HEAT TRANSFER AND CHEMICAL PROCESSES IN CHEMICAL VAPOR DEPOSITION REACTOR FOR SYNTHESIS OF CARBON NANOTUBES

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ABSTRACT OF DISSERTATION

Wahed Rezk Wasel

The Graduate School
University of Kentucky
2006
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ABSTRACT OF DISSERTATION

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Engineering at the University of Kentucky

By
Wahed Rezk Wasel
Lexington, Kentucky

Director: Dr. Kozo Saito, TVA Professor of Mechanical engineering
Lexington, Kentucky
2006

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ABSTRACT OF DISSERTATION

HEAT TRANSFER AND CHEMICAL PROCESSES IN CHEMICAL VAPOR DEPOSITION REACTOR FOR SYNTHESIS OF CARBON NANOTUBES

A small-scale model of a CVD reactor was built. Axial and radial of major species concentrations and temperature profiles were obtained with a micro gas chromatograph and a fine thermocouple. Those temperature and species concentrations revealed detailed thermal and chemical structures of the CVD reactor.

The concentrations of argon plus hydrogen, methane, and C₂Hₓ (C₂H₂ + C₂H₄ + C₂H₆) resulting from xylene decomposition were measured along the CVD at different temperatures. Ferrocene was added to xylene to investigate the effect of a catalyst on composition profiles. The results with ferrocene indicated an increase in CH₄ and C₂Hₓ concentrations. At 1000 °C and above, the increase of C₂Hₓ concentration is higher than that for CH₄. The effect of ferrocene was very minor on the concentration of the gases. Finally composition and temperature profiles were measured and plotted for the radial direction at X=75 cm and T=1200 °C.

The overall rate constant for the gas-phase reaction was calculated based on the measured species concentration data using the Benson and Shaw reaction mechanism. Our study showed that the Benson and Shaw mechanism could be used in the temperature range lower than 800 °C.

Also the effect of hydrogen in the syntheses of CNTs, in the CVD reactor using xylene and ferrocene, was studied. Both single-step and two-step methods were applied. In the single-step method, the ferrocene was dissolved in the xylene. In the two step-method the catalyst preparation step was performed first; ferrocene powder was placed in the preheater for a certain period of time and carried by a mixture of argon and hydrogen at fixed concentration to get catalyst nanoparticles deposited on the reactor wall. Xylene then was injected to the reactor. To study the effect of hydrogen, the synthesized materials were observed by SEM and TEM. The results showed that the presence of hydrogen is essential for CNTs to be synthesized by the CVD method, and also the concentration of hydrogen in the reactor has a great effect on the quality of
CNTs. The yield of CNTs in the two-step method was slightly higher than that in the one-step method.

KEYWORDS: Carbon Nanotubes CNTs, Chemical Vapor Deposition CVD, Xylene decomposition, Hydrogen role, Thermal and Chemical structures

Wahed R. Wasel

04-13-2006
HEAT TRANSFER AND CHEMICAL PROCESSES IN CHEMICAL VAPOR DEPOSITION REACTOR FOR SYNTHESIS OF CARBON NANOTUBES

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By
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2006
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To my parents and my teacher Abdelmoneim M. Abouzeid;
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CHAPTER ONE

INTRODUCTION

1.0 Introduction

Carbon is the lightest atom in column IV of the periodic table and is an element with unique properties. The recent discoveries of fullerenes (a zero-dimensional form of carbon) and carbon nanotubes (a 1 D form) have stimulated great interest in carbon materials overall [1,2].

Also carbon is considered as one of the three basic elements (C, O, H) in the earth that constitute several kinds of organisms compounding with other elements. Formally, carbon nanotubes and fullerenes have a number of common features and also, many differences. In reviewing the theoretical literature, the focus is on single–wall tubules, cylindrical in shape, either infinite in the length or with caps at each end such that the two caps can be joined to form a fullerene. Formally, the cylindrical portions of the tubules consist of a single graphene sheet, rolled to form the cylinder [3]. Carbon fibers result from the filamentary growth $sp^2$-bonded graphitic carbon along an axis parallel to the basal plane, leading to a very high length-to-diameter ratio called the aspect ratio Figure 1.1 shows the very high aspect ratio of commercial polyacrylonitrile (PAN) and mesophase pitch-based carbon fibers, and also of vapor-grown carbon fibers,
which are typically not continuous. CNTs have aspect ratios comparable to vapor-grown carbon fibers, while fullerenes have aspect ratios close to unity similar to carbon blacks [1].

Regarding diameter dimensions, commercial PAN-based and mesophase pitch-based fibers are in the 7 to 20 \(\mu m\) range, while vapor-grown carbon fibers are considered to have diameters ranging from 1000 \(\sigma A < d < 1 \text{ mm}\), as indicated in Figure 1.2 Though much smaller in diameter, carbon Nanotubes bear a close to resemblance to vapor-grown carbon fibers regarding microstructure and morphology, and often are grown concurrently[1].
Figure 1.1 Comparison of aspect ratios for various carbon fibers (which are relevant to carbon CNTs) and carbon blacks (which are relevant to fullerenes)[1]
Figure 1.2 Structure of CNT, fullerenes, Graphite, and Diamond [1].
Figure 1.3 Comparison of diameters of various CFs, GW, VGCFs, CNTs, and fullerenes [1]
1.1 History of Carbon materials to Carbon Nanotubes

The early history of carbon fibers was stimulated by needs for materials with special properties, both in the 19th century, and more recently, after World War II. The first carbon fiber was prepared by Thomas A. Edison to provide a filament for an early model of an electric light bulb. Specially selected Japanese Kyoto bamboo filament were used to wind a spiral coil that was then pyrolyzed to produce a coiled carbon resistor, which could be heated ohmically to provide a satisfactory filament for use in an early model of an incandescent light bulb. Following this initial pioneering work by Edison, further research on carbon filament proceeded more slowly, since sturdier tungsten filaments in the electric light bulb soon replaced carbon filaments.

Nevertheless, research on fibers and filaments preceded steadily over a longtime-frame, through the work of Schutzenberge in 1890, Pelabon, and others. Efforts were mostly directed toward early phases of research on oil vapor-grown carbon filaments, showing filament growth from the thermal decomposition of hydrocarbons.

The second applications-driven stimulus to carbon fiber research came in the 1950s from the needs of the space and aircraft industry for strong, stiff, lightweight fibers that could be used for building lightweight composite materials with superior mechanical properties. This stimulation led to great advances in the preparation of continuous carbon fibers based on polymer precursors, including rayon, PAN, and later, mesophase pitch. The late 1950s and 1960s were a
period of intense activity at the Union Carbide Corporation, the Aerospace Corporation, and many other laboratories worldwide. This stimulation also led to the growth of a carbon whisker, which has become a benchmark for the discussion of the mechanical and elastic properties of carbon fibers. The growth of carbon whiskers was also inspired by the successful growth of single-crystal whisker filaments at that time for many metals such as iron, nonmetals such as Si, and oxides such as Al₂O₃, and by theoretical studies showing superior mechanical properties for whisker structures. Parallel efforts to develop new bulk synthetic carbon materials with properties approaching single-crystal graphite led to the development of highly oriented pyrolytic graphite (HOPG) in 1962 by Ubbclohde and co-workers, and HOPG has since been used as a benchmark for the general characterization of carbon materials.

While intense effort continued toward perfecting synthetic filamentary carbon materials, and great progress was indeed made in the early 1960s, it was soon realized that long-term effort would be needed to reduce fiber defects and to enhance structure resistance to crack propagating. Because of the difficulty in improving the structure and microstructure of polymer-based carbon fibers for high-strength and high-modulus applications, and in developing graphitizable carbons for ultrahigh modulus fibers and because of the desire to synthesize more crystalline filamentous carbon under more-controlled conditions, synthesis of carbon fibers by a catalytic CVD (CCVD) process proceeded, laying the scientific basis for the mechanism and thermodynamics for the vapor phase growth of carbon fibers in the 1960s and early 1970s. Parallel to these scientific
studies, other research studies focused on control of the process for the synthesis of vapor-grown carbon fibers, leading to current commercialization of vapor-grown carbon fibers in the 1990s for various applications. Concurrently, polymer-based carbon fiber research has continued worldwide, mostly in industry, with emphasis on greater control of processing steps to achieve carbon fibers with ever-increasing modulus and strength and fibers with special characteristics, while decreasing costs of the commercial products.

As research on oil vapor-grown carbon fibers on the micrometer scale preceded, the growth of very small diameter filaments, such as shown in Figure 1.4, was observed, but not detailed, systematic studies of such thin filaments were reported. In studies of filaments carbon growth of the initial hollow tube and the subsequent thickening process and very thin vapor-growth tubules (<100 °A) were reported. An example of such early work is shown in Figure 1.4 [1].
Figure 1.4 High-resolution TEM micrograph showing carbon nanotubes with diameters less than 10 nm [1]
Nanotechnology is a catchall phrase for materials and devices that operate at the nanometer ($10^{-9}$ m) scale. In the metric system of measurement, "Nano" equals a billionth and therefore a nanometer is one-billionth of a meter. This length scale reaches the atomic level providing the opportunity to explore micro and macro phenomena and properties. References to nano materials, nano electronics, nano devices, and nano powders simply mean the material or activity can be measured in order of nanometers.

Nanotechnology is the science that creates functional materials and devices on the CNTs, which were first discovered in 1991 as a by-product of fullerene production [5], which represent a new class of materials. With a size that meets the nanometer scale, this new one-dimensional carbon structure is the ideal nanomaterial. CNTs have the most strength and highest thermal conductivity of any material. According to the orientation of the carbon network, CNTs can be either metals or semiconductors. These unique electronic and mechanical properties of CNTs have stimulated intensive research to characterize their structure and to explore their applications both by direct measurement and through theoretical calculation. The exploitation of CNTs in a wide range of applications, including electronic and sensing devices, composite materials, energy storage, Nano-scale probes, and field emission devices, becomes one of the most important topics in today’s materials and physical science.

Besides the outstanding physical properties, over the past few years the chemical properties of CNTs have also aroused an increasing interest from
scientists. The chemical functionalization is of significant importance since it can tailor the properties of CNTs and therefore aid in the development of applications. Functionalization has been demonstrated at the ends and sidewalls of CNTs. CNTs have great potential; on the other hand, there are still many challenges in CNT research. These challenges include large-scale production of CNTs, their purification from catalyst residues and carbonaceous impurities, the manipulation of individual tubes, and the separation by different length, diameter, and chirality.

1.2 Carbon Nanotubes (CNTs)

Carbon Nanotubes are fullerene-related structures which consist of graphene cylinders closed at either end with caps containing pentagonal rings as shown in Figure 1.5. They 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. He found that the central core of the cathodic deposit contained a variety of closed graphitic structures including nano particles and nanotubes, of a type which had never previously been observed. 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. This paved the way to an explosion of research into the physical and chemical properties of carbon nanotubes in laboratories all over the world [4].
Figure 1.5 Schematic Representation of CNTs Structure
1.3 *Single-layer Nanotubes and Nanotubes "ropes"*

A major event in the development of carbon nanotubes was the synthesis in 1993 of single layer-nanotubes. The standard arc-evaporation method produced only multilayered tubes. It was found that addition of metals such as cobalt to the graphite electrodes resulted in extremely fine tube with single-layer walls. The availability of these structures should enable experimentalists to test some of the theoretical predictions, which have been made about nanotube properties.

Smalley’s group described an alternative method of preparing single-walled Nanotubes in 1996. Like the original method of preparing C$_{60}$, this involved the laser-vaporization of graphite, and resulted in a high yield of single-walled tubes with unusually uniform diameters. These highly uniform tubes had a greater tendency to form aligned bundles than those prepared using arc-evaporation, and led Smalley to christen the bundles nanotube ropes. Initial experiments indicated that the rope samples contained a very high proportion of nanotubes with a specific armchair structure. Subsequent work has suggested that the rope samples may be less homogeneous than originally thought. Nevertheless, the synthesis of carbon nanotube ropes gave an important boost to nanotubes research, and some of the most impressive work has been carried out on these samples [4].
1.4 Carbon Nanotubes Properties

CNTs are predicted to possess novel mechanical and electrical properties owing to both their regular, periodic structure and quantum size [9-11].

1.4.1 Mechanical Properties

Due to its strong in-plane bonding, graphite is a very stiff material with an extremely high Young's modulus (800 GPa) and a very high in-plane tensile strength (20 GPa), where the numerical values given are for graphite whiskers. The high tensile strength of graphite in the basal plane is exploited in most of the applications of carbon fibers when used in woven ropes or in composites as construction materials [1]. Young's modulus, tensile strength and density of CNTs are compared with some other materials in Table 1-1[12].

Lower tensile strength and Young's modulus are also attributed to defects in MWNTs. But the weak inter-wall coupling makes one treat the MWNTs as few decoupled two dimensional single wall tubules. So the results may be useful for their applications [13].
Table 1—1 Different materials mechanical properties [12].

<table>
<thead>
<tr>
<th>Material</th>
<th>Young's modulus (GPa)</th>
<th>Tensile Strength (GPa)</th>
<th>Density (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single wall nanotube</td>
<td>1054</td>
<td>150</td>
<td>NA</td>
</tr>
<tr>
<td>Multi wall nanotube</td>
<td>1200</td>
<td>150</td>
<td>2600</td>
</tr>
<tr>
<td>Steel</td>
<td>208</td>
<td>0.4</td>
<td>7800</td>
</tr>
<tr>
<td>Epoxy</td>
<td>3.5</td>
<td>0.005</td>
<td>1250</td>
</tr>
<tr>
<td>Wood</td>
<td>16</td>
<td>0.008</td>
<td>600</td>
</tr>
</tbody>
</table>
1.4.2 Electronic Properties

The electronic and transport properties of carbon fibers are strongly related to those of graphite.

The single-walled carbon nanotubes (SWNTs) can be either metallic or semi-conducting, depending on their helicities, (i.e., how the graphene sheet is rolled up). Further interesting physical properties, such as superconductivity, ferromagnetism, have also been found or expected in them [14].

1.4.2.1 Electrical Conductivity

The analysis of the temperature-dependent conductivity of carbon Nanotube bundles shows that the simple two-band model that has been successfully used for vapor-grown carbon fibers VGCFs is also valid for carbon nanotube bundles. However, scanning tunneling microscopy (STM) studies show that both conducting and semi-conducting carbon nanotubes can be observed [9].

1.4.2.2 Electron Energy Loss Spectroscopy (EELS)

EELS concerns the inelastic scattering of an electron beam by solid and is carried out by directing an energetic (typically -100 KeV) beam of electrons onto a thin region of material (typically <1 00 nm) and measuring the intensity of the transmitted beam as a function of energy loss (AE) EELS spectra have been
reported for polarizations both parallel and perpendicular to the tubule axis for CNTs [15].

1.4.2.3 Magneto-resistance

Magneto-resistance measurements on a bundle of CNTs show a negative magneto-resistance, as is normally found in carbon fibers showing 2D weak localization effects. However, at low T (<1 K) anomalous behavior is found in the magneto-resistance, different from previous observations in VGCFs [16].

1.4.3 Optical Properties

Graphite is a relatively good conductor; hence, its optical properties are often investigated by optical reflectivity measurements. Because of the low carrier density of graphite, the free carriers do not give rise to a clear plasma response in the reflectivity spectrum [1]. Sun et al. has done some numerical work in the optical for fullerene and CNTs [17].

1.4.4 Thermal Properties

The heat capacity, thermal conductivity, and thermal expansion coefficients of graphite are all unusual. The high degree of anisotropy ($k_a/k_c \approx 300$) and the large magnitude of the in-plane thermal conductivity are simultaneously reduced by crystal imperfections and by defects, which act as
phonon scatterers [1]. Che, Cagin, and Goddard [17] numerically calculated the thermal conductivity of a nanotube to approach 2,980 W/m-K as the current applied to it is increased. In 2000, Berber, Kwon, and Tomànek [20] determined the thermal conductivity of CNTs and its dependence on temperature. They confirmed the suggestion of Hone et al. in 1999 by suggesting an unusually high value of 6,600 W/m-K for the thermal conductivity at room temperature.
Table 1—2 Facts about Carbon Nanotubes

<table>
<thead>
<tr>
<th>Carbon Nanotubes Fact-sheet</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Equilibrium Structure</strong></td>
</tr>
<tr>
<td>Average Diameter of SWNT’s</td>
</tr>
<tr>
<td>1.2-1.4 nm</td>
</tr>
<tr>
<td>Distance from opposite Carbon Atoms (Line 1) 2.83 Å</td>
</tr>
<tr>
<td>Analogous Carbon Atom Separation (Line 2) 2.456 Å</td>
</tr>
<tr>
<td>Parallel Carbon Bond Separation (Line 3) .45 Å</td>
</tr>
<tr>
<td>Carbon Bond Length (Line 4) 1.42 Å</td>
</tr>
<tr>
<td>C-C Tight Bonding Overlap Energy ~ 2.5 eV</td>
</tr>
<tr>
<td>Group Symmetry (10, 10) C5V</td>
</tr>
<tr>
<td>Lattice Bundles of Ropes of Nanotubes: Triangular Lattice(2D)</td>
</tr>
<tr>
<td>Lattice Constant 17 Å</td>
</tr>
<tr>
<td>Lattice Parameter:(10, 10) Armchair 16.78 Å</td>
</tr>
<tr>
<td>(17, 0) Zigzag 16.52 Å</td>
</tr>
<tr>
<td>(12, 6) Chiral 16.52 Å</td>
</tr>
<tr>
<td><strong>Density:</strong></td>
</tr>
<tr>
<td>(10, 10) Armchair 1.33 g/cm³</td>
</tr>
<tr>
<td>(17, 0) Zigzag 1.34 g/cm³</td>
</tr>
<tr>
<td>(12, 6) Chiral 1.40 g/cm³</td>
</tr>
<tr>
<td><strong>Interlayer Spacing:</strong></td>
</tr>
<tr>
<td>(n, n) Armchair 3.38 Å</td>
</tr>
<tr>
<td>(n, 0) Zigzag 3.41 Å</td>
</tr>
<tr>
<td>(2n, n) Chiral 3.39 Å</td>
</tr>
</tbody>
</table>
1.5 Applications of CNTs

Because of their outstanding electronic and mechanical properties CNTs have and will have applications in many fields. These applications include field emitters for scanning tunneling electron microscope tips; nano-scale electronics, nano-electronic devices; catalyst supports; hydrogen and energy storage media; battery electrodes; reinforcing material in carbon composite materials such as polymers, ceramics, and metals; hydrogen; gas; humidity; chemical and biological sensors; and controlled drug release.

1.5.1 Reinforcement for Composite Materials

Because of their excellent mechanical properties, CNTs are perfect fiber candidates for composite materials such as reinforcement of polymers. Significant breakthroughs have been reported in processing CNTs [19–21] and carbon nanotube/polymer composite films [22–28] and fibers [29–31].

By adding CNTs, the strength, elasticity, toughness, durability, and conductivity of the composite material can be improved. The major challenge in using CNTs for composite materials is achieving a homogeneous dispersion of CNTs throughout the matrix without destroying their integrity. The second important point to be considered is the interfacial bonding, which is required to achieve load transfer across the nanotube-matrix interface. In some special cases, CNTs aligned parallel to the axis of the composite are desired.
In practice, a solution or suspension of matrix material is mixed thoroughly with CNTs to create a uniform composition. Sometimes chemical functionalization or physical wrapping is used to improve the affinity of CNTs for the matrix [32].

