Flame synthesis of carbon-nanostructures

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FLAME SYNTHESIS OF CARBON-NANOSTRUCTURES

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science in Mechanical Engineering

in

The Department of Mechanical Engineering

by

Saritha Perla
B.E., Osmania University, 2002
December 2005
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LIST OF SYMBOLS AND ACRONYMS

a  Lattice constant for graphite
a₁, a₂  Unit vectors in two-dimensional hexagonal lattice
aₐ-c  Bond length between two carbon atoms
Cₖ  Chiral vector
dₜ  Diameter of the tube
D  Diffusivity
D₀  Outer diameter of the CNT/CNF
h  Height above the burner
L  Size of nanoparticle
m,n  Integers
r  Radial distance in a diffusion flame
t  Sampling time
T  Temperature
Tₐₚₜ  Ambient temperature
V  Volumetric flow rate
φ  Fuel equivalence ratio
θ  Chiral angle

Acronyms
BET  Brauner Emmet Teller
CNFs  Carbon Nanofibers
CNS  Carbon Nanostructures
CNTs  Carbon Nanotubes
CVD  Chemical vapor deposition
EDS  Electron Diffraction Spectroscopy
MWNT  Multi walled carbon nanotube
PAH  Poly nuclear aromatics
SWNT  Single wall carbon nanotube
SEM  Scanning electron microscopy
TEM  Transmission electron microscopy
ABSTRACT

Ever since their discovery carbon nanostructures (nanotubes and nanofibers) have attracted a lot of interest, due to their striking physical, chemical, mechanical and electrical properties, and paves the path to a wide range of applications. Large quantities of these structures are necessary to make their applications viable. The challenge is to produce them in bulk and in an economical way. Current methods like Arc discharge have the disadvantages of short tube lengths, CVD generated nanomaterials are often riddled with defects and although laser ablation method produces pure and high yield of nanotubes, is a costly technique with expensive lasers and high power equipment. Flame synthesis is one such technique, which meets the standards of commercial scalability. Also flame-generated particles are known for their low density and high surface areas, which are likely to enhance the adsorption properties of the materials.

In this study flame synthesis is selected as a tool, to study in detail the growth mechanisms of these structures with different catalyst materials, and to establish the conditions (fuel equivalence ratio, residence time, type of metal catalyst) for maximum yield of these nanostructures. Three catalysts, Stainless steel (Fe/Cr/Ni), Nickel (99.8% pure) and Monel (Ni/Cu/Fe) wires were used to grow the carbon nanotubes and nanofibers. All these carbon nanostructures were characterized using scanning and transmission electron microscopy.

The shape and size of carbon nanotubes and nanofibers produced was found to vary with the composition of catalyst material. TEM and SEM analysis shows that these carbon nanostructures are multiwalled nanotubes (MWNT’s) with diameter 27–40nm and nanofibers
with diameter 0.125 to 0.5 microns. It was found that vertically aligned nanostructures can be produced using premixed flames.
1. INTRODUCTION

1.1 Study Motivation

The study of Carbon Nanotubes on a great part is driven by its properties that make them both interesting and potentially useful. Nanotubes are extremely flexible, have an extremely high young’s modulus, and high aspect ratio, notable electrical properties ranging from metallic to semiconductors depending on their unique quantum mechanical structure, they have mechanical strength greater than steel and electrical conductivity as high as diamond. Because of these properties nanotubes are avidly sought for nanoelectronics, catalyst support media, gas adsorption media, electromechanical storage, reinforcing agents in composite materials and hydrogen storage media [6]. The latter applications require large quantities of carbon nanotubes. The challenge is to supply them in bulk at competitive prices to be economically feasible.

Current methods such as Chemical Vapor Deposition (CVD), laser ablation, arc discharge are energy intensive and batch processes and lack demonstrated scalability for the bulk synthesis. The basic ingredients for all these processes are a hydrocarbon gas and catalyst metal particles. All these approaches follow the principle of the generation of particles in the presence of the reactive hydrocarbon species at elevated temperatures.

Flame synthesis is a cost effective technique, which incorporates all the features of the above-mentioned approaches for carbon nanotube synthesis. Flame synthesis is easily scalable to industrial production. As first step towards the optimization of carbon nanotube synthesis a thorough study of the parameters influencing the nanotube growth in well-defined flame system is needed. With these motivations, flame synthesis of carbon nanotubes was
investigated. The scope, details and results of this investigation are presented in the sections that follow.

1.2 Research Objective

In the present work carbon nanotubes collected from a premixed propane/oxygen flame at different heights above the burner for different flow rates and fuel equivalence ratios are analyzed for their structure and properties. The main objective is to establish the optimized conditions for nanotubes synthesis by use of hydrocarbon fuels with different C/H ratio in the flame with different fuel/oxygen ratios. Also to establish whether temperature, residence time and fuel equivalence ratios have any effect on the structure of carbon nanotubes in terms of their diameter, length, relative surface density and graphitic structure. Different catalyst materials, Ni-gird, pure Ni, Monel (alloy of Ni/Cu/Fe) and Stainless steel wires were used as probes for nanotube synthesis. The specific objective was to three fold; to study the type of carbon nanotubes produced (SWNT or MWNT’s or Carbon nanofibers)

a) As a function of the flame parameters like fuel equivalence ratio, residence times and sampling times.

b) To identify the type of catalyst probe that can yield the maximum nanostructures yield and

c) To identify the prevailing mechanism for carbon nanostructures synthesis in this type of reactor.

Structural characterization of the nanotubes is accomplished through Transmission Electron Microscopy (TEM) of various samples collected at different heights above the burner. Electron Diffraction Spectroscopy (EDS) is used to determine the amount of carbon
and metal catalyst present. From the TEM images the type of nanotube growth mechanism is proposed.

The nanotubes so obtained are tested for their properties such as Surface area using BET, specific heat, using Differential Scanning Calorimeter (DSC) and absorbtivity of hydrogen using Thermo Gravimetric Analysis (TGA).

### 1.3 Methodology

The goal in this investigation is to study the variation of structure of carbon nanotubes in premixed flames in which properties vary according to one spatial variable only. The premixed flame is supported on a water-cooled, sintered metal burner. While details concerning experimental procedures are left as the subject of chapter three, a general description of the experimental methodology follows.

The samples are collected within the flame at different heights by the technique of thermophoresis, i.e., particle drift down a temperature gradient [9], which provides an effective way of collecting samples with minimum disturbance to the flame. This sampling procedure provides a “snapshot” look at the structure of nanotubes produced at different heights and fuel/air ratios by way of viewing them through a transmission electron microscope for which magnifications as high as 250 KX are possible.

### 1.4 Analysis Overview

The thesis consists of seven chapters. In chapter one, a brief introduction, motivation for the study and objective are described. In chapter two the significant contributions of eminent researchers is reviewed. Chapter three thoroughly describes the experimental facilities and procedures used in the present study. The data collected and analysis of the
results are presented in chapters four. Finally, the summary of results is presented in chapter five followed by recommendations for the work in chapter six.
2. LITERATURE SURVEY

The most relevant work performed to date on the synthesis of nanotubes is presented in this chapter. Emphasis is placed on the flame synthesis of carbon nanotubes.

2.1 Carbon Nanotube Structure

Carbon nanotubes are layers of graphite wrapped into cylinders of few nanometers in diameters, and approximately 10-20 microns in length. There are two main types of nanotubes Single wall nanotubes (SWNT) and Multi wall nanotubes (MWNT). Rolling a single graphite sheet into a cylinder forms SWNT. MWNT comprised of several nested cylinders with an inter layer spacing of approximately 0.34 to 0.36nm [1]. SWNT’s are usually closed at both ends by fullerene like half spheres that contain both hexagons and pentagons.

In order to understand the structure of a nanotube, let us consider the structure of graphite, which consists of a layer of carbon atoms arranged in a honeycomb structure. These honeycomb layers are stacked on top of each other. In graphite sp\(^2\) hybridization takes place where three sp\(^2\) orbitals are formed at 120\(^0\) to each other within a plane. The in plane bond called the sigma bond is a covalent bond that strongly binds the atoms in the plane. The pi bond is out of plane (perpendicular to the plane) and much weaker than the in plane bond.

A carbon nanotube is formed when a layer of graphite is wrapped with the edges joined. The structure of a nanotube can be defined by using a chiral vector. Three types of nanotubes are possible, called armchair, zigzag and chiral nanotubes, depending on how the two-dimensional graphene sheet is “rolled up”[2].
The different types are most easily explained in terms of the unit cell of a carbon nanotube in other words, the smallest group of atoms that defines its structure. The so-called chiral vector of the nanotube, $C_h$ shown in Fig. 1, is defined by $C_h = na_1 + ma_2$ where $a_1$ and $a_2$ are unit vectors in the two-dimensional hexagonal lattice, and $n$ and $m$ are integers [2]. Another important parameter is the chiral angle, which is the angle between $C_h$ and $a_1$.

When the graphene sheet is rolled up to form the cylindrical part of the nanotube, the ends of the chiral vector meet each other. The chiral vector thus forms the circumference of the nanotube’s circular cross-section, and different values of $n$ and $m$ lead to different nanotube structures. Armchair nanotubes Fig.2 are formed when $n=m$ and the chiral angle is $30^\circ$. Zigzag nanotubes are formed when either $n$ or $m$ is zero and the chiral angle is $30^\circ$. Zigzag nanotubes are formed when either $n$ or $m$ is zero and the chiral angle is $0^\circ$. All other nanotubes, with chiral angles intermediate between $0^\circ$ and $30^\circ$, are known as chiral nanotubes.

Note that for the hexagonal lattice a unit cell is made of two atoms. Also, $a_1$ and $a_2$ are defined as two vectors with $120^\circ$ openings [2]. With this definition in the figure $a_1$ and $a_2$ can be expressed using the Cartesian coordinate $(x, y)$ as shown in the Fig.2

$$a_1 = \left(\frac{3}{2}a_{cc}, \frac{\sqrt{3}}{2}a_{cc}\right)$$

$$a_2 = \left(\frac{3}{2}a_{cc}, -\frac{\sqrt{3}}{2}a_{cc}\right)$$

Here, $a_{cc}$ is the bond length between the carbon atoms. For graphite $a_{cc} = 1.421$ Å. This same value is often used for nanotubes. But, probably, $a_{cc} = 1.44$ Å is a better approximation for nanotubes. It should really depend on the curvature of the tube. A slightly larger value for more curvature is known. Since the length of $a_1$, $a_2$ are both are equal i.e.
Figure 1: A layer of graphene sheet showing the chiral vector [99]

Figure 2: Unit cell of graphite
\[ |a_1| = |a_2| = \sqrt{3}a_{cc} \equiv a \]

This ‘a’ is the lattice constant [2] Hence,

\[ a_1 = \left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right)a \]
\[ a_2 = \left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right)a \]

Length of the Chiral vector \( C_h \) is the peripheral length of the nanotube:

\[ C_h = \sqrt{3}a_{e-c} \sqrt{n^2 + nm + m^2} \]

For Armchair nanotube \((m = n)\):

\[ C_h = 3na_{e-c} \]

Further examples, for \((5,5)\):

\[ C_h = 15a_{e-c} \]

For \((10,10)\):

\[ C_h = 30a_{e-c} \]

For zigzag nanotubes \((m = 0)\):

\[ C_h = \sqrt{3}na_{e-c} \]

Further examples, for \((10,0)\):

\[ C_h = 10\sqrt{3}na_{e-c} \]

For \((16,0)\):

\[ C_h = 16\sqrt{3}a_{e-c} \]

Hence, the diameter of nanotube \( d_t \) is
\[ d_t = \frac{C_h}{\pi} = \frac{\sqrt{3} a_{c-c}}{\pi} \sqrt{n^2 + nm + m^2} \]

For armchair \((n=m)\):

\[ d_t = \frac{3n}{\pi} a_{c-c} \]

For zigzag \((m=0)\):

\[ d_t = \frac{\sqrt{3}n}{\pi} a_{c-c} \]

Also the chiral angle is given as:

\[ \theta = \sin^{-1} \left[ \frac{\sqrt{3} m}{2(n^2 + nm + m^2)} \right] \]

Figure 3: Armchair SWNT, Zig-Zag, Chiral nanotubes [2]
It turns out that the way in which the sheet is rolled up correlates to the electronic properties of the tube. Researchers quantify this by using the chiral vector to describe which overlaps with the starting hexagon. For example, if the image shown in Fig.4 is printed on a transparent page and the (0,0) hexagon overlaps with the (8,0) hexagon, the result would be a (8,0) SWNT [3].

