Synthesis of carbon nanotubes from waste polyethylene plastics

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Abstract

Generation of non-biodegradable wastes, such as plastics, and resulting land as well as water pollution therefrom discarded plastics have been continuously increasing, while landfill space decreases and recycling markets dwindle. Exploration of novel uses of such materials becomes therefore imperative. Here I present an innovative and unique partial conversion of plastic waste to valuable carbon nanomaterials. It is an overall exothermic and scalable process based on feeding waste plastics to a multi-stage, pyrolysis/combustion-synthesis reactor. Plain stainless steel screens are used as substrates as well as low-cost catalyst for both carbon nanomaterials synthesis and pyrolyzates generation. Nano carbon yields of as high as 13.6% of the weight of the polymer precursor were recorded. This demonstration provides a sustainable solution to both plastic waste utilization, and carbon nanomaterials mass production.
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Chapter 1

Introduction

Over the past fifty years the proliferation of non-biodegradable man-made materials, such as plastics, has increased dramatically. It is estimated that more than 30 million tons of plastic wastes are generated yearly in the USA[1] and Europe[2], and polyethylene (PE) accounts for over 60 wt% of those amounts. As plastics are mass produced and inexpensive, they are readily discarded thereby creating a vast solid waste and pollution issue, contaminating land and coastal waters. Recycling efforts in past years have attempted to alleviate this problem, but as recycled plastics are generally devalued products the economics of this practice do not always work out. Although the recycling rate in the U.S. went from approximately 6% to 33% of all municipal solid waste (MSW) over the past 50 years, a further increase of recycling is not only desirable but, rather, essential due to continuously decreasing landfill space available. However, it has been limited by a dramatic slump of the recycling market with the recent global economic downturn. For instance, prices of used plastic bottles have been falling from 25 cent/lb to 2 cent/lb over the last year[3]. This threatens to erode the recycling markets, the associated infrastructure and, perhaps eventually, the public’s mindset for recycling. Therefore, creation of a new market for recycled plastics, particularly leading to high-value products, would be beneficial. Generating high-end value products, such as combustion-generated-carbon-nanofibers (CGCF), specifically, carbon nanotubes (CNT) and carbon nanofibers (CNF), from recycled waste plastics may reverse this trend and restore, even enhance, the motives for recycling. The major barrier to the industrial
application of either CNT or CNF, on the other hand, lies on the cost of their carbonaceous precursors. Even those facilities with large-scale production ability, two decades after the discovery of CNT[4], still have to rely on large volume, high-purity light hydrocarbons as carbon source[5], such as methane, ethane, ethylene, etc. However, such chemicals are of high demand by many diverse industries and are, thus, costly. Considering their high carbon and hydrogen content, as well as their high energy content, waste plastics present a distinct alternative to the aforementioned carbon sources. The use of such relatively inexpensive feedstock for the manufacture of well-defined CGCF, could lower prices of nanostructured carbonaceous materials and accelerate their large-scale use in an increasing number of commercial products, such as batteries or composites. This work utilized waste polyethylene (PE) as a feedstock. Other waste plastics are currently being examined.
1.1 Literature review on plastic waste and its combustion

Experiments involving combustion of solid fuels in furnaces were also conducted and provided additional challenges. Transient combustion of solid wastes was studied in a two-stage electric muffle furnace. Under conditions often encountered in these systems as well as in practical systems, polycyclic aromatic hydrocarbon (PAH) and soot are generated and once they form they are difficult to destroy; the partial pressure of some may even increase in post-flame gases. This illustrates the needs for identification of operating conditions that minimize pollutant formation and for understanding the underlying chemical processes. Efforts were made to approximate the physics of such cases and to appropriately apply the kinetic model. The fuels burned were polystyrene (PS), polyethylene (PE), polyvinyl chloride (PVC), medical waste latex gloves, cotton pads, as well as tire chips and waste liquid styrene.

Apart of the modeling efforts, the practical goals of prior study, especially conducted in our lab, were to compare the emission characteristics and yields of the different fuels but, most importantly, to find operating conditions which minimize them. To minimize products of incomplete combustion (PIC) from the batch combustion of solid fuels four techniques were investigated: (i) The gas temperature of the main gasifier/combustor was varied in the range of 500-1000 °C. (ii) The effluent of this furnace was mixed with additional air in a venturi, and it was channeled to a secondary furnace (afterburner) for further treatment, lasting 0.6 to 0.8s. (iii) The gas temperature of the afterburner was varied between 900-1100 °C. (iv) The effluent of the primary furnace was first subjected to high-temperature flue-gas filtration and then channeled to the afterburner. These studies illustrated large variations in the emissions from the various wastes. For instance,
combustion of liquid styrene proved to be the most uncontrollable; combustion of polystyrene and latex were the most soot emitting; combustion of polystyrene and polyethylene were the most PAH emitting; tire chips burned in a well-controlled manner; PVC combustion resulted in low yields of PIC; overall, cotton pads were the ‘‘cleanest’’-burning waste fuel.

Technique (ii), i.e., mixing the effluent of the primary furnace/gasifier with additional air and then implementing the afterburner treatment, was often beneficial in reducing PIC, but not always[6, 7]. Its effectiveness depended on the afterburner operating conditions, on the operating conditions of the primary furnace, on the fuel type and on the kind of PIC. Thus, the afterburner may, under certain circumstances, increase emission levels for some species. Fuels undergoing relatively controlled decomposition, such as PS, and/or with relatively low volatile hydrocarbon mass (PVC, tire, cotton pads) typically benefited from aftertreatment[8]. Fuels with fast decomposition, e.g., PE, or even abrupt decomposition, e.g., styrene, did not always benefit. Regarding technique (i), at low primary furnace temperatures the decomposition of all fuels was smoother and the flux of volatiles was smaller[9], the ensuing diffusion flames were the steadiest and the afterburner was found to be most effective. For instance, in the case of the primary furnace operated at 600 °C the formation and emission of PAH and soot were suppressed. When this effluent was mixed with additional air and was treated in the afterburner it benefited in nearly all cases. Increasing the operating temperature of the afterburner in the range of 900-1100 °C (technique iii) had a beneficial effect in decreasing the PAH emissions but increased the soot emissions, while it had little effect on CO[8]. Generally, it was concluded that once PIC are formed in a diffusion flame, they are not easily
oxidized under subsequent post-flame conditions. Prevention of their formation to any possible extent must be targeted, and this is the focus of the current work. Experiments were also conducted with a high-temperature ceramic honeycomb barrier filter (such as those currently used as automotive diesel filters), placed just before the exit of the primary furnace (technique iv). High-temperature filtration drastically reduced the soot emissions from the overall system, but it did not always reduce those of all volatile PAH[10-13]. Some conditions worked superbly for some fuels. For instance, in the case of waste-tire-derived-fuel the combination of the high-temperature ceramic filter with the afterburner treatment reduced the final emissions of CO by factors of 2-6, NO\textsubscript{x} by factors of 2-3, particulates by two orders of magnitude (both PM\textsubscript{2.5} and PM\textsubscript{10}), and most individual PAH species by more than one order of magnitude.

In separate experiments, augmenting the oxygen partial pressure in the venturi drastically decreased PAH and particulate emissions, it increased CO\textsubscript{2} yields, whereas CO yields first increased and then decreased. At the elevated oxygen partial pressure (0.47 atm) in the afterburner soot was absent; this provided an opportunity to deduce global oxidation rate constants for PAH species. They were found to range from \(\approx1\times10^4\) to \(1\times10^6\) cm\textsuperscript{3} mole\textsuperscript{-1} s\textsuperscript{-1}, at \(T_{gas} = 900\text{-}1100\) °C. Based on these global kinetic data, rate constants describing soot formation from PAH were determined at 0.14 and 0.21 atm partial oxygen pressures, under sooting conditions. These rate constants were found to be between \(\approx1\times10^8\) and \(3\times10^{10}\) cm\textsuperscript{3} mole\textsuperscript{-1}s\textsuperscript{-1}. Therefore, conversion of PAH to soot appears to be significantly faster than PAH oxidation.
1.2 Literature review on CNT, its properties, application, and synthesis

1.2.1 Carbon Nanotube Properties and Applications

Carbon nanotubes (CNT) including single-wall carbon nanotubes (SWNT) are a category of fullerenic materials and their increasing use in commercial products is part of the beginning nano-technological revolution. The ability to produce CNT of specified characteristics in large quantities and low prices is therefore of major importance for continuous growth and competitiveness of the national economy. The appealing properties of CNT fall essentially in three categories: (i) Electrical: semiconducting or metallic behavior. (ii) Mechanical: very high tensile strength (100 × steel), high thermal stability and thermal conductivity[14, 15]. (iii) Chemical: extremely high surface area, biological interface affinity. Properties of nanotubes depend in many cases on their detailed structure. For instance, chirality of single-wall nanotubes determines their metallic or semi-metallic properties.

