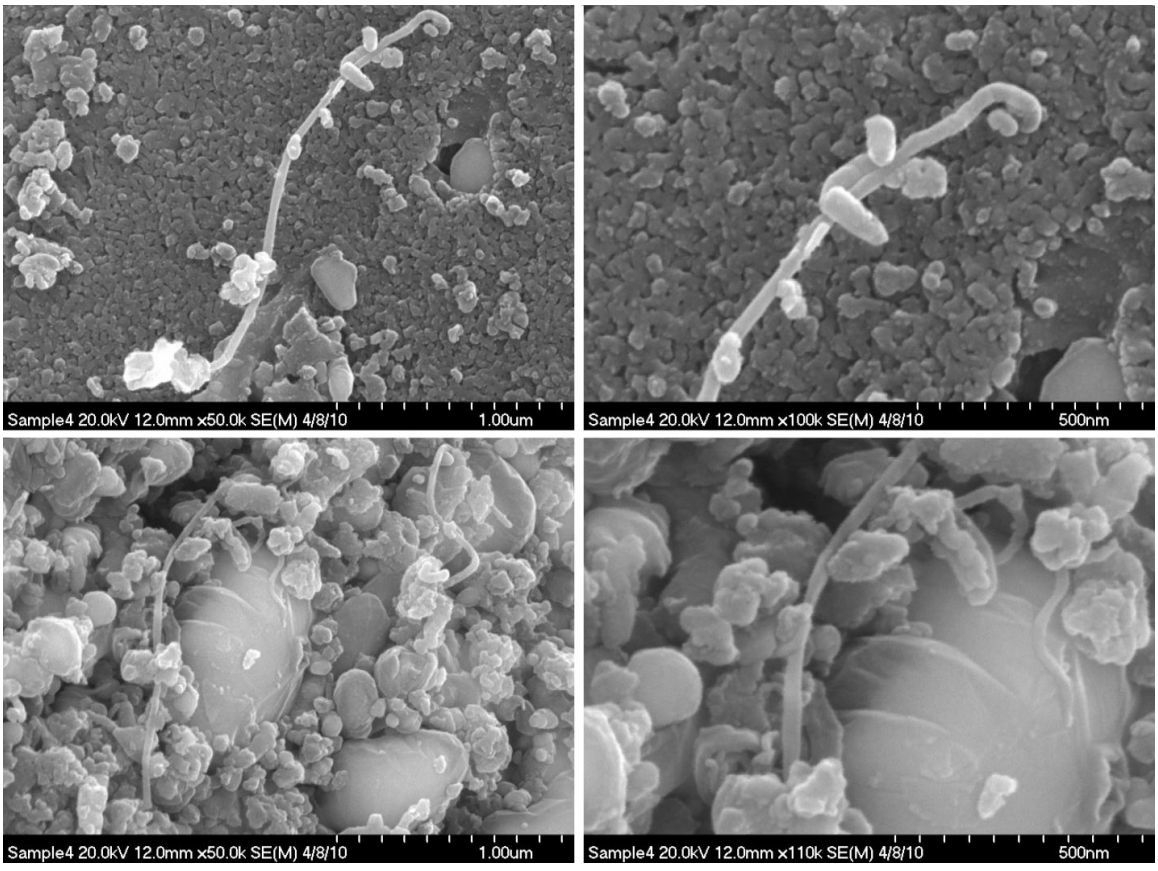

Figure 8: Multi-walled carbon nanotubes produced from methane on Co-Mo catalysts.

Another set of similar experiments were performed using iron-cobalt catalyst on magnesium oxide support particles and a mixture of methanol and ethanol as the carbon source. Similar results were observed compared to the previous experiments in that very few carbon nanotubes were present in one sample of these experiments. Figure 9 displays a set of SEM images of thin multi-walled carbon nanotubes on Fe-Co catalyst particles.