Ultra-sonication is often applied to prepare the dispersion of CNTs. After evaporating the solvent, the composite material is obtained in bulk or film form. This method has been used to produce composite materials, such as MWNT/silane [33], MWNT/PmPV [34, 35] and SWNT/PmPV [37].

Polyacrylonitrile (PAN)/CNTs composite fibers were spun from solutions in dimethyl acetamide (DMAc), using single wall (SWNTs), double wall (DWNTs), multi-wall (MWNTs), and vapor grown carbon nanofibers (VGCNFs). In each case, CNTs content was 5 wt% with respect to the polymer. While all nanotubes contributed to property improvements, the maximum increase in modulus (75%) and reduction in thermal shrinkage (up to 50%) was observed in the SWNT containing composites, and the maximum improvement in tensile strength (70%), strain to failure (110%), and work of rupture (230%) was observed in the MWNTs containing composites as shown in Table 1.3 [37].

CNTs reinforced polymer composites are seen as a potentially fruitful area for new, tougher or fatigue resistant materials [38].
Table 1—3 Structural parameters and properties of control PAN and PAN/CNT composite fibers [37]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Control PAN</th>
<th>PAN/SWNTs</th>
<th>PAN/DWNTs</th>
<th>PAN/MWNTs</th>
<th>PAN/VGCNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus (GPa)</td>
<td>7.8±0.3</td>
<td>13.6±0.5</td>
<td>9.7±0.5</td>
<td>10.8±0.4</td>
<td>10.6±0.2</td>
</tr>
<tr>
<td>Strength at break (MPa)</td>
<td>244±12</td>
<td>335±9</td>
<td>316±15</td>
<td>412±23</td>
<td>335±13</td>
</tr>
<tr>
<td>Strain to failure (% strain)</td>
<td>5.5±0.5</td>
<td>9.4±0.3</td>
<td>9.1±0.7</td>
<td>11.4±1.2</td>
<td>6.7±0.3</td>
</tr>
<tr>
<td>Toughness (MPa)</td>
<td>8.5±1.3</td>
<td>20.4±0.8</td>
<td>17.8±1.7</td>
<td>28.3±3.3</td>
<td>14.0±1.0</td>
</tr>
<tr>
<td>Shrinkage at 160°C (%)</td>
<td>13.5</td>
<td>6.5</td>
<td>11.5</td>
<td>8.0</td>
<td>11.0</td>
</tr>
<tr>
<td>$T_S^*$ (°C)</td>
<td>100</td>
<td>109</td>
<td>105</td>
<td>103</td>
<td>103</td>
</tr>
<tr>
<td>$I_{PAN}$</td>
<td>0.52</td>
<td>0.62</td>
<td>0.53</td>
<td>0.60</td>
<td>0.57</td>
</tr>
<tr>
<td>$I_{CNT}$</td>
<td>–</td>
<td>0.98</td>
<td>0.88</td>
<td>0.91</td>
<td>0.91</td>
</tr>
<tr>
<td>Crystal size (nm)</td>
<td>3.7</td>
<td>5.0</td>
<td>4.1</td>
<td>5.0</td>
<td>4.4</td>
</tr>
<tr>
<td>Crystallinity (%)</td>
<td>58</td>
<td>54</td>
<td>57</td>
<td>55</td>
<td>55</td>
</tr>
</tbody>
</table>

* $T_S^*$ peak temperature.
The addition of CNTs fillers to poly (methyl methacrylate)–CNTs nano composite thin films, can have a dramatic reinforcement effect on the nature of degradation by both sources of high-energy radiation, where polymer-free radicals are mainly responsible for the proliferation of degradation. In addition, CNT networks can effectively disperse the radiation [39]. CNTs composites may find application in electronic devices.

Polypyrrole (PPy) is a conducting polymer and has been used to make composite films with MWNTs by electrochemistry [40].

**1.5.2 Electronic applications**

**1.5.2.1 Battery electrodes**

For applications in micro batteries and nano-scale devices, controlled growth of vertically aligned nanotubes is important. Future work will involve improving the synthesis techniques of carbon nanotubes for a better control over alignment, density, purification, nanotube diameter, wall thickness and improving our prototype batteries by applying carbon nanotubes as electrodes and fabricating true nano-battery systems with nanotube electrical connections [41]. Nano composites of carbon nanotubes (CNTs) with Sb and SnSb$_{0.5}$ particles were prepared by chemical reduction of SnCl$_2$ and SbCl$_3$ precursors in the presence of CNTs. These CNT–metal composites are active anode materials for lithium ion batteries, showing improved cyclability compared to unsupported Sb.
and Sn–Sb particles and higher reversible specific capacities than CNTs [42] as shown in Table 1.4.

### 1.5.2.2 Semi-conducting applications

The single electron transistor (SET) is formed by two quantum dots connected by a conductive tunnel (island). Several groups have reported SET devices made of individual metallic SWNTs [43] and chemically modified individual SWNT bundles that operate at room temperature [44].

The SiO$_2$ islands formed by excess anodization of Si-based are the starting growth points of the CNTs as shown in Figure 1.6. This kind of Si-based CNTs array is expected to have significant applications in nano electronics and nano devices [45].

Nano-electronic devices using CNTs, such as Field-Effect Transistors (FETs) and Single-Electron Transistors (SETs) attracted many researches [46-48]. FET is one of the most important electronic devices using CNTs in electronics applications. A simple FET involves two main electrodes (“source” and “drain”) connected by a semi-conducting channel. For CNTs based FETs as shown in Figure 1.7 the channel is made of an individual semi-conducting CNTs. A third electrode, the “gate”, is separated from the channel by a thin insulator. The channel of a p-type FET (hole-conducting, like CNT) becomes conductive when a negative charge is placed on the gate and a certain threshold voltage is exceeded [32].
Table 1—4 Comparison of electrical capacities in first cycle Li insertion and extraction reactions between 0 and 2 V and at 50 mA g [42]

<table>
<thead>
<tr>
<th>Electrode</th>
<th>1st Li-insertion (mAh g⁻¹)</th>
<th>1st Li-extraction (mAh g⁻¹)</th>
<th>1st cycle efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNTs</td>
<td>822</td>
<td>199</td>
<td>24.2</td>
</tr>
<tr>
<td>Sb</td>
<td>1023</td>
<td>648</td>
<td>63.3</td>
</tr>
<tr>
<td>SnSb₆₃ alloy</td>
<td>951</td>
<td>726</td>
<td>76.3</td>
</tr>
<tr>
<td>CNTs–Sb (36 wt.%)</td>
<td>1266</td>
<td>462</td>
<td>36.5</td>
</tr>
<tr>
<td>CNTs–SnSb₆₃ (56 wt.%)</td>
<td>1092</td>
<td>518</td>
<td>47.4</td>
</tr>
</tbody>
</table>
Figure 1.6: (a) Schematic diagram of Si-based nano scale SiO$_2$ islands (b) A cross-sectional and (c) a planar images of Si-based [44].
Figure 1.7: A scheme of FET made by individual SWNT (middle) the upper picture is imaged by AFM, and the bottom is a diagram of the circuit [48].
1.5.3 Hydrogen or Gas Storage

Hydrogen has been employed in different fields such as hydrogenation processes, petroleum transformation, welding, cryogenic cooling, chemical production of substances, and rocket engines. Considering that fossil fuels (petroleum and natural gas), traditionally used as main energy sources, are pollutant and exhaustible (extinguish) agents, the hydrogen utilization as a clean energy source in fuel cells has been recently researched. Fuel cells are currently used in vehicle and power generators. They are electrochemical devices that can directly convert chemical energy to electrical energy obtaining water as the only waste (residual) product. Hydrogen, a colorless and odorless gas is inflammable for concentrations higher than 4%. Accordingly its transport and storage raises many safety questions [49]. CNTs possess hollow cavities, creating excellent nano-containers for hydrogen storage. Hydrogen molecules can be physically adsorbed on the exterior surface of CNTs or interstitial spaces between them.

The science and technology related with CNTs in hydrogen storage has evidently progressed in recent years. Hydrogen is a carrier of high energy density, and is regarded as an ideal energy carrier because of its non-pollution property. Hydrogen is the most universal element existing in nature. As an energy source, hydrogen is of the lightest weight of all the elements and can transit heat energy most easily among all the gases, but the main obstacle of using it lies in the hydrogen storage with high-energy density [50].
The application of CNTs in the electrodes of hydrogen storage battery [51] is being carried out to improve the electrochemical hydrogen storage ability. The hydrogen storage capacity of CNTs depends on several factors, such as tube diameter, length, and purity. Theoretical calculations predict that the hydrogen storage capacity of SWNTs can be larger than 14 wt. % (160 kg H₂/m³). The predicted hydrogen storage capacity of SWNTs increases linearly with the tube diameter [52].

1.5.4 Gas or Humidity sensors

The high aspect ratio, surface area, size, hollow geometry, and chemical inertness are all remarkable properties of CNTs, which make them attractive for demanding applications in the field of gas sensing. To date studies on possible applications of CNTs have been focused either on individual SWNTs as sensitive materials towards O₂, NO₂ and NH₃ [53-58] or on MWNTs (CNTs) mats as NH₃, CO, CO₂ humidity and O₂ gas sensors [59–60]. Nanotube sensors offer significant advantages over conventional metal-oxide-based electrical sensor materials in terms of sensitivity and small sizes needed for miniaturization and the construction of massive sensor arrays [61].

A novel microelectronic gas sensor utilizing carbon nanotubes in a thin-layered Pd/CNTs/n⁺-Si structure for hydrogen detection has been achieved. The sensor is fabricated on an n-type silicon wafer, which is needed as an ohmic supporting substrate as shown in Figure 1.8. MWNTs were grown selectively on the substrate via catalytic activation with microwave plasma enhanced chemical
vapor deposition. The I–V characteristics of the sensor exhibit Schottky diode behavior at room temperature with marked sensitivity or current changes in the presence of hydrogen as shown in Figure 1.9. Increasing detection sensitivity in hydrogen sensing was observed with increasing operating temperature. The results demonstrate that CNTs configured as a gas sensor has high sensitivity to hydrogen over a wide temperature range. The successful utilization of CNTs in gas sensors may open a new door for the development of novel nano-structure gas-sensing devices [62].

A low humidity sensor was made of a quartz crystal microbalance (QCM) coated with multi-walled carbon nanotubes/Nafion (MWCNTs / Nafion) composite material films [63].
Figure 1.8 Schematic diagram of the experimental setup of the CNTs-based gas sensor [62].
Figure 1.9 Plot of measured current vs. applied voltage (I–V) of the CNTs-based sensor in air and after exposure to constant flow of H₂ (concentration, 100%; flow rate, 10 ml/min) at room temperature [62].
1.5.5 Chemical and Biological Sensors

Because of its 1-D structure, CNTs are ideal candidates for the development of a new generation of biological and chemical sensors. SWNTs have small dimensions, which make them easily introduced into cells with little disturbance of the cell function.

The incorporation of enzymes with a transducer allows one to fabricate highly sensitive and selective enzyme-based biosensors. Many different methods of enzyme immobilization have been proposed such as gels, conductive salts, carbon pastes, organic polymer hosts (Tess and Cox, 1999; Wang, 2001; Cardosi and Turner, 1990) and recently nanostructured materials. In the case of nanostructured materials, nanosized colloidal gold (Liu and Ju, 2003), SiO$_2$ nanoparticles (Qhobosheane et al., 2001) and carbon nanotubes (Davis et al., 1997; Azamian et al., 2002) have been successfully used to immobilize enzymes and apply for biosensing. The direct electron transfer (DET) of various redox proteins has been observed when such nanomaterials are used to modify the surfaces of the working electrodes. Of particular interest is the use of the carbon nanotube as an electrochemical transducer [64].

A sensitive detection method is required for some viruses, specific antibodies, metabolized materials, and heavy metal ions in serum or body fluid. Such a method would not just facilitate the examination of blood for transfusions or be used in evaluating environmental pollution, but also aid in the investigation of the binding processes of bio-molecules while using small sample amounts. Sensitivity and size of equipment are crucial factors for biosensors, especially for
outdoor use. Nanotubes are expected to exhibit excellent properties as transducers. Moreover, they are ideal materials for ultra-small sensors because they have a large surface area and are known to exhibit charge-sensitive conductance. Semi-conducting SWNTs have high mobility; all their atoms are located on the surface. CNT sensors detected anti-hemagglutinin (HA) is shown in Figure 1.10 [65].
Figure 1.10: Schematic model of I–V measurement using the CNT sensors [65].
1.5.6 Controlled Drug Delivery

The search for new and effective drug delivery systems is a fundamental issue of continuous interest. A drug delivery system is generally designed to improve the pharmacological and therapeutic profile of a drug molecule. The ability of f-CNT to penetrate into the cells offers the potential of using f-CNT as vehicles for the delivery of small drug molecules. However, the use of f-CNT for the delivery of anticancer, antibacterial or antiviral agents has not yet been fully ascertained. The development of delivery systems able to carry one or more therapeutic agents with recognition capacity, optical signals for imaging and/or specific targeting is of fundamental advantage. For example in the treatment of cancer and different types of infectious diseases. For this purpose, a new strategy was developed for the multiple functionalisation of CNT with different types of molecules (Figure 1.11 a). A fluorescent probe for tracking the cellular uptake of the material and an antibiotic moiety as the active molecule were covalently linked to CNT. MWNT were functionalised with amphotericin B and fluorescein. The antibiotic linked to the nanotubes was easily internalized into mammalian cells without toxic effects in comparison with the antibiotic incubated alone (Figure 1.11 b) [66].
Figure 1.11: Functionalization and imaging of CNT with amphotericin B[66].

(a) Covalent attachment of amphotericin B and fluorescein isothiocyanate to CNT. MWNTs are treated with acids to generate carboxylic groups, subsequently modified with a mono-protected diaminetriethylene glycol. The CNTs are then subjected to 1,3-dipolar cycloaddition. Selective cleavage of the orthogonal protecting groups allows the introduction of the fluorescein moiety and amphotericin B. (b) Epifluorescence microscopy image of f-CNT inside Jurkat cells. Bright-field image (left) and fluorescent image (right) after internalisation of f-CNT incubates for 16 h at 37°C. Jurkat cells have an average diameter of 10 μm.
2.1 CNTs Synthesis Methods

Many Synthesis methods are used to produce CNTs. The most commonly used methods are the arc discharge, laser ablation, flame and chemical vapor deposition.

2.2. Laser Ablation Method

This method involves shooting a laser at a graphite target in the presence of a metal catalyst. When the target is hit with the Laser, the carbon ablates and jets out. The ablated carbon phase includes the metal catalysts, which then cool and crystallize into nano-particles from which the MWNTs or SWNTs grow.

A continuous flow of a gas, such as Ar, is used to move the product to the collector [67]. Figure 2.1 shows a schematic of a laser ablation setup.
Figure 2.1 Schematic of a laser ablation set-up [67].
2.3 Arc Method

In this method a high current electric arc goes through graphite electrodes in the presence of catalytic particles to form CNTs and soot as shown in Figure 2.2. The MWNTs produced by this method were first made as a byproduct of the production of fullerenes. Currently the largest commercial suppliers of MWNTs material utilize the core material from arc production [67,68].
Figure 2.2 Schematics of an arc-discharge apparatus, along with TEM pictures of the products obtained with doped and pure anodes [67].
2.4. Chemical Vapor Deposition (CVD) Method

An alternative to the arc discharge and laser ablation methods is the catalytic growth of Nanotubes. This method is based on the decomposition of a hydrocarbon gas over a transition metal to grow CNTs in a chemical vapor deposition (CVD) reactor such as the one shown below in Figure 2.3 [69].

Carbon filaments and fibers have been produced by thermal decomposition of hydrocarbons since the 1960s. Usually, a catalyst is necessary to promote the growth.

For the production of MWNTs acetylene is usually used as source of carbon atoms at temperatures typically between 600 – 800°C. To grow SWNTs the temperature has to be significantly higher (900 – 1200°C) due to the fact that they have a higher energy of formation. In this case carbon monoxide or methane may be used because of their increased stability at higher temperatures as compared to acetylene [69].
Figure 2.3: Schematics of a CVD deposition oven.
2.5 Flame Method

Flame synthesis is an economical means of bulk synthesis of a variety of aerosol materials such as carbon black. Flame synthesis of CNTs could potentially realize an economy of scale that would enable their use in common structural materials such as car-body panels. Figure 2.4 is a TEM micrograph of MWNTs. The image shows a cross section of the atomic structure of the Nanotubes. This sample was obtained by the supported catalyst method, whereby the nanoscale catalysts are dispersed on a substrate providing their support. The substrate with catalyst particles was immersed within an acetylene diffusion flame to which nitrogen had been added to eliminate soot formation. Upon removal from the flame, the nanotubes were dispersed on a holder suitable for electron microscopy. Although not seen in the figure, the tube diameter reflects that of the catalyst particle [70, 71].

The right figure is a TEM of a SWNT. Only a single graphite layer of carbon (one layer plane of graphite) is rolled upon itself so as to form a seamless cylinder. The nanotubes were obtained by sampling material from a flame using a probe that was rapidly inserted and retracted from the flame to minimize flame perturbations. In these experiments, catalyst particles were seeded into the flame by thermal decomposition of a suitable precursor compound [70].
Figure 2.4 Up cross section of MWNTs down SWNT.
This section will include the works, which have been done by other researchers related to the flame synthesis of Carbon Nanotubes in both diffusion and pre-mixed flames. During the last few years Single and Multi wall carbon nanotubes syntheses have been reported for both diffusion [72,73] and Pre-mixed flames [74].

2.5.1 Diffusion Flame

In 1987 K. Saito conducted SEM analyses of materials deposited on a stainless steel grid from methane, acetylene and other hydrocarbon flames [71, 75, 76]. This analysis indicated the rough surface material to be soot and the initial light brown material to be soot and polyhedral shaped crystal-like particles. Surprisingly, a deposit from the acetylene flame had a spider-web shape of entangled, long, narrow diameter strings, but its detailed structure remained unknown until the present TEM analysis revealed entangled carbon nanotubes [70]. This work was repeated using a stainless steel grid with a holding wire of a 0.4 mm diameter bare Ni-Cr to collect deposit materials from a methane flame. At an appropriate position in the flame, brown material was deposited on the stainless steel grid, and black material was deposited on the Ni-Cr wire. SEM and TEM analyses showed the black materials to be almost purely multi-walled carbon nanotubes whose diameters ranged from 20 to 60 nm.
This is the first evidence from the synthesis of such carbon nanotubes from a methane diffusion flame under normal atmospheric pressure. In this work unseeded methane air diffusion flame was employed. Figure 2.5 shows a schematic diagram of the experimental apparatus. Methane (99.9% purity) issued from a 1.1 cm diameter stainless-steel tube, which surrounded by a 5 cm diameter tube through which air flowed with the average linear fuel flow rate of 16.3 cm$^3$/s and the average airflow rate 63.0 cm$^3$/s, a steady and stable laminar flame with a visible flame height of 65 mm was established on the burner port at atmospheric pressure. A stainless-steel grid was employed with a holding wire of 0.4 mm diameter bare Ni-Cr (60% Ni, 26 % 14 % Fe) to collect deposit materials on the grid [70].