In recent years literature describing potential applications of nanotubes has become overwhelmingly large[16-18], major fields of interest can be divided as follows: a) Actuators: Conversion of electrical energy to mechanical energy and vice versa. Potential use in robotics, optical fiber switches and displays, prosthetic devices etc., has been explored[19, 20]. b) Sensors: Correlations between adsorption of gases such as oxygen and conductance and thermoelectric power have been observed[21]. c) Composites: Employing nanotubes as additive to polymer composites can give improved strength performance[22, 23]. The challenge of anchoring nanotubes to polymeric structures has been addressed by functionalizing nanotube walls[24]. d) Biological: Due to their physical dimensions similar to that of biologically active macromolecules such as proteins, and
DNA, carbon nanotubes are finding increasing utility in biology related applications including sensors, drug delivery, enzyme immobilization and DNA transfection[25]. For instance, single-wall nanotubes (SWNT) have been shown to be ideal probe tips for atomic-force microscopy (AFM) imaging of biomacromolecules[26]. e) Electronics: Significant research efforts have investigated numerous applications taking advantage of electronic properties[27]. Depending on structural characteristics, carbon nanotubes are metallic or semiconducting. Sizes of transistors and logic devices can be reduced significantly, e.g., a logic devices made of a single nanotube with a transition between chiralities along its length has been reported[28]. The potential use of highly-ordered carbon nanotube arrays for a variety of electronics application ranging from data storage, displays, and sensors to smaller computing devices has been described[29]. Commercial application of carbon nanotubes in the area of flat panel displays (FPD) is expected in the near future. Vertically grown arrays of nanotubes serve as field emitters that project electrons onto phosphorescent pixels. Prototypes of nanotube-based field emission displays (FED) have been presented and, taking into account the 18.5 billion dollars in sales of FPD in 1999, the market potential is significant[30]. f) Hydrogen storage: Single-wall nanotubes are potentially suitable for hydrogen storage systems necessary in hydrogen-powered vehicles allowing for a reduction of the nation’s dependence on foreign oil, lower greenhouse gas emissions and the improvement of regional air quality [31]. Significant hydrogen storage capacities have been observed[32-34], but depend strongly on sample characteristics and preparation[32]. Other applications for CNT are in catalyst supports[35], and optical limiters[36].
1.2.2 Nanotube Synthesis Overview

Desired characteristics of CNT such as diameter, length or chirality depend strongly on the targeted application. After the discovery of multi-wall and then single-wall carbon nanotubes by carbon vaporization in electric arcs[37, 38], several varieties of this technique such as metal doping, different configurations of the electrodes or different types of carbon sources[39, 40] have been described. Synthesis of improved-quality single-wall carbon nanotubes has been reported using rather expensive laser irradiation of metal-doped carbon targets[41-44]. Chemical vapor deposition (CVD), i.e., growing materials from pyrolyzing hydrocarbons to a gas from the gas phase onto solid surfaces, by a) Surface deposition and b) Floating catalyst methods. The generation of well-aligned and uniform mats of multi-wall as well as single-wall nanotubes has been demonstrated[45, 46]. Readily vaporized metal carbonyl (e.g., Fe(CO)$_5$) and metallocene (e.g, Fe[((C$_5$H$_5$)$_2$)]) have been used in conjunction with different carbon sources such as acetylene or benzene[47-49]. In the (HiPCO) process[50, 51], catalysts have been formed in-situ by thermal decomposition of iron pentacarbonyl (Fe(CO)$_5$) in a heated flow of carbon monoxide at pressures of 1 to 10 atm and temperatures between 800 and 1200 °C. The need for continuous external heating is a serious drawback for CVD’s use on an industrial scale for all but the highest end-value applications. Another drawback of CVD is that most experiments reported require the injection of H$_2$ to achieve the reduction conditions needed to synthesize nanotubes, so increasing the risks of potential explosion due to H$_2$ compressed gas handling.
Carbon nanotubes have also been generated by combustion synthesis. Compared to CDV pyrolysis, combustion synthesis has the advantage of being an exothermic process. Carbon sources such as carbon monoxide or small hydrocarbons are generated in-situ by means of a combustion process while a catalyst is introduced, similar to the above-described CVD techniques. The use of suitable combustion equipment and precise setting of operating conditions such as fuel/oxygen ratio, dilution with inert gas, fresh gas velocity and pressure allows for accurate control of the nanotube-forming process. Sufficient understanding of the correlations of the parameter space with the characteristics of nanotubes is expected to lead to a large-scale and high-yield production process of carbon nanotubes with well-defined and homogeneous properties. Formation of multi-wall carbon nanotubes by immersion of metallic substrates in methane- and ethylene-fueled, co-flow diffusion flames[52-54] and of single-wall nanotubes by addition of metallocenes to the fuel-stream of acetylene- or ethylene diffusion flames[55] has been reported. Multi-wall carbon nanotubes were also observed in opposed-flow methane-oxygen diffusion flame with and without immersion of metal catalysts[56-58]. Small amounts of single-wall carbon nanotubes (SWCNT) were identified in the condensed material of partially premixed sooting acetylene and ethylene flames in which metallocenes (Fe(C₅H₅)₂ and Ni(C₅H₅)₂) were vaporized and added to the flame feed whereas multi-wall carbon nanotubes (MWCNT) were observed in corresponding benzene flame[59].

Significant insight in carbon nanotube formation in combustion environments has been gained by the studies of Vander Wal and co-workers using a) “pyrolysis flames” with injected catalyst precursors[60-62] and b) premixed flames with a supported catalyst[63,
In “pyrolysis flames”, reactive mixtures consisting of CO/H\(_2\), C\(_2\)H\(_2\)/H\(_2\) or CO/C\(_2\)H\(_2\)/H\(_2\), with helium or argon as inert gas, were introduced into a surrounding fuel-rich acetylene/air flame, serving as energy source. Iron as well as nickel catalysts have been introduced with the reactive mixture after sublimation of organometallics, thermal evaporation of pure metals or nebulization of solutions containing metal salts. In “premixed flames”, Vander Wal and co-workers used cobalt as catalyst, and cobalt-coated stainless steel meshes were introduced into the post-flame area of a series of rich premixed fuel (CH\(_4\), C\(_2\)H\(_2\), C\(_2\)H\(_4\), C\(_2\)H\(_6\) and C\(_3\)H\(_8\))-air flames. Correlations between experimental parameters such as the composition of the reactive mixture or temperature with formation of single- or multi-wall nanotubes were established and competing processes such as coating of the catalyst were addressed. A supported cobalt catalyst has been investigated and conditions suitable for carbon nanotubes growth were identified. For a nominal post-flame temperature of 800°C, best carbon nanotubes growing conditions were found with fuel-rich flames below the soot onset limit, with the ideal equivalence ratio, \(\phi\), which is defined as \(\phi = (m\text{_{fuel}}/m\text{_{O}_2})\text{_{actual}}/(m\text{_{fuel}}/m\text{_{O}_2})\text{_{stoichiometric}}\), value varying as a function of the original pre-mixed fuel. Ethylene seemed to be the most appropriate fuel. The authors presented a striking correlation map of the H\(_2\) and CO equilibrium concentrations that result in the formation of nanotubes, showing that the best equilibrium concentrations for nanotubes growth fall in a small area around CO and H\(_2\) mole fraction of 0.1, each. They proposed that CO and H\(_2\) were the active contributors to CNT synthesis, with CO serving as carbon source and H\(_2\) being responsible for controlling the velocity of carbon deposition over the catalyst due to its ability to co-adsorb in the catalyst and dissociate.
and, so, re-combining and restructuring the elemental carbon deposited by CO. H$_2$O and CO$_2$ were regarded as playing secondary roles in CNT growing, based on the water-gas shift equilibrium. Finally, in a study related to the above, but also relevant to the current work, Jiang and co-workers[65] mixed a polymer (polypropylene) and a catalyst, placed the mixture in the crucible, positioned over a gas/O$_2$ flame at 830°C. After the end of a luminous yellow flame period the crucible was removed from the flame and the products were purified to obtain the nanotubes. The catalyst was a mix of nickel compounds (oxides and hydroxides) with organic-modified montmorillonite clays and a polypropylene maleate (PPMA) as a compatibilizer. Although nanotubes were obtained, the reproducibility of the flame conditions and scale-up of this synthetic route is deemed difficult.