Table 1: Comparison of Armchair, Zig-Zag and Chiral Nanotubes

<table>
<thead>
<tr>
<th>Armchair nanotubes</th>
<th>Zig-Zag nanotubes</th>
<th>Chiral nanotubes</th>
</tr>
</thead>
<tbody>
<tr>
<td>It is called so based on the shape of the cross-sectional ring, which can be visualized like a chair with side structures to support the arms or elbows shape of an armchair.</td>
<td>In this case the cross-sectional ring is zig-zag in shape.</td>
<td>These exhibit spiral symmetry.</td>
</tr>
<tr>
<td>Mirror image of the structure has an identical structure with the original one [2].</td>
<td>Mirror image of the structure has an identical structure with the original one [2]</td>
<td>Because of the spiral symmetry mirror image cannot be superposed on to the original one [2].</td>
</tr>
<tr>
<td>Always metallic in nature [2].</td>
<td>Metallic only when ( n ) is a multiple of 3 [2].</td>
<td>Chiral nanotubes are mostly semiconductors [2].</td>
</tr>
</tbody>
</table>
Figure 4: Possible vectors specified by the pairs of integers \((n, m)\) for general carbon nanotubes, including armchair, zigzag, and chiral. The hollow denote metallic tubules while the small dots are for semi conducting tubules \([4,3]\).
2.2 Properties and Applications of Carbon Nanotubes

Nanotubes possess many fundamental properties that make them interesting and potentially useful as shown in the following Table 2.

Table 2: Properties and Applications of Nanotubes

<table>
<thead>
<tr>
<th>Properties</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mechanical Properties</strong></td>
<td></td>
</tr>
<tr>
<td>High Young’s Modulus (1500-5000 GPa), high flexibility and expansion by charge injection</td>
<td>As reinforcements in composites, atomic force microprobe tips, space and aircraft body parts.</td>
</tr>
<tr>
<td><strong>Electrical Properties</strong></td>
<td></td>
</tr>
<tr>
<td>Nanotubes have metallic or semiconductor behavior based on the chirality of the tubes. Easy tunable field emission.</td>
<td>Conductive Plastics, electronic nanocomponents (diodes, transistors etc). Electron gun, Field emission display etc.</td>
</tr>
<tr>
<td><strong>Physical and Chemical Properties</strong></td>
<td></td>
</tr>
<tr>
<td>High surface area (&gt;1000 m$^2$/g). High porosity enabling the storage of molecules in the tubes.</td>
<td>Hydrogen storage media for fuel cell applications. Batteries with improved life.</td>
</tr>
</tbody>
</table>

Out of these applications our interest is on the applications of carbon nanotubes as a primary source of hydrogen storage media for fuel cells. Because of their high surface area to weight ratio these can be seen as ideal candidate for hydrogen storage.
2.3 Synthesis Methods for Carbon Nanotubes

The first tubular structures were discovered in 1991 by the Japanese electron microscopist Sumio Iijima who was studying the material deposited on the cathode during the arc evaporation synthesis of fullerenes. Moreover, under certain conditions these tubes sealed themselves by joining with the two halves of a split bucky ball as end caps. A short time later, Thomas Ebbesen and Pulickel Ajayan, from Iijima's lab, showed how nanotubes could be produced in bulk quantities by varying the arc evaporation conditions.

The predominant methods of nanotube synthesis are:

1. Arc discharge
2. Laser ablation
3. Chemical vapor deposition, and
4. Flame synthesis

A brief description of the first three methods is given in the following paragraphs, whereas flame synthesis is discussed in detail.

2.3.1 Arc Discharge

This method creates nanotubes through arc-vaporisation of two carbon rods placed end to end as shown in Fig.4, separated by approximately 1mm, in an enclosure that is usually filled with inert gas (helium, argon) at low pressure (between 50 and 700 mbar). A direct current of 50 to 100 A driven by approximately 20 V creates a high temperature discharge between the two electrodes [9]. The discharge vaporizes one of the carbon rods and forms a small rod shaped deposit on the other rod. Producing nanotubes in high yield depends on the uniformity of the plasma arc and the temperature of the deposit form on the carbon electrode [8].
Carbon nanotubes synthesized by arc discharge see Fig.5 normally have multiwalled nanotubes. If holes are bored in the graphite rods and then filled with appropriately proportional composites of graphite powder and catalytic Co, Fe or Ni powder, SWNT’s can be produced [9].

Nanotubes produced by this process are covered with a large amount of carbon deposits or carbon particles and partially exposed. In order to study basic properties, structure and applications of carbon nanotubes, they should be purified [9].

Figure 5: Schematic diagram of Arc discharge apparatus [9]

Figure 6: SEM images of MWNT’s produced by arc discharge (Kunsan National Univ)
2.3.2 Laser Ablation

In 1995, Smalley's group at Rice University reported the synthesis of carbon nanotubes by laser vaporization. The laser vaporization apparatus used by Smalley’s group is shown in Fig.6. A laser is used to vaporize a graphite target in an oven at a temperature of 1200°C [9]. Then Helium or Argon gas is added to keep the pressure in the oven at 500 Torr. Carbon clusters from the graphite target are cooled, adsorbed, and condensed on the Cu sheet collector at a low temperature. The condensates obtained this way are mixed with carbon nanotubes and nanoparticles. MWNT would be synthesized in the case of pure graphite, but uniform SWNT could be synthesized if a graphite of a mixture of Co, Ni, Fe, and Y were used instead of a pure graphite [9]. SWNT’s synthesized this way exist as 'ropes'. Fig. 7(a) and (b) show a SEM and a TEM image synthesized by Smalley's group using laser-vaporization. It is found from the SEM image that carbon nanotubes had curved shapes and carbon particles were stuck on the surface of the nanotubes [9]. The structures and forms of graphene sheets are stable and clean, but carbon particles are stuck on the surface. The TEM image showing a cross-section of a carbon nanotube reveals that several SWNT’s are clustered and typical 'ropes' shapes as mentioned before. Laser vaporization is higher in yield than arc-discharge and can yield high quality SWNT’s [9].

2.3.3 Chemical Vapor Deposition

Chemical vapor deposition (CVD) synthesis is achieved by placing a carbon source in the gas phase and using an energy source, such as plasma or a resistively heated coil, to transfer energy to a gaseous carbon molecule [9]. Commonly used gaseous carbon sources include methane, carbon monoxide and acetylene.
Figure 7: Schematic diagram of the laser vaporization apparatus for CNT synthesis [9]

Figure 8: SEM and TEM image of ropes of SWNT synthesized by laser ablation [9]
The energy source is used to “crack” the molecule into reactive atomic carbon [9]. Then, the carbon diffuses towards the substrate, which is heated and coated with a catalyst (usually a first row transition metal such as Ni, Fe or Co) where it will bind. Carbon nanotubes will be formed if the proper parameters are maintained [9]. Excellent alignment [11], as well as positional control on nanometer scale [12], can be achieved by using CVD. Control over the diameter, as well as the growth rate of the nanotubes can also be maintained. The appropriate metal catalyst can preferentially grow single rather than multi-walled nanotubes [13].

CVD carbon nanotube synthesis is essentially a two-step process consisting of a catalyst preparation step followed by the actual synthesis of the nanotube [9]. The catalyst is generally prepared by sputtering a transition metal onto a substrate and then using either chemical etching or thermal annealing to induce catalyst particle nucleation. Thermal annealing results in cluster formation on the substrate, from which the nanotubes will grow. The temperatures for the synthesis of nanotubes by CVD are generally within the 650-900 °C range [11,12,14,and15]. Typical yields for CVD are approximately 30%. These are the basic principles of the CVD process. In the last decennia (1991-2001), different techniques for the carbon nanotubes synthesis with CVD have been developed, such as plasma enhanced CVD, thermal chemical CVD, and alcohol catalytic CVD, vapor phase growth, aero gel-supported CVD, laser assisted CVD, CoMoCat process and high pressure CO disproportionation process.

**Plasma Enhanced CVD:** The plasma method generates glow discharge in a chamber or a reaction furnace by a high frequency applied to both electrodes. A substrate is placed on the grounded electrode. In order to form a uniform film, the reaction gas is supplied from the opposite plate. C₂H₂, CH₄, C₂H₄, C₂H₆, CO gases are typically used to synthesize carbon
nanotubes. The deposited metal on substrate can be etched using ammonia or H\textsubscript{2} gas. After nanoscopic fine metal particles are formed, carbon nanotubes are grown on the metal particles on the substrate by glow discharge generated from high frequency power.

**Thermal Chemical CVD:** The synthesis method of carbon nanotubes using thermal chemical vapor deposition is as follows. Fe, Ni, Co, or alloy of the three catalytic metals is initially deposited on a substrate. After the substrate is etched in diluted HF solution with distilled water, the specimen is placed in a quartz boat. The boat is positioned in a CVD reaction furnace, and nano-size fine catalytic metal particles are formed after an additional etching of the catalytic metal film using NH\textsubscript{3} gas at a temperature in 750 to 1050 °C. Carbon nanotubes are grown on these fine catalytic metal particles in CVD synthesis.

**Vapor Phase Growth:** Vapor phase growth is a synthesis method of carbon nanotubes, directly supplying reaction gas and catalytic metal in the chamber without a substrate [9,101]. Fig.8 shows a schematic diagram of a vapor phase growth apparatus. Two furnaces are placed in the reaction chamber. Ferrocene is used as catalyst. In the first furnace, vaporisation of catalytic carbon is maintained at a relatively low temperature. Fine catalytic particles are formed and when they reach the second furnace, decomposed carbons are absorbed and diffused to the catalytic metal particles. Here, they are synthesized as carbon nanotubes. The diameter of the carbon nanotubes by using vapor phase growth are in the range of 2 – 4 nm for SWNTs40 and between 70 and 100 nm for MWNTs [9,101].