The sampling time was 15-30 min: the longer time resulted in the larger accumulation of deposit materials, but SEM and TEM images of these deposited materials remain the same regardless of the sampling time. Figure 2.6 reveals the magnified image of each spaghetti-shaped CNT with a tube diameter range between 20 and 60 nm [70].
Figure 2.5: A schematic diagram for the experimental apparatus for the diffusion flame [70]
This work reported that the region in the flame where nanotubes growth occur is not large but it is limited to certain conditions and the optimum yield condition for carbon nanotubes was at h/H = 0.2-0.3 and r/R = 0.6 - 0.9, where h is the axial height, H is the visible flame height, r is radial distance from the axial height, and R is the flame radius. Catalyst particle formation and nanotube formation are two different processes that do not interact chemically, but in that work, these two processes affect each other. The existence of oxygen affects not only the catalyst particle formation (nickel oxide) but also pyrolysis process of methane. This self-formation process of catalyst particle may provide a cost effect on production method to synthesize a large amount of multi-walled CNTs. The optimum nanotube growth rate and yield seem to depend on oxygen concentration, temperature, and residence time [70].

Flame synthesis, a technique that is widely used for commercial synthesis of a broad range of materials, such as carbon black, does offer these features. While flame synthesis of other novel carbon nano-structures such as fullerenes has been reported [74], flame synthesis of pure CNTs has met with little success [75]. The synthesis of single-wall nanotubes (SWNTs) via a simple laboratory-scale diffusion flame was demonstrated. The method, which was employed, is a metal nanoparticle catalyst formed from a metallocene lowers the energetic constraints for the formation of CNTs and hence acts as an effective interface between the gas-phase reactants and solid carbon precipitate [73, 2].
Figure 2.6: SEM images for the deposit material from methane diffusion Flame [70].
A laminar diffusion flame served as the hot, reactive hydrocarbon environment for the synthesis. Nitrogen dilution of the fuel acetylene or ethylene produced a fuel concentration commensurate with that typically used in the floating catalyst approach in conjunction with high-temperature furnaces. Typical flow rates were 0.150 slm (slug per minute) \([3.65 \times 10^{-2} \text{ kg/s}]\) of acetylene and 1.75 slm \([4.26 \times 10^{-1} \text{ kg/s}]\) of nitrogen. All syntheses were performed at atmospheric pressure. An additive, when used, was introduced into the flow at a rate of 0.050 slm \([1.22 \times 10^{-2} \text{ kg/s}]). Metalloocene vapor was entrained within the inert gas that was the major component of the pyrolysis flame. Estimated introduction rates ranged between 0.1 and 2 mg/min. Nanotubes were collected from the flame for subsequent transmission electron microscopy (TEM) analysis by thermophoretic sampling. In this technique, a probe holding a TEM grid is rapidly inserted into a hot gas environment allowed to remain for some period of time, tens to hundreds of milliseconds, and then retracted. The temperature gradient between the cold probe initially at room temperature and the hot flame gases drives the motion of particles towards the cold surface, resulting in deposition. Sampling times were typically maintained at 250 ms [71].

According to Randall L. Vander Wal work [77, 79] diffusion flames of methane or nitrogen-diluted methane did not yield a detectable number of nanotubes. Acetylene gave a tenfold increase over ethylene in relative nanotube yield as observed through a survey of TEM images. The additives of hydrogen, air and methane to the nitrogen diluted fuel stream were tested individually. Hydrogen only slightly enhanced the Nanotube yield in either ethylene or
acetylene diffusion flames. The presence of air in concentrations similar to hydrogen resulted in nanotube yields similar to those obtained with hydrogen. Methane addition in similar concentrations gave SWNT yields that were several times greater than those observed in the absence of additive. Dilution of the fuel stream with an inert gas was critical to Nanotube synthesis. Absence of the inert carrier resulted in soot formation and the complete encapsulation of the metal nanoparticles within a carbonaceous matrix with no nanotubes being formed. Substitution of argon for nitrogen as the inert carrier produced little change in the observed nanotube yield for a given acetylene and hydrogen concentration. Inert concentrations greater than 1.0 slm lowered the Nanotube yield, presumably due to decreased reactant concentration. Figure 2.7 shows TEM micrographs at different magnifications of the material collected from the flame [78].

The absence of SWNT stubs protruding from the carbonaceous matrix indicates that the SWNTs were not formed by carbon dissolution and precipitation from the carbonaceous matrix in which the particles are embedded. It is concluded that the SWNTs observed here formed via the same aerosol gas-phase synthesis process reported for high-temperature furnace methods, proceeding first with catalyst particle formation followed by Nanotube growth via the mechanism discussed above. For the present flame conditions, the majority of catalyst particles were simply deactivated prior to nanotube inception, reflecting less than optimized growth conditions [78].

Flame synthesis of CNTs provides unique features not realized in current synthetic methods utilizing an arc discharge or high-temperature furnace.
Combustion of a portion of the hydrocarbon gas provides the elevated temperatures required with the remaining fuel quite naturally serving as the hydrocarbon reagent. Hence the flame constitutes an efficient source of energy and hydrocarbon reactant. Perhaps the most significant aspect of the flame synthesis approach is the very short residence times realized for catalyst inception and nanotube growth. Reported results from the high-temperature furnace approach suggest reaction times on the order of seconds. In contrast, the flame synthesis method realizes residence times on the order of tens of milliseconds, an attribute that underscores the potential of flame synthesis for large-scale production of nanotubes [73].

Flame synthesis of Ni-catalyzed nanofibers is illustrated and the experimental setup is shown in Figure 2.8. Ni Nanoparticles are formed by thermal decomposition of a nebulized Ni nitrate solution entrained into a reactive fuel mixture. Although at the earliest stages of growth, the Ni Nanoparticles are sufficiently small to catalyze single-wall Nanotubes (SWNTs), only the larger particles appear catalytically active yielding only nanofibers [79]. Flame synthesis of single-walled carbon nanotubes and nanofibers is demonstrated using a pyrolysis flame configuration. Fe reacts preferentially with CO/H₂/He mixtures to produce single-walled Nanotubes (SWNTs). In contrast, Ni reacts preferentially with C₂H₂/H₂/He mixtures to yield nanofibers. Both catalyst metals exhibit a marked size dependent reactivity towards these reactant gas mixtures.
Figure 2.7: TEM image Nanotubes and HRTEM image of a SWNT [71].
The yarmulke mechanism and a carbon solvation/diffusion/precipitation account for the different catalyzed products; SWNTs and nanofibers, respectively. Consequences of the size dependent reactivities of Fe and Ni Nanoparticles and the respective growth mechanisms for the SWNTs and nanofibers are discussed [80]. Using different reactive gas mixtures consisting of CO or C\textsubscript{2}H\textsubscript{2} or their combination, Ni nanoparticles exhibited a high preferential reactivity towards C\textsubscript{2}H\textsubscript{2} to form nanofibers.

Variation of the CO/C\textsubscript{2}H\textsubscript{2} ratio in reactant mixtures of CO/C\textsubscript{2}H\textsubscript{2}/H/He alters the nano-fibers morphology very little; instead the relative yield varies dramatically. Ni appears to be relatively uncreative towards CO within the flame environment used here for all particle sizes observed here (0.5–5nm). In contrast, Ni is catalytically active towards C\textsubscript{2}H\textsubscript{2}, but only the larger nano-particles (4–5nm) exhibit this activity. A synergism between CO and C\textsubscript{2}H\textsubscript{2} is observed as an increase nano-fibers yield in reactant mixtures containing both CO and C\textsubscript{2}H\textsubscript{2}.

Electronic interaction between the adsorbents, mediated by the metal nanoparticles and physical protection of active sites are consistent with the variation in yield with varying CO/C\textsubscript{2}H\textsubscript{2} ratios. High C\textsubscript{2}H\textsubscript{2} concentrations lead to encapsulation, indicative of too rapid a supply carbon and likely deposition of PAHs that deactivate active sites. By variation of the gas composition, extraneous deposition of amorphous carbon on the nanofibers walls and soot formation may be prevented. Thus only nanofibers are produced as the flame synthesized aerosol product [79]
Figure 2.8 Experimental schematic [79].
Formation of carbon nanotubes in counter flow, oxy-methane diffusion flames without catalysts has been studied. Figure 2.9 shows oxygen enriched methane diffusion flames, and carbon nanotubes discovered to be formed in the region on the fuel-rich side of the flame front at an oxygen enrichment of 50%. No catalyst was employed. An opposed flow diffusion flames with varying strain rate and oxygen content in the oxidizer stream was used. Substantial quantities of nanotube material are produced at atmospheric pressure in this continuous (non-batch) process. Thermophoretic sampling of the flame and collecting the carbon material deposited near the exhaust was done. Both confirm the growth of carbon nanotubes and other carbon clusters [80].

Ethylene flame synthesis of well-aligned multi-walled carbon Nanotubes was also reported by using Cobalt electrodeposited stainless steel applied to the nitrogen-diluted ethylene diffusion flame; well-aligned and well-graphitized CNTs consisting of 20 nm diameters and 10 mm long element were obtained [82].
Figure 2.9 Schematic of counter-flow burner [80].
2.5.2 Pre-mixed Flame

In addition to their appeal as a practical method for Nanotube production, flames also offer an ideal system in which to study the mechanisms of Nanotube formation. There are three key requirements for Nanotube formation:

1) Source of carbon,
2) Source of heat, and
3) Presence of a metallic catalyst particle.

A fuel-rich flame is a high temperature, carbon-rich environment that can be suitable for nanotube formation if metals are introduced into the system. Furthermore, a premixed 1-dimensional flame can serve as a convenient system in which to perform a variety of systematic measurements to characterize the dynamics of Nanotube formation.

A premixed acetylene/oxygen/argon flame formed the basis of this study. An argon dilution of 15 molar percent, cold gas feed velocity of 30 cm/s, and burner pressure of 50 Torr (6.7 KPa) were used throughout the experiments. A variety of fuel equivalence ratios rang from 1.4 through to 2.2 was considered. Iron pentacarbonyl (Fe (CO) 5) was used as the source of metallic catalyst necessary for nanotube synthesis. A controlled flow of iron pentacarbonyl vapor was supplied through a temperature-controlled (4°C) single-stage bubble saturator unit using argon as the carrying gas. The argon gas flow could be accurately proportioned between the saturator and a bypass line, allowing control of the catalyst feed rate. Typical iron pentacarbonyl feed concentrations were 4,000 PPM.
The burner, as shown in Figure 2.10, consists of a 100 mm diameter copper plate with 1500 uniformly spaced 1.00 \( \mu \)m diameter holes drilled through the surface. Only the inner 70mm diameter burner section was utilized for this study with the outer annular section used during flame startup. The burner plate is attached to a burner cavity filled with stainless steel wool to facilitate uniform flow distribution of the premixed gases entering from the base of the cavity. A flow of cooling water passes through copper tubing coiled around the outside of the burner body. Burner plate temperatures were typically 70-80°C.

The burner is mounted on a vertical translation stage, which allows measurements to be taken at various height above the burner (HAB). The burner and translation stage are contained in a stainless-steel pressure chamber. The upper chamber plate is water-cooled and exhaust gases are withdrawn through two ports in the upper flange. A variety of ports in the sidewall of the chamber provide access to sampling and diagnostic instruments. A large (15 cm) window is provided for visual observation of the flame. An electronic proportioning valve and PID controller coupled to the exhaust extraction system allows accurate control of the chamber pressure. Flame characterization sampling was performed on flames with fuel equivalence ratios (\( \phi \)) between 1.4 and 2.2. For each flame, samples were obtained along the axis-line in the post-flame region between 10 and 75 nm above the burner [73].
Figure 2.10  Premixed flame burner and burner chamber showing flow metering and pressure control systems.

*The burner can be translated vertically to allow sampling at a series of heights above burner [73].*
A typical progression of nanotube morphologies observed in a flame with equivalence ratio of 1.6 is shown in Figure 2.11. The initial post-flame region (up to 40 mm) is dominated by the presence of discrete particles. The composition of the particles is most likely metallic iron as observed in flames of higher equivalence ratio. CNTs are observed after an inception time of approximately 30 ms. A small number of discrete Nanotube segments with length of the order of 100 nm are observed as early as 25 ms and longer tube lengths up to a micron in length are observed to form in the following 10 ms [73].

It appears that the metallic particle population has reached a critical level after 25 ms and Nanotube growth proceeds rapidly after this point for the next 10 to 20 ms. The critical condition may be: sufficiently large particle size, carbon content, surface properties, internal lattice structure transition, or point of relative concentrations for CO and H₂ within the flame gases. For times after 40 ms the dominant mechanism appears to be coalescence of the condensed material in the flame gases. Disordered networks of nanotube bundles form tangled webs decorated with metallic and soot-like particles. The complexity and size of the webs increases significantly in the upper region of the system, between 45 and 70 ms [73].
Figure 2.11: TEM images showing a representative progression of Nanotube morphologies with increasing HAB. Scale bars represent 100nm ($\phi=1.6$) [73].
The effect of different equivalence ratios upon Nanotube formation was also investigated. Samples were extracted from 70 mm above burner (approx. 67 ms) for equivalence ratios between 1.4 and 2.0. Representative TEM images over the range of equivalence ratios are shown in Figure 2.12. Nanotubes are observed to form between equivalence ratios of 1.5 and 1.9 only [73] SWNTs have been observed in a premixed acetylene/oxygen/argon flame operated at 50 Torr with iron pentacarbonyl vapor used as a source of metallic catalyst necessary for nanotube growth. Catalyst particle formation and growth is observed in the immediate post-flame region, 10 to 40 mm HAB, with coagulation leading to typical particle sizes on the order of 5 to 10 nm. Nanotubes were observed to be present after 40 mm (34 ms) with Nanotube inception occurring as early as 30mm HAB (~ 25 ms). Between 40 and 70 mm HAB (period of approx. 30 ms), nanotubes are observed to form and coalesce into clusters. Based on the rapid appearance of nanotubes in this region, it appears that once initiated, nanotube growth is quite rapid, on the order of 10 \( \mu \text{m} \) per second. A nanotube formation 'window' is evident with formation limited to fuel equivalence ratios between a lower limit of 1.5 and an upper limit of 1.9.
Figure 2.12: TEM image showing a bundle of SWNs (φ = 1.6, HAB=70mm) [73].
CHAPTER THREE

CNTs GROWTH IN THE CVD REACTOR

*Background*

Chemical vapor deposition (CVD) is one of the most widely used method for production of high quality CNTs. By vapor phase thermal catalytic deposition of a carbon source (C\(_6\)H\(_{10}\), C\(_8\)H\(_8\), C\(_6\)H\(_6\), C\(_2\)H\(_2\), C\(_6\)H\(_{14}\), CO, CH\(_4\), etc.) with metal nano-particles catalyst as Fe, Co, Ni, Co-Ni, and CoSi\(_2\), CNTs can be synthesized. The catalyst can be seed on the substrate or can be introduced into the CVD reactor in-situ as a floating catalyst. The pyrolysis of the carbon source or metal catalyst is performed in an Ar/H\(_2\) environment at relatively high temperature inside the CVD reactor. The CVD process, by which CNTs were grown using metal particles as the reaction catalyst, has several advantages over other synthesis methods. The CNTs can grow at relatively low temperature, and varying the size of the metal catalyst can control the size of CNT. Furthermore, it is relatively easy to obtain vertically aligned CNTs, which are important for the application of field emission display.
The process parameter control for the growth of CNT, however, still remains empirical manner, because the reaction kinetics and the growth mechanism are not fully understood [83]. Deposition behavior of CNT in CVD process can be compared with that of the carbon filaments [84]. The CVD method has been widely used to synthesize both SWNTs [85-91] and MWNTs [92-96]. A schematic for a horizontal CVD is shown in Figure 3.1.
Figure 3.1  Schematic of horizontal flow reactor for CNTs growth [83].
3.1 Parameters Affecting CNTs Synthesis by CVD

Among the different techniques that have been applied for the production of carbon Nanotubes, catalytic chemical vapor deposition (CCVD) or thermal catalytic CVD appears to be the most promising method due to its relatively low cost and potentially high yield production [97-99]. The CCVD technique has been applied both in the absence and in the presence of a substrate. The former is a gas phase homogeneous process where the catalyst is in the gas phase; the latter is a heterogeneous process using a supported catalyst [100].

There are some technical and economical factors that affect CNTs synthesis by the CVD method. Examples of the technical factors are type of catalyst, operating pressure and temperature, and reactor type such as Plasma Enhanced CVD (PE-CVD) or Microwave Plasma CVD (MP-CVD).

The most important economical factors affecting CNTs productions are:

- The scale of production,
- The carbon source or feedstock used (e.g., xylene, toluene ethane or natural gas),
- The reactor type and related type of operation,
- The yield of CNTs,
- The reaction time and temperature.
The CVD of various hydrocarbon gases on transition-metal catalysts has been used successfully in obtaining carbon fibers and multi-walled nanotubes (MWNTs) [101-106]. The CVD methods are attractive because of their efficiency in generating carbon feedstock and the straightforward scale-up. Furthermore, it could be possible to gain control over the types of nanotubes grown by controlling various parameters that are involved in CVD experiments.

Figure 3.2 shows a schematic diagram of the essential requirements for CNTs synthesis by the CVD method.
Figure 3.2 CNTs synthesis by CVD essentials.
3.1.1 Catalyst Effect

The type of catalyst support is found to control the formation of individual or bundled SWNTs. Advanced treatment for catalyst resulted in modulating of metallic catalyst particle diameter, which leads to control of CNTs diameter [107]. Table 3.1 shows the effect of advance treatment for the catalyst and its results on the CNTs diameter sanitized by the CVD method.

The catalyst effect on the growth and structure of the CNTs using thermal CVD have been studied by C. J. Lee et al [107-108]. The growth rate of CNTs indicates that the performance of catalyst follows in the order of Ni>Co>Fe. The size effect of catalyst particle would be another factor to determine the growth rate of CNT even though the growth rate mainly depend on the diffusion rate of carbon at the catalyst particle.

The bamboo-like structured CNTs are exclusively produced irrespective to the catalyst. The CNTs grown on Fe catalyst reveals the best crystallinity among the three catalysts. On the other hand, the CNTs grown on Co catalyst exhibit much lower degree of crystalline character compared with Fe or Ni catalyst.

The growth rate, the diameter, and the crystallinity of CNTs can be manipulated by selecting the catalysts. The CNTs grown on Fe catalyst have a larger diameter and a broad diameter distribution compared with Co or Ni catalyst. The Fe catalyst particles had the largest diameter and the broadest size distribution among the three catalysts (Fe>Co>Ni) before the CNT growth. The lower density of CNTs grown on Ni catalysts is rationalized by the easy
agglomeration of the small sized Ni particles compared with Fe or Co particles [108].

Table 3.2 shows the growth rate, diameter, and density of CNTs grown on Fe, Co, and Ni catalysts using thermal CVD of C2H2 at 950°C. Figure 3.3 shows TEM images for the bamboo-like structured CNTs grown on (a) Fe, (b) Ni, and (c) Co catalysts, showing the closed tip without encapsulated catalyst particles and the compartment layers with a curvature directed to the tip. HRTEM images for the graphitic sheets of CNTs grown on (d) Fe, (e) Ni, and (f) Co catalysts, also are in the same figure.

Fe is widely used as a catalyst by many researchers in the CVD syntheses of both MWNTs and SWNTs [93, 108-110].
Table 3—1 The average diameter of CNTs depending on average particle (Fe) diameter [107].