A major breakthrough toward the manufacture of SWCNT at an industrial scale was achieved in the laboratory of Jack B. Howard in the Department of Chemical Engineering at MIT[66-68]. The formation of SWCNT without other carbonaceous materials such as MWCNT, fullerenes or soot was demonstrated in fuel-rich but non-sooting premixed acetylene/oxygen/argon flames at reduced pressure while injecting iron pentacarbonyl as catalyst precursor. Combustion synthesis of SWCNT was further developed in view of its use for large-scale manufacture[69, 70]. In-line filtration allowing for continuous operation of SWCNT and product recovery was implemented using commercial metallic cartridges. Major improvements of the SWCNT yields and their quality have been achieved by using natural gas or methane as fuel.
1.3 Reference


Chapter 2

Methods

2.1 Pyrolysis of waste polyethylene plastics

Similar to previous work at Northeastern University (NEU)\textsuperscript{1}, a two-stage furnace was utilized, see Figure 2.1, a. Samples of polymer powder (high-density PE, 250 to 297 \(\mu\)m, purchased from Sigma-Aldrich) were loaded in a porcelain boat and inserted into the laminar-flow muffle furnace. Nitrogen served as carrier gas at the flow rate of 4 l min\(^{-1}\) ensuring the absence of oxygen and, therefore, pyrolytic conditions prevailed in the first stage of the furnace. In order to optimize PE decomposition to ethylene monomers, two furnace temperatures (650 °C and 800 °C) were explored. Samples of pyrolysis gas were withdrawn with syringes mounted on a syringe pump and analyzed by gas chromatography (Agilent 6890A) using flame ionization detection (FID). PE pyrolyzates were found to include more than twenty \(C_{1-8}\)-hydrocarbon species. Based on our quest of maximizing the ethylene gas concentration, an operating temperature of 800 °C was selected for the first stage of the furnace (the pyrolyzer).

![Figure 2.1. Apparatus Setup for pyrolysis (A) and synthesis (B)](image-url)
2.2 Combustion of waste polyethylene plastics

After the identification of optimized pyrolyzer operating conditions, the second stage of the apparatus was modified to accommodate requirements of the present project, as shown in Figure 2.1, b. This apparatus consists of three sections of quartz tubing. The first section (3.7 cm ID × 87 cm) is the pyrolyzer, as described above, the second section (3.7 cm ID × 26 cm) is connected to a mixing venturi (0.8 cm ID) where the pyrolyzer gases (pyrolyzates) come in intimate contact with jets of oxygen or of an oxygen-nitrogen mixture leading to an average equivalence ratio $\phi = 1.62$ (or higher). After some optimization, a flow rate of 5 l min$^{-1}$ of nitrogen entering the first stage followed by the addition of 1.33 l min$^{-1}$ of oxygen at the venturi was used for nanocarbon synthesis. As a result of the blending of the pyrolyzates with the preheated oxidizing gases, ignition occurred and a premixed flame was established at the exit of the venturi. The combined use of the pyrolyzer reactor to gasify the solid polymer and of the venturi to establish a premixed flame, as described in the section printed in italic needs to be considered as proprietary information for the development of this process. The combustion gases were then channeled into the third section of the apparatus (3.7 cm ID × 38 cm) where catalyst-coated screens were placed perpendicular to the flow and maintained at a predetermined temperature, controlled by the second muffle furnace. As described above, solid polymer powder was uploaded in porcelain boats (Coors 60035) and pyrolyzed in the first section under inert gas (nitrogen) flow. The combustion of this pyrolysis gas, upon mixing with oxygen at the venturi, lasted for approximately 30 s. To generate additional effluent for the growth of nanostructures, two sequential boatloads of polymer were
inserted in the furnace. Whereas the equivalence ratios in these experiments were targeted to be below expected sooting thresholds for ethylene, the non-steady nature of the flames herein could not preclude the formation of some soot. Therefore, to prevent deposition of soot formed in the flame onto the catalyst-bearing screens and resulting catalyst deactivation, a high-temperature barrier filter was placed inside the furnace. This filter had a honeycomb structure and was made out of silicon carbide (SiC), see Figure 2.2. This is a high filtration efficiency filter (97% retention for 1 micron particles) manufactured by Ibiden, Co[2].

While any formed soot particulates are retained in the filter, gaseous combustion products, i.e., CO, CO₂, H₂, light hydrocarbons and small PAH, enter the third stage of the apparatus in which catalyst-coated stainless steel screens have been inserted. The use of the high-temperature barrier filter, as described in the section printed in italic needs to be considered as proprietary information. Finally, the growth of carbonaceous nanostructures is occurring on the screen surface using the products of the exothermic combustion process as carbon supply. Hydrogen and water, also formed in situ during the combustion of the PE pyrolyzates, are expected to prevent catalyst deactivation and poisoning by continuous surface cleaning.
In the next step, the fuel pyrolysis temperature was optimized for the synthesis of carbonaceous nanomaterials. Taking into account the importance of CO as potentially direct precursor of nanomaterials, its maximized concentration was targeted and the establishment of a stable flame at the venturi was verified. As some instability has been observed below 700 °C and high CO concentrations and yields were found for most initial sample masses at 800 °C, as shown in Figure 2.3, this pyrolysis temperature has been used for all subsequent experiments.

![Figure 2.3 Averaged CO concentrations and yields per gram of PE for different masses of initial fuel at pyrolysis temperatures of 700°C and 800°C.](image)

Prior to the experiments, catalyst-coated supports were prepared by means of physical vapor deposition (PVD). For this purpose, small screens (one square inch) of type 304 stainless steel (400 × 400 mesh with 0.002 cm diameter wire) were used as received. The effectiveness of cobalt (Co) and nickel (Ni) catalysts in generating carbon nano-structures was investigated at two different film thicknesses, 4 and 8 nm.

### 2.4 Synthesis of carbonaceous nanomaterials

In order to avoid oxidation of the catalyst prior to the nanostructure synthesis, the system was purged with nitrogen. Taking into account the time required to pyrolyze PE, addition of oxygen (1.33 l min⁻¹) through the ejector nozzles of the venturi was delayed by 1 min 25 s after the start of the pyrolysis process. The resulting mixture auto-ignited readily at the exit of the venturi. Upon completion of the reaction, as indicated by the
extinction of the visible flame, oxygen was turned off immediately to avoid any oxidation of the material grown on the screens. While remaining in the reactor, the catalyst-coated screens were then allowed to cool-down under a stream of nitrogen until the temperature decreased below 200 °C. Finally, the screens were removed and prepared for analysis by means of SEM and TEM.

2.5 SEM

SEM was conducted on a Hitachi 4800 using a voltage of 3 kV and a working distance of 8.2 mm.

2.6 TEM

For TEM, a JEOL 1010 instrument was used with an accelerating voltage of 70 kV, whereas a JEOL 2010 instrument was also used with an accelerating voltage of 200 kV. In the present work, the material deposited on the surface of the stainless steel mesh was dispersed in ethanol, assisted by sonication. Drops of the resulting dispersion were deposited on a holey carbon film (200 copper mesh, EMS Com.) which was then inserted in the specimen chamber of the TEM instrument.

2.7 TGA

Material grown on metal screens has been removed by suspension in alcohol followed by solvent removal. The resulting powder was analyzed in a TGA i 1000 instrument, (Instrument Specialists, Twin Lakes, WI) using a heating rate of 5 K/min.

2.8 Surface Area

The BET (Brunauer-Emmett-Teller) method was applied using a Micromeritics Gemini 2375 Surface Area Analyser. Prior to analysis, the sample was degassed at 160 °C.
2.9 Electrical Conductivity

Approximately 4 mg of the material finally used for the surface area measurement was dissolved in 20 mL of methanol assisted by sonication. The solution was then transferred to a beaker with a diameter of 4 cm and evaporated at reduced pressure and a temperature of 40 to 45 °C. A layer covering the whole bottom of the beaker was formed and its conductivity across the diameter measured using a two probe diameter and a standard digital multimeter.

2.10 Reference

Chapter 3
Experimental parameters and results

3.1 Temperature of pyrolysis

Light hydrocarbons as aforementioned are considered to be the major carbon suppliers for the growth of carbon nanostructured materials[1, 2], and therefore are our major focus. 800°C was chosen as the pyrolysis temperature to maximize the gaseous pyrolyzates while minimizing the generation of tars and oils[3, 4]. The latter are the precursors of soot[5], which can eventually deactivate the catalyst[2].