**Aero Gel Supported CVD:** In this method SWNTs are synthesised by disintegration of carbon monoxide on an aero gel-supported Fe/Mo catalyst.

**Laser Assisted CVD:** In laser-assisted thermal CVD (LCVD) a medium power, continuous wave CO\textsubscript{2} laser, which was perpendicularly directed onto a substrate, pyrolyses sensitized
mixtures of Fe(CO)$_5$ vapor and acetylene in a flow reactor. The carbon nanotubes are formed by the catalyzing action of the very small iron particles.

**CoMoCat Process**: In this process SWNTs are grown by disproportionation of CO on a Co-Mo catalyst at about 700-950 °C.

**High Pressure CO Disproportionation Process**: In this process SWNTs are produced by continuous flowing of CO, mixed with a small amount of Fe(CO)$_5$ through a heated reactor.

### 2.3.4. Flame Synthesis

A fuel-rich flame is a high-temperature carbon-rich environment that can be suitable for nanotube formation if transition metals like (Fe, Ni) are introduced into the system. As such, flame synthesis is a continuous-flow, scalable method with potential for considerably lower cost nanotube production than is available from other methods.

The earliest observation of intriguing tube like structures in flames was reported by Singer [16] in the 1950’s and within the last decade from 1990’s there have been occasional reports on nanotube structures [17-22].
2.3.4.1. Diffusion Flames

Saito et al. [20, 23] immersed metallic substrates in methane and ethylene fueled co-flow diffusion flames and observed multi-walled carbon nanotubes that had formed on the substrate [24]. Vander Wal and coworkers have observed single-walled nanotubes in a hydrocarbon (acetylene or ethylene)/air diffusion flame with nitrogen diluent and metallocene catalyst precursor compound added to the fuel stream [22]. Merchan-Merchan et al. [21] observed multi-walled carbon nanotubes in an opposed-flow methane diffusion flame without the additions of metallic catalyst.

2.3.4.2. Premixed and Hybrid Flames

An extensive amount of research related to the formation of fullerenes and fullerenic nanostructures in flames has been reported in the last decade [24, 25-30]. In particular, there have been two studies in a group at MIT where carbon nanotubes have been observed in condensed material collected from flames [24,25,26]. In these studies, Howard and coworkers employed a premixed flame configuration operated at low pressure (20-97 torr), and burner gas velocity between 25 and 50cm/s. a variety of fuel and fuel/oxygen compositions (C/O ratios) were explored including acetylene (C/O 1.06, $\phi =2.65$), benzene (C/O 0.86-1.00, $\phi =2.15-2.65$) and ethylene (C/O 1.07, $\phi =3.21$) and diluent concentrations between 0% and 44 mol%. Here the equivalence ratio ($\phi$) is defined as the actual fuel/oxygen ratio divided by the stoichiometric fuel/oxygen ratio corresponding to conversion of all carbon to CO$_2$ and all hydrogen to H$_2$O. These flames are all considered ‘sooting’ flames as they spontaneously generate condensed carbon in the form of soot agglomerates suspended in the flame gases. Similarly, Duan et al. [18], Grieco [29] and Richter et al. [19] reported producing nanotubes in flames under sooting conditions. Samples of condensed
material were obtained directly from the flame using a water-cooled gas extraction probe (between 2 and 7 cm above burner), and also from the water-cooled surfaces of the burner chamber [24]. Nanostructures were also extracted from the collected soot material by sonification of soot material dispersed in toluene. High-resolution electron microscopy of the extracted material allowed visual analysis of the fullerenic nanostructures, including spherical, spheroidal, tubular and triangular structures, typically composed of multiple, graphitic carbon planes [24]. Multiwalled nanotubes were also observed, typically with more than five concentric walls of monatomic carbon thickness. Also Murray and Howard [24] synthesized single-wall nanotubes with a premixed acetylene/oxygen/argon flame with argon dilution of 15 molar percent, cold gas feed velocity of 30 cm/s, and a burner pressure of 6.7 KPa (50 Torr) and used Fe(CO)$_5$ as the source of metallic catalyst. Typical Fe(CO)$_5$ concentration were 6000±500 ppm (molar).

In 2000, Diener et al. [31] reported the synthesis of single-walled carbon nanotubes in sooting flames. A partially mixed flame configuration was used with fuel gases (acetylene, ethylene or benzene) issued through a sintered-metal plate through which oxygen flows, drafting past the fuel tubes. Iron and nickel bis (cyclopentadiene) compounds were vaporized and included in the flame feed as a metal catalyst precursor. Single-walled nanotubes were observed in acetylene and ethylene flames (over equivalence ranges of 1.7-3.8) while multi-walled nanotubes were observed in benzene flames (over equivalence ratios of 1.7-3.4).

Diener and coworkers did not report the level of dilution with argon, the concentration of metal species added to the flame, or the inlet velocity for the feed gas mixture-all of which are parameters influencing nanotube formation in flames [24]. Diener et al. emphasized the use of sooting flames for the synthesis of their materials in an analogous
approach to that reported earlier by Howard et al. [25-27], Richter et al. [19], and Duan et al [18]. The reported range of equivalence ratios are stated as 1.7-3.8, which is very much focused on exploiting sooting conditions. Furthermore, the quantities of nanotubes observed in the condensed material are a very small percentage (<1%) of the condensed material [24].

Vander Wal and coworkers have made extensive use of an annular burner configuration consisting of a 50mm diameter sintered metal plate with a central tube of 11mm diameter that is mounted flush with the surface of the burner plate [32]. For most experiments Vander Wal established a fuel-rich premixed flame supported on the outer annular section of a burner plate while reactant gas mixture, including metal catalyst species of interest were fed through a central tube [24]. This configuration is termed a ‘pyrolysis flame’ in the papers as the central gas flow does not undergo combustion due to lack of oxygen in this low, but reactions (and nanotube formation) do proceed in the flow by virtue of the heating influence of the surrounding annular flame [24]. The central gas flow is in effect a reactive streamtube rather than a flame. A stabilizing chimney (7.5x2.5cm diameter) immersed vertically in the flame gases provides a stabilizing effect and nanotube (single-wall nanotubes, multi-wall nanotubes and nanofiber) samples are collected at the exit of the chimney. There are some important distinctions to note regarding this configuration. The outer (annular) flame is primarily a source of heat and the central gas mixture flow is the primary source of carbon and metallic catalyst. Combustion is not supported in the central gas flow. Therefore, heating and material synthesis processes are substantially separated functions [24].

Vander Wal and Ticich [33,34] explored a wide variety of methods to introduce metallic catalyst species to the system and performed comparative experiments, synthesizing
nanotubes in both the ‘pyrolysis flame’ and tube reactor setups. The premixed flame in the outer annulus used acetylene/air mixtures of equivalence ratios between 1.4 and 1.62. The reactant gas mixtures used in this instance consisted of either carbon monoxide/hydrogen or acetylene/hydrogen mixtures, and iron or nickel nanoparticles were entrained in the central feed gases [24]. In an analogous study [34], Vander Wal and Ticich used a carbon monoxide/hydrogen reactant feed mixture and used a nebulized solution of iron colloid (ferrofluid) and a spray drying technique as the source of catalyst particles. Nanotube samples were collected once again at the exit of the chimney [34]. Single-walled nanotubes were observed in a similar flame setup where Vander Wal and Hall introduced metallocene (ferrocene and nickelocene) vapor to the central reactive feed gases using a controlled sublimation technique [35]. Vander Wal observed single-walled nanotubes in an identical flame arrangement using a nebulizer system to introduce iron nitrate salt solution to the flame as the catalyst particle precursor [35]. Vander Wal also reports the formation of nanofibers (similar to multi-walled nanotubes except the walls tend to be irregular and non-graphitic) in an identical flame configuration with nickel nitrate solution nebulized into the flame [36].

Another variation of the catalyst feed technique with this burner configuration is reported by burning a piece of paper coated in metal particles and the resulting aerosol entrained in a fuel-rich mixture of carbon monoxide, hydrogen and air [24]. The resulting gas mixture is fed to the central tube of an annular fuel rich acetylene air flame and in this instance the central gas flow does in fact lead to a premixed flame (as opposed to a pyrolysis reaction streamtube in previous experiments) where the premixed flame composition is carbon monoxide, hydrogen and air with entrained iron nanoparticles [24]. Single-wall nanotubes were once again collected at the exhaust of the stabilizing chimney [37].
Vander Wal and co-workers have also synthesized multi-walled nanotubes and nanotubes and nonofibers on cobalt nanoparticles supported on a metal substrate immersed in premixed flames of various hydrocarbon fuels and equivalence ratios [38,39]. This configuration is truly a premixed flame and all three functions necessary for nanotube synthesis (heat source, carbon source, and metal catalyst) are present in the same flame environment, and in this instance the catalyst particles are supported on an externally affixed substrate immersed in the flame gases.

2.3.4.3. Other Flame Studies

There have been a number of combustion studies that did not observe the formation of carbon nanotube material for the both premixed and diffusion flames using the hydrocarbon mentioned in the above studies. Rumminger and Linteris [40,41] introduced a vapor of iron pentacarbonyl into premixed flames of methane/air and also carbon monoxide/hydrogen/air. The focus of their studies was on flame inhibition due to the presence of iron pentacarbonyl. No nanotube material was reported, most likely a result of low equivalence ratio employed in the studies. Feitelberg and coworkers [42] also injected metal compounds into the premixed flames in order to examine the effect upon soot formation in fuel rich flames. Nanotube-like material was not observed, most likely because the equivalence ratios they employed were too high. Janzen and Roth [43] examined the formation of iron oxide particles in premixed hydrogen/oxygen/argon flame injected with iron pentacarbonyl and did not observe any nanotube formation. Zhang and Charalampopoulos [44] have conducted experiments on formation of chain like aggregates in a CO-air diffusion flame seeded with iron pentacarbonyl, with their emphasis on the composition of aggregates and their morphological parameters.
With these merits of flame synthesis of carbon nanostructures over other methods, it was selected as a tool in this investigation to produced carbon nanostructures. The experimental methods used in this study are discussed in the following chapter.
3. EXPERIMENTAL SET-UP

In this chapter the information on the experimental facilities used in this study are discussed. A description of the burner system used to produce the premixed flat flames, followed by the type of sampling system used to collect the samples from the flame is presented.

3.1 Burner System

In this thesis the structural variation of nanotubes produced in premixed flames varying according to one spatial variable is studied. The advantages of premixed flames over diffusion flames are given below. Hence the burner that supports the flame must be designed in such a way that the requirement of one-dimensionality is strictly met. In addition, a precise translation mechanism of the burner is desired for accurate sampling at different heights within the flame. Both of these requirements were met by the set-up used in this investigation and are discussed in detail in the next two sections. In this study the burner used was the same as one previously used by Munoz [98].