<table>
<thead>
<tr>
<th>Number of experimental runs</th>
<th>NH$_3$</th>
<th>C$_2$H$_2$</th>
<th>Average Fe particle diameter (nm)</th>
<th>Average CNT diameter (nm)</th>
<th>CNT length (μm)</th>
<th>Growth rate (μm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>100</td>
<td>30</td>
<td>200</td>
<td>130</td>
<td>12</td>
<td>1.2</td>
</tr>
<tr>
<td>3</td>
<td>300</td>
<td>30</td>
<td>130</td>
<td>60</td>
<td>18</td>
<td>1.8</td>
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<tr>
<td>2</td>
<td>300</td>
<td>30</td>
<td>400</td>
<td>240</td>
<td>8</td>
<td>0.8</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>30</td>
<td>200</td>
<td>130</td>
<td>3.6</td>
<td>1.2</td>
</tr>
<tr>
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<td>100</td>
<td>30</td>
<td>200</td>
<td>130</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>30</td>
<td>200</td>
<td>130</td>
<td>28</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Table 3—2. The growth rate, diameter, and density of CNTs grown on Fe, Co, and Ni catalysts using thermal CVD of C$_2$H$_2$ at 950°C [108].

<table>
<thead>
<tr>
<th>Catalyst type</th>
<th>Growth rate (µm/min)</th>
<th>Diameter distribution (nm)</th>
<th>Averaged diameter (nm)</th>
<th>Density (cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1 ± 0.2</td>
<td>80-200</td>
<td>130</td>
<td>4 × 10$^4$</td>
</tr>
<tr>
<td>Co</td>
<td>1.7 ± 0.3</td>
<td>80-130</td>
<td>110</td>
<td>4 × 10$^4$</td>
</tr>
<tr>
<td>Ni</td>
<td>2 ± 0.3</td>
<td>90-110</td>
<td>100</td>
<td>2 × 10$^4$</td>
</tr>
</tbody>
</table>
Figure 3.3 TEM images for the bamboo-like structured CNTs grown on Fe, Ni, and Co [108].

(a) Fe, (b) Ni, and (c) Co catalysts, showing the closed tip without encapsulated catalyst particles and the compartment layers with a curvature directed to the tip. HRTEM images for the graphitic sheets of CNTs grown on (d) Fe, (e) Ni, and (f) Co catalysts [108]
Catalysts supported on crystalline alumina Nano-particles produce abundant individual SWNTs and small bundles. Catalysts supported by amorphous silica particles produce only SWNT bundles. Studies of the ends of SWNTs lead to an understanding of their growth mechanism. In J. Kong et al work for methane CVD experiment; 10 mg of the catalyst was placed in a quartz tube mounted in a tube furnace. An argon flow was passed through the quartz tube as the furnace was heated to reach 1,000°C. The Ar flow was then replaced by methane (99% purity) at a flow rate of 6,150 cm³/min under 1.25 atm head pressure. The methane flow lasted for 10 min and was replaced by argon and the furnace was cooled to room temperature.

First, methane was chosen as carbon feedstock at temperature 1,000°C. Methane is known to be the most kinetically stable hydrocarbon that undergoes the least pyrolytic decomposition at high temperatures. Therefore, the carbon atoms needed for nanotube growth are supplied by the catalytic decomposition of methane on transition metal surfaces. This is one of the main reasons that the synthesized Nanotubes are nearly free of amorphous carbon coatings caused by self-pyrolysis of methane.
Secondly, CVD reaction times were limited to 10 min at a high methane flow rate to prevent amorphous carbon accumulation. Previous methane CVD syntheses of carbon fibers and MWNTs have found and utilized the build up of carbon over-coating to an appreciable thickness over a time period of several hours near 1,000°C temperatures.

Thirdly it was found that supported Fe$_2$O$_3$ catalysts produce SWNTs much more efficiently than NiO, Co, and the NiO/Co mixture [109].

### 3.1.2 Temperature Effect

Measuring CNTs growth temperature is very important especially at growth locations either it is substrate or reactor walls but sensing of substrate temperature in CVD reactors is one challenge encountered in implementing active thermal control. Because invasive temperature measurement devices disrupt film growth and preclude substrate rotation, the substrate temperature must be measured with non-invasive techniques or inferred (through model-based observer).
Much work has been done to model and measure reactor heat transfer dynamics in rapid thermal processing (RTP) reactors [112]. Some researchers have investigated the effect of growth temperature on both quantity and quality of CNTs [113-114]. Lee et al [113] reported that vertically aligned CNTs were grown on iron-deposited silicon oxide substrates by thermal CVD of acetylene gas at temperature range 750-950°C and as the growth temperature increased from 750°C to 950°C, the growth rate increases by four times and the average diameter also increases from 30 nm to 130 nm, as shown in Figure 3.4, while the density decreases by a factor of about two. The relative amount of crystalline graphitic sheets increases progressively with the growth temperature and a higher degree of crystalline perfection can be achieved at the growth temperature [113]. Figures 3.5 and 3.6 show the effect of temperature on the quality of CNTs, synthesized by the CVD method.
Figure 3.4 The growth rate and diameter of CNTs as a function of the growth temperature [113].
Figure 3.5 The average outer and inner nanotube diameters for various growth temperatures of nanotubes produced at 590 and 760 °C [114].
Figure 3.6 HRTEM images for CNTS grown at (a) 750°C, (b) 850°C, and (c) 950°C [113].
C.C. Chiu et al [115] reported that vertically aligned carbon nanotubes (CNTs) were synthesized on a lithographically patterned silicon/silica substrate coated with an ultra thin iron film. The process was performed using different thickness of iron using a rapid heating and cooling system (RHCS) in a thermal chemical vapor deposition (CVD) chamber. The substrate was placed on the heater, which can be heated from room temperature to 900°C within 20 s, and cooled from 900°C to 250°C within 25 s. Once the silica patterns on silicon substrate are made, selective growth of CNTs on the patterned silica can be achieved when the processing temperature over 850°C was used in the RHCS CVD system. Moreover, this study also presents an effective method for growing ultra long aligned vertical CNT array with a very high growth rate.

The CNT array with a length near 500 µm was synthesized within 10 min under a low pressure [115]. Also it has been reported that the graphitic character of CNTs improved as the CVD reactor temperature was increased from 500°C to 800°C. Figure 3.5 shows the length of CNTs synthesized under different temperatures on silicon and silica substrates. Samples showed progressive increase in metallic appearance and layered tube wall structure and decrease in electrical resistance. No further enhancement of graphitization was observed among samples formed at 800, 900, and 1000°C. Table 3.3 shows qualitative evaluation of the degree of non-catalytic sample [116].
Figure 3.7. The plot of the length of CNTs synthesized under different temperatures on silicon and silica substrates [115].
Table 3—3 Qualitative evaluation of the degree of non-catalytic sample [34].

<table>
<thead>
<tr>
<th>CVD Temperature</th>
<th>Surface Appearance</th>
<th>Structure of CNT Wall</th>
<th>Electrical Resistance</th>
<th>Raman Analysis</th>
<th>XRD Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 °C</td>
<td>Shiny Black</td>
<td>Amorphous</td>
<td>&gt;$10^6 , \Omega$</td>
<td>Insuff. Sample</td>
<td>Insuff. Sample</td>
</tr>
<tr>
<td>600 °C</td>
<td>Glassy Black</td>
<td>Amorphous</td>
<td>&gt;$10^3 , \Omega$</td>
<td>+ Nanographite</td>
<td>Insuff. Sample</td>
</tr>
<tr>
<td>700 °C</td>
<td>Shiny Slate</td>
<td>Incipient Layers</td>
<td>&lt;100 , \Omega</td>
<td>+ Nanographite</td>
<td>Insuff. Sample</td>
</tr>
<tr>
<td>800 °C</td>
<td>Reflective Silver Mirror</td>
<td>Well-Defined Layers</td>
<td>&lt;2 , \Omega</td>
<td>+ Nanographite</td>
<td>No Long-Range Order</td>
</tr>
<tr>
<td>900 °C</td>
<td>Dull Metallic Gray</td>
<td>Well-Defined Layers</td>
<td>&lt;1 , \Omega</td>
<td>No Sample</td>
<td>No Long-Range Order</td>
</tr>
<tr>
<td>1000 °C</td>
<td>Dull Metallic</td>
<td>Well-Defined</td>
<td>&lt;1 , \Omega</td>
<td>+ Nanographite</td>
<td>No Sample</td>
</tr>
</tbody>
</table>
### 3.1.3 Pressure Effect

In the CVD process pressure has sensible effect on microwave plasma chemical vapor deposition (MP-CVD) and electron cyclotron resonance chemical vapor deposition (ECR-CVD). Effects of plasma pressure and the presence of nitrogen on growth of carbon nanotubes (CNTs) and their properties were studied by C. H. Lin et al. [117] using microwave plasma chemical vapor deposition (MPCVD) (pressure=600-3300 Pa) and electron cyclotron resonance chemical vapor deposition (ECR-CVD) (pressure=0.3-0.6 Pa) systems.

CH$_4$/H$_2$ and CH$_4$/N$_2$ were used as source gases, and Co as the catalyst. The morphology change from spaghetti-like to well-aligned CNTs is discussed in terms of directed ions. The change in field emission properties is reasoned in terms of geometric enhancement factor and screening effect for different tube morphologies. The presence of nitrogen plasma can have the following effects: increasing tube diameter, increasing straightness of CNTs, forming of bamboo-like CNTs, deterioration of field emission properties, and shifting of Raman peak toward lower frequency side (or increasing residual tensile tress)[117].
3.2 Different types of Chemical Vapor Deposition (CVD)

The decomposition of carbon-bearing precursors in the presence of catalysts to produce CNTs seems to be more suitable for large-scale synthesis [118]. Thus, nowadays various chemical vapor deposition (CVD) techniques became dominant in the mass synthesis of carbon nanotubes, such as thermal CVD [119,120], plasma enhanced CVD (PECVD) [121,122], alcohol catalytic CVD (ACCVD) [123], laser assisted CVD (LCVD) [124] or the high pressure CO-disproportionation (HiPCO) [125].

Although up to 450 mg/h SWNTs can be produced with the HiPCO method in a continuous flow [125], or a large output of zeolite supported SWNTs was reported with ACCVD [123], the most common and promising methods for large-scale carbon nanotube production are the thermal and plasma enhanced CVD [126], which results in MWCNTs supported on substrates that were previously coated with catalytic nano-particles or the catalyst was co-deposited from a precursor.

Depending on the diameter of the catalytic particles MWCNTs with diameters up to 100 nm, in a narrow size distribution, with highly accessible surface area, low resistivity, and high stability are obtained. Using NH3 to control the catalytic reaction and the hot filament variant of the CVD method [122,127] or by application of an electric field [128] the MWCNTs can be highly vertically aligned.
3.2.1 Fluidized bed catalytic CVD

Multi-walled carbon nanotubes have been produced with high yield on an iron-supported catalyst by catalytic chemical vapor deposition in a fluidized bed reactor [100]. The choice of such a technique allows reaching high selectivity towards the desired material. A remarkable feature of this process is the huge bed expansion observed during the nanotubes growth that affects the fluidization regime due to the evolution of the apparent density of the composite powder.

In the work done by M. Corrias et al. [100] a fluidized bed reactor was entirely constructed from a 304 L stainless steel; its dimensions are 5.3 cm internal diameter and 1 m height. It has an expansion zone of 10 cm ID, to allow entrained particles to drop back into the bed. The gas distributor is a stainless steel perforated plate, with a porosity of 1.2%. A chromel alumel thermocouple of 0.5 mm in diameter can be moved all along the reactor axis. An electric furnace allows the monitoring of the fluidized bed temperature via a thermocouple fixed on the outer reactor wall.

Electronic grade ethylene, hydrogen, and nitrogen gases are supplied to the bed through a mass flow meter for the former and by ball rota-meters for the two others. A pressure sensor allows monitoring the differential pressure drop between the bottom and the top parts of the reactor. After its exit out of the reactor, the gaseous effluents flow through a bag filter, to collect the elutriated particles or fines formed during the experiments. The initial fluidized powders are
classical meso-porous alumina (Al$_2$O$_3$) particles, previously treated in another reactor, in order to obtain a 2.5% Fe/Al$_2$O$_3$ catalyst.

The Al$_2$O$_3$ particles mean diameter is about 100 mm, and their minimum fluidization velocity at 650 °C is 0.14 cm/s.

The operating procedure is quite simple: initially a controlled amount of particles is loaded into the reactor and then the bed is fluidized with a constant flow rate of pure nitrogen and hydrogen and heated. As soon as the thermal regime is reached, the flow rate of nitrogen is lowered to a pre-calculated value of deposition and simultaneously ethylene is introduced into the bed. In that work an initial bed weight of 100 g has been used, corresponding to a fixed bed height of 3.5 cm; it will be seen later why small bed height has been employed. The average bed temperature was maintained at 650°C; whereas ethylene, hydrogen and nitrogen flow rates were fixed to 250, 500 and 250 standard cm$^3$/min, respectively, for runs 11–14, and to 405, 800, 250 standard cm$^3$/min for the other runs. The mass of introduced carbon was determined from the flow rates and time measurements. The experiment duration together with the initial fluidization $U_0/U_{mf}$ ratio are reported in Table 3.4. After each run, the whole bed particles were chemically treated in an acid bath, in order to completely dissolve the alumina and most of the iron catalyst [100].
Table 3—4: Experimental results for fluidized bed CVD [100].

<table>
<thead>
<tr>
<th>Run</th>
<th>$U_0/U_mf$</th>
<th>Duration (min)</th>
<th>Final bed weight (g)</th>
<th>Weight of introduced carbon (g)</th>
<th>Final fixed bed height (cm)</th>
<th>Deposition rate (g/min)</th>
<th>Carbon yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>7.14</td>
<td>120</td>
<td>127</td>
<td>30</td>
<td>48</td>
<td>0.225</td>
<td>90.4</td>
</tr>
<tr>
<td>12</td>
<td>7.14</td>
<td>120</td>
<td>126.4</td>
<td>30</td>
<td>48</td>
<td>0.22</td>
<td>88.1</td>
</tr>
<tr>
<td>13</td>
<td>7.14</td>
<td>120</td>
<td>126.8</td>
<td>30</td>
<td>48</td>
<td>0.22</td>
<td>89.4</td>
</tr>
<tr>
<td>14</td>
<td>7.14</td>
<td>120</td>
<td>125.7</td>
<td>30</td>
<td>48</td>
<td>0.24</td>
<td>85.8</td>
</tr>
<tr>
<td>15</td>
<td>12.3</td>
<td>10</td>
<td>102.3</td>
<td>4</td>
<td>6.8</td>
<td>0.23</td>
<td>56.9</td>
</tr>
<tr>
<td>16</td>
<td>12.3</td>
<td>20</td>
<td>104.7</td>
<td>8</td>
<td>14.7</td>
<td>0.235</td>
<td>58.1</td>
</tr>
<tr>
<td>17</td>
<td>12.3</td>
<td>60</td>
<td>116.3</td>
<td>24</td>
<td>42</td>
<td>0.27</td>
<td>67.2</td>
</tr>
<tr>
<td>18</td>
<td>12.3</td>
<td>60</td>
<td>118.5</td>
<td>24</td>
<td>44.6</td>
<td>0.3</td>
<td>76.3</td>
</tr>
</tbody>
</table>
The deposition efficiency is characterized by the following parameters:

- The weight of produced material during each run, and the resulting deposition rate,
- The carbon yield, corresponding to the weight of deposited carbon in comparison with the introduced quantity,
- The weight of elutriated particles collected in the bag filter, and
- The evolution with time of the bed temperature at 5 cm above the distributor, and of the mean pressure drop between the bottom and the top parts of the reactor.

This final parameter enables the bed weight increase, by assuming that the pressure drop is proportional to the apparent bed weight. Of course, it can also give information about the fluidization quality of catalytic powders and nanotubes. Thermo gravimetric analysis (TGA) were conducted so as to measure the amount of carbon deposited in each experiment and also to evaluate the percentage of other forms of carbon. The mean deposition rate for the conditions tested is close to 0.22 gm/min. The amount of elutriated fines is always negligible, which means that Nanotubes remain anchored on the alumina powder in the fluidized bed. This last result was absolutely not expected a priori.

The nanotubes formed are of multi-walled type, composed of around 13 walls and present occasionally some graphene layers that grow perpendicularly to the growth axis of the tube Figure 3.8. The mean nanotube outer diameter is about 17 nm and the inner diameter around 8 nm, whereas their length is very difficult to measure, varying roughly between 100 nm and several microns.
Nanometric iron particles are present either at the nanotubes tip or in their middle part [100].

These first feasibility experiments clearly demonstrate the high efficiency of the CVD fluidized bed process to manufacture carbon nanotubes. The carbon yield often exceeds 95%, and the nanotubes selectivity is close to 100%. Under the tested conditions, no decrease of the fluidization quality has been detected, at least after 1 h of run. It is also worth noting that, in pre-industrial equipment that may operate in a continuous mode, the problem of bed height elevation and fluidization ratios evolution during runs will disappear [100].

### 3.2.2 Thermal CVD

Thermal chemical Vapor Deposition has been widely used to synthesize carbon materials [129-132] especially for CNTs synthesis. A schematic for a thermal vapor deposition reactor is shown in Figure 3.9.
Figure 3.8 (a) Low magnification TEM, (b) HRTEM and (c) high magnification TEM micrographs of nanotubes of run 13 [100].
Figure 3.9 Schematic diagram for the thermal CVD for ethanol decomposition [129].
3.2.3 Plasma Enhanced CVD (PE-CVD)

Plasma enhanced chemical vapor deposition (PE-CVD) has been used in CNTs synthesis [133-135]. The main advantage of this method is the low deposition temperature [136]. A schematic diagram for plasma enhanced chemical vapor deposition working under atmospheric pressure is showing in Figure 3.10. Another type of PE-CVD reactors is shown in Figure 3.11. In this type of PE-CVD reactors, radio frequency was utilized [137].

3.2.4 Microwave Plasma CVD (MP-CVD)

Microwave plasma chemical vapor deposition (MP-CVD) has been used in CNTs synthesis [137]. A schematic diagram for this method is shown in Figure 3.12.
Figure 3.10 Schematic diagram of the capillary dielectric discharge-type AP-PECVD [136].
Figure 3.11. Schematic diagram of TCP type RF plasma enhanced CVD [137].
Figure 3.12 Schematic diagram of a large volume MP-CVD system.

1, Discharge area; 2, magnet coil; 3, glass windows for viewing & sample entering; 4, graphite protected ring; 5, graphite cap (sample platform); 6, stainless steel cylinder; 7, ceramic cylinder; 8, temperature controller; 9, coil of 2.8 kW inductuner; 10, high vacuum valve; 11, mechanical vacuum pump; 12, low vacuum valve; 13, valve for gas release; 14, vacuum gauge; 15, flow meter; 16, flow switch; 17, quartz window. [28]
CHAPTER FOUR

EXPERIMENTAL SETUP

Background

The experimental set up used in this study is similar to the one reported by other researchers [93,139-143]. The main difference is that our setup includes a Gas Chromatograph (GC) for measuring different gas species taken from inside the reactor from both preheating and heating zones along the reactor centerline at different temperatures in the heating zone.

The experimental set up was designed, assembled, and installed by me in IEAS group laboratory on RGAN Building in Mechanical Engineering at University of Kentucky.
Figure 4.1 Schematics of the experimental set-up.

(H₂ 9.3 %; Ar 89.7 %; C₈H₁₀ 1.0 %)
4.1 Setup components

The experimental setup shown in Figure 4.1 consists of a chemical vapor deposition reactor, a programmable syringe pump to deliver the carbon source or feedstock, flow meters to control argon and hydrogen flow respectively, temperature controllers to control the preheater and the heater temperatures, a sampling probe which is used to carry the gas samples to the GC. That probe is 1.6 mm inner diameter and 4.75 mm outer diameter and cooled by nitrogen to keep the species frozen at suction conditions.