3.2 Time for the pyrolysis

While large polymer mass could provide more LHC and its pyrolysis process could last longer, only 0.75 gram of high density polyethylene (HDPE) pellets were inserted each batch as the solid fuel, since it is the highest amount that the size of current apparatus could handle. The corresponding pyrolysis and combustion processes are completed within approximately thirty seconds.

3.3 Gas addition to the venturi,

3.3.1 O₂

It has been suggested that carbon monoxide (CO) is the primary growth agent for nanomaterials [6-8], its maximized concentration was targeted and the establishment of a stable flame at the venturi was verified. Pure oxygen (O₂) was injected through the venturi at three different flowrates to result in concentrations of 19%, 21%, and 25%, upon mixing with the nitrogen stream of the pyrolyzer. There was an unusual increase of CO with increasing O₂, which normally indicates fuel-richer condition. The
corresponding averaged CO emissions were: 12%, 14%, and 17%, respectively. The corresponding averaged CO$_2$ emissions were: 6.4%, 6.7%, and 8.7%, respectively. The more consumption of O$_2$ normally relates to better oxidation of pyrolysis gas, and therefore the combustion effluent will be much cleaner. The synthesis stage temperature was set at 750$^\circ$C in most experiments where catalyst effect occurred optimized. Here the corresponding products show the differences. As shown in Figure 3.1, b, tar-like materials were evident embedded along with tubular nanomaterials in the lowest oxygen conditions, where the combustion condition is too fuel-rich. The combustion effluent for the CGCF synthesis could even contain unburned hydrocarbons. By contrast, the products with the median oxygen concentration (21%) look much cleaner than the others. This could be attributed to the optimized synthesis conditions provided by this combustion effluent. Hydrogen and water, also formed in situ during the combustion of the PE pyrolyzates, are expected to prevent catalyst deactivation and poisoning by continuously cleaning surface[9, 10].

The theoretically calculated averaged bulk equivalence ratios for all the tests were higher than $\Phi= 2.0$, and this is evident from the amount of soot captured and visible at the ceramic filter after each experiment. A critical investigation of the penetration length ($Y_{\text{max}}$) in the venturi as suggested by Lefebvre[11], was then conducted to check how the pyrolysis gas and the oxygen mixed within the venturi. The corresponding penetration lengths for those three experiments turn out to be far away from the centerline. It is evident that the penetration depth was largely affected by the velocity of the injecting oxygen, thus its concentration. By better utilizing the pyrolysis gas and its combustion
effluents, especially the unburned hydrocarbons and carbon monoxide, more carbon source could be provided for the CGCF synthesis and therefore higher conversion rate.

Two boats of polymer powers were inserted consequently into the furnace, aiming to provide with more carbon source. The product yields, rather than double, keep almost the same as the single batch. One possible explanation is that the synthesis process terminated sometime before the insert of the second boat so that no extra benefit could be received.

Figure 3.1 SEM images of material grown from combustion effluents of PE pyrolyzates.
**3.3.2 N₂ (pyrolysis only)**

Realizing the fact that light hydrocarbons themselves could also serve as the growth agents for nanomaterials, especially in a CVD apparatus[12], those chemical agents have been detected at the exit of the synthesis chamber when there is no catalyst present in this chamber and therefore no synthesis happened. The results have also been compared with those detected at its entrance, and it is shown that the mass fractions of methane, ethylene, propylene, and benzene increase after the chamber, which indicate that more pyrolysis gases got further decomposed. This is attributed by the prolonged reaction time when gases passing this chamber, now an extended pyrolysis chamber[3, 4]. Besides, when the temperature of the extended pyrolysis chamber increase, fractions of methane, acetylene, ethylene and benzene increase while there were less ethane, propane, propylene, propane, n-butane, toluene and ethylbenzene decrease. Attractively, propane, propane, n-butane, and ethylbenzene almost disappear. The results suggested that different temperatures affect a lot the decomposition of the pyrolyzates along with the CNT synthesis, and the further study of its correlations are currently on the way.

With current apparatus, CNT could also be achieved without the help of combustion. This interesting result comes out when there is no combustion occurs. As the products shown in Figure 3.1, j and k, the surfaces of the tubes are not as smooth as those using the synthesis gas from the combustion process. Comparisons of the chemical products with and without CNT synthesis reveals that without oxidation, those twenty C1- to C8-hydrocarbon species were abundance that any difference before and after the synthesis on these species were very remarkable, as shown in Figure 3.2, a.
The gases after the synthesis were also analyzed by gas chromatography. All the experiments were repeated at least twice to minimize the uncertainty and the results exhibited the same tendencies. At the synthesis chamber temperature of 750°C, major hydrocarbons emitted within the synthesis process increased by 54.29wt% in total, compared those without synthesis process in place, while it was 2.84wt% increment at 900°C. All the comparisons were based on the averaged values of repeated measurements. We believe that the stainless steel catalyst works not only for the CNT synthesis process, but also for the pyrolysis process. The whole process therefore turns out to be a multi-functional one, providing high value carbon nanomaterials along with the high-energy content byproducts, such as light hydrocarbons and hydrogen.

Besides, by calculating the difference of each individual hydrocarbon species before and after the synthesis process, we realized that only at relatively lower temperature, which is 750°C here, acetylene (C$_2$H$_2$) is the only species for which a negative increment was recorded(Figure.5, a). Assuming that the amount of individual hydrocarbon species pyrolyzed increases with catalysts, the reduction of acetylene indicates that this shortest alkyne was largely consumed during the synthesis process, which suggests that it was the principle carbon source for carbon nanomaterials growth at lower temperature. At 900°C, the amount of emitted hydrocarbons also increases, but less than that at 750°C. As contrasted with the increment of methane (27.91%), benzene (16.14%) and ethylene (2.32%), all other hydrocarbons of interest, including acetylene, decreased. We believe that these changes are the joint results of both catalyzed pyrolyzates decomposition, which produces more light hydrocarbons within the same period, and catalyzed nanocarbon synthesis process, which consumes a major portion of those decompounds.
The light hydrocarbon measurements release that, in general, the synthesis process prefers to utilize alkynes as carbon course. Those with smaller carbon numbers were consumed first when relatively lower temperatures were adopted, and the hydrocarbon species spread to higher carbon numbers when synthesis happens at higher temperatures.

![Figure 3.2 Typical emission products from the polyethylene pyrolyzates and its combustion: a, light hydrocarbon emissions, and b, CO and CO₂ emissions](image)

### 3.4 Temperature of the synthesis chambers

The CNT synthesis was achieved at all experimental temperatures tested, i.e., 600°C, 750°C, and 900°C (Figure 3.1, g, h and i). The dominant difference among different temperatures is that the tubes grow longer with higher temperatures, while there is no evident difference in terms of morphology. Therefore most experiments were conducted at 750°C and 900°C.

### 3.5 Time of synthesis

The synthesis normally finished within thirty seconds, which were the duration time of the combustion. Considering that the synthesis process is a highly complex and sensitive one, the suitable synthesis window may be even shorter. With the length in the order of several micrometers, the CGCF products showed their potential to be as long as centimeters if the optimized synthesis condition could last for hours.
3.6 Type of screens

3.6.1 Effects of Extra-coated Catalysts

Four series of experiments were conducted to investigate correlations between either the catalyst identity or the thickness of its layer, deposited by means of physical vapor deposition (PVD), and the characteristics of the resulting materials. For this purpose, material grown on the 4 and 8 nm thick nickel and cobalt layers has been examined by means of TEM. In addition, samples grown on 8-nm-thick nickel and 4-nm-thick cobalt have been imaged using SEM. SEM images of material grown on the 4-nm-cobalt- and the 8-nm-nickel-coated stainless steel meshes, are shown in Figure 3.1, a and b, respectively. While nanostructural materials could be identified in both cases, more distinct features were observed when 4-nm cobalt was used as catalyst. As shown in Figure 3.1, a, material grew on the surface of the wires of the mesh (A) and dendritic branching (B) occurred as arrowed. It also revealed that these tube-shape structures are at a length on the scale of micrometers, but of various diameters. Structures consisting of straight, tortuous and even coiled (arrowed) shapes were observed at higher magnification. In the case of 8 nm nickel, nanostructured wires were also observed but appear to have a more uniform diameter distribution (Figure 3.1, b). No coiled or irregular structures were found in this sample. In order to gain insight in detailed features of the structures identified by means of SEM, additional characterization was conducted using TEM.