3.1.1 Flat Flame Burner

Flat flame burners are known for their one-dimensional flame in which a planar and stationary reaction zone is formed near the burner surface. This design allows for subsequent movement of the combustion products away from the reaction zone, as an undisturbed column of gas. The use of porous sintered metals to attain the flat flame features has proven successful in the past [94] and the same is used in this study. The burner used is shown schematically in Figure 9. A stainless chamber encases a sintered bronze plug (60 mm diameter) through which the premixed gases (fuel plus oxygen) flow.
Table 3: Premixed Vs Diffusion Flames

<table>
<thead>
<tr>
<th><strong>Premixed flames</strong></th>
<th><strong>Diffusion flames</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Premixed nature of the fuel and air promotes rapid combustion, with a short,</td>
<td>As the flame length is inversely proportional to the stoichiometric fuel mass fraction, i.e. only fuels, which require less air for complete combustion, produce shorter flames, hence limiting the use of fuels.</td>
</tr>
<tr>
<td>easily controlled flame for laboratory purposes facilitating use of wide variety</td>
<td></td>
</tr>
<tr>
<td>of fuels.</td>
<td></td>
</tr>
<tr>
<td>2. Easily adjustable stoichiometry of the reacting gases and hence the flame</td>
<td>Chemistry of diffusion flames cannot be described by a single equivalence ratio.</td>
</tr>
<tr>
<td>chemical compositions.</td>
<td></td>
</tr>
<tr>
<td>3. Dilution of the premixed gases with an inert gas is not required, as the soot</td>
<td>Dilution of fuel stream with inert gas is critical to nanotube synthesis as absence of inert gas resulted in soot formation and the complete encapsulation of the metal nanoparticles with no nanotubes [104].</td>
</tr>
<tr>
<td>produced in premixed flames is less when compared to diffusion flames.</td>
<td></td>
</tr>
<tr>
<td>4. They are not diffusion limited hence the reactive gas profile can be made</td>
<td>Mixing of gases is limited to diffusion.</td>
</tr>
<tr>
<td>uniform by the burner system [38].</td>
<td></td>
</tr>
<tr>
<td>5. Less safe as there is scope for detonation.</td>
<td>No such problem</td>
</tr>
<tr>
<td>6. Premixed flames sustain the growth of particles on a wide range of conditions</td>
<td>Diffusion flames are less flexible, but allow a faster growth and a better control on the final product as the particles can be removed from the fuel side of the flame, thus preventing undesired oxidation with air [121].</td>
</tr>
<tr>
<td>(fuel, stoichiometry, temperature) producing a wide variety of particles.</td>
<td></td>
</tr>
</tbody>
</table>
In order to prevent any flashbacks and to preserve its integrity, the plug is embedded with copper tubing (three passes) through which cooling water circulates. In addition, the steel casing also houses an annular bronze plug where an inert gas (nitrogen) is passed to prevent entrainment of outside air into the flame. At steady state conditions, the premixed gas stream flows through the pores of the plug and out to the surface of the burner where combustion takes place. To safely start the flame, a low fuel-only flow is ignited by a spark and oxidation is allowed to occur by diffusion of surrounding air. Afterwards, the oxygen supply is opened and both gases (fuel and oxygen) are adjusted to the desired fuel equivalence ratio. The process is completed by forcing the nitrogen flow through the annular region and thus, forming a shroud, which prevents entrainment of the surrounding room air.

The gases used in these experiments were ultra high purity grade and were directed to the burner by a series of needle valves and interconnected Teflon and metallic tubing. Prior to mixing, the flow rates of fuel (i.e. propane) and oxygen were monitored by standard Matheson rotameter (Model number-FM-1050). The nitrogen shroud flow rate was monitored by a standard rotameter (Brooks 1110-06F1D1A) and was adjusted to a maximum flow such that no disturbance to the flame profile was observed.

The cold premixed gas velocity of 3cm/sec was chosen for this study. Once the velocity was set, all the flow variables in the system were fixed by choosing a fuel equivalence ratio, $\phi$ which is defined as [95]:

$$\phi = \frac{\left(\frac{\text{moles fuel}}{\text{moles oxygen}}\right)_{\text{actual}}}{\left(\frac{\text{moles fuel}}{\text{moles oxygen}}\right)_{\text{stoichiometric}}}$$ (1)
Figure 10: Flat flame burner [96]
By varying the fuel equivalence ratio, a range of conditions can be tested to assess the evaluation of flame properties on premixed-gas composition. Table 3 gives the details of the flame settings used in this study. Finally, in order to stabilize the rate of efflux of combustion products, the burner set-up also included a ceramic grid (honeycomb) placed at approximately 25mm above the plug surface.

### Table 4: Flow Rates of Fuel and Oxygen at Desired Equivalence Ratios

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>( \phi )</th>
<th>Flow rate Oxygen (SLPM)</th>
<th>Flow rate Fuel (SLPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_3)H(_8)</td>
<td>1.8</td>
<td>3.45</td>
<td>1.21</td>
</tr>
<tr>
<td>C(_3)H(_8)</td>
<td>1.9</td>
<td>3.4</td>
<td>1.26</td>
</tr>
<tr>
<td>C(_3)H(_8)</td>
<td>2.0</td>
<td>3.35</td>
<td>1.31</td>
</tr>
<tr>
<td>C(_3)H(_8)</td>
<td>2.1</td>
<td>3.31</td>
<td>1.35</td>
</tr>
</tbody>
</table>

### 3.1.2. Burner Positioning

In this study the probes were fixed in position and a translation mechanism in the burner system allowed for spatially varied sampling in the axial direction of the flame as shown in fig 12. The translation mechanism consists of a number of gears that provide swift adjustment of a lead screw connected to the base of the burner. The gears are driven by a 1/50 horsepower electric motor. Burner displacement is measured by detection of infrared light pulses passing through equidistant holes located around the circumference of a disk attached to the bottom output, the electric motor drives a pair of spur gears. When driven by those gears, the screw causes rotation of the disk which is sandwiched between the infrared emitter and a protodetector; thus, creating a pulse with the passing of each hole. The pulses
are then recognized by a digital counter that registers 10 pulses per millimeter of vertical burner movement [98].

3.2. Sampling System

The sampling system used in this study is a simple bar sliding mechanism on which the required wires or probes were mounted as shown in Fig.11. The collected material on the wires was then scraped into a glass vial and taken for SEM and TEM analysis.

3.3. Experimental Procedure for Synthesis of Carbon Nanostructures

A premixed flame of propane-oxygen with a total flow rate of 4.66SLPM was set up on a porous plug burner described above. The Ni grid, Ni & Monel and Stainless steel wires, which acted as the catalyst material, were exposed for <1min, 10min and 15min respectively for enough material to be deposited. The collected samples were imaged using SEM for composition and micro structural characterization.

3.4. Composition and Microstructural Characterization

3.4.1. TEM

High resolution (HR) Transmission Electron Microscope (TEM) analysis of the deposited carbon material was performed on a JEOL JEM 2010 electron microscope operated at 200 KeV with a point-to-point resolution of 2.3 Å. TEM samples were prepared by dispersion of the carbon material in alcohol and drops of dispersed material were placed on copper TEM grids and dried for TEM analysis.
Figure 11: (a) Temperature profile (b) Schematic of the burner and sampling system.
3.4.2. SEM

The surface morphology and composition of the deposited material was studied using a Hitachi S-3600N Scanning Electron Microscope (SEM), equipped with an Energy Dispersive Spectroscopy (EDS) detector.

Thus obtained results are discussed in the next chapter.
4. RESULTS AND DISCUSSION

The material deposited on Nickel grid (3mm), Stainless steel wire (0.68mm dia), pure Ni-99.8% (1.0mm dia) and Monel (Ni/Cu/Fe) (2.5mm dia) probes (wires) were imaged using SEM, to characterize the structure and morphology of the CNT’s. The material deposited on the nickel grid was negligible. Thus, in order to increase the yield of CNTs the amount of catalyst supplied and the sampling times had to be increased, so our choice was to use Nickel, Monel and Steel wires extensively in order to collect sufficient amount of material for further analysis.

4.1. Effect of Catalyst Composition and Local Flame Conditions on the Morphology

In this investigation the effect of catalyst particles on the CNT morphology with different residence and sampling times and with increasing $\phi$ along the flame centerline was studied.

4.1.1. Catalyst and CNT Morphology

As shown in Fig 12 MWNTs are grown on Ni-grid when exposed to the flame for less than a minute. Nickel and Monel (Ni/Cu/Fe) wires produced helical, spiral and zig-zag nanotubes as shown in Fig 13 (a) and (b) respectively.

Steel wire enabled the growth of straight and aligned nanotubes as shown in Fig 14. The white dots observed at the tip of the tubes in the SEM images are the catalyst particles. With Steel as catalyst material a layer of catalyst particles are seen at the tip of the compact bundle of tubes as shown in Fig 14.
Figure 12: TEM images of MWNTs grown on Ni-grid at $\phi = 1.9$, $t = <1 \text{min}$, $h = 15 \text{mm}$.
Figure 13: (a) SEM images of Helical and spiral nanotubes with Ni-wire, $\phi = 1.9$, $t = 10$ min, $h = 15$ mm. (b) Spiral nanotubes with Monel-wire $\phi = 1.9$, $t = 10$ min, $h = 15$ mm
Figure 14: SEM image of aligned nanofibers on Steel wire for $\phi = 1.9, t = 15\text{min}, h = 15\text{mm}$
4.1.2. Variation of CNT Morphology with Different Residence Times

There were no filamental structures found on the Nickel, Monel and steel wires at a height of 5mm above the burner for $\phi=1.9$. The temperature at this location was measured to be 1382K, with an S-type thermocouple. With melting point temperatures of Steel and Ni wires being $\sim1420^°$K and $1726^°$K respectively, enough catalytic particles are generated but probably insufficient precursors would not have facilitated the growth of the nanostructures.

At 10mm height above the burner with Steel as a catalyst material produced long and entangled nanofibers as shown in Fig15 &16. At 15mm height above the burner-aligned nanotubes of short lengths are seen as in Fig 17, at 20mm height above the burner bundles of straight nanotubes are present as shown in Fig 18. The temperatures at these locations are measured to be 1240 K (at 15mm) and 1197 K (20mm) respectively.

Figure 15: SEM images of Nanofibers with Steel wire for $\phi=1.9$, $t=15$min, $h=10$mm.
Figure 16: SEM images of Nanofibers with Steel- wire for $\phi=1.9$, $t=15\text{min}$, $h=10\text{mm}$.
Figure 17: SEM images of Nanofibers with Steel-wire for $\phi=1.9$, $t=15\text{min}$, $h=15\text{mm}$. 
Figure 18: SEM images of Nanofibers with Steel- wire for φ =1.9, t = 15min, h = 20mm.

As seen in Figs 19 &20 there was not much difference in the structure of nanofibers produced with Ni-wire at 15mm and 20mm height above the burner. The material deposited on the Ni-wire consisted of helical, zigzag and coiled nanofibers. The lengths of these tubes are around 20μm and diameters of these fibers are around 0.5μm as shown in the TEM images in Fig.21.