4.1.1 CVD Reactor components

The reactor consists of:

1. A quartz tube (From Quartz Scientific Inc.) having an inner diameter of 85.1 mm, an outer diameter of 90.00 mm and a length of 1524 mm as shown in Figure 4.2a.

2. A set of six 2-phase electric heaters 304 mm long, 95.00 mm inner diameter, 126.5 mm outer diameter, as shown in Figure 4.2b. Each heater has 220 V, and 1630 W (From Applied Test Systems, Inc.); two of them are used for pre heating zone and the other four are connected together to heat up the heating zone.

3. Two temperature controllers (From Omega Inc.), as shown in Figure 4.2b, one is used to control the pre heating zone heater
temperature (350°C) and the other one was used to control heating zone heater temperature (600°C to 1200°C).

4.1.2. Feedstock supply and Sampling probe

1. Two flow meters from KI inc., as shown in Figure 4.2 b. One is used to control H₂ flow rate at around $2.5 \times 10^{-6}$ m³/s while the other is used to control Ar flow rate at around $2.25 \times 10^{-5}$ m³/s.
2. Two gas cylinders one for Ar and the other for H₂.
3. Programmable syringe pump from New Era Pump System, as shown in Figure 4.2 d, to deliver and control xylene flow rate.
4. Sampling probe, which is shown in Figure 4.2 f, equipped with a cooling system as shown in Figure 4.2 c and connected to the GC.
Figure 4.2 A photo showing the set up.
Figure 4.3 Photos showing the set up components.
4.2 Gas Chromatographer (GC) configuration and calibration

Background

The GC, which has been used in this experiment, is a very compact micro GC and it has its own vacuum pump to suck the samples. The GC also has three columns: Channel A = Polo Pack Q (PPQ), channel B = MolSieve 5A (MSA), and channel C = Composite Pack (CB).

A thermal conductivity detector (TCD) is used in the analysis of the gases by packed column gas chromatography. The TCD utilizes the difference of the thermal conductivities of the carrier gas and the mixture of the analyzed gas. The carrier gas has to give an electrical response that is interpreted into an area that corresponds to the different concentrations of the analyzed gas.

Helium was used as a carrier gas at 80 Psi through a two-stage regulating valve. The main purpose of using the GC is to measure the hydrocarbons concentrations resulting from xylene decomposition inside the CVD reactor and, due to technical difficulties in separating hydrogen from argon, the combined concentration of argon and hydrogen instead of measuring their individual concentrations. Measuring the concentration of heavy hydrocarbons, such as xylene, toluene, and benzene was difficult because of condensation which has occurred in the suction line connecting the sampling probe and the GC but most of the condensates were trapped in the GC filter prior to the columns entrance.
The GC was calibrated by using a certified gas mixture cylinder from AIR LIQUIDE starting with a cylinder contains 76.815 % Ar, 14.97% H₂, 5% CH₄ %, 2.00 % C₂H₆, 1.01 % C₂H₄ %, 0.203 % C₂H₄, 265 PPM xylene, 549 PPM toluene, and 1143 PPM benzene. The gas mixture cylinder was connected to the GC, and the area counted resulted from the GC standard report was recorded. The procedure was performed using six gas cylinders, one for each gas, and flow meters to control gas flow rate. The different gases were introduced to the GC at different concentrations. This calibration procedure was done after each 12 samples were taken.

4.2.1 Gas Chromatographer configuration

4.2.1.1 Instrument Description

The Varian, Inc. CP-4900 Micro-GC, which is shown in Figure 4.3, is configured for the use with either He (or H₂) as a carrier or transport gas. It is recommended to use gases with a minimum purity of 99.995%. Since the injection valve is operated pneumatically, there is a limit of 550 ± 10 kPa (80 ± 2 PSI) to the main gas supply, therefore a two-stage regulating vale was used to control the flow of 99.999 He at 80 PSI (5.5x10⁶ Pa).

For assurance of the dryness of the gas sample and to prevent solid particles from entering the GC, a filter is placed in the sample line between the injector and sampling device as shown in Figure 4.4. CP-Gas Clean filters are recommended to remove any traces of moisture and oxygen.
For low-level analysis a better grade of carrier gas should be considered. The difference between the relative thermal conductivity of the carrier gas and the sample components should be as high as possible. Table 4.1 gives relative thermal conductivities for several gases.

4.2.1.2 Micro Electronic Gas Control (EGC)

The CP-4900 Micro-GC has built-in Micro EGC regulators that can be adjusted to obtain a constant or programmed pressure control, which result in a constant or programmed flow through the injector, column and detector. The pressure range of the Micro EGC is between 50-350 kPa (7-49 Psi). This pressure sets a continuous flow of carrier gas of about 0.2-4.0 mL/min. A typical pressure rise is 200 kPa/min, which will give a significant pressure increase during the run, without excessive baseline disturbance. In most cases baseline subtraction may improve the quality of chromatograms that suffer from baseline drift. Figure 4.5 shows a schematic for the EGC location in the GC.
Figure 4.4 CP-4900 Micro GC 4-CH.
Figure 4.5 Filter is placed in the sample line.
Table 4—1 Relative thermal conductivity for several gases.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>47.1</td>
</tr>
<tr>
<td>Helium</td>
<td>37.6</td>
</tr>
<tr>
<td>Methane</td>
<td>8.9</td>
</tr>
<tr>
<td>Oxygen</td>
<td>6.8</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>6.6</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>6.4</td>
</tr>
<tr>
<td>Ethane</td>
<td>5.8</td>
</tr>
<tr>
<td>Propane</td>
<td>4.8</td>
</tr>
<tr>
<td>Argon</td>
<td>4.6</td>
</tr>
<tr>
<td>Carbondioxide</td>
<td>4.4</td>
</tr>
<tr>
<td>Butane</td>
<td>4.3</td>
</tr>
</tbody>
</table>
4.2.1.3 Injector

The injector has a built-in **10µL** sample loop that is filled with the gaseous sample. The pressure of the sample should be between **0-100 kPa (0-15 psi)** and the sample temperature within **5-40 °C ±5 °C** of the analyzer. By activating the START option within the data-handling package, a vacuum pump will draw the gas sample through the loop, and then the injector will inject the gas sample from the sample loop into the gas stream. The minimum pressure required by the injector is **550 ± 10 kPa (80 ± 2 psi)**. A typical injection time is **40 milliseconds (ms)**. This equals an average injection volume of **0.20 µL**. Injection time will be rounded to a multiple of 5 ms. A practical minimum value is **40 ms**. In most cases a value of **0 - 20 milliseconds** will result in no injection. Figure 4.5 shows a schematic for the injector location in the GC.

4.2.1.4 Back-flush option

Back flushing to vent is an advanced technique, which is used to prevent later eluting compounds for reaching the analytical column and detector. The main reason for applying this technique is to keep the analytical column clean and reduce analysis time.

The Varian CP-4900 Micro-GC is available with GC modules that incorporate back-flush capabilities. A back-flush system always consists of a pre-column and an analytical column. The two columns are coupled with a so-called
pressure point, which makes it possible to invert the carrier gas flow direction through the pre-column at a preset time, the "back-flush time."

When all compounds which are to be quantified are transferred to the analytical column, the back-flush valve switch (at the back-flush time) on the pre-column then the flow is inverted and all compounds left on the pre-column are now (back) flushed to the vent (see back-flush diagram). On the analytical column the separation goes on because the flow there is not inverted. Back flushing will ensure that the pre-column will be in good condition for the next run. Figure 4.6 shows a schematic of the back-flush option and two chromatographs one without back-flush and the other with back-flush.

4.2.1.5 Detector

The CP-4900 Micro-GC is equipped with a thermal conductivity detector (TCD). This detector responds to the difference in thermal conductivity between the carrier gas and the sample components. The construction of a TCD is such that the changing thermal conductivity of the carrier gas stream, due to components present, is compared to the thermal conductivity of a constant reference gas stream.
Figure 4.6 Schematic of sampling loop showing EGC and injector.
Figure 4.7 schematic of the back-flush option and two chromatograph one without back-flush and the other with back-flush
4.2.1.6 Columns

A variety of column configurations are possible on the CP-4900. The required columns for the specific analysis have been installed at Varian. Table 4.2 shows the columns used in this study and their application.

- Column Molsieve 5 Å

The Molsieve 5Å column is designed to separate: hydrogen, carbon monoxide, methane, nitrogen, oxygen, and some noble gases. Higher molecular weight components have much higher retention times on this column. Example of the peaks for gases separated by this is shown in Figure 4.7.
Table 4—2 Some Varian, Inc columns and applications

<table>
<thead>
<tr>
<th>Column</th>
<th>Main applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molsieve 5A PLOT</td>
<td>Hydrogen (H₂), oxygen (O₂), nitrogen (N₂), methane (CH₄), carbon monoxide (CO), noble gases.</td>
</tr>
<tr>
<td>CP-Sil 5CB</td>
<td>Natural gas, vapor of common solvents, EPA volatile priority pollutants. Separation primarily by boiling point where the last eluting compound has the highest boiling point.</td>
</tr>
<tr>
<td>PPQ</td>
<td>Air, ethylene (C₂H₄), ethane (C₂H₆), acetylene (C₂H₂), natural gas</td>
</tr>
</tbody>
</table>
Figure 4.8 Sample of the peaks resulted from MS5A column.

Column temperature : 100 °C
Inject time : 40 ms
Detector sensitivity : medium
Sample pressure : 100 kPa
Sample time : 5 s
Run time : 100 s
Column pressure : 80 - 160 kPa [11.6 - 23.2 Psi (Helium)]
• Conditioning of Molsieve columns

On a properly activated column nitrogen and oxygen will be very well separated. However, these two peaks will start to merge together. This is caused by water, present in the sample or carrier gas, adsorbing to the stationary phase. To restore the columns efficiency, it will suffice to raise the oven temperature to 180 °C (max. column oven temperature) and, with the normal operating pressure on the column head, leave it to condition for about an hour. It is recommended to switch the detector filaments off during this period. After reconditioning the column, performance can be tested by injecting plain air. If there is a proper separation between nitrogen and oxygen again the column separation power has been restored. If the CP-4900 Micro-GC’s frequency of use is very high, a standard reconditioning procedure of leaving the instrument with the oven temperature at 180°C overnight might be adopted. The longer the reconditioning period, the better the column performance without damage.

• CP-Sil 5CB Column

The natural gas components, mostly hydrocarbons, separate in the same order on the non-polar and medium-polar CP-Sil CB columns. Nitrogen, methane, carbon dioxide, and ethane are not separated on these columns. They produce a composite peak. Example of the peaks for gases separated by this is shown in Figure 4.7
Figure 4.9 Sample of the peaks resulted from CP-Sil 5CB column.

- **Column temperature**: 50°C
- **Inject time**: 40 ms
- **Detector sensitivity**: medium
- **Sample pressure**: 100 kPa
- **Sample time**: 5 s
- **Run time**: 50 s
- **Column pressure**: 80 - 160 kPa [11.6 - 23.2 Psi (Helium)]
4.2.1.7 EXTERNAL DEVICES

The CP-4900 is equipped with several external I/O’s in order to control external devices or to synchronize with external devices. External devices can be external pump(s), alarms, Auto Sampler, etc.

The following I/O’s are standard:


2. Two external relays (contact closures). The CP-4900 driver supports alarming purposes, Auto-Sampler control via solenoids and external pump control.

3. External Start In. The CP-4900 driver supports the start of the CP-4900 Micro-GC by an external device (Flow computer or PLC). The CP-4900 Micro-GC processes this event (start run) and passes the event to the CP-4900 driver.

4. External Start Out. The “External Start Out” signal is directly controlled from the CP-4900 Micro-GC.

5. External Ready In. The “External Ready In” signal is not processed in the CP-4900 Micro GC. The CP-4900 driver acquires this event. It can be used to synchronize with an external device.

6. External Ready Out. The “External Ready Out” signal is directly controlled from the CP-4900 Micro-GC.
7. Six External Analog Input signals. The CP-4900 driver supports the acquisition and processing of the External Analog Input signals.

Figure 4.9 Shows a photo for the VICI electric actuated multi positional valve used in the Micro GC CP 4900.

4.2.2 Gas Chromatograph calibration

The gases are sampled in a multi positional gas-sampling valve, which is shown in Figure 4.9, with a sample loop of 10 mL. The carrier gas, helium, flows into the column with the analyzed gas into the TCD chamber. The TCD compared the thermal conductivities of two gas flows: carrier gas (also known as the reference gas) and the analyzed gas. The Varian Star Workstation collects the signals generated from the micro GC.

Figures 4.10, 4.11, and 4.12 show some of the analysis conditions for the method used in this study.

Table 4.3 shows the operating conditions for the analysis of (Ar+ H₂), CH₄, and C₂Hₓ by using helium as the carrier gas.
Figure 4.10 The VICI electric actuated multi positional valve
Figure 4.11 Detectors conditions for the method used in this study.
Figure 4.12 Integration parameters for the method used in this study.
Figure 4.13 Chromatograph for the method used in this study.
Table 4—3 Analysis Conditions for the method used in this study.

<table>
<thead>
<tr>
<th>Sample time</th>
<th>30 s</th>
<th>Run time</th>
<th>265 s</th>
<th>Stabilizing time</th>
<th>5 s</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A (PPQ)</strong></td>
<td></td>
<td><strong>B (MSA)</strong></td>
<td></td>
<td><strong>C (CB)</strong></td>
<td></td>
</tr>
<tr>
<td>Column dimensions</td>
<td>10 m</td>
<td>10 m</td>
<td>8 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carrier Flow:</td>
<td>4.00 mL/min</td>
<td>4.00 mL/min</td>
<td>4.00 mL/min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature:</td>
<td>150°C</td>
<td>100°C</td>
<td>150°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial Pressure</td>
<td>21.8 psi</td>
<td>21.8 psi</td>
<td>21.8 psi</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Injection time</td>
<td>40 ms</td>
<td>40 ms</td>
<td>40 ms</td>
<td></td>
<td></td>
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<tr>
<td>Detector</td>
<td>TCD</td>
<td>TCD</td>
<td>TCD</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Data Handling**

<table>
<thead>
<tr>
<th>Initial S/N ratio</th>
<th>5</th>
<th>4</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial peak width</td>
<td>0.5 s</td>
<td>4 s</td>
<td>4 s</td>
</tr>
<tr>
<td>Initial Peak reject value</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
</tbody>
</table>
4.2.2.1 GC Calibration Procedure

The GC was calibrated in two steps. The first step was performed by using a gas mixture cylinder (from AIR LIQUIDE), that contains: 76.815 % Ar, 14.97% H₂, 5% CH₄ %, 2.00 % C₂H₆, 1.01 % C₂H₄ %, 0.203 %C₂H₄, 265 PPM xylene, 549 PPM toluene, and 1143 PPM benzene. The second step was performed by using six gas cylinders (Ar, H₂, CH₄, C₂H₂, C₂H₄, C₂H₆). Argon concentration was fixed at 90% and hydrogen concentration was changing to have (Ar +H₂) at 94.5, 95.5, 96.5, 97.5, 98.5, 99, 99.50, 99.75, 99.8 and 99.90 %. The gas mixture cylinder was connected to GC and the area counted resulted from GC standard report was plotted at each concentration. Methane (CH₄) mole concentrations were 3.50, 2.75, 2.00, 1.5, 0.75, 0.5, 0.25, 0.125, 0.10, and 0.05. C₂Hₓ (C₂H₂+ C₂H₄+ C₂H₆) concentrations were 2.00, 1.75, 1.5, 1.00, 0.75, 0.50, 0.25, 0.125, 0.10, and 0.05 %.
Table 4—4 Area counts resulted from the gases analyzed by the Micro-GC.

<table>
<thead>
<tr>
<th>Mol%</th>
<th>A (Ar=H₂)</th>
<th></th>
<th>Mol%</th>
<th>A (CH₄)</th>
<th></th>
<th>Mol%</th>
<th>A (H₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>91.79</td>
<td>97890176</td>
<td>98717492</td>
<td>98543256</td>
<td>98010344</td>
<td></td>
<td>2689991</td>
<td>2321065</td>
</tr>
<tr>
<td>94.50</td>
<td>99564120</td>
<td>100481436</td>
<td>100216200</td>
<td>99677301</td>
<td>3.50</td>
<td>1613995</td>
<td>1392639</td>
</tr>
<tr>
<td>95.50</td>
<td>101198068</td>
<td>102050794</td>
<td>101898148</td>
<td>101348475</td>
<td>2.75</td>
<td>1479495</td>
<td>1276586</td>
</tr>
<tr>
<td>96.50</td>
<td>102910538</td>
<td>103697325</td>
<td>103600185</td>
<td>103106172</td>
<td>2.00</td>
<td>1075996</td>
<td>928426</td>
</tr>
<tr>
<td>97.50</td>
<td>104565858</td>
<td>105410267</td>
<td>105200308</td>
<td>104670119</td>
<td>1.5</td>
<td>806997</td>
<td>696320</td>
</tr>
<tr>
<td>98.50</td>
<td>106220895</td>
<td>107040210</td>
<td>106865977</td>
<td>106331709</td>
<td>0.75</td>
<td>403499</td>
<td>348160</td>
</tr>
<tr>
<td>99.00</td>
<td>107874852</td>
<td>108710182</td>
<td>108536018</td>
<td>108001280</td>
<td>0.5</td>
<td>268999</td>
<td>232107</td>
</tr>
<tr>
<td>99.50</td>
<td>109540121</td>
<td>110365432</td>
<td>110300862</td>
<td>109857999</td>
<td>0.25</td>
<td>134500</td>
<td>116053</td>
</tr>
<tr>
<td>99.75</td>
<td>111206728</td>
<td>111929046</td>
<td>112014808</td>
<td>111921306</td>
<td>0.125</td>
<td>67250</td>
<td>58027</td>
</tr>
<tr>
<td>99.8</td>
<td>113556972</td>
<td>113752981</td>
<td>113528749</td>
<td>113258374</td>
<td>0.10</td>
<td>53800</td>
<td>46421</td>
</tr>
<tr>
<td>99.99</td>
<td>115183347</td>
<td>115130773</td>
<td>114687549</td>
<td>115540210</td>
<td>0.05</td>
<td>26900</td>
<td>23211</td>
</tr>
</tbody>
</table>

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4.2.2.2 Mathematical model for the GC calibration

Figure 4.14 Diagram of predicted and measured values and residual [143].

Where:

\[ Y = \text{Measured or known percentage molar concentration of the gas (\%)} \]

\[ X = \text{Area counted from the GC results report} \]

\[ Y' = b_0 + b_1 X = \text{Predicted value} \]
• Analysis of Variance (ANOVA) and Linear regression

\( n=11 \) ; \( n \) is the sample population.

\( m=4 \) ; \( m \) sample size.

\( Df_{av.} = (n-2)m=9*4 =36 \) ; Degree of freedom based on the total samples.

\( DF_p = n-2 \) ; Degree of freedom based on the samples population

\( X = X/n \) ; \( X \) is the mean of the area counted.

\( Y = Y/n \) ; \( Y \) is the mean of the molar concentration.

\( S_{XX} = X^2 - [X]^2/n \)

\( S_{XY} = XY - X \cdot Y/n \)

\( S_{YY} = Y^2 - [Y]^2/n \)

\( b_1= S_{XY} /S_{XX} \)

\( b_0= Y - b_1 \cdot X \)

\( S^2 = (S_{YY} - b1S_{XY})/(n-2) \) ; \( S^2 \) is the common variance of the error.