A TEM image of material grown on 4 nm cobalt catalyst is given in Figure 3.3, a, and the coiled tubes can be seen in longitudinal orientation. Some transparent parts including the side surface (T) and the cross section of the tube (arrow) could be identified. The
variance of the tube diameters is significant ranging from approximately 20 to 100 nm. For comparison, the corresponding SEM micrographs was previously shown in the Figure 3.1, a.

Figure 3.3 TEM images of material grown from combustion effluents of PE pyrolyzates after dispersion in ethanol and deposition on holey carbon grids. Scale bar: 5nm except specified within the image.
Assessing the impact of the thickness of the catalyst layer, TEM image of material grown on 8-nm-cobalt is shown in Figure 3.3, b. General features appear to be very similar, for instance coiled tubes were found again. While no quantitative analysis has been conducted, no striking difference in tube diameters and wall thickness could be observed. Overall, nanostructures grown on 4-nm-thick Co occur to be cleaner than in the case of the corresponding 8-nm-thick catalyst layer. However, due to the possible impact of sample preparation on the resulting images, definitive conclusions should be avoided at the current stage. TEM images of samples generated after deposition of 4-nm- and 8-nm thick nickel layers are shown in Figure 3.3, e and f. In both cases, catalyst particles (arrow in e) are evident and, in addition, a catalyst particle connected to two tubes could be identified (arrow in f). For the latter, the diameters of both tubes show a marked difference, growth could have occurred either from different edges of the fractal structures or two initially distinguished structures combined at some point. In contrast, no coiled tubes were found from cobalt-coated substrates.

3.6.2 Type of substrates (with and without extra coated catalyst)

Energy dispersive X-ray spectroscopy (EDS) revealed that the nanoparticles covered on one end of the CGCF consists of nickel, iron, chromium, and manganese, which are typical compounds of stainless steel used here as catalyst. As shown in the EDS profile (Figure 3.4, b), the estimated density was 5.62g/cm³, the ratio of the weights on iron, chromium and nickel is 11.49 : 1.29 : 1. The exclusive catalysis effect of Ni on CGCF synthesis therefore becomes uncertain in our case. In other words, 304 stainless steel, a compound of several elements, could also work as catalyst. This hypothesis was
confirmed by repeating the synthesis with the same operating conditions while no extra Ni or Co was coated on the surface of the inserted plain stainless steel meshes. The HRTEM also showed that either CNT or CNF (Figure 3.3, g and h) could be produced, compared with those from the catalyst coated meshes (Figure 3.3, c and d). The estimated density is the 8.68g/cm$^3$, while the ratio among three elements turned out to be Fe : Cr : Ni=11.41 : 1.17 : 1. (Fig.3.4, d)

Successful CGCF formation using uncoated stainless steel has been observed and a study of the effect of the different nickel contents in commercially available stainless steels has been conducted, inspired by the discovery described above. Samples were produced using 304 SS (Ni: 8~10.5wt%, Figure 4, e), 316 SS (Ni: 10~14wt%, Figure 4, f) and 330 SS (Ni: 34~37wt%, Figure 4, l). It was shown that 330 SS can even produce
tubes with diameters smaller than 10nm. Compared with 304 SS, it tends to have less variance of the tube diameter on the 316 SS. This reveals an interesting study field which relates the CNT growth mechanism, especially its formation (initialization), and the crystal structures on various catalysts.

3.7 Number of screens

The catalyst surface was increased by the use of three-dimensional “rolled” (as opposed to flat screens) substrates and formation rates relative to the initial amount of waste plastic as high as 13.6% could be achieved. Increased production could be carried out by utilizing larger amounts of catalysts. Pieces of SS meshes were rolled in the synthesis chamber, and the volume of catalyst together with its reacting surface is hundreds of times than that in the tentative tests. With this new technique, pyrolyzing 0.75 grams of polymer produced as much as 0.102g CNT. Considering the amount of plastic waste produced every year, and this effective conversion rate (13.6%), the utilization of CNT in the industrial scale could be achieved though this pyrolysis-(combustion)-synthesis process.

3.8 Nature of plastics

Other recent findings include the demonstration of CGCF formation from actual waste plastics, instead of commercial virgin PE (or polypropylene, PP). Pieces of milk jugs (made of HDPE), and plastic bags (made of LDPE) are adopted as solid fuels in the same operation conditions, and the results were compared with those using virgin HDPE and LDPE. Due to some additives, dyes, and other conditioners mixed in the jugs, there is white residual left in the crucible after the experiments. The products using this recycled raw polymer look irregular and its process shows less productivity.
3.9 Additional characterization results

Sample characterization by means of transmission electron microscopy (TEM) and scanning electron microscopy (SEM) is to a large extent complementary. Whereas the possibility of higher resolution using TEM enables the identification of detailed structures on the nanoscale such as the differentiation between single-walled, multi-walled carbon nanotubes and nanofibers, SEM allows for a general view of the major sample features. In SEM analysis, samples can be imaged without any prior sample preparation and larger areas can be visualized at different magnifications. Typical SEM and TEM images at different resolutions are given in Figure 3.1 and 3.3. While combustion-generated-carbon-nanofibers (CGCF) usually appeared to be hollow, a more detailed assessment of the wall structure was required to confirm the presence of multi-walled CNT (MWCNT) characterized by the parallel graphitic walls[13]. As shown in Figure 3.3, the use of high-resolution TEM (HRTEM) has revealed MWCNT, which is comparable with current commercial products[14]. CNF was also confirmed under HRTEM, which contains solid, rather than a hollow cavity as shown in the MWCNT.

Figure 3.5 Thermogravimetric analysis (TGA) results of carbon nanomaterials
The abundance of carbonaceous material has been assessed by means of thermogravimetric analysis (TGA) under air[15]. As shown in Figure 3.5, after a rather slow weight decrease until approximately 450 °C, nearly quantitative oxidation is completed around 600 °C. While the initial weight loss can possibly be attributed to the oxidation of soot-like structures, the consumption of most of the material beyond 525 °C is consistent with the presence of stable nanotube structures. Remaining residues, likely consisting of either metal or metal oxide, have ranged from approximately 2 to about 20%, depending on operating conditions. Such high abundances of nanotubes are in agreement with observations using SEM or TEM, discussed above.

A surprising low value of the Brunauer-Emmett-Teller (BET) surface area[16] as 76.28 ± 0.90 m²/g was determined for one of the samples. Such, compared to other nanostructured carbon materials as, e.g., single-walled nanotubes[17], small surface area may be of significant interest for Li storage in Li-ion batteries as high surface areas are likely to lead to irreversible adsorption. In addition, the electrical conductivity has been assessed in-house. An average resistance of 2724 ± 691 Ω was measured.
REFERENCES

Appendix 1

3-D Simulation of Flow Field and Heat Transfer in a Quartz Tube with a Venturi Using GAMBIT® and FLUENT®

Submitted as the Final Project for the Course

“Computational Fluid Dynamics with Heat Transfer”

MTMG310

Chuanwei Zhuo

NUID: 000492503

Dec. 17, 2008
Objective

This simulation model is derived from one part of my ongoing research. A quartz tube with venture, which is illustrated in Figure A.1.1, is set for my material synthesis experiment.

During my experiment, Solid polymers were uploaded in the porcelain boats (Coors 60035), which is covered by another porcelain boat (Coors 60036), and inserted into the first section, where they get pyrolysized and carried by the inert gas (99.9% Nitrogen, Med-Tech). This pyrolysis gas (fuel) then passed through venture where it gets mixed with extra adding oxygen, all the fuel gets burned within the second section of the chamber. The flame moves together with the combustion products (CO, CO$_2$, H$_2$, light hydrocarbon, PAH, Soot, etc.) into a ceramic filter (IBIDEN CO., LTD, Japan), which is installed at the beginning of the third stage, where the solid particles got captured. The gaseous combustion products will then provide a chemical reaction environment inside the third section where material synthesizing will occur.

In order to the control the quality of the synthesized materials precisely, it is very important to know and even predict the distributions of the temperature, the velocity and
the pressure inside the tube, especially in the third section. As the first step of the research, I am very interested to see the how the flow field turned out to be at the steady state, plus the study domain has been simplified where no additional oxygen adding at this time. The tube has been modified as the whole wall of it will have a uniform and stead state temperature, which is 800°C (1073°K). This modified modal is shown in Figure A.1.2.