These nanofibers are hollow in nature as shown in Fig.22 where a catalyst particle got detached from its tip. The growth mechanism for these structures is explained in detail in section 4.2. As seen in Fig 23 a few nanofibers grew to 1μm in cross section on the pure Ni-wire as the catalyst material.
Figure 19: SEM images of Nanofibers with Ni-wire for $\phi = 1.9$, $t = 10\text{min}$, $h = 15\text{mm}$. 
Figure 20: SEM images of Nanofibers with Ni- wire for $\phi = 1.9$, $t = 10\text{min}$, $h = 20\text{mm}$.
Figure 21: TEM images of helical nanofiber of length 20μm and diameter 500nm.
Figure 22: SEM images of hollow Nanofibers with Ni-wire for $\phi=1.9$, $t=10\text{min}$, $h=20\text{mm}$. 
In order to see the effectiveness of Ni-based alloys on the structures when compared to pure metal, Monel an alloy of Ni/Cu/Fe was exposed to the flame for 10 min. As seen in Fig. 24 there were ball shaped deposits (low magnification) covered on the top with amorphous carbon with hidden nanofibers (high magnification). There was no difference in the shape of these structures when compared to pure Ni. As shown in Fig 25 there was a large variation in the tube sizes ranging from ~125 nm-1 μm. TEM images in Fig 26 represent a few nanofibers formed on the Monel wire with diameters ranging from ~125-200 nm.
Figure 24: (a) SEM low magnification image of carbon deposit on Monel wire (b) SEM high magnification image showing the hidden carbon nanostructures covered by amorphous carbon.
Figure 25: SEM images of carbon nanofibers with Monel wire (a) Zig-Zag entangled nanofibers and (b) Nanofibers hollow in nature.
Figure 26: Carbon nanofibers with Monel wire, diameters ranging from 125-200nm.
4.1.3. Effect of Probe Exposure Time on the CNT Morphology

When the probes were exposed for 5min in the flame at 15mm height above the burner for \( \phi =1.9 \), very few nanofibers were found when compared to those produced for 10 min. Fig. 27(a) and (b) are the SEM images of nanofibers produced by Ni-wire for 5 and 10 min respectively. As shown in these images with increase in sampling times these fibers grew larger in diameters, also helicity and spirality increased. The growth rate of these structures was 168nm/min.

4.1.4. Effect of Fuel Equivalence Ratio on the CNT Morphology

Monel (Ni/Cu/Fe) probe produced Carbon nanofibers (CNFs) for \( \phi =1.9 \) at a height of 20mm where the yield of carbon nanostructures was maximum. The CNFs produced are similar to those produced by pure Ni-wire. With increasing \( \phi \), the carbon nanofibers diameters, lengths and yield decreased as is evident from Fig. 29. This is obvious as with increasing \( \phi \) soot dominates the growth of carbon nanostructures. Also the temperature in the respective flame location decreases with increasing \( \phi \), decreasing the number of catalyst particles generated, which act as nucleation sites for growth of these nanofibers.

4.2. Growth Mechanism for Carbon Nanostructures

From the experimental data we have carbon nanotubes and nanofibers grown on different catalyst particles as a function of the flame reactor operating conditions. These carbon nanostructures are helical, coiled, zig-zag and vertically aligned with catalyst particles at their tips. The growth mechanisms of these structures are discussed in detail in this section. Also a comparison of our results with previous studies is given.
Figure 27: (a) SEM images of relatively straight Nanofibers grown on Ni-wire for $\phi = 1.9$, $t = 5\text{min}$, $h = 15\text{mm}$. as compared to (b) nanofibers grown on Ni-wire for $\phi = 1.9$, $t = 10\text{min}$, $h = 15\text{mm}$. 
Figure 28: (a) SEM images of Nanofibers grown on Fe-wire for $\phi=1.9$, $t=5$min, $h=15$mm. (b) Aligned Nanofibers grown on Fe-wire for $\phi=1.9$, $t=15$min, $h=15$mm.
Figure 29: SEM images of Nanofibers with increasing $\phi$ grown on (a) Monel wire for $\phi = 1.9$, $t = 10$ min, $h = 20$mm. (b) SEM images of Nanofibers grown on Monel wire for $\phi = 2.0$, $t = 10$ min, $h = 20$mm (c) SEM images of Nanofibers grown on Monel wire for $\phi = 2.1$, $t = 10$min, $h = 20$mm.
The growth of carbon nanostructures can be divided into two steps:

1. Molecular Growth of solid carbon.
2. Building up of solid carbon into various carbon nanostructures.

### 4.2.1. Molecular Growth of Solid Carbon

Growth of solid carbon in fuel rich flames is attributed to insufficient oxygen, to oxidize all the carbon atoms to CO$_2$. Polynuclear aromatic hydrocarbons (PAHs) are considered to be the building blocks for soot formation. PAH formation in the current propane-oxygen fuel rich (aliphatic hydrocarbon) flame can be explained by two distinct reactions pyrolysis and pyrosynthesis [105]. Pyrolysis is the process where the fuel molecules partially crack to form smaller unstable fragments (radicals) at higher temperatures. In the pyrosynthetic step these radicals combine to form larger and more stable aromatic compounds through cyclization reaction as shown in Fig 30. Agglomeration of these aromatics leads to PAHs that contain eight or more aromatic rings. By virtue of their size (over 10nm), these molecules are solids, and are referred to as soot.

Solid carbon is also produced by the reduction/hydrogenation and disproportionation [106,107] of CO.

$$\text{CO} \xrightleftharpoons{\text{metal}} \text{C}_{\text{solid}} + H_2O \quad \text{reduction reaction} \quad (2)$$

$$2\text{CO} \xrightleftharpoons{\text{metal}} \text{C}_{\text{solid}} + \text{CO}_2 \quad \text{disproportionation} \quad (3)$$

### 4.2.2. Building Up of Solid Carbon into Carbon Nanostructures

The formation of carbon into multiwalled nanotubes and nanofibers in this experiment is dependent upon parameters like the catalyst particle size, residence time, temperature and stoichiometry.
Figure 30: Schematic representation of possible process involved in the formation of CNTs and CNFs [98,116].
Figure 31: TEM image of a carbon nanofiber showing the tip growth mechanism with a catalyst particle at its tip.
These carbon nanostructures followed the tip growth mechanism with a catalyst particle at the tip of the tubes as shown in the TEM image of a nanofiber in Fig.31.

Growth of carbon nanostructures formed is explained via the carbon solvation, diffusion and precipitation mechanism [108]. There are four accepted mechanisms for the carbon nanotubes and nanofibers, which although not completely proven, are supported by experimental evidence.

These growth mechanisms are based on the introduction of catalyst particles either as deposited salts on a substrate or as aerosols suspended catalyst particles in the flame environment.

Yarmulke growth mechanism as shown in Table 4 [115] occurs on suspended catalyst particles whose size is limited to ~1nm. According to observations the carbon in this case decomposes from CO disproportionation on the catalyst particle and then diffuses along the surface till adding to the growing particle. Thus a SWNT is formed whose diameter is same as that of the catalyst particle and has a wall with mono-atomic layer of carbon. It was observed and hypothesized that Fe based catalyst particles grow carbon particles (nanotubes) immediately after forming and in turn these carbon particles prevent the catalyst from growing further [116].

Carbon solvation, diffusion and precipitation growth mechanism as shown in Table 4 [108] also occurs on suspended catalysts whose size exceeds 5nm. The carbon in this mechanism would originate from acetylene and solvate into the particle and diffuses through the interstitial sites, and when saturated precipitates out of the catalyst particle to grow MWNT and nanofibers whose cross section and number of walls matches with the crystallographic interstitial planes through which the carbon precipitated our to the catalyst particle [117]. This
is a general case with nickel, which through observations was hypothesized as that the growth of carbon nanotubes with demands a longer time, and thus nickel grows larger and more crystalline when compared with iron particles [116].

Base and Tip growth mechanisms as shown in Table 4 [118,38] occur on deposited catalyst particles via three steps. In the first step carbon solvates and diffuses through the catalyst particles. In the second step the growth of tubes depends upon the source of carbon available. In abundance of acetylene, forms a layer of amorphous carbon over the catalyst particle. Hence carbons can solvate through the substrate only. In the third step when it precipitates out of the catalyst particle it would push the layer of amorphous carbon away from the catalyst particle, thus leaving the particle at the base and the amorphous layer forms a cap.

In abundance of CO, continuous layers of amorphous carbon are etched from the surface hence carbon can solvate into the particle from the gaseous interface and precipitates on the opposite side of the particle, hence upholding the particle at the tip [116].

We know from the above discussion that interstitial diffusion leads to MWNTs and nanofibers where as surface diffusion leads to growth of SWNTs. The growth of MWNTs and nanofibers is favored as the characteristic time for interstitial diffusion is less than that for surface diffusion. The diffusivity of carbon in metals at high temperatures 1000°C is of the order 10⁻⁷ cm²/sec [109,110,111]. The characteristic time ‘τ’ taken for diffusion of carbon through a metal particle of characteristic length ‘L’ is given as

\[ L^2 = D \times t \]  \hspace{1cm} (4)

where \( D \) is the diffusivity. So for a particle of 10nm the time taken for interstitial diffusion is of order 0.01ms. The diffusivity of CO molecule diffusing on the surface of Ni (110) was
studied by Xiao et al. [112] and reported it to be of the order $10^{-10}$ cm$^2$/sec. Based on the characteristic time equation defined above the time taken for diffusion of CO to the opposite side of a 10nm particle is of order 10ms. Thus the growth of MWNTs and nanofibers is favored in this case.

Table 5: Growth Mechanisms

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspended particles</td>
<td>Suspended particles</td>
<td>Deposited Catalyst particles.</td>
<td>Deposited Catalyst particles.</td>
</tr>
<tr>
<td>Nanoparticle size~1nm</td>
<td>Nanoparticle size $&gt;$5nm</td>
<td>C$_2$H$_2$ layer formed</td>
<td>Amorphous carbon layers are etched from the surface.</td>
</tr>
<tr>
<td>Surface Diffusion of carbon over the Nanoparticle</td>
<td>Interstitial diffusion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time scale ~10ms.</td>
<td>Time scale~0.01ms</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SWNTs</td>
<td>MWNTs,CNFs.</td>
<td>C$_2$H$_2$</td>
<td></td>
</tr>
</tbody>
</table>

![Diagram](image)
The size of catalyst particle increased with increase in sampling time. Depending upon the size of the catalyst particle the type of carbon structures formed differ. As seen in Fig: 12 MWNTs (~27nm dia) are formed where the catalyst particle size was 31nm and nanofibers (~0.5μm dia) are formed as shown in Fig.13, the size of the catalyst particle was 630nm Fig30. Thus the diameter of the carbon nanostructures is directly proportional to the diameter of the catalyst particle.

With increased sampling times as seen in Figs 27 (a) and (b) the helicity and spirality of the nanofibers increased, this can be attributed to the increased supply of carbon by direct disproportionation of CO on the metal surface, forming pentagonal and heptagonal carbon rings. The incorporation of a pentagon into a graphite layer produces an outer curvature, while the incorporation of a heptagon would produce an inner curvature as shown in Fig 32. Regular pairing of these pentagons and heptagons without any twist in the growth direction leads to spiral nanofibers as shown in Fig 33 where as periodic paring of pentagons and heptagons with a twist along the growth of the nanofiber results in helical nanofibers as shown in Fig 21 [114].