\( SSM = S(Y' - Y)^2 \) ; \( SSM \) is the sum of squares for the model.

\( SSE = S(Y - Y')^2 \) ; \( SSE \) is the sum of squares of the error or residual.

\( SST = S(Y - Y)^2 \) ; \( SST \) is the total sum of squares.

\( MSM = S(Y' - Y)^2 \) ; \( MSM \) is the sum of squares for the model.

\( MSE = S(Y - Y')^2 /(n-2) \)

\( R^2 = SSM/SST \)
Table 4.5 consists of the calculated parameters of the analysis of variance and linear regression for the gases analyzed by the Micro-GC using helium as the carrier gas. It is clear from results that the area response is linear for the three categories. The standard or average relative error for (Ar+H₂) for this experiment is around 0.11 %, for CH₄ is 6.45 %, and for C₂Hₓ is 8.27 %.
Table 4—5 ANOVA and Linear Regression parameters for the gases analyzed by the Micro-GC.

<table>
<thead>
<tr>
<th></th>
<th>A (Ar+H₂)</th>
<th>A(CH₄)</th>
<th>A(C₂Hₓ)</th>
</tr>
</thead>
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<tr>
<td>b₀</td>
<td>58.00</td>
<td>0.00115</td>
<td>0.0483</td>
</tr>
<tr>
<td>b₁</td>
<td>4.20E-07</td>
<td>2.03E-06</td>
<td>8.76E-07</td>
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<tr>
<td>S²</td>
<td>82.00</td>
<td>1.83</td>
<td>0.9438</td>
</tr>
<tr>
<td>SSM</td>
<td>55.30</td>
<td>26.9</td>
<td>9.9447</td>
</tr>
<tr>
<td>SSE</td>
<td>0.92</td>
<td>0.204</td>
<td>0.1049</td>
</tr>
<tr>
<td>SST</td>
<td>56.20</td>
<td>2.71</td>
<td>10.0495</td>
</tr>
<tr>
<td>MSM</td>
<td>1.54</td>
<td>0.748</td>
<td>0.2762</td>
</tr>
<tr>
<td>MSE</td>
<td>0.102</td>
<td>0.00226</td>
<td>0.0117</td>
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<tr>
<td>F</td>
<td>15.03</td>
<td>33.04</td>
<td>23.71</td>
</tr>
<tr>
<td>F₀.₀₁ (from tables)</td>
<td>2.15</td>
<td>2.15</td>
<td>2.15</td>
</tr>
<tr>
<td>R²</td>
<td>0.984</td>
<td>0.992</td>
<td>0.9896</td>
</tr>
<tr>
<td>R</td>
<td>0.992</td>
<td>0.996</td>
<td>0.9948</td>
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CHAPTER FIVE

CHEMICAL AND THERMAL STRUCTURES OF A XYLENE-BASED CVD REACTOR TO SYNTHESIZE CNTS

5.1 Abstract

A small-scale model chemical vapor deposition (CVD) reactor was built. Axial and radial temperature profiles were measured with a fine thermocouple; axial and radial profiles of major species concentrations were measured and analyzed by a micro gas chromatograph. Those temperature and species concentrations revealed detailed thermal and chemical structures of the CVD reactor.

The concentrations of argon plus hydrogen (Ar +H₂), methane (CH₄), and C₂Hₓ (C₂H₂ + C₂H₄ + C₂H₆) resulted from xylene decomposition were measured along the CVD in both preheating and heating zones at different temperatures. Also the axial and radial temperatures distributions were measured. Additional experiments were performed adding ferrocene to xylene to investigate the effect of catalyst on composition profile. The results without ferrocene indicated that there is an increase in CH₄ and C₂Hₓ concentrations. The increase was noticeable after 10 cm in the heating zone; also the rate of increase was much
higher at a higher temperature. At high temperatures (1000°C and above) the increase of C$_2$H$_x$ concentration is higher than that for CH$_4$.

The effect of ferrocene was very minor on the concentration of the gases but the presence of ferrocene increased both CH$_4$ and C$_2$H$_x$ concentrations. Finally composition and temperature profiles were measured and plotted for the radial direction at X=75 cm and T=1200°C.

The overall rate constant for the gas-phase reaction was calculated based on the measured species concentration data using the Benson and Shaw reaction mechanism. Despite the fact that the Benson and Shaw mechanism is based on relatively short residence time (order of 1 s) and our CVD is based on longer residence time (order of 100 s), our study showed that the Benson and Shaw mechanism can be used in the temperature range lower than 800°C [165].

5.2 Introduction

The chemical vapor deposition (CVD) method can produce large amounts of carbon nanotubes (CNTs) [93,145]. To improve the performance of the full scale CNT-CVD reactor, reduced scale model reactors have been employed for both experimental [93] and numerical [146–148] studies. These scale model reactors have merits over the full scale because the reduced scale models are easy to operate under desired boundary conditions and checking repeatability of data is relatively easy [149]. Scale model CVD reactors are desirable to
establish a reliable experimental database, which can be used to validate reactor-scale computer models [146–148, 150–152].

Emori and Saito [153] developed scaling laws for chemically reacting flow systems and identified key pi-numbers for scaling up. The scaling laws will be discussed separately from the current study where our focus is to measure thermal and chemical structures of a scale model CVD reactor because there are little experimental data available on the detailed chemical structure in CVD reactors for CNT synthesis [154]. Some papers report exhaust-gas concentrations [146, 147], while many other papers do not report species concentration profiles along the reactor, which are necessary to identify the direct carbon precursors for formation of CNTs [155, 156].

The aim of this experimental study is to construct the chemical and thermal structures of the xylene-based CVD process using a scale model CVD reactor. Xylene was chosen because it has been widely used by other researchers to produce CNTs [93] and computer models based on xylene [146–148] are available for comparison.

A scale model CVD reactor was designed and the profile of temperature and concentrations of gas-phase reaction products were measured at five different reactor temperature conditions (600, 700, 800, 1000, and 1200°C). To investigate the role of iron as a catalyst on concentrations of intermediate gas species, species concentration measurements were made with and without the presence of the catalyst (ferrocene).
The decomposition of hydrocarbons in flames has been studied before [156] but there is lack in the same studies for CVD reactor used to synthesize carbon nanotubes. Carbon nanotubes, discovered by Iijima [5] have attracted the interest of many researchers due to their pioneer mechanical and electrical properties [158, 159]. CNTs can be synthesized by different methods such as arc discharge [160], flame [161, 162], and CVD [93] which is considered one of the most scalable methods that can be used commercially in producing large amounts of CNTs. Therefore the growth and reaction mechanism of carbon nanotubes formation in chemical vapor deposition reactors becomes an important issue for many researchers [163, 139-142].

This chapter presents an experimental study investigating the chemical and thermal structures for xylene decomposition inside the CVD reactor at different reactor temperatures. Xylene has been chosen because it has been used widely as a carbon source for CVD to synthesize CNTs [164].

Results presented here demonstrate the variation of gases concentrations and the temperature profile along the centerline of the reactor. Another purpose of this study is to be part of a larger research project to build a numerical model for CVD reactors synthesis of CNTs using xylene as a carbon source.
5.3 Experimental and Procedure

5.3.1 Experimental set up

Figure 5.1a shows the experimental set-up, described in detail in chapter 4, used for this study consisting of a quartz-made main CVD reactor tube (8.5 cm in diameter and 1.52 m in length), the gas supply unit, and the sampling and analysis unit. The main CVD reactor is divided into four sections which are in the order of the direction of flow; the entrance section (30 cm long), the pre-heater section (30 cm long), the main heating section (60 cm long), and the tail-off exit section (32 cm long). Temperature of the pre-heater section and the main heater section was independently controlled by two separate electric heaters of the same type. The temperature controller attached to the electric heaters provided a steady and stable temperature field.

The gas supply unit consists of two compressed gas cylinders (Ar and H₂) and liquid xylene. A rotor meter attached in the down stream of the supply line provided an accurate control of flow rate of each gas. A known amount of liquid xylene was directly injected into the CVD reactor and mixed with Ar and H₂.

The sampling and analysis section consists of a stainless-steel made sampling probe (2.0 long and 1.6 mm inner and 4.75 mm outer diameter) which is connected to a prove cooling unit and a gas chromatograph. The sampling probe was placed at the exact sampling location using a probe holder shown in Figure 5.1b, which is a quartz disc with the total of twenty-five 0.63 cm diameter
holes. The gas chromatographer is Varian micro GC-4900 where three different columns (PPQ, MSA, and 5 CB) were installed. Column PPQ was used to separate gas species C$_2$H$_x$ (C$_2$H$_2$ + C$_2$H$_4$ + C$_2$H$_6$). Column Molsieve (MS5A) was used for separation of gas species (Ar+H$_2$) and CH$_4$. Column Cp-Sill 5 CB was used for xylene, toluene, and benzene. This GC has its own vacuum pump installed inside the unit and operated with PC. The sampling volume was 10µL, which had very little effect on the bulk flow of Ar and H$_2$. 
Figure 5.1 Schematic diagram for the sampling probe holder.
5.3.2 Procedure

At the beginning and before each run, the sampling probe was placed at the desired location inside the reactor by means of the sampling probe holder, (a schematic diagram for that sample holder is shown in Figure 5.1 b), and then the reactor was purged from air by flowing argon at 5.0x10^{-5} m^3/s for 45 minutes prior to turning the heaters on. Then the temperature controllers were set to the desired temperatures and after that the feedstock was allowed to flow (Argon at 2.25x10^{-5} m^3/s, H_2 at 2.5x10^{-6} m^3/s, and Xylene at 8.33x10^{-8} m^3/s). Then the furnace was allowed to sit at the desired temperature for 30 minutes to allow the furnace's heat zone to stabilize at the target temperature and to give xylene enough time to decompose. Once the whole sampling system is ready, the cooling gas, nitrogen, was turned on to cool down the gas samples stopping further reactions inside the sampling probe. Using the Micro GC configuration program the GC was programmed to execute a sampling list of four samples automatically once the run icon of that sample list was clicked on, the GC started withdrawing four samples one every 5 minutes after the first sample. The GC used those 5 minutes as follows: 30 second for sampling, 265 second for running, and 5 second for stabilizing and calculation. The four samples were taken from one location; the operating conditions remained the same for each one of the four samples. A thermocouple was attached to the sampling probe tip to measure temperature at the desired location. After taking the samples at the desired location the sampling probe was moved back manually 5 cm to the next location, and the system was allowed to run for 5 minutes to overcome the
disturbances occurred due to sampling probe movement. That procedure was repeated until the end of the reaction zone along the reactor centerline at 600, 700, 800, 1000, and 1200°C. A set of samples was taken in the radial direction at 1200°C at a certain horizontal location (X= 75 cm) to study the variation in both composition and temperature profiles along the radial direction. Another two sets of samples were taken at 700 and 800°C with the same reactor conditions except for the addition of ferrocene at approximately 8.25% mole concentration to xylene (to get a solution with 1.00% Fe/C ratio).

The presented species concentration data are the average over the four samplings. The standard error for the combined concentration of argon and hydrogen in the reaction zone was 0.1%; this high accuracy is due to the nearly constant concentration of argon and hydrogen as discussed above. The standard error for both methane and C₂ concentrations in the reaction zone was less than 8%. 
5.3.3 Error Analysis

Error may be defined as the difference between the measured result and the true value of the quantity being measured. Most errors can be placed into one of two general classes. The first type is the bias errors, also referred to as systematic errors, are those that occur the same way each time a measurement is made. The second one is the precision errors, also called random errors, are different for each successive measurement but have an average value of zero. If enough readings are taken, as shown in this study in which 4 readings were taken, the distribution of precision errors will become apparent. In contrast, bias errors cannot be treated using statistical techniques, because such error are fixed and not show a distribution [186].

For gas species measurements, it is clear from ANOVA table for the calibration of the GC that the goodness of fit of the data is acceptable at different confidence levels. For the temperature measurements, the change in the measured value was negligible because of using the same thermocouple at the same location.
5.4 Results and discussion

5.4.1 Thermal structure

Figure 5.2 shows the temperature profile along the centerline (X-axis) at five different heater temperatures. The preheater temperature was kept constant at 350 °C for all the cases. For X < 30 cm, temperature is independent of the reaction temperature and increases with an increase in the X distance. Considering that the effect of radiation on the thermocouple reading is minor in this temperature range, the temperature increase is due to thermal conduction from the preheater. The flow rate and the reactor diameter yield the average axial flow velocity of about $2.33 \times 10^{-3}$ m/s at the pre-heater temperature. The Péclet number is on the order of 1 based on the reactor diameter and argon properties at the pre-heater temperature. In such a case, the thermal conduction in the axial direction cannot be ignored unlike conditions in references [151] and [152].

In the preheating zone (30 < X < 60 cm), temperature again increases with an increase in X. For 30 < X < 40 cm, temperature is lower than the preheater temperature (350°C) due to the conduction heat loss in the region of X < 30 cm. By contrast, temperature for 40 < X < 60 cm is higher than 350°C due to the heat transfer from the reaction zone (X > 60 cm) to the preheating zone. In the preheating zone, the temperature slightly increases with an increase in the heater temperature.
Figure 5.2  Temperature profile along X-axis at 5 different heater temperatures.

*The preheater temperature is fixed at 350°C.*
In the heating zone (X > 60 cm), temperature sharply increases and becomes nearly constant for 75 < X < 100 cm at a slightly lower temperature than the heater temperature. The difference between the temperature at Y = 0 and the heater temperature increases with an increase in heater temperature, because the heat loss (due to convection and conduction) increases with an increase in temperature. At X = 100 cm, temperature starts decreasing due to heat loss to the environment.

The temperature profile shows that from the reactor entrance until the beginning of the preheating zone where X>30 cm the temperature increased suddenly by more than 50% from around 195 °C to almost 300°C. It increased gradually during the preheating zone until it reached a value of 437°C which is about 28% higher than the targeted preheater temperature. That seems to be the result of the radiation and heat diffusion coming from the heating zone heater then the temperature staying almost constant at 687°C along the heating zone. It decreased by the end of the heating zone because the effect of the ambient temperature on the unheated part of the quartz tube at the reactor exit.

Table 5.1 presents the summary of the measured temperature at some specific locations along the reactor such as the surface temperature of the outside reactor wall right before the preheating zone area entrance and right after it, temperature at the middle and end of the preheating zone, temperature at the beginning of the heating zone, and the maximum temperature inside the heating zone.
Figure 5.3 shows the temperature profile in the $y$-axis at $X = 75$ cm at $1200^\circ C$. The temperature at $Y = 0$ is about $46^\circ C$ lower than the heater temperature ($1200^\circ C$) due to the heat loss to the preheating zone and the environment as discussed before.
Table 5—1 Summary of Measured Temperature of Preheating and Heating Zones.

<table>
<thead>
<tr>
<th>$T_{HZS}$ ($^\circ$C)</th>
<th>$T_{PHZO}$ ($^\circ$C)</th>
<th>$T_{PHZE}$ ($^\circ$C)</th>
<th>$T_{PHZM}$ ($^\circ$C)</th>
<th>$T_{PHZD}$ ($^\circ$C)</th>
<th>$T_{HZE}$ ($^\circ$C)</th>
<th>$T_{HZMax}$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>195.87</td>
<td>297.15</td>
<td>351.24</td>
<td>433.54</td>
<td>547.08</td>
<td>590.98</td>
</tr>
<tr>
<td>700</td>
<td>196.75</td>
<td>298.88</td>
<td>352.38</td>
<td>437.46</td>
<td>634.76</td>
<td>687.21</td>
</tr>
<tr>
<td>800</td>
<td>197.32</td>
<td>303.37</td>
<td>354.88</td>
<td>445.96</td>
<td>731.07</td>
<td>780.26</td>
</tr>
<tr>
<td>1000</td>
<td>209.82</td>
<td>316.85</td>
<td>368.98</td>
<td>456.77</td>
<td>939.57</td>
<td>970.86</td>
</tr>
<tr>
<td>1200</td>
<td>211.83</td>
<td>319.14</td>
<td>388.71</td>
<td>487.98</td>
<td>1132.19</td>
<td>1154.43</td>
</tr>
</tbody>
</table>

$T_{HZS}$ : Set Temperature of the Heating Zone  
$T_{PHZO}$ : Measured Temperature of quartz tube wall right before Preheating Zone entrance  
$T_{PHZE}$ : Measured Temperature at Preheating Zone entrance  
$T_{PHZM}$ : Measured Temperature at the middle of the Preheating Zone  
$T_{PHZD}$ : Measured Temperature at the end of the Preheating Zone  
$T_{HZE}$ : Measured Temperature at the Heating Zone entrance  
$T_{HZMax}$ : Maximum Measured Temperature in the Heating Zone
Figure 5.3 Temperature Profile along Y-axis at x = 75 cm and 1200°C.
5.4.2 Chemical structure

5.4.2.1 Hot zone temperature (HVT) = 600°C

At X = 60 cm, where the hot zone starts, there was a measurable increase in CH₄ and C₂Hₓ concentrations. That increase becomes very high for CH₄ at X = 65 cm which is about 5 cm from the heating zone entrance. After that the increase was smooth until the end of the heating zone. For C₂Hₓ the increase was smooth and less than the increase of CH₄ concentration which could be because of the lower reactor temperature and the need of C₂Hₓ for a higher temperature to have a faster reaction rate. The maximum concentrations for CH₄ and C₂Hₓ at that temperature were 0.27% and 0.10% respectively, and at the end of the heating zone those concentrations were reached. Figure 5.4 shows the molar concentration for (Ar + H₂), CH₄, and C₂Hₓ, which resulted from xylene decomposition without the presence of ferrocene. For argon plus hydrogen the concentration increased gradually along the reactor center. The average (Ar + H₂) was 96.92% at the heating zone end while it was 95.11 % at the beginning of the preheating zone.

At that temperature, the combined concentration of (Ar + H₂) was nearly constant throughout the reactor. Also, only very little CH₄ and total C₂Hₓ species were detected for X < 60 cm, indicating that there is no significant gas-phase reaction at the preheater temperature (350°C). Therefore, we only consider isothermal reactions in the reaction zone (X > 60 cm).
Figure 5.4 Measured concentration profiles for (Ar + H2), CH4 and C2Hx along the x-axis at 600 °C.

\[ C_2 \text{ or } C_2H_x = (C_2H_2 + C_2H_4 + C_2H_6) \]
5.4.2.2 Hot zone temperature (HZT) = 700°C

At X = 60 cm, where the hot zone starts, there was a measurable increase in CH₄ and CₓHₓ concentrations. That increase becomes very high for CH₄ at X = 65 cm which is about 5 cm from the entrance of the heating zone. After that the increase was smooth until the end of the heating zone. For CₓHₓ the increase was smooth and less than the concentration of CH₄ which could be because of the lower reactor temperature and the need of CₓHₓ for a higher temperature to have a faster reaction rate. The maximum concentrations for CH₄ and CₓHₓ at that temperature were 0.31% and 0.14% respectively, and at the end of the heating zone those concentrations were reached. For argon plus hydrogen the concentration increased gradually along the reactor center. The maximum (Ar + H₂) concentration was 97.03% at the heating zone end while it was 95.46 % at the beginning of preheating zone.

Figure 5.5 shows the concentration of (Ar + H₂), CH₄, and total CₓHₓ species (C₂H₆ + C₂H₄ + C₂H₂) at 700°C without the presence of ferrocene. At that temperature, the combined concentration of (Ar + H₂) was nearly constant throughout the reactor. Also, only little CH₄ and total CₓHₓ species were detected for X > 60 cm, indicating that there is significant gas-phase reaction in the heating or reaction zone temperature 700°C.