![Figure A.1.2 Simplified computation domain](image)

After simplification, the goal of this project is to simulate the temperature, velocity and pressure distributions inside a two-stage tube connected with a venturi.

The geometry in 3-D and its dimension are shown in Figure A.1.3 and Figure A.1.4, respectively. The velocity of air at the inlet is 3.125m, the absolute pressure at the inlet is 1atm (101325 Pascal), and the wall temperature is constant at 800°C (1073°K)
Here are assumptions applied to this model:

* There is no radiation in the system, so only heat conduction and heat convection are considered.

* There is only laminar flow occurs inside the tube, even in the venturi part.

- **Problem Solving Procedure, instead of Algorithm**

  General 3-D simulation process was conducted, which includes:

  A. Create 3-D geometry;
  
  B. Mesh the surface; Mesh the volume, which will create grids and cells;

  All the work above were finished using GAMBIT®, while FLUENT® is used to finish the following steps:

  C. Check whatever the output from GAMBIT®, including the grids, elements, and cells, etc.;
  
  D. Scale the model to match the reality;
  
  E. Define the models for solver, energy, and viscous;
  
  F. Define the materials’ properties;
  
  G. Define the operation condition and the boundary condition;
  
  H. Set the solution control, the initial values, and the residuals;
  
  I. Iterate the equation to get the solution while monitor the residuals;
  
  J. Modify the model if needed, and
K. Plot the results as well as the summary of the operation condition.

- Conditions Setting

  The conditions set in the FLUENT®, such as models’ definition for solver, energy, and viscous; materials’ properties; operation condition and the boundary conditions; solution control, the initial values, and the residuals, etc., have been recorded, summarized and attached in the supporting document.

- Major Results

  The geometry of the model has been shown in Fig.3, however, due to the difficulty to build the model using cylindrical coordinates, especially the converge-diverge part of the venturi, a square geometry was built instead of the circular one. Besides, only one quarter of the whole domain is applied due to the symmetry. The geometry with and without mesh is illustrated in Figure A.1.5~7:

  ![Figure A.1.5 Geometry without Mesh, one quarter of the solution domain is built (left top), the surfaces on x-z plan and x-y planes are of symmetry (left bottom), the zoom-in area of venturi part has been simplified (right)](image)
Figure A.1.6 Geometry with Mesh, the interval size of the mesh for the volume is 10. One quarter of the solution domain is built (left top), the surfaces on x-z plane and x-y planes are of symmetry (left bottom), the zoom-in area of venturi part has been simplified (right).

Figure A.1.7 Geometry with Mesh, the interval size of the mesh for the volume is 20. One quarter of the solution domain is built (left top), the surfaces on x-z plane and x-y planes are of symmetry (left bottom), the zoom-in area of venturi part has been simplified (right).
The results of two different cell sizes are shown in the images marked from Figure A.1.8 ~ 15:

Figure A.1.8 Residuals in two simulation using different interval size: iteration converges slower in smaller cell size (left: interval size is 10) than in bigger cell size (right: interval size is 20).

Figure A.1.9 Residuals Comparison between the simulations with original boundary setting (left) and with the boundary setting which has been adapted (right).
Figure A.1.10 The Absolute Pressure distributions in two simulations with different interval sizes. (Zoom-in) Left: interval size is 10, and right: interval size is 20.

Figure A.1.11 The Absolute Pressure distributions in two simulations with different interval sizes. Left: interval size is 10, and right: interval size is 20.

Figure A.1.12 The velocity contours in two simulations with different interval sizes. (Zoom-in) Left: interval size is 10, and right: interval size is 20.
Figure A.1.13 The velocity contours in two simulations with different interval sizes. Left: interval size is 10, and right: interval size is 20.

Figure A.1.14 The Static Temperature contours in two simulations with different interval sizes (zoom-in). Left: interval size is 10, and right: interval size is 20.

Figure A.1.15 The Static Temperature contours in two simulations with different interval sizes. Left: interval size is 10, and right: interval size is 20.
Estimate of accuracy, Discussion and Conclusion

General speaking, there are differences between the simulation and experiment. Compared the temperature along the central line of the tube which I measured using K type thermocouple (OMEGA Engineering, INC), the temperature in the first section is around 50°C lower than the wall temperature, and the temperature in the third section is almost the same as the wall temperature. This measurement is conducted during such a circumstance when air is passing through the whole tube without extra gas adding to the venturi. However, the pressure distributions reveal the difference of the pressures between the inlet and the outlet. This result matches what I found by measuring the difference of the pressure using a pressure gauge. Normally it reads around 0.5psi (~3500 Pa) of the pressure loss at outlet referred to the inlet pressure. This value is almost the same as predicted by the simulation using the interval size number of 10. Since I have not measured the velocity of flow at the outlet, I am not able to make a judgment on how the simulations work on the prediction.

In view of converge, finer solution leads to longer iteration, which is shown in Figure A.1.8. What is more, finer solution also reveals more detail about how the distributions of temperature, velocity and pressure looks like, as can been seen in the left part of the images from Figure A.1.10~15. Other than the differences caused by the change of the grid size, the adaption function come with this software can help lead the iteration to converge more smoothly, which is already shown in Figure A.1.9.
Based on the laminar viscous model I chose as to simplify the solution, one can predict that the results should be some distance away it naturally should be. In order to improve my simulation, more complicated viscous model should be tried and the corresponding adjustments should be made. Furthermore, the geometry itself should be modified to the circular shape, adding two (or four) extra tubes at the venturi part, and a porous section should be used in order to simulate the actual experiment circumstance. Ultimately, phase transfer and combustion models should be utilized if I would like to achieve my goal of precise process control of material synthesis.

- Acknowledgements

First of all, I would like to thank Dr. Ahmet Umit COSKUN, who is not only a good lecturer of the CFD class, but also good leader who guides me to explore the magical power of simulation. I would also like to thank Parnian Boloorizadeh and Salih Saran, who helped me a lot for project discussion. Last but not least, I would like to thank Brendan Hall for his tutorial about using SOLIDWORKS®, and Reza Khatami for his assistance on operating GAMBIT® and FLUENT®.
• Supporting document

Conditions set for simulation in FLUENT®

Models

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Y-Coordinate of Point on Cone Axis (m)                    0
Z-Coordinate of Point on Cone Axis (m)                    0
Half Angle of Cone Relative to its Axis (deg)             0
Relative Velocity Resistance Formulation?                 yes
Direction-1 Viscous Resistance (1/m2)                     0
Direction-2 Viscous Resistance (1/m2)                     0
Direction-3 Viscous Resistance (1/m2)                     0
Choose alternative formulation for inertial resistance?   no
Direction-1 Inertial Resistance (1/m)                     0
Direction-2 Inertial Resistance (1/m)                     0
Direction-3 Inertial Resistance (1/m)                     0
C0 Coefficient for Power-Law                              0
C1 Coefficient for Power-Law                              0
Porosity                                                  1
Solid Material Name                                       fused-quartz

wall

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<tr>
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<td>X-component of shear stress (pascal)</td>
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**innersymmetry**

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**outflow**

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### inlet

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<td>Temperature (k)</td>
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is zone used in mixing-plane model? no

default-interior

<table>
<thead>
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<tbody>
<tr>
<td>Solver Controls</td>
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<tr>
<td>Equations</td>
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</table>
Equation Solved

-----------------
Flow      yes
Energy    yes

Numerics

Numeric     Enabled
-----------------------------
Absolute Velocity Formulation yes

Relaxation

Variable     Relaxation Factor
-------------------------------
Pressure     0.30000001
Density      1
Body Forces  1
Momentum     0.69999999
Energy       1

Linear Solver

Solver     Termination Residual Reduction
Variable     Type Criterion Tolerance
--------------------------------------------------------
Pressure     V-Cycle 0.1
X-Momentum   Flexible 0.1 0.7
Y-Momentum   Flexible 0.1 0.7
Z-Momentum   Flexible 0.1 0.7
Energy       Flexible 0.1 0.7

Pressure-Velocity Coupling
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**Discretization Scheme**

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<td>Energy</td>
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**Solution Limits**

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<td>Minimum Temperature</td>
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**Material Properties**

**Material: air (fluid)**

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<tr>
<td>Density</td>
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<td>constant</td>
<td>1.225</td>
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<tr>
<td>Cp (Specific Heat)</td>
<td>j/kg-k</td>
<td>constant</td>
<td>1006.43</td>
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<tr>
<td>Thermal Conductivity</td>
<td>w/m-k</td>
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<tr>
<td>Viscosity</td>
<td>kg/m-s</td>
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<tr>
<td>Molecular Weight</td>
<td>kg/kgmol</td>
<td>constant</td>
<td>28.966</td>
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</table>
L-J Characteristic Length  angstrom  constant  3.711
L-J Energy Parameter  k  constant  78.6
Thermal Expansion Coefficient  1/k  constant  0
Degrees of Freedom  constant  0
Speed of Sound  m/s  none  #f

Material: fused-quartz (solid)

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
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<th>Value(s)</th>
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Appendix 2

Mechanical Properties of Carbon Nanotubes

Chuanwei Zhuo

April 20, 2009

MTMG350 2009 Spring

by Prof. Yung Joon Jung
Carbon nanotube (CNT) is a type of materials which belongs to the fullerene, a family of carbon allotropes. This kind of carbon allotrope is featured by its $sp^2$ carbon-carbon bonds. For CNT’s structure, people can visually imagine it as a roll of sheet by wrapping up a layer (s) of graphene. The study of CNT’s structure predicts its unique advantages in mechanical strength.