<table>
<thead>
<tr>
<th>Sampling Times</th>
<th>Diameter of Carbon Nanofibers</th>
</tr>
</thead>
<tbody>
<tr>
<td>5min</td>
<td>~660nm</td>
</tr>
<tr>
<td>10min</td>
<td>~1.5μm</td>
</tr>
</tbody>
</table>

The yield of nanofibers produced with the Stainless Steel and Monel wires was higher as compared to pure Nickel. This is supported by the fact that alloys reduce the melting point of
metal, onward forming more catalyst particles, which in turn increase the nucleation sites for nanotubes and nanofibers formation. Also the solubility of carbon in alloys is higher as compared to single metals [113]. This is the reason for the decrease in the diameter of the nanofibers (~125nm) produced by Monel wire as compared to those produced by pure Nickel.

![Hexagon, Pentagon and Heptagon Carbon Rings](image)

Figure 32: (a-c) Hexagon, pentagon and heptagon carbon rings in a graphite layer [114].

With increasing fuel equivalence ratio it is observed that the lengths of nanofibers and their yield decreased as shown in Fig 25 and 26. This can be attributed to the fact that increase in equivalence ratio yields more soot which dominates the growth of carbon nanostructures. Table 7 shows the variation in the diameters of the tubes with increasing $\phi$.

<table>
<thead>
<tr>
<th>Increasing $\phi$</th>
<th>Change in Diameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min-Max</td>
</tr>
<tr>
<td>1.9</td>
<td>~125-1 $\mu$m</td>
</tr>
<tr>
<td>2.0</td>
<td>~95-470nm</td>
</tr>
<tr>
<td>2.1</td>
<td>~60-375nm</td>
</tr>
</tbody>
</table>

Table 7: Fuel Equivalence Ratio Vs diameter of the Tubes
Figure 33: Spiral Nanofibers formed with pure Ni-wire for $\phi = 1.9$, $t = 1\text{min}$, $h = 15\text{mm}$.
4.2.3. TEM Analysis of Vertically Aligned Nanostructures

The TEM images of vertically aligned structures revealed that these structures are indeed bundles of nanotubes as shown in Fig 34. The outer diameter of the bundle was ~32nm. The bundle comprised of individual nanotubes, which might be either SWNT or MWNT (the nature of the tubes is not yet known as they could not be separated individually). The composition of the layer of catalyst particles at the tip of the tubes was found to be that of Ni-Cr. The size of the catalyst particles was in the range of ~9-20nm as is evident from the TEM image.

Figure 34: (a) TEM image of a bundle of carbon nanotubes. (b) TEM image of Ni-Cr catalyst particles.
4.2.4. Comparison of Vertically Aligned Nanostructures in Flames

In order to test the effect of catalyst composition on the nanostructures a stainless steel wire was introduced into the flame. We found aligned structures as shown in Fig.15 with a layer of catalyst particles at their tips. Aligned structures have been previously reported in diffusion flames but this is the first time that they are found in a premixed flame. A comparison of the aligned structures with those obtained in other studies is shown in Table 8.

Table 8: Comparison of Aligned Nanostructures

<table>
<thead>
<tr>
<th>Diffusion flame</th>
<th>Premixed flame</th>
<th>Diffusion flame</th>
</tr>
</thead>
<tbody>
<tr>
<td>➢ Fusheng Xu et al [119].</td>
<td>➢ Present study ➢ Propane-oxygen Premixed flame</td>
<td>➢ Claudya P. Arana [120]</td>
</tr>
<tr>
<td>➢ Methane Inverse Diffusion flame</td>
<td>➢ 316 Stainless steel wire</td>
<td>➢ Ethylene Diffusion Flame</td>
</tr>
<tr>
<td>➢ Ni/Cr/Fe (60%, 16%, 24%)</td>
<td>➢ Compact bundles of CNTs.</td>
<td>➢ 302 Stainless steel wire (Fe/Cr/Ni)</td>
</tr>
<tr>
<td>➢ MWNTs ~15-20nm</td>
<td></td>
<td>➢ CNFs~0.5µm.</td>
</tr>
</tbody>
</table>

![Image](image_url)
It was also found that the vertical alignment of nanostructures formed with the stainless steel wire with respect to height was more precise as shown in Fig.17 & 18. This trend was similar to one reported by Fusheng Xu et al in a methane diffusion flame with increase in the radial position ‘r’. A comparison of the structures is shown in the following Table 9.

Table 9: Comparison of Vertically Aligned Nanostructures

<table>
<thead>
<tr>
<th>Diffusion Flame (Fusheng Xu et al. [119])</th>
<th>Premixed Flame (Present Study)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="c.png" alt="Image" /></td>
<td><img src="f.png" alt="Image" /></td>
</tr>
<tr>
<td><strong>60% Ni / 16% Cr / 24% Fe probe</strong></td>
<td><strong>Stainless steel (Fe/Cr/mi)</strong></td>
</tr>
<tr>
<td>r = 2 to 3 mm</td>
<td>h = 10 mm</td>
</tr>
<tr>
<td><img src="i.png" alt="Image" /></td>
<td><img src="g.png" alt="Image" /></td>
</tr>
<tr>
<td>r = 1.75 to 3.25 mm</td>
<td>h = 15 mm</td>
</tr>
<tr>
<td><img src="h.png" alt="Image" /></td>
<td><img src="i.png" alt="Image" /></td>
</tr>
<tr>
<td>r = 2 to 4.5 mm</td>
<td>h = 24 mm</td>
</tr>
</tbody>
</table>
In the above mentioned diffusion flame synthesis of CNTs [119] it was found that well aligned CNTs were formed where there is almost no C\textsubscript{2}H\textsubscript{2} but copious amount of CO as indicated by Raman spectroscopy. Hence it can be inferred that CO is the main precursor for the formation of CNT’s. Now it is clearly seen that the layer of catalyst material at their tips is justified via the tip growth mechanism discussed in section 4.2.2.

A comparison of the present study with other premixed flame studies is shown in Fig.35. In 1959 J.M.Singer reported the growth of filamental structures in a premixed, eight percent propane-air flame. These filamental structures grown on steel grid are indeed MWNTs and nanofibers with lengths 1.5-5microns and diameters 49 – 470nm.

In 2000 Diener et al. reported the formation of MWNTs in benzene-oxygen and SWNTs in acetylene-oxygen flame with $\phi$ ranging from 1.7-3.8 with the catalyst being nickelocene and ferrocence vapors.

In 2002 Vander Wal et al. conducted a series of experiments on the synthesis of carbon nanotubes in premixed flames, with ethane, ethylene, acetylene as the fuels and with cobalt coated stainless steel grid as the catalyst material and reported the optimal yield of MWNTs in premixed ethylene-air flame with $\phi$ =1.62.

The carbon nanostructures produced in the present study with Ni and Steel wires with fuel equivalence ratio 1.9 are highly ordered in terms of helicity, spirality and vertical alignment. Also the vertically aligned nanostructures appear as dense and consist of compact bundles of individual tubes.

These nanostructures are hollow in nature as discussed earlier. Also we achieved a maximum yield of 2mg/min with Monel wire as the catalyst material.
Figure 35: Comparison of the carbon nanostructures produced in the present study with previous investigations.
5. SUMMARY OF RESULTS

The main findings in this investigation may be summarized as follows:

1. Carbon nanotubes and nanofibers were produced using a propane-oxygen flame with \( \phi \) ranging from 1.9 to 2.1.

2. The effect of four catalysts Ni-grid, pure Ni-wire, Monel an alloy of Ni/Cu/Fe and Stainless steel wires on the structure and yield of the carbon nanostructures was tested.

3. The diameter of these nanostructures is strongly dependent upon the size of the catalyst particle. The diameter of the tubes increases with increasing catalyst particle size. MWNTs with diameters 27-40nm were observed with catalyst particle sizes 31-45nm, while CNFs with diameters \(~125\text{nm-}500\text{nm}\) were observed with catalyst particle sizes 130-630nm.

4. As the fuel equivalence ratio increased the diameters, lengths and the yield of the carbon nanofibers decreased.

<table>
<thead>
<tr>
<th>Increasing ( \phi )</th>
<th>Change in Diameters</th>
<th>Min-Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9</td>
<td>~125-1( \mu )m</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>~95-470nm</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>~60-375nm</td>
<td></td>
</tr>
</tbody>
</table>

5. It was shown that alloyed catalysts increase the yield of the carbon nanostructures when compared to pure metals, due to their decrease the melting temperature and
hence supply more catalyst particles as nucleation sites for the growth of these nanostructures. Typical yield was found to be 2mg/min.

6. With increase in sampling times diameters, helicity and spirality of the tubes increased.

<table>
<thead>
<tr>
<th>Sampling Times</th>
<th>Diameter of Carbon Nanofibers</th>
</tr>
</thead>
<tbody>
<tr>
<td>5min</td>
<td>~660nm</td>
</tr>
<tr>
<td>10min</td>
<td>~1.5μm</td>
</tr>
</tbody>
</table>

7. With increase in residence times it was found that there was not much variation in the shape and size of the tubes grown on pure Ni wire. While the carbon nanostructures vertically aligned themselves into bundles of nanotubes with increasing residence times on a steel wire.

8. Premixed flames are capable of producing vertically aligned nanostructures.

9. It was identified that tip growth mechanisms prevails for all the structures formed in this flame reactor owing to the abundance of CO and due to the fact that tip growth mechanism occurs on deposited catalysts.

10. In the present study highly ordered structures in terms of helicity, spirality and vertical alignment were produced when compared to previous premixed flame studies.
6. RECOMMENDATIONS FOR FUTURE WORK

The recommendations for future work are as follows:

1) To study the properties of these nanostructures like density, surface area, electrical conductivity, specific heat and hydrogen absorption capabilities.

2) To carry out a detailed study on the synthesis of these structures in both premixed and diffusion flames in order to identify the best method to produce them in bulk.

3) To develop simple methods to purify the as grown carbon nanostructures from other flame generated particles.

4) To scale flame synthesis as an industrial technique for nanotube synthesis.
REFERENCES


99. Maruyama’s molecular dynamics and nano heat website.

100. I.P.E Nanotube premier website.


APPENDIX A: HYDROGEN STORAGE

A.1 Introduction to Hydrogen Storage

Carbon nanotubes due to their low densities and high surface areas posses the potential for hydrogen storage. Hence there is need to study the hydrogen absorbtivites and analyze their suitability as hydrogen storage material. A discussion on this issue is presented in this section.

Hydrogen is one such element which when burns, as fuel does not emit any pollutants [46]. With this the question arises as to how to store hydrogen efficiently and safely. In order to meet the current standards set by DOE, the amount of hydrogen to be stored is 6.5wt%. The four notable systems for hydrogen storage investigated upto date are compressed hydrogen gas, liquid hydrogen, and chemical storage in chemical and metal hydrides and gas on solid adsorption [45]. All of these methods have their shortcomings. Because of high pressure Compressed gas hydrogen storage systems suffer due to permeability and embrittlement of metal tanks [46]. Liquid storage systems suffer due to losses form evaporation and require expensive insulation. Metal hydrides storage till date has shown only a reproducible storage of hydrogen of 3-wt% and hence falls short of the DOE requirements [45].