Figure 5.6 Shows SEM image for the materials collected from the reactor after its run at 700°C.
Figure 0.5 Measured concentration profiles for (Ar + H₂), CH₄ and C₂Hₓ along X-axis at 700°C.
Figure 5.6 SEM image for the materials collected at 700°C.
5.4.2.3 HZT = 800°C

The results are very similar to that for 700 °C and the trends for all the variables were the same but the maximum concentrations for CH₄ and C₂Hₓ at that temperature were 0.39% and 0.25% respectively. For (Ar + H₂) it was 97.58%. The steady state maximum temperature in the heating zone was 780 °C as indicated in Table 5.1.

Figure 5.7 shows the concentration of (Ar + H₂), CH₄, and total C₂Hₓ species (C₂H₆ + C₂H₄ + C₂H₂) at 800 °C without the presence of ferrocene. At that temperature, the combined concentration of (Ar + H₂) was nearly constant throughout the reactor. Also, relatively little CH₄ and total C₂Hₓ species were detected for X > 60 cm, indicating that there is significant gas-phase reaction in the heating or reaction zone temperature 800 °C.

Figure 5.8 Shows SEM image for the materials collected from the reactor after its run at 800 °C.
Figure 5.7 Measured concentration profiles for (Ar + H\textsubscript{2}), CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{x} along the x-axis at 800°C.
Figure 5.8 SEM image for the materials collected from at 800°C.
5.4.2.4 HZT = 1000°C

The temperature and the (Ar + H₂) concentration profiles are similar to the previous two cases, but the maximum temperature was 970°C, and the maximum (Ar + H₂) concentration was 97.82 %. The concentrations of both CH₄ and C₂Hₓ are much different than those resulting from 700°C and 800°C reactor temperatures. First the increases in concentrations are much higher: the maximum concentrations for CH₄ and C₂Hₓ were 0.77 % and 0.95%. The second CH₄ concentration was higher than that for C₂Hₓ until the location where X > 100 cm and then the C₂Hₓ concentration becomes higher than CH₄ concentration. Figure 5.9 shows the concentration of (Ar + H₂), CH₄, and total C₂Hₓ species (C₂H₆ + C₂H₄ + C₂H₂) at 1000°C without the presence of ferrocene. At that temperature, the combined concentration of (Ar + H₂) was nearly constant throughout the reactor. Also, considerably more CH₄ and total C₂Hₓ species were detected for X > 60 cm, indicating that there is highly significant gas-phase reaction is more significant in the heating zone temperature 1000°C.

Figure 5.10 Shows SEM image for the materials collected from the reactor after its run at 1000°C.
Figure 5.9 Measured concentration profiles for (Ar + H₂), CH₄ and C₂Hₓ along the X-axis at 1000°C.
Figure 5.10 SEM image for the materials collected at 1000°C.
5.4.2.5 HZT = 1200°C

At this relatively high temperature the behavior of most parameters showed a higher increase, especially for the C\textsubscript{2}H\textsubscript{x} concentration which reaches a maximum value of 1.25\% and becomes to be higher than the CH\textsubscript{4} concentration earlier in the hot zone at X ≥ 90 cm. The CH\textsubscript{4} concentration remains almost unchanged. The maximum CH\textsubscript{4} concentration was 0.79 \%, which could be because of the high temperature at which some of CH\textsubscript{4} converted into C\textsubscript{2}H\textsubscript{x}.

The maximum temperature for this case was 1154°C, and the maximum (Ar + H\textsubscript{2}) concentration was 98.88 \%. For the radial temperature profile at X = 75 cm, it shows a reasonable trend where the temperature is minimum at the center and it increases gradually until it reaches its maximums at the walls. In the upper half of the reactor the temperature was slightly higher which is resulted from buoyancy effect. The gases concentration profile shows a very slight effect, which indicates that the (Ar + H\textsubscript{2}) concentration at the upper half of the reactor is slightly higher than in the lower half. For CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{x} concentrations the profiles show a slight decrease in the upper half of the reactor.

Figure 5.11 shows the concentration of (Ar + H\textsubscript{2}), CH\textsubscript{4}, and total C\textsubscript{2}H\textsubscript{x} species (C\textsubscript{2}H\textsubscript{6} + C\textsubscript{2}H\textsubscript{4} + C\textsubscript{2}H\textsubscript{2}) at 1000°C without the presence of ferrocene. At that temperature, the combined concentration of (Ar + H\textsubscript{2}) was also nearly constant throughout the reactor. Also, more CH\textsubscript{4} and total C\textsubscript{2}H\textsubscript{x} species were detected for X > 60 cm, indicating that there is much gas-phase reaction in the heating or reaction zone temperature (1200°C).
Figure 5.12 Shows SEM image for the materials collected from the reactor after its run at 1200°C.

5.4.2.6 Radial Species Concentrations at X = 75 cm

Figure 5.13 shows the temperature and concentration profiles along the y-axis at x = 75 cm at 1200°C. The observed uniform concentration profiles along the Y-axis indicate little buoyancy effect, which also agrees with our computational studies [146, 147]. On the other hand, temperature at Y = 0 is about 46°C lower than the heater temperature (1200°C) due to the heat loss to the preheating zone and the environment as discussed before.
Figure 5.11 Measured concentration profiles for (Ar +H₂), CH₄ and C₂Hₓ along the X-axis at 1200°C.
Figure 5.12 SEM image for the materials collected at 1200°C.
Figure 5.13  Temperature and concentration profiles along the y-axis at X = 75 cm and 1200°C.
5.5 Reactions Analysis and Mechanism

Benson and Shaw [165] identified the following key reactions of xylene decomposition and consequent toluene decomposition:

\[ \text{C}_8\text{H}_{10} \leftrightarrow \text{C}_8\text{H}_9 + \text{H}, \quad (1) \]

\[ \text{C}_8\text{H}_9 + \text{H}_2 \leftrightarrow \text{C}_8\text{H}_{10} + \text{H}, \quad (2) \]

\[ \text{C}_8\text{H}_{10} + \text{H} \rightarrow \text{C}_7\text{H}_8 + \text{CH}_3, \quad (3) \]

\[ \text{C}_7\text{H}_8 \leftrightarrow \text{C}_7\text{H}_7 + \text{H}, \quad (4) \]

\[ \text{C}_7\text{H}_7 + \text{H}_2 \leftrightarrow \text{C}_7\text{H}_8 + \text{H}, \quad (5) \]

\[ \text{C}_7\text{H}_8 + \text{H} \rightarrow \text{C}_6\text{H}_6 + \text{CH}_3. \quad (6) \]
They calculated the value of the overall rate constant for this reaction mechanism and validated the obtained value with experimental data for reaction temperatures lower than 1200°C [165].

Reactions (3) and (6) show the formation of methyl radical. According to Westbrook and Dryer [167], CH₄ and C₂H₆ will be formed by the following reactions:

\[ \text{CH}_3 + \text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}, \quad (7) \]

\[ \text{CH}_3 + \text{CH}_3 \leftrightarrow \text{C}_2\text{H}_6. \quad (8) \]

Our results support this mechanism. With an increase in temperature, reaction (8) becomes more important than reaction (7). Other C₂ species (C₂H₄ and C₂H₂) will be formed by the following mechanism [166]:

\[ \text{C}_2\text{H}_6 + \text{H} \leftrightarrow \text{C}_2\text{H}_5 + \text{H}_2, \quad (9) \]

\[ \text{C}_2\text{H}_5 \leftrightarrow \text{C}_2\text{H}_4 + \text{H}, \quad (10) \]

\[ \text{C}_2\text{H}_4 + \text{H} \leftrightarrow \text{C}_2\text{H}_3 + \text{H}_2, \quad (11) \]

\[ \text{C}_2\text{H}_3 \leftrightarrow \text{C}_2\text{H}_2 + \text{H}. \quad (12) \]
Reactions (1), (2), (4), and (5) will indirectly setup the equilibrium of hydrogen:

\[ H_2 = 2H. \]  \hspace{1cm} (13)

Applying the partial equilibrium assumption, the rate equation for xylene and toluene is

\[
\frac{d[C_{8}H_{10}]}{dt} = -K_{13}^{1/2}k_3[C_{8}H_{10}][H_2]^{1/2}, \hspace{1cm} (14)
\]

\[
\frac{d[C_7H_8]}{dt} = K_{13}^{1/2}k_3[C_{8}H_{10}][H_2]^{1/2} - K_{13}^{1/2}k_6[C_7H_8][H_2]^{1/2}. \hspace{1cm} (15)
\]

Since \([H_2]\) can be regarded as constant in our case and in \(K_{13}^{1/2}k_3 \approx K_{13}^{1/2}k_6\) [166], the rate equation for methyl formation from xylene and toluene yields

\[
\frac{[CH_3]}{[C_{8}H_{10}]}_0 = 2 - (2 + kt)e^{-kt}, \hspace{1cm} (16)
\]

Where \(k\) is the overall rate constant defined as \(k \equiv K_{13}^{1/2}k_3[H_2]^{1/2}\). Using measured CH₄ and C₂ concentrations, we obtained the apparent value of \(k\) and plotted it in Figure 5.14 the value \(k\) determined by measured CH₄ and C₂ concentrations, agrees with the value calculated by Benson and Shaw [165] at 700°C. With an increase in temperature, however, the difference between the experimentally determined \(k\) and the Benson and Shaw value increases, indicating that the reaction mechanism (1)–(12) is not valid at temperatures
higher than 1000°C. At those higher temperatures, C₂ species, especially acetylene are consumed to form polycyclic aromatic hydrocarbons (PAHs) and soot [156, 169], thus lowering the apparent value of \( k \). This interpretation was supported by the fact that a considerable amount of brown tar-like material was deposited on the reactor wall at temperatures higher than 1000°C.
Figure 5.14  Experimentally obtained apparent value of overall rate constant \( (k) \) at four different temperatures. Experimental data of other researchers are from Ref. [165].
5.6 Ferrocene effect

The effect of adding ferrocene to xylene was almost negligible, but it shows that there is an increase in both CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{x} concentrations with the addition of ferrocene more than without ferrocene. The increase in C\textsubscript{2}H\textsubscript{x} concentration is relatively more than the increase in CH\textsubscript{4}.

With the presence of ferrocene, interestingly, both CH\textsubscript{4} and total C\textsubscript{2} species concentrations increased by 5–10\% at both 700°C and 800°C, implying that methyl radicals are likely produced via a C-C bond split during catalytic decomposition of xylene on the surface of iron particles.

Figures 5.15 and 5.16 show the gas species concentration for xylene decomposition in the presence and absence of ferrocene (i.e. with and without Fe particles).
Figure 5.15 Measured concentration profiles for CH₄ and C₂Hₓ along the X-axis with and without ferrocene at 700°C.
Figure 5.16 Measured concentration profiles for CH$_4$ and C$_2$H$_x$ along the X-axis with and without ferrocene at 800°C.
5.7 Temperature effect on xylene decomposition

Some of the data collected from gas species concentrations along the reactor at different locations and temperatures have been treated in another way to investigate the effect of temperature on xylene decomposition. The selected locations are at X=65, 75, 85, 95, and 110 cm. These locations represent the reaction zone, which starts at X=60 cm and end at X=120 cm.

Figures 5.17 to 5.21 show the effect of reaction zone temperature on combined argon plus hydrogen, CH$_4$, and C$_2$H$_x$ concentrations at that selected locations.

It is clear from the figures that the molar concentrations of (Ar+H$_2$), CH$_4$, and C$_2$H$_x$ increase with the temperature increasing.
Figure 5.17 Temperature effect on the species concentrations at X=65 cm.
Figure 5.18 Temperature effect on the species concentrations at X=75 cm.
Figure 5.19 Temperature effect on the species concentrations at X=85 cm.
Figure 5.20 Temperature effect on the species concentrations at X=95 cm.
Figure 5.21 Temperature effect on the species concentrations at X=110 cm.
5.8 Conclusions

Using our scale model CVD reactor, an experimental study has been done to measure the major gas species concentrations inside a CVD reactor for xylene decomposition at temperatures 600–1200°C. The temperatures were measured along the reactor center at the same location, as the sampling probe was located. This study showed that the CH₄ and C₂Hₓ concentrations increased along the reactor heating zone, and this increase is related to temperature and is much higher at higher temperatures 1000°C and above. The increase in (Ar+H₂) concentration is relatively small compared with those for CH₄ and C₂Hₓ.

The temperature profiles for axial and radial measurements are in agreement with the theoretical profiles for laminar flow in a hot wall tube. The radial measurements for species concentrations did not show much difference.

The following conclusions were made. The overall rate constant for the gas-phase reaction was calculated based on the measured species concentration data using the Benson and Shaw reaction mechanism [157]. Despite the fact that the Benson and Shaw mechanism is based on relatively short residence time (order of 1 s) and our result is based on longer residence time (order of 100 s), our study showed that the Benson and Shaw mechanism could be used in the temperature range lower than 800°C.
CHAPTER SIX

HYDROGEN ROLE IN XYLENE DECOMPOSITION IN CVD REACTOR USED TO PRODUCE CNTS

6.1 Abstract

An experimental study was conducted to examine the role or effect of hydrogen in the syntheses of carbon nanotubes CNTs in the chemical vapor deposition CVD reactor using xylene as a carbon source and ferrocene as catalyst. Both single-step and two-step methods were applied in this study. In the single-step method the catalyst (ferrocene) was dissolved in the carbon source xylene but for the two-step method the catalyst preparation step was performed first; ferrocene powder was placed in the preheated zone for a certain period of time and carried by a mixture of argon and hydrogen (at a fixed concentration of 90% argon and 10% hydrogen) to get catalyst nanoparticles deposited on the reactor wall and then pure xylene was injected to the reactor. SEM and TEM images of the synthesized materials have been taken to study the effect of hydrogen. The results showed that the presence of hydrogen is essential for CNTs to be synthesized by the CVD method, and also the concentration of hydrogen in the reactor has a great effect on the quality of CNTs synthesized by that method.
The yield of CNTs in the two-step method was formed slightly higher than that in the one-step method.

6.2 Introduction

The catalytic decomposition of hydrocarbons in CVD reactor has been widely used in CNTs production [170-174]. The reaction mechanisms of this decomposition and the roles of different gases and parameters need to be understood fully to control both the quantity and quality of the CNTs production in CVD processes. There have been some recent works to understand the growth mechanism of carbon nanotubes in chemical vapor deposition. In a kinetic study of the synthesis of CNTs by catalytic decomposition of acetylene by M. Perez_cabero et al. [163] showed a significant influence of the reaction conditions (feed mixture, reaction temperature, etc.) on the final yield and on the structural and morphological characteristics of the carbon products. The influence of hydrogen partial pressure ($P_{H_2}$) and the role of different gases, such as nitrogen in carbon nanotubes or nano-fibers formation have been investigated [175-177], and those studies showed that nitrogen containing plasma can induce bamboo-like CNTs.

The catalytic reactions during CNT growth involve very complicated processes. The first process involves the selectivity effect (composition effect) of the catalyst so that the same precursor through different catalytic reactions may result in different products. The second involves desorption or adsorption on the
catalyst surface, which would change the catalyst surface energy and its electronic state. The third involves the structure of the catalyst, such as particle size, crystallographic structure and surface composition because the catalytic reaction is often structure-sensitive.

6.2.1 Nitrogen effect on CNTs growth

The role of nitrogen in CNT growth or bamboo-like CNT formation is basically to prolong the passivity of the front catalyst surface to enhance carbon diffusion [178].

What is the formation mechanism of the bamboo-like CNTs? According to previous research [178], the following parameters seem to help in promoting the formation of the bamboo-like CNTs:

1. The presence of nitrogen or other heavy gases,
2. Keeping an active and clean top surface of the catalyst particles,
3. Prolonging carbon bulk diffusion of the catalysts,
4. Larger catalyst size, and
5. Passivation layer on the catalyst surfaces.

Conditions (2) and (3) can explain the reasons why Electron Cyclotron Resonance chemical vapor deposition (ECR-CVD) often forms bamboo-like CNTs. The presence of nitrogen is essentially to fulfill conditions (2) and (3). Bartsch [11] showed in his study the dependence of the formation of bamboo-like CNTs on the deposition time. After longer deposition time the structure of bamboo-like CNTs was dominant.
6.2.2 Hydrogen Effect on the Floating Catalyst Method

An improved apparatus was designed for better control of experimental parameters. The schematic diagram of the apparatus is given in Figure 6.1. The quartz tube is 22 mm in diameter and 600 mm long. Benzene was used as the carbon source, hydrogen as the carrier gas and ferrocene as the catalyst precursor [179]. Table 6.1 shows the effects of hydrogen flow rate on the products. At the beginning of the experiments, all of the hydrogen bubbled through the benzene. It was found that only amorphous carbon was obtained at hydrogen flow rates, 200 ml/min. Carbon fibers and strand-like products were produced when the hydrogen flow rate increased to 250 ml/min.

In order to control the amount of benzene carried by the hydrogen, two paths for the hydrogen were adopted. In one path (H$_2$I) hydrogen bubbled through the benzene, and in the other path (it flowed directly through the reactor). The results are shown in Table 6.1. A total hydrogen flow rate of 300 ml/min was maintained during the above experiments and different ratios of hydrogen flow were adopted. SEM and TEM observations showed that as the hydrogen flow bubbling through the benzene increased, the amount of amorphous carbon in the products increased, and the diameter of carbon nanofiber increased. At a low H$_2$I/ H$_2$I ratio, a high quality carbon nanofiber films was obtained [179].
Figure 6.1 Schematic diagram of an experimental apparatus for the floating catalyst method [179].
Table 6—1 the effect of hydrogen flow rate on the products [179].

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Temperature °C</th>
<th>H\textsubscript{2} flow rate (ml/min)</th>
<th>Products\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H\textsubscript{2}I</td>
<td>H\textsubscript{2}II</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1120</td>
<td>&lt;200</td>
<td>AC</td>
</tr>
<tr>
<td>2</td>
<td>1120</td>
<td>250</td>
<td>AC, CF</td>
</tr>
<tr>
<td>3</td>
<td>1120</td>
<td>300</td>
<td>CF, SC</td>
</tr>
<tr>
<td>4</td>
<td>1150</td>
<td>80</td>
<td>SC + FC</td>
</tr>
<tr>
<td>5</td>
<td>1150</td>
<td>100</td>
<td>CF + SC + FC</td>
</tr>
<tr>
<td>6</td>
<td>1150</td>
<td>120</td>
<td>CF + SC + FC</td>
</tr>
<tr>
<td>7</td>
<td>1150</td>
<td>150</td>
<td>AC + CF + SC + FC</td>
</tr>
</tbody>
</table>

\textsuperscript{a} AC represents amorphous carbon; CF carbon fibers in powder form; SC strand-like product; FC film-like product. (Observed through SEM and TEM).
Argon is used as the carrier gas in many CVD reactors, and hydrogen is mixed with argon specifically when a liquid hydrocarbon (xylene, toluene, benzene …etc) is used as the carbon source. What is the role of hydrogen in CNTs formation? This study is a partial contribution in trying to the answer of that question. Although there is some previous work to explain the effect of hydrogen in carbon fiber formation [180-183] and recent work to study the effect of hydrogen on CNTs formation [114], it is needed to do more research to have a better understanding of the role of hydrogen in catalytic decomposition of hydrocarbon especially for CNTs syntheses.