The CNT has the diameter in the scales from 1nm to 100nm, while its length can achieve as long as centimeter. So it can be considered as one-dimensional material because of its high aspect ratio, which is the ratio of subject’s longer dimension to its shorter dimension. This character leads to the unique mechanical properties, which are among the best in both two fields: the Young’s modulus and the tensile strength. There are two factors determining the mechanical properties of a solid material: inter atomic forces and the spatial arrangement of atoms. In case of CNT, the spring constant $k$ of the carbon-carbon bond is around 300-1000 N·m$^{-1}$, and the interatomic distance $r$ is around 0.14 nm. Since the Young’s modulus is in direct proportion to the value of $k\cdot r^{-1}$, these two parameters determinate its unique properties intrinsically.

The experiment along with the theoretical calculation reveals that CNT’s Young’s modulus can be in the order of 1 terapascals (TPa). This value holds the clear advantage compared with that of stainless steel, which is around 0.2TPa. The tensile strength of CNT has been measured as higher as 63 gigapascals (GPa).This value is almost 50 times than that of stainless steel. In some field, such as aerospace application, people care more about the specific strength, which is defined as the force per unit area at failure. Attributed from the ultra low density of carbon, 1.3–1.4 g·m$^{-3}$, the specific strength of
CNT turns out to be around 47,000 kN·m·kg\(^{-1}\), probably the highest among the known materials.

There are four major experimental methods for Young’s modulus test: vibrations under transmission electron microscopy (TEM), electromechanical excitation under TEM and scanning electron microscopy (SEM), tensile loading test under SEM and atomic force microscope (AFM).

In the paper ‘Young’s modulus of single-walled nanotubes’, the authors first simplified the vibration profile to be that of a clamped cantilever, and they derived the following equation:

\[
\sigma^2 = 0.8486 \cdot \frac{L^2 \cdot k \cdot T}{Y \cdot W \cdot G \cdot (W^2 + G^2)} ,
\]

where \(\sigma\) is the rms displacement at the tip, \(L\) is tube length, \(k\) is constant, \(T\) is temperature, \(Y\) is Young’s modulus, \(W\) is the nanotube width, and \(G\) is the graphite interlayer spacing of 0.34 nm. By recording and measuring the displacement at each tube’s tip, the authors calculated that the averaged Young’s modulus for those CNT samples is \(Y=1.25+0.35/-0.45\) TPa. Actually, the image Inserted with each micrograph is the simulated one. They correspond to the best least-square fit for the adjusted length \(L\) and tip vibration amplitude \(\sigma\).

Figure A.2.1 TEM images of vibrating single-walled nanotubes, after A. Krishnan et al.[4]
The nanotube length, diameter $W$, tip amplitude and the estimated Young’s modulus $E$, are (a) $L = 36.8$ nm, $\sigma = 0.33$ nm, $W = 1.50$ nm, $E = 1.33 \pm 0.2$ TPa; (b) $L = 24.3$ nm, $\sigma = 0.18$ nm, $W = 1.52$ nm, $E = 1.20 \pm 0.2$ TPa; and (c) $L = 23.4$ nm, $\sigma = 50.30$ nm, $W = 1.12$ nm, $E = 1.02 \pm 0.3$ TPa.

For electromechanical excitation method, the Young’s modulus can be achieved after calculating the following equation:

$$v_j = \frac{\beta_j}{8 \pi} \cdot \frac{1}{l^2} \cdot \sqrt{(D^2 + D_i^2)} \cdot \frac{E_b}{\sqrt{\rho}}$$

where $D$ is the outer diameter, $D_i$ is the inner diameter, $E_b$ is the elastic modulus, $\rho$ is the density, and $b_j$ is a constant for the $j^{th}$ harmonic: $b_1 = 1.875$, $b_2 = 4.694$. Using that method, the authors conducted the experiments in terms of: 1) in the absence of a potential, 2) Resonant excitation of the fundamental mode of vibration ($n_1$ = 631 kHz), and 3) Resonant excitation of the second harmonic ($n_2$ = MHz). In the nanotube tip was 6.25 mm long and 14.5 nm in diameter. It was vibrated in the absence of a potential because of thermal effects. The same tube (in B) was then vibrated under the resonant excitation of the fundamental mode of vibration ($n_1$ = 530 kHz). The image in C shows the vibration of the tube under the resonant excitation of the second harmonic ($n_2$ = 3.01 MHz). For this nanotube, $E_b = 0.21$ TPa. The similar relationship between resonance frequency and Young’s modulus can also be observed in SEM. In the right part of Figure A.2.2, the MWCNT was vibrated at its fundamental resonance frequency (a) along with its second order harmonic (b), the Young’s modulus were in the range of 0.1 to 1TPa.
By using SEM, the Young’s Modulus can also be derived from the strain-stress curve in the tensile test. As shown in Figure A.2.3, the tensile-loading experiment can be conducted by first anchoring the both ends of CNT on the tips (left, A to D) and then pull the CNT via moving two tips apart (Right). After analyzing the curve, the Young’s Modulus was estimated to be varied from 270 to 950 GPa.

Figure A.2. 2 Nanotube response to resonant alternating applied potentials under TEM (left), and electric field induced resonance of an individual MWCNT under SEM (right). After Philippe Poncharal [5]
AFM can be used as a tool for the nano manipulation, which can create large curvature bends in MWCNTs (Figure A.2.4 Left, a to d), buckles and periodic ripples were observed. In the right section of the image, from e to h, it shows the height and curvature of the bent tubes along its centerline. These authors estimated that, based on the local curvature of the bend found, some MWCNTs could sustain up to 16% strain without obvious structural or mechanical failure.

Figure A.2.3 Tensile-loading experiment. After Min-Feng Yu [6]

Figure A.2.4 Curvature and height of buckles along a bent carbon nanotube. After M. R. Falvo [7]
REFERENCE:

1. Nicole Grobert, Materials today, Volume 10, Number 1-2, JAN-FEB 2007, ‘Carbon nanotube – becoming clean’;


Appendix 3

Calculation of Penetration Depth

Dimension of the venturi section:
\[ d_g = 8\text{mm}, \quad d_j = 2\text{mm}, \quad \Delta t = 30\text{s}, \quad Q_{N_2} = 5\text{lpm}, \quad Q_{O_2} = 1.33\text{lpm}, \quad m_{\text{HDPE}} = 0.75\text{g}, \quad \text{and} \quad [O_2] = 21\%. \]

\[ \rho_{N_2} = 1251\text{g/m}^3, \quad \rho_{O_2} = 1430\text{g/m}^3, \]

The penetration length, suggested by Lefebvre[1]:

\[ Y_{\text{max}} = 1.25 \cdot d_j \cdot J^{0.5} \cdot \left[ \frac{m_g}{m_g + m_j} \right], \] where

\[ J \] is the momentum flux, and

\[ J = \frac{\rho_{\text{g}} \cdot u_{\text{g}}^2}{\rho_{\text{j}} \cdot u_{\text{j}}^2}, \] where

\( g \) refers to the circular duct, and \( j \) refers to the round jet.