The gas on solid adsorption has been investigated in recent years with carbon nanostructures as a promising media for hydrogen storage. But the challenge ahead lies as to the reproducibility of the results as there exist conflicting amounts of hydrogen storage by various research groups.

The two basic phenomena of hydrogen storage in carbon nanostructures are by physisorption, a process in which the hydrogen atoms condense on the surface of the
nanostructures and are held by weak molecular forces like the Vander Waals forces, and hence minimum energy is required for the desorption process. The second phenomenon is chemisorption is a strong short-range bonding, and involves a direct chemical bond and charge transfer.

A summary of the reported hydrogen storage in carbon nanotubes and nanofibers by various research groups as reported in a recent review is given in Table 2. [47].

The hydrogen adsorption by various research groups has been based on the hydrogen measurements techniques addressed in the next topic. The discrepancies in the hydrogen adsorption measurements may be related to the error in measuring techniques, which are discussed to an extent in the following topic.

**A.2 Hydrogen Storage Measurement Techniques**

The main methods used for determining the hydrogen storage capacities are temperature-programmed desorption (TPD), volumetric analysis, thermogravimetric analysis (TGA), and the electrochemical method [47].

TPD is a technique, which uses a mass spectrometer to measure the hydrogen desorped from a sample during controlled heating [48]. TPD is highly sensitive, allowing the study of samples with masses below 1mg. for calibration, the hydrogen desorption of a well-known metal hydride or an alloy of known hydrogen content has to be measured [49]. The activation energy of desorption can be directly measured from the temperature at which hydrogen appears in the spectrometer. As different adsorption mechanisms and sites will have different activation energies, each peak in the thermogram will indicate a different site or mechanism. Carbon adsorbents have adsorption peak around 130K, and nanotubes have one (at~300K) or more additional peaks. The amount of hydrogen desorbed requires
integration of the signal, and may have significant errors [48]. In volumetric analysis, the adsorption of hydrogen is measured by a pressure change in a fixed volume, with pressure variations attributed to adsorption or desorption.

A complication with this technique is the presence of thermal effects during the filling of the sample cell. Hydrogen has an appreciable temperature-dependent compressibility that needs to be taken into account as the temperature changes due to compressing the gas during filling and the exothermic adsorption. Unless this problem is specifically addressed, the change in pressure caused by temperature fluctuations will cause overestimation of the amount of hydrogen adsorbed [50].

The TGA analysis consists of measuring weight of a sample as the temperature is varied under constant pressure. The technique is known, with the difficulty being the sensitivity of the instrumentation on the relatively small sample sizes used in these studies. The gravimetric analysis is capable of measuring very low sample masses of about 10mg in specially designed devices, but it is a nonselective analysis. The high specific area of carbon nanotubes increases the possibility of the adsorption of residual gases. Therefore, the apparatus has to be extremely clean, and high-purity hydrogen has to be used [47].

Hydrogen can also be stored by the electrochemical storage. In this technique a carbon electrode is prepared by mixing it with conductive powder, for example, nickel or gold and compacted [51-53]. The counter electrode is, for example, metallic nickel. Both electrodes are placed in KOH solution, which provides the hydrogen atoms, and a polymer separator separates them.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Purity (%)</th>
<th>T (K)</th>
<th>P (Mpa)</th>
<th>wt%</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT</td>
<td>Assumed 100</td>
<td>133</td>
<td>0.04</td>
<td>5-10</td>
<td>Dillon et al. [58]</td>
</tr>
<tr>
<td>SWNT</td>
<td>high</td>
<td>ambient</td>
<td>0.067</td>
<td>3.5-4.5</td>
<td>Dillon et al. [59]</td>
</tr>
<tr>
<td>SWNT</td>
<td>~50</td>
<td>300</td>
<td>10.1</td>
<td>4.2</td>
<td>Liu et al. [60]</td>
</tr>
<tr>
<td>Aligned SWNT</td>
<td>Purified</td>
<td>ambient</td>
<td>11</td>
<td>4</td>
<td>Liu et al. [61]</td>
</tr>
<tr>
<td>SWNT</td>
<td>Purified</td>
<td>77-300</td>
<td>8</td>
<td>1-1.5</td>
<td>[62]</td>
</tr>
<tr>
<td>SWNT</td>
<td>high</td>
<td>80</td>
<td>~7</td>
<td>8.25</td>
<td>Ye et al. [63]</td>
</tr>
<tr>
<td>MWNT</td>
<td>Purified</td>
<td>~300-</td>
<td>Ambient</td>
<td>0.25</td>
<td>Wu et al. [64]</td>
</tr>
<tr>
<td>MWNT</td>
<td>Purified</td>
<td>ambient</td>
<td>4.8</td>
<td>1.2</td>
<td>[65]</td>
</tr>
<tr>
<td>SWNTTiAl0.1V0.4</td>
<td>Sonicated&gt;98</td>
<td>ambient</td>
<td>0.067</td>
<td>6.5</td>
<td>Dillon et al. [66]</td>
</tr>
<tr>
<td>SWNT-Ti-6Al-4V</td>
<td>Purified</td>
<td>ambient</td>
<td>0.08</td>
<td>1.47</td>
<td>Hirscher et al. [67]</td>
</tr>
<tr>
<td>SWNT-Fe</td>
<td>Purified</td>
<td>ambient</td>
<td>0.08</td>
<td>&lt;0.05</td>
<td>Hirscher et al. [67]</td>
</tr>
<tr>
<td>Ball-milled SWNT</td>
<td>&lt;50</td>
<td>ambient</td>
<td>0.08</td>
<td>&lt;0.1</td>
<td>Hirscher et al. [68]</td>
</tr>
<tr>
<td>Ball-milled SWNT</td>
<td>&lt;50</td>
<td>ambient</td>
<td>0.9</td>
<td>1.0</td>
<td>Hirscher et al. [68]</td>
</tr>
<tr>
<td>CNT</td>
<td>Purified</td>
<td>298-773</td>
<td>0.1</td>
<td>0.4</td>
<td>Hirscher et al. [68]</td>
</tr>
<tr>
<td>Doped CNT</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>0.5-1.0</td>
<td>Zidan [69]</td>
</tr>
<tr>
<td>Li-CNT</td>
<td>Purified</td>
<td>473-673</td>
<td>0.1</td>
<td>20</td>
<td>Chen et al. [70]</td>
</tr>
<tr>
<td>K-CNT</td>
<td>Purified</td>
<td>&lt;313</td>
<td>0.1</td>
<td>14</td>
<td>Chen et al. [70]</td>
</tr>
<tr>
<td>Li-CNT (wet H2)</td>
<td>Purified</td>
<td>473-663</td>
<td>0.1</td>
<td>12</td>
<td>Yang [71]</td>
</tr>
<tr>
<td>Li-CNT (dry H2)</td>
<td>Purified</td>
<td>473-663</td>
<td>0.1</td>
<td>2.5</td>
<td>Yang [71]</td>
</tr>
<tr>
<td>K-CNT (wet H2)</td>
<td>Purified</td>
<td>&lt;313</td>
<td>0.1</td>
<td>21</td>
<td>Yang [71]</td>
</tr>
<tr>
<td>K-CNT (dry H2)</td>
<td>Purified</td>
<td>&lt;313</td>
<td>0.1</td>
<td>1.8</td>
<td>Yang [71]</td>
</tr>
<tr>
<td>Li-CNT</td>
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<td>473-663</td>
<td>0.1</td>
<td>0.7-4.2</td>
<td>Pinkerton [72]</td>
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<tr>
<td>SWNT</td>
<td>80-90</td>
<td>273</td>
<td>0.04</td>
<td>7</td>
<td>Dillon et al. [66]</td>
</tr>
<tr>
<td>SWNT (90-vol%)</td>
<td>298</td>
<td>-------</td>
<td>0.63</td>
<td>0.63</td>
<td>Ritschel et al. [73]</td>
</tr>
<tr>
<td>MWNT</td>
<td>unpurified</td>
<td>298</td>
<td>-------</td>
<td>0.05</td>
<td>Ritschel et al. [73]</td>
</tr>
<tr>
<td>MWNT</td>
<td>unpurified</td>
<td>293</td>
<td>6.5</td>
<td>2.0</td>
<td>Ding et al. [74]</td>
</tr>
<tr>
<td>CNT</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>0.5</td>
<td>Adu et al. [75]</td>
</tr>
<tr>
<td>SWNT</td>
<td>Purified</td>
<td>77</td>
<td>0.2</td>
<td>6</td>
<td>Pradhan et al. [76]</td>
</tr>
<tr>
<td>Aligned MWNT</td>
<td>High</td>
<td>298</td>
<td>10</td>
<td>3.0</td>
<td>Zhu et al. [77]</td>
</tr>
<tr>
<td>Aligned MWNT</td>
<td>High</td>
<td>290</td>
<td>10</td>
<td>2.4</td>
<td>Cao et al. [78]</td>
</tr>
<tr>
<td>Random MWNT</td>
<td>High</td>
<td>298</td>
<td>10</td>
<td>0.68</td>
<td>Zhu et al. [77]</td>
</tr>
<tr>
<td>MWNT</td>
<td>High, untreated</td>
<td>300</td>
<td>1.0</td>
<td>5.7</td>
<td>Chen et al. [79]</td>
</tr>
<tr>
<td>MWNT</td>
<td>High, acid</td>
<td>300</td>
<td>1.0</td>
<td>13.8</td>
<td>Chen et al. [79]</td>
</tr>
<tr>
<td>MWNT</td>
<td>High</td>
<td>300</td>
<td>7.0</td>
<td>0.7-0.8</td>
<td>Badzian et al. [80]</td>
</tr>
<tr>
<td>SWNT</td>
<td>Unpurified</td>
<td>295</td>
<td>0.1</td>
<td>0.93</td>
<td>Nishimiya et al. [81]</td>
</tr>
<tr>
<td>SWNT</td>
<td>Unpurified</td>
<td>77</td>
<td>0.1</td>
<td>2.37</td>
<td>Nishimiya et al. [81]</td>
</tr>
<tr>
<td>MER MWNT</td>
<td>10-15%</td>
<td>298</td>
<td>3.6</td>
<td>0.03</td>
<td>Tibbetts et al. [82]</td>
</tr>
<tr>
<td>Rice SWNT</td>
<td>High</td>
<td>298</td>
<td>3.6</td>
<td>0.05</td>
<td>Tibbetts et al. [82]</td>
</tr>
<tr>
<td>CNT</td>
<td>-------</td>
<td>298</td>
<td>11.35</td>
<td>11.26</td>
<td>Chambers et al. [83]</td>
</tr>
<tr>
<td>GNF (herringbone)</td>
<td>-------</td>
<td>298</td>
<td>11.35</td>
<td>67.55</td>
<td>Chambers et al. [83]</td>
</tr>
<tr>
<td>GNF (platelet)</td>
<td>-------</td>
<td>298</td>
<td>11.35</td>
<td>53.68</td>
<td>Chambers et al. [83]</td>
</tr>
<tr>
<td>GNF</td>
<td>-------</td>
<td>77-300</td>
<td>0.8-1.8</td>
<td>0.08</td>
<td>Ahn et al. [84]</td>
</tr>
<tr>
<td>CNF</td>
<td>-------</td>
<td>300</td>
<td>12</td>
<td>6.5</td>
<td>Browing et al. [85]</td>
</tr>
<tr>
<td>GNF</td>
<td>-------</td>
<td>300</td>
<td>10.5</td>
<td>0.7</td>
<td>Poirier et al. [86]</td>
</tr>
<tr>
<td>CNF</td>
<td>-------</td>
<td>293</td>
<td>10</td>
<td>1</td>
<td>De la Casa-Lillo et</td>
</tr>
<tr>
<td>CNF</td>
<td>-------</td>
<td>298</td>
<td>12</td>
<td>1.4</td>
<td>Hwang et al. [87]</td>
</tr>
<tr>
<td>Ball milled GNF</td>
<td>-------</td>
<td>ambient</td>
<td>0.9</td>
<td>0.5</td>
<td>Hirscher et al. [68]</td>
</tr>
<tr>
<td>GNF</td>
<td>-------</td>
<td>300</td>
<td>11</td>
<td>&lt;0.1</td>
<td>Hirscher et al. [68]</td>
</tr>
<tr>
<td>VGCFL</td>
<td>-------</td>
<td>298</td>
<td>3.6</td>
<td>&lt;0.1</td>
<td>Tibbetts et al. [82]</td>
</tr>
<tr>
<td>CNF</td>
<td>-------</td>
<td>300</td>
<td>12.5</td>
<td>1.6</td>
<td>Strobel et al. [88]</td>
</tr>
<tr>
<td>Herringbone GNF</td>
<td>Purified</td>
<td>77-300</td>
<td>1.5</td>
<td>1-1.8</td>
<td>Strobel et al. [89]</td>
</tr>
<tr>
<td>GNF</td>
<td>-------</td>
<td>300</td>
<td>12</td>
<td>10</td>
<td>Gupta et al. [90]</td>
</tr>
<tr>
<td>GNF</td>
<td>-------</td>
<td>300</td>
<td>12</td>
<td>10</td>
<td>Gupta et al. [91]</td>
</tr>
<tr>
<td>CNF</td>
<td>-------</td>
<td>77</td>
<td>12</td>
<td>12.38</td>
<td>Fan et al. [92]</td>
</tr>
<tr>
<td>CNF</td>
<td>-------</td>
<td>300</td>
<td>11</td>
<td>5.7</td>
<td>Cheng et al. [93]</td>
</tr>
</tbody>
</table>