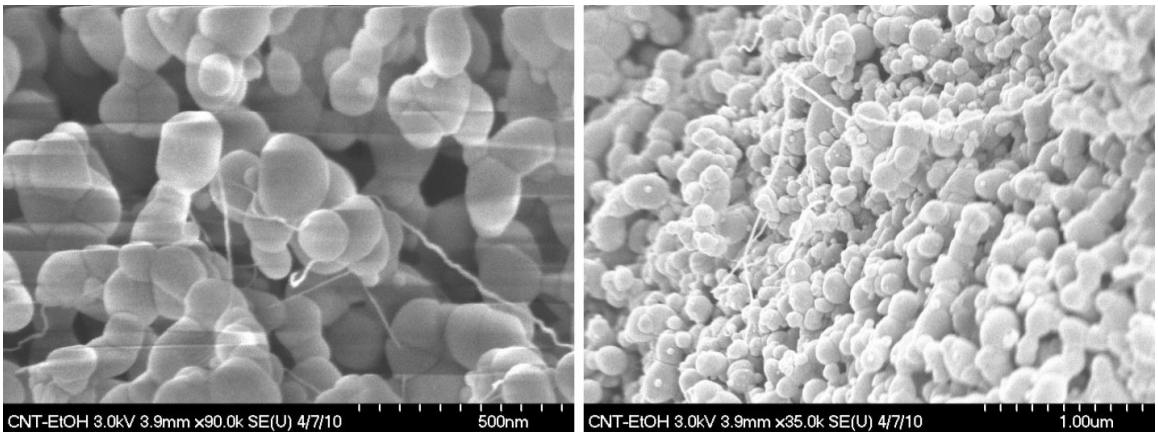

Figure 9: Multi-walled carbon nanotubes produced from alcohol on Fe-Co catalysts.

Future Work

Evaluating the experimental work done and the analysis of results, additional work was identified that would provide further research, improve experimental result analysis, and narrow down the paths to draw distinct conclusions in producing single-walled carbon nanotubes. Following the results of the current experiments, additional experiments could be performed by investigating higher methane flow rates for the present catalysts (Co-Mo on silica gel), investigating the effects of pressure above one atmosphere along with the construction of a pressurized fluidized bed, investigating different combinations of carbon source and metal catalysts, and utilizing other characterization methods such as TEM, AFM, and Raman spectroscopy.

Following the research on the carbon nanotube “super-growth” by the Kenji Hata Research Center for Advanced Carbon Materials [7], a different set of experiments could be performed using the “super-growth” method to produce carbon nanotubes efficiently.

This method calls for the construction of a non-fluidized chemical vapor deposition reactor.

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Appendix: Experimental Procedures

Preparation of Catalyst

Cobalt-molybdenum catalyst on silica gel support was prepared using the impregnation method as described by Kitiyananm et al [12]. Ammonium molybdate (3.531 g) and cobalt nitrate (2.9102 g) were mixed in a beaker. Water (20 mL) was added to the mixture to dissolve the compounds. Once dissolved, silicon gel beads (100-mesh, 41.8 g) was added to the beaker, and the mixture was stirred continuously until the mixture was uniform. The catalyst mixture was then placed in an oven, with vacuum and purge, overnight at 65-70°C. The following day, the beaker was taken out and was cooled to room temperature. The resulting catalyst was a brick-red colored powder containing 6 wt% metals and has a 1:2 Co-Mo molar ratio.

Experimental Procedure

The following procedure was followed for each experiment in the factorial analysis of control variables.

1. Insert 3.0 grams of catalyst into the quartz tube reactor and insert the tube into the heater.
2. Purge the reactor with argon gas.
3. Turn on the heater to the designated temperature.
4. When the designated temperature is reached, switch on the methane flow and run for 30 minutes.
5. After 30 minutes, switch off the methane and turn off the heater. Continue to purge with argon.
6. When the quartz tube has reached room temperature, transfer the catalyst sample into a vial and clean the inside of the tube.

Table 7: Factorial analysis of control variables for nanotube experiments.

Sample	Temp (°C)	Methane (sccm)	Argon (slpm)	Ratio (sccm/slpm)
1	900	10.5	2.00	5.25
2	900	10.5	2.50	4.20
3	900	8.5	1.62	5.25
4	900	8.5	2.02	4.20
5	950	10.5	2.00	5.25
6	950	10.5	2.50	4.20
7	950	8.5	1.62	5.25
8	950	8.5	2.02	4.20