So,

\[ m_{g,N_2} = \frac{5 \times 28}{(60 \times 22.40)} = 0.104\text{g/s} \]

\[ m_{g,\text{HDPE}} = \frac{0.75}{30} = 0.025\text{g/s} \]

Hence,

\[ m_g = m_{g,N_2} + m_{g,\text{HDPE}} = 0.104 + 0.025 = 0.129\text{g/s}, \]

Besides,

\[ \frac{\rho_{N_2}}{\rho_g} = \frac{m_{N_2}/V}{m_g/V} = \frac{m_{N_2}}{m_g} = \frac{m_g}{m_g}, \]

therefore,

\[ \rho_g = \rho_{N_2} \cdot \frac{m_g}{m_g} \cdot 1251 \times \frac{0.129}{m_g \cdot 0.104} = 1552\text{g/m}^3, \]

Since \( \rho_{\text{HDPE}} \geq 0.941\text{g/cm}^3 \), set \( \rho_{\text{HDPE}} = 0.941\text{g/cm}^3 \) for simplicity,
\[ V_{\text{HDPE,vapor}} = \frac{0.75 \times 1000}{0.941} = 797 \text{ cm}^3, \] after expansion by one thousand times within thirty seconds.

Since \( d_g = 8 \text{ mm}, \ A_j = \pi r_g^2 = \pi \cdot \frac{d_g^2}{4} = \pi \cdot \frac{8^2}{4} = 50.27 \text{ mm}^2 \)

\[ U_g = U_{g,N_2} + U_{g,\text{HDPE (vapor)}} = \frac{5 \times 1000000}{1000 \times 50.27 \times 60} + \frac{797 \times 1000000}{1000000 \times 50.27 \times 30} = 1.65771501 + 0.528 = 2.186 \text{ m/s} \]

In terms of inject ports, for each single inject

\[ \dot{m}_j = \dot{m}_{O_2} = 1.33 \times 32 / (60 \times 22.40 \times 2) = 0.0158 \text{ g/s}, \]

\[ \rho_{O_2} = 1430 \text{ g/m}^3, \]

\[ d_j = 2 \text{ mm}, \ A_j = \pi r_j^2 = \pi \cdot \frac{d_j^2}{4} = \pi \cdot \frac{2^2}{4} = 3.14 \text{ mm}^2, \]

\[ U_j = U_{O_2} = \frac{1.33 \times 1000000}{1000 \times 3.14 \times 60 \times 2} = 3.53 \text{ m/s}, \]

So,

\[ J = \frac{\rho_j U_j^2}{\rho_g U_g^2} = \frac{1430 \times 3.53^2}{1552 \times 2.186^2} = 2.40, \]

\[ Y_{\text{max}} = 1.25 \cdot d_j \cdot j^{0.5} \cdot \sqrt{\frac{m_g}{m_g + m_j}} = 1.25 \times 0.002 \times 2.40^{0.5} \times \frac{0.129}{0.129 + 0.0158} = 0.0035 \text{ m} < 0.004 \text{ m}, \] which is the critical value of the central line.
If the vapor of HDPE was not taken into account, then

\[ m_g = m_{g,N_2} = 5 \times 28 / (60 \times 22.40) = 0.104 \text{g/s} \]

\[ U_g = U_{g,N_2} = 5 \times 10^3 / (1000 \times 50.27 \times 60) = 1.66 \text{m/s} \]

\[ U_f = U_{O_2} = 1.33 \times 10^3 / (1000 \times 3.14 \times 60 \times 2) = 3.53 \text{m/s} \]

So,

\[ J = \frac{\rho_f U_f^2}{\rho_g U_g^2} = \frac{1430 \times 3.53^2}{1552 \times 1.66^2} = 4.17 \]

\[ Y_{max} = 1.25 \cdot d_j \cdot f_{0.5} \cdot \sqrt[5]{\frac{m_g}{m_g + m_f}} = 1.25 \times 0.002 \times 4.17 \times \left( \frac{0.104}{0.104 + 0.0158} \right) \]

\[ = 0.0044 \text{m} > 0.004 \text{m}, \text{ which is the critical value of the central line.} \]

As listed in the table below, the penetration depths in the venturi section varied with the change of oxygen concentration.

<table>
<thead>
<tr>
<th>[O_2] (%)</th>
<th>( Q_{O_2} ) (lpm)</th>
<th>( Y_{max} ) With HDPE vapor</th>
<th>( Y_{max} ) Without HDPE vapor</th>
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</thead>
<tbody>
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<td>1.173</td>
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<tr>
<td>21%</td>
<td>1.329</td>
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<tr>
<td>23%</td>
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<td><strong>24%</strong></td>
<td><strong>1.579</strong></td>
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<td>25%</td>
<td>1.667</td>
<td>0.0042</td>
<td>0.0054</td>
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Reference:

Appendix 4

Effects of Heat Treatment on Stainless Steel

This is the primary study of an attempting looking for an alternative, inexpensive and sustainable catalyst for CNT synthesis. The results will eventual serve as the technical storage for large volume, well defined CNT production.

In case of CNT synthesis, catalyst works as a critical element. First, the size of catalyst will determine the type of CNT produced, such as multi-walled CNT or single-walled CNT[2]. Second, the type of catalyst will affect the morphology of CNT. Current preparations of catalyst include but not limit to physical vapor deposition (PVD)[3], dip coating[4], catalyst precursor solution followed by evaporation[5] and so on. Though they are successful for CNT synthesis in lab scale, all the popular methods are either high energy consumption or concentration sensitive.

Plain stainless steel, however, is an important material applied in construction, manufacture among others. It contains iron and nickel, both of which are acknowledged as catalysts for CNT growth. My previous research reveals that plain stainless steel as a compound could work as catalyst together as the substrate for CNT/CNF synthesis, compared with those with extra catalyst layers coated. It has mature manufacture technology, and is in commercial scale. It could work as a platform to enlarge the production of relatively inexpensive catalyst. The new problem comes out when the synthesis is finished and products have been removed from the surface of stainless steel, whether they could be reused without degradation, and whether its properties need recovery after every usage.
As the first step, study was conducted on the effects of heat treatment on the surface morphology of the stainless steel meshes. For this purpose, small screens (one square inch) of type 304 stainless steel (400 × 400 mesh with 0.002 cm diameter wire) were used as received. The surface of the meshes had been cleaned using acetone, and then dried under well-ventilated atmosphere.

Three types of treatments had been applied: extended heating durations at the same temperatures, various heating temperatures within same time, and the water solution as the additive.

For the experiment, each sample was inserted inside the hottest zone of the electric heating furnace under nitrogen, which works as inert gas. 750°C was chosen and three time spans were conducted: 6 minutes, 30 minutes, and 60 minutes. 900°C and 1050°C were also applied to bake the sample, and both lasted for 6 minutes. Besides, sample before heat treatment was dipped into purified water in such a way that there was a visible thin water film covered and surround the sample.

The SEM images of those samples together with the experimental description were listed below:

<table>
<thead>
<tr>
<th>Item Number</th>
<th>Temperature (°C)</th>
<th>Duration (min)</th>
<th>W/ water</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>750</td>
<td>6</td>
<td>No</td>
</tr>
<tr>
<td>1B</td>
<td>750</td>
<td>6</td>
<td>Yes</td>
</tr>
<tr>
<td>1C</td>
<td>750</td>
<td>30</td>
<td>No</td>
</tr>
<tr>
<td>1D</td>
<td>750</td>
<td>60</td>
<td>No</td>
</tr>
<tr>
<td>2A</td>
<td>900</td>
<td>6</td>
<td>No</td>
</tr>
<tr>
<td>3A</td>
<td>1050</td>
<td>6</td>
<td>No</td>
</tr>
<tr>
<td>3B</td>
<td>1050</td>
<td>6</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Results:

No evident CNT/CNF growth was observed after using any of these pretreated meshes. The surface of these treated meshes turned out to be with lots of crystallographic structures. In terms of morphology, these treated meshes looks similar whenever pre-immersion of water was applied in both low and high treating temperatures. The crystallization both enhanced with the larger dimensions when the treating temperatures increase and when the treating time increase. These are the primary studies about the metallography of catalysts, and more work needs to be done in this field.

![Figure A.4.1 Plain SS without treatment](image)

![Figure A.4.2 SS Heat treated at 750°C for 6mins](image)
Figure A.4.3 SS Heat treated at 750°C for 6mins, dipped inside the water before the treatment

Figure A.4.4 SS Heat treated at 750°C for 30mins

Figure A.4.5 SS Heat treated at 750°C for 60mins
Figure A.4.6 SS Heat treated at 900°C for 6mins

Figure A.4.7 SS Heat treated at 1050°C for 6mins

Figure A.4.8 SS Heat Treated at 1050°C for 6mins, dipped inside the water before the treatment