Note: ------ represents data not available
During the charging process, water dissociates at the negative working electrode, and atomic hydrogen may intercalate into the carbon material [47]. The discharge process results in the recombining of water. By maintaining a constant current, the voltage is measured across the two electrodes during the charging and discharging. The amount of desorbed hydrogen is determined by measuring the electric charge in a galvanostatic setup [47].

The chief areas where hydrogen adsorption experiments may be in error are as follows [47].

The first is that leaks can be difficult to distinguish from hydrogen storage. Hydrogen molecules escape from a pressurized reservoir. If hydrogen molecules leak from a system of volume V at a nearly constant rate \( L = \frac{dP}{dt} \) over the period of the experiment t, an observer could incorrectly attribute the pressure decrease to a wt% hydrogen stored in a sample of mass \( m \) proportional to \( VL/m \). For small sample masses, the consequences of this can be particularly treacherous.

A second source of error is that, in a high-pressure experiment, pressure changes arising from ambient temperature variations can be mistakenly interpreted as substantial sorption. At 10 MPa and 300K, the pressure change with temperature is 33.3 kPa/K. If this were interpreted as sorption by a 1g sample in a 1L volume, the result would be 2.6 wt% per degree temperature drop. Most reports in the literature have samples smaller than 1g.

It is worth noting that the metal hydride research community has devised experimental techniques to handle all of these problems [54]. First, to avoid spurious readings form gas cooling to ambient, use two calibrated volumes connected by a valve, one an initially pressurized reservoir and the other containing the sample. Then determine the precise equilibrium temperatures and pressures of both volumes before and after opening the
connecting valve. Second, to unambiguously establish that there are no leaks, measure not only the gas adsorbed, but also the gas desorbed from the sample. Third, present a complete pressure composition isotherm that precisely defines the pressure and composition at which the hydrogen-adsorbent bond is formed and decomposes. A complete pressure composition isotherm would show an interesting change in curvature with pressure that would be very useful in classifying the sorption, and lending credibility to the research [55].

### A.3 Comparison of Hydrogen Storage in Metal Hydrides and Nanotubes

The volumetric density of hydrogen in metal hydrides reaches approximately double the density of liquid hydrogen the hydrogen intercalates in its atom state in the host metal and acts like a metal atom in the host lattice. According to the Westlake criteria [57], the hydrogen atoms in metal hydrides have an inter-atomic distance of at least 0.21nm. This corresponds to an atomic volume of 0.00485 nm$^3$ and a maximum volumetric density of 187 kg m$^{-3}$.

The volumetric density of hydrogen in hydrocarbons reaches 100–110 kgm$^3$. The line for nanotubes is universal, i.e. all types of nanotubes are on this line as long as the above-described hydrogen adsorption mechanism is correct. Therefore, the only way to increase the volumetric hydrogen density above the density of liquid hydrogen is the dissociation of hydrogen molecules in combination with a tight binding (covalent) or an electron transfer to the host material as in metal hydrides [56].

The preceding review provides the necessary concepts to understand hydrogen adsorption in carbon nanotubes in detail and constitutes the basis for future work on hydrogen adsorpptivities in carbon nanostructures.
Figure 36: Specific volumetric hydrogen density versus the gravimetric hydrogen density for various hydrogen storage media. The SWNT line represents the calculated values according to the model presented in the paper [56]. Dashed lines and values on top of the figure indicate the gravimetric density of the storage material.
APPENDIX B: CATALYST METAL COMPOSITIONS

B.1 Composition of Pure Nickel Wire

The Ni- wire, which was used as catalyst material, was 99.8% pure.

B.2 Composition of Monel Wire

The Monel wire used was, Unibraze 60 ERrNiCu-7. The composition of this alloy is as follows [122]:

Table 11: Composition of Monel Wire

<table>
<thead>
<tr>
<th>Ingredients of The Product</th>
<th>CAS No.</th>
<th>Approx. %</th>
<th>OSHA PEL Mg/M3</th>
<th>ACGIH TLV Mg/M3</th>
<th>Carcinogenicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>*Nickel</td>
<td>7440-02-0</td>
<td>35.99</td>
<td>1</td>
<td>1</td>
<td>Yes</td>
</tr>
<tr>
<td>Iron</td>
<td>7439-89-6</td>
<td>0-20</td>
<td>5</td>
<td>10 (as Fe₂O₃)</td>
<td>No</td>
</tr>
<tr>
<td>*Chromium</td>
<td>7440-47-3</td>
<td>0-26</td>
<td>.05 (Chromium VI)</td>
<td>.05 (Chromium VI)</td>
<td>Yes</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>7439-98-7</td>
<td>0-30</td>
<td>15</td>
<td>10</td>
<td>No</td>
</tr>
<tr>
<td>*Manganese</td>
<td>7439-96-5</td>
<td>1-4.0</td>
<td>5</td>
<td>1</td>
<td>No</td>
</tr>
<tr>
<td>Silicon</td>
<td>7440-21-3</td>
<td>1-1.25</td>
<td>5 (as SiO₂)</td>
<td>1</td>
<td>No</td>
</tr>
<tr>
<td>Columbium</td>
<td>7440-03-1</td>
<td>0-5</td>
<td>5</td>
<td>5</td>
<td>No</td>
</tr>
<tr>
<td>Copper</td>
<td>7440-50-8</td>
<td>0-30</td>
<td>.1</td>
<td>.2</td>
<td>No</td>
</tr>
<tr>
<td>*Aluminum</td>
<td>7429-90-5</td>
<td>0-2</td>
<td>5 (as Al₂O₃)</td>
<td>10</td>
<td>No</td>
</tr>
<tr>
<td>Titanium</td>
<td>7440-32-6</td>
<td>0-3.5</td>
<td>15 (as TiO₂)</td>
<td>10 (as TiO₂)</td>
<td>No</td>
</tr>
<tr>
<td>*Vanadium</td>
<td>7440-62-2</td>
<td>0-.6</td>
<td>.1</td>
<td>.05 (as V₂O₅)</td>
<td>No</td>
</tr>
<tr>
<td>Tungsten</td>
<td>7440-33-7</td>
<td>0-4.5</td>
<td>Not Registered</td>
<td>1</td>
<td>No</td>
</tr>
</tbody>
</table>

*The ingredients marked with an asterisk are covered under the reporting requirements of Section 513 of
B.2 Composition of Stainless Steel Wire

The Stainless Steel wire used in this investigation was a Unibraze ER316 wire with the composition as follows [122].

<table>
<thead>
<tr>
<th>Flux or other Ingredients</th>
<th>% Of Weight</th>
<th>CAS No.</th>
<th>Exposure Limit (mg/m3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>OSHA PEL</td>
</tr>
<tr>
<td>Chromium (Cr) a, c</td>
<td>4.6 – 32.0</td>
<td>7440-47-3</td>
<td>1</td>
</tr>
<tr>
<td>Nickel (Ni) a, c</td>
<td>0.50 – 36.0</td>
<td>7440-02-0</td>
<td>1</td>
</tr>
<tr>
<td>Molybdenum (Mo) c</td>
<td>0.45 – 5.2</td>
<td>7439-88-7</td>
<td>15 T/5 R</td>
</tr>
<tr>
<td>Columbium (Cb) plus Tantalum (Ta) c</td>
<td>0.05 – 0.30</td>
<td>7440-03-1</td>
<td>10</td>
</tr>
<tr>
<td>Manganese (Mn) c</td>
<td>.050 – 13.5</td>
<td>7439-96-5</td>
<td>5/1 F/3**</td>
</tr>
<tr>
<td>Copper (Cu) c</td>
<td>0.75 – 4.0</td>
<td>7440-50-8</td>
<td>0.1 F</td>
</tr>
<tr>
<td>Silicon (Si) a, c</td>
<td>0.15 – 4.5</td>
<td>7440-21-3</td>
<td>5 OF/5 R</td>
</tr>
<tr>
<td>Iron (Fe) a</td>
<td>45 - 80</td>
<td>7439-89-6</td>
<td>5 / 5 R</td>
</tr>
</tbody>
</table>

* = Exposure limits for oxides, dust, fume and mist where applicable  F=Fume  R=Respirable fraction  T=Total dust
VITA

Saritha Perla was born in India on July 20, 1980. She received her bachelor’s degree in mechanical engineering with a specialization in production engineering from Osmania University, India, in June 2002. She came to the United States to pursue a master’s degree in mechanical engineering in January 2003 at Louisiana State University, Baton Rouge, Louisiana. She is expected to fulfill the requirements for a master’s degree in mechanical engineering in December 2005.