There have been some recent works to understand the growth mechanism of carbon nanotubes (CNTs) in chemical vapor deposition [139, 142,163].

The aim of this study is to make a partial contribution in understanding the role or effect of hydrogen on xylene catalytic decomposition in CVD reactors. Also the effect of using two-steps reaction instead of using a single-step reaction has been studied.
6.3 Experimental

The experimental set up, shown in Figure 6.2 and similar to the ones in [170] and our numerical studies [146, 147] consists of a quartz tube having 85 mm diameter and 1,520 mm long, 304 mm pre heater and 608 mm heater, a programmable syringe pump to deliver xylene (or xylene + ferrocene) the flow rate of xylene (or xylene + ferrocene) of 4.0 mL/hr, flow meters to control argon and hydrogen flow rates respectively, and temperature controllers to control both preheater and heater temperatures. The reactor walls were used as substrates for CNT growth. In the single-step method a mixture of xylene (C₈H₁₀) and ferrocene (Fe C₁₀H₁₀) with ferrocene at approximately 8.25 % mole concentration to xylene (to get a solution with 1.00 % Fe/C ratio) was used as a feedstock. The synthesized materials were collected from the reactor walls after each run. Hitachi-900 SEM and JEOL-2000 TEM were used to take SEM and TEM images for that synthesized materials.

In the two-step method iron catalyst particles (nano-particles) were deposited on the furnace wall by thermal decomposition of ferrocene [180]. Therefore 0.5 grams of ferrocene was placed in the preheating zone area for 10 minutes prior to each run. The carrier gas (argon) and hydrogen have a fixed flow rate of 1,500 sccm in both single-step and two-step methods. The synthesized materials were collected from the reactor walls after each run. Hitachi-900 SEM, JEOL 2010 HRTEM, and JEOL-2000 TEM were used to take SEM and TEM images for those synthesized materials.
Figure 6.2 Schematic diagram for the experimental set up.
6.4 Procedure

At the beginning of each run the reactor was purged from air to avoid oxidation of carbon by oxygen by flowing argon at 3,000 sccm/min for 45 minutes prior to turning the heaters on, and then the temperature controllers were set to the desired temperatures after that the furnace was allowed to sit at the desired temperatures (350°C for preheating zone and 875°C for heating zone) for 10 minutes to stabilize the system. Starting with the hydrogen flow rate at 0.0 sccm the reactor was running for 45 minutes as a fixed duration time during each run in both single-step and two-step methods. Then the reactor was shut off and let to cool down and the deposited materials were collected from the inside walls of the reactors. The hydrogen flow rate was increased by a certain amount and argon flow rate was decreased by the same amount to maintain the total mixture flow rate at 1,500 sccm. Those steps were repeated at different conditions as shown in Table 6.2.
Table 6—2 Hydrogen and argon concentrations at each run for single-step method.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>H₂  m³/s</th>
<th>(%)</th>
<th>Ar. m³/s</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>00.000</td>
<td>(00.0)</td>
<td>2.500x10⁻⁵</td>
<td>(100.0)</td>
</tr>
<tr>
<td>1-2</td>
<td>6.250x10⁻⁷</td>
<td>(02.5)</td>
<td>2.375x10⁻⁵</td>
<td>(097.5)</td>
</tr>
<tr>
<td>1-3</td>
<td>1.250x10⁻⁶</td>
<td>(05.0)</td>
<td>2.333x10⁻⁵</td>
<td>(095.0)</td>
</tr>
<tr>
<td>1-4</td>
<td>2.500x10⁻⁶</td>
<td>(10.0)</td>
<td>2.250x10⁻⁵</td>
<td>(090.0)</td>
</tr>
<tr>
<td>1-5</td>
<td>3.333x10⁻⁶</td>
<td>(13.3)</td>
<td>2.167x10⁻⁵</td>
<td>(086.7)</td>
</tr>
<tr>
<td>1-6</td>
<td>4.167x10⁻⁶</td>
<td>(16.7)</td>
<td>2.083x10⁻⁵</td>
<td>(083.3)</td>
</tr>
<tr>
<td>1-7</td>
<td>5.000x10⁻⁶</td>
<td>(20.0)</td>
<td>2.000x10⁻⁵</td>
<td>(080.0)</td>
</tr>
</tbody>
</table>
In the two-step method, the first step was to prepare catalyst by placing 0.5 gm of ferrocene powder in the preheater. The temperature controllers were set to 250 °C for the preheater and 500°C for the heater. Those temperatures were fixed during the catalytic preparation step in all runs. The ferrocene vapor was swept down the reactor to the reaction (or heating) zone by the carrier gas (argon) and hydrogen. For 30 minutes under these conditions, iron nanoparticles were deposited on the furnace wall to form the catalytic base for CNT growth.

After the catalyst particles were prepared, the ferrocene powder container was removed from the reactor to prevent any disturbance to the flow inside the reactor. The preheater temperature was increased to 350°C and the furnace temperature to 875°C. Xylene in liquid form was continuously fed into the reactor by using a programmable syringe pump at the rate of 4.0 ml/hr. Those steps were repeated, several times varying both hydrogen and argon flow rates but keeping the mixture flow rate fixed at 1500 sccm as indicated in Table 6.3, which is similar to the single-step method. Then the synthesized materials were collected from the reactor walls after each run and the same electronic microscopy was used to get SEM, TEM, and HRTEM images for the collected materials.
Table 6—3 Hydrogen and argon concentrations at each run for the two steps method.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>H₂</th>
<th>m³/s</th>
<th>(%)</th>
<th>Ar.</th>
<th>m³/s</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
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<td>2-1</td>
<td>00.000</td>
<td>(00.0)</td>
<td></td>
<td>2.500×10⁻⁵</td>
<td>(100.0)</td>
<td></td>
</tr>
<tr>
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<td>6.250×10⁻⁷</td>
<td>(02.5)</td>
<td></td>
<td>2.375×10⁻⁵</td>
<td>(097.5)</td>
<td></td>
</tr>
<tr>
<td>2-3</td>
<td>1.250×10⁻⁶</td>
<td>(05.0)</td>
<td></td>
<td>2.333×10⁻⁵</td>
<td>(095.0)</td>
<td></td>
</tr>
<tr>
<td>2-4</td>
<td>2.500×10⁻⁶</td>
<td>(10.0)</td>
<td></td>
<td>2.250×10⁻⁵</td>
<td>(090.0)</td>
<td></td>
</tr>
<tr>
<td>2-5</td>
<td>3.333×10⁻⁶</td>
<td>(13.3)</td>
<td></td>
<td>2.167×10⁻⁵</td>
<td>(086.7)</td>
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</tr>
<tr>
<td>2-6</td>
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<td>(16.7)</td>
<td></td>
<td>2.083×10⁻⁵</td>
<td>(083.3)</td>
<td></td>
</tr>
<tr>
<td>2-7</td>
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<td>(20.0)</td>
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<td>2.000×10⁻⁵</td>
<td>(080.0)</td>
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6.5 Results

The main purpose of this work is to investigate the effect of hydrogen concentration on carbon materials synthesized by thermal CVD. Therefore it was better to conduct all observations on the as grown material without any special purification or treatment processes, in order to have good knowledge of the nature and morphology of the obtained carbon materials. The synthesized materials were collected and then observed by scanning electron microscope (SEM Hitachi-900) and transition electron microscope (TEM JEOL-2000 & HRTEM JOEL 2010).

6.5.1 Single Step Method

For run number 1-1, where is no hydrogen, the collected materials were completely soot with small amount of some other carbon materials. Figures 6.3, 6.4 and 6.5 show SEM and HRTEM images for samples of the materials collected from this run. The diameters or the length of those deposited materials range approximately from 50 nm to 250 nm. Some of these materials look like nano-balls and others like agglomerated soot. Arrow (a) in Figure 6.4 is pointing toward a nano particle with a size of about 50 nm. Arrow (b) in Figure 6.5 is pointing toward a nano iron particle encapsulated inside the deposited materials.
Figure 6.3  SEM images for soot collected from run No. 1-1.
Figure 6.4 SEM images for soot collected from run No. 1-1.
Figure 6.5  HRTEM image for soot collected from run No. 1-1.
For run 1-2 where there is a little hydrogen concentration presented in the reactor, the collected materials were composed of soot, carbon fibers, carbon tubes, and other carbon materials, with barely one or two CNTs. Figures 6.6 and 6.7 show SEM images for samples of the materials collected from this run. Diameters of those materials range from ~35 to ~180 nm. Arrow (a) in Figure 6.6 is pointing toward a carbon fiber, which has a piece of carbon materials at its end. A small amount of the agglomerated soot reached a size of more than 350 nm as indicated by arrow (b) in Figure 6.6. Some carbon layers with sizes were ranging from 0.5 µm to 1.75 µm as shown by arrow (C) in Figure 6.7, have appeared in this run. This carbon layers at some location were attached to the end or beginning of a carbon fiber, carbon tube or CNT.
Figure 6.6 SEM images for soot, carbon fiber, carbon tubes and carbon materials collected from run No. 1-2.
Figure 6.7 SEM images for soot carbon fiber, carbon tubes and carbon materials collected from run No. 1-2 at different location inside the reactor.
For runs number 1-3 where the hydrogen concentration increased in the reactor, but its concentration in the argon and hydrogen mixture was still less than 10%, the collected materials were composed of soot, carbon fibers, carbon tubes, and a small amount of CNTs and other carbon materials.

Figures 6.8 and 6.9 show SEM images for samples of the materials collected from this run. Diameters of those materials range from ~35 to ~180 nm, with the exception of some larger size carbon tubes, such as the one in Figure 6.8 as indicated by arrow (a). The carbon fibers collected from this run have some special characteristics over the one collected from previous runs. The first characteristic is its obvious length as indicated by arrow (c) in Figure 6.9. The second characteristic was that some of them ended with a nano carbon ball or sphere as shown in figure 6.6 b and pointed to by arrow (b). The size of that nano ball is almost twice the diameter of the original carbon fiber.
Figure 6.8 SEM images for carbon fiber, carbon tubes, CNTs, soot and carbon materials collected from run No. 1-3.
Figure 6.9 SEM images for carbon fiber, carbon tubes, CNTs, soot and carbon materials collected from run No. 1-3 at different location inside the reactor.
For run 1-4, where the hydrogen concentration was around 10%, the collected materials were mainly composed of CNTs, and a small amount of other carbon materials like carbon fibers and carbon tubes. Diameters of those materials range from ~25 to ~160 nm. Figure 6.10 shows a SEM image for samples of the materials collected from this run. Arrow (a) is pointing toward one carbon fiber collected from this run. The diameter of this carbon fiber is around 150 nm and it is clear that it is an exception among the collected materials. Also arrow (b) is pointing toward one carbon fiber and arrow (b) is pointing toward one carbon tube collected from this run. The diameter or size of this carbon tube is around 350 nm and it is clear that it is also an exception among the collected materials.

Figures 6.11a shows a TEM image for one of the multi-wall carbon nanotubes collected from this run. Figures 6.11b shows TEM image for some of the carbon fibers that appeared in this run. Some of those carbon fibers are straight as shown by arrow (c) and some are not (or curved) as shown by arrow (d) in Figure 6.8 b.
Figure 6.10  SEM images for, CNTs, carbon fiber, carbon tubes, and carbon materials collected from run No. 1-4.
Figure 6.11 TEM images for (a) one CNT & (b) collected from run No. 1-4.
For run 1-5, at which hydrogen concentration is 13.33 %, the collected materials were well-aligned MWNTs and a very small amount of other carbon materials. Figure 6.12 shows a SEM image for this run. Diameters of those materials rang from ~20 nm to ~120 nm.

A small amount of those CNTs have a very small diameter as small as 17 nm as shown by arrow (a) in Figure 6.12 and a very small number of those have a bigger diameter or size as shown by arrow b in the same figure. It is clear from the image that the CNTs collected from this run are long and straight and the amount of other carbon materials are minimal.

Figure 6.13 shows TEM images for a sample of the materials collected by this run. It is also clear from the image that most of the CNTs are long and straight.
Figure 6.12 SEM image for CNTs, and carbon materials collected from run No. 1-5.
Figure 6.13 TEM image for CNTs, and carbon materials collected from run No. 1-5.
For runs 1-6 and 1-7, at which hydrogen concentrations are 16.67 % and 20 %, the collected materials were very well-aligned MWNTs, with a negligible amount of other carbon materials. Figures 6.14 and 6.15 show SEM images for runs 1-6 and 1-7. Figures 6.12a and 6.12b show TEM images for this run. Figure 6.13 shows HRTEM image for run number 1-7. There is no measurable change in the size or diameter range for the materials collected from these runs than that from run number 1-5. The collected materials in runs 1-6 and 1-7 are in the same range (~25 nm to ~140 nm).

A small amount of those CNTs, which might be single wall CNTs, have a very small diameter, as small as 15 nm as shown by arrow (a) in Figure 6.14 and a very small number of those have a bigger diameter. It is also clear from the image that the CNTs collected from this run are long and very straight and there are almost no other carbon materials or amorphous carbon.

Some of helical or spring shape CNTs appeared at these conditions as shown in Figure 6.15 by arrow (b). Some of these helical shape CNTs have an extended spring shape as indicated by arrow (c) in Figure 6.16a and some others have a compressed spring shape as indicated by arrow (d) in Figure 6.16b. An HRTEM image for CNTs sample collected by this run is shown in Figure 6.17. It is also clear from the image those CNTs are very straight.
Figure 6.14 SEM image for CNTs collected from run No. 1-6.
Figure 6.15 SEM image for CNTs collected from run No. 1-7.
Figure 6.16 TEM image for CNTs collected from run No. 1-7.
Figure 6.17 HRTEM image for, CNTs collected from run No. 1-7.
6.5.2 Two-step Method

For run 2-1, where there is no hydrogen, the collected materials were similar to those collected from run 1-1 and they were completely soot with a small amount of some other carbon materials. Figures 6.18 and 6.19 show SEM and HRTEM images for samples of the materials collected from this run. The diameters or the length of those deposited materials range approximately from 50 nm to 250 nm. Some of those materials look like nano-balls and others like agglomerated soot.
Figure 6.18 SEM image for soot and carbon materials collected from run No. 2-1.
Figure 6.19 HRTEM image for soot and carbon materials collected from run No. 2-1.
For runs 2-2 and 2-3, where there is a little hydrogen presented in the reactor, the collected materials were composed of short but yet very organized carbon fibers, carbon tubes soot, and a small amount of CNTs. Diameters of those materials are also ranging from 25 to 160 nm. Figure 6.20 shows an SEM images for carbon nanofiber sample collected from these runs at different magnification. The main difference between the materials collected from this run and runs number 1-2 and 1-3 is the appearance of carbon nanofiber rings as indicated by arrows (a), (b), and (c) in Figures 6.20a, 6.20b, 6.20c and 6.20d respectively and arrow (b) in Figure 6.21c. Arrow (a) in Figure 6.18a pointing toward some amorphous carbon materials synthesized among the collected materials.

Figures 6.21 shows a SEM image for a sample of carbon fiber collected from run number 2-3. In this run, a different carbon material appeared with a size of about 1.0 µm as indicated by arrow (b), and it has pits as indicated by arrow (d) in Figure 6.21b.
Figure 6.20 SEM images short carbon fiber, nano rings and carbon materials collected from run No. 2-2.
Figure 6.21 SEM images carbon fiber, carbon tubes and carbon materials collected from run No 2-3.
For run 2-4, where the hydrogen concentration was around 10%, the collected materials were mainly composed of CNTs, and a small amount of other carbon materials such carbon fibers, and carbon tubes, which is similar to the results from run 1-4. Some of the carbon fiber collected from this run is shown in Figure 6.22 and it is clear that some of those carbon fibers have a nano-ball or a nano sphere at their end as shown by arrow (a) in Figure 6.22b.

Diameters of the materials collected from this run range from ~25 to ~150 nm. Some of those collected materials, either which are carbon fibers or carbon tubes, have a V-shape as shown in Figure 6.22d.
Figure 6.22 SEM images carbon nanofiber, carbon tubes and carbon materials collected from run No. 2-4.
For runs 2-5 to 2-7 at which hydrogen concentration is 13.33 %, 16.67 % and 20 %, hydrogen concentration considerably exceeding 10 %, the collected materials were very well-aligned MWNTs, and a negligible amount of other carbon materials. Figures 6.23, 6.24, 6.25 and 6.26 show SEM, TEM, and HRTEM images for some of the materials collected from these runs practically the carbon fiber materials. The change in the diameter range for the materials collected from these runs was minimal compared to 2-4. The average sizes are still in the same range (~25 nm to ~140 nm).

It is clear from the SEM images in Figure 6.23 that the carbon fibers collected from this run are long and very straight as indicated by arrow (a) in Figure 6.23a and also the majority of the carbon fiber are ended by a soot-like carbon nano-ball as shown in Figures 6.23a and 6.23b. There are almost no other carbon materials or amorphous carbon.

SEM images for CNTs synthesized among the materials collected from these runs are shown in Figures 6.24. TEM and HRTEM image of CNTs and carbon fibers samples collected by these run are shown in Figure 6.25 and Figures 6.26. It is also clear from the image that CNTs are very straight.
Figure 6.23 SEM images for carbon nanofiber, carbon tubes and carbon materials collected from runs No. 2-5 (a), 2-6 (b) and 2-7 (c, d).
Figure 6.24 SEM images for carbon nanofiber (a, b) for runs No. 2-5, 2-7 and CNTs (c, d) for runs No. 2-6 & 2-7.
Figure 6.25 TEM images for CNTs and carbon nanofiber materials collected from runs No. 2-5 & 2-7.
Figure 6.26 TEM and HRTEM images for CNTs and other carbon materials collected from runs No. 2-5 (a, d), 2-6 (b) and 2-7 (c).
6.6 Discussion

CNTs are more thermodynamically stable than soot because of the lack of dangling bonds [181]. Hydrogen concentration inside CVD is an important factor in hydrocarbon decomposition, which has an effect on the nature of the synthesized materials. In the case of the absence of hydrogen or at a very low concentration inside the reactor, the diffusion rate of hydrogen from the hydrocarbon is very fast and will not give the carbon enough time to rearrange into the most thermodynamically stable configuration [182]. Thus the resulting materials are soot as indicated of the results of run number one. When hydrogen concentration increased, the diffusion rate of hydrogen from hydrocarbon decreased. In this case, carbon will have enough time to rearrange into carbon tubes, CNTs or carbon fibers, which matches with the results from runs numbers 2 to 7. More increase in hydrogen concentration resulted in better quality of CNTs and an increase in the percentage of CNTs among the amount of synthesized materials.

The TEM and HRTEM images show that there were almost no encapsulated iron particles inside the CNTs produced by two-step method and also the alignment of the CNTs produced by the two-step method is better than those produced by the single-step method.

Another difference between the materials produced by the single-step method and the two-step method is that the carbon fiber collected from the two-
The step method is more uniform and longer than the carbon fibers produced from the single-step method as shown in SEM images especially in Figure 6.23a.

It is important to understand the effect of hydrogen on carbon formation. The effect of hydrogen can be both accelerating and suppressing. The accelerating effect of hydrogen on carbon fiber formation may be interpreted in two ways. One interpretation (mechanism 1) suggests that hydrogen decomposes inactive metal carbides to form catalytically active metals [146, 147]. The other (mechanism 2) is that hydrogen removes the graphite over layer, which hinders the catalytic action of the metal [184]. The suppressing effect has also been reported to be due to the surface hydrogenation reactions and also hydrogasification of carbon to form methane [184,185].

The results from this study agree with accelerating effect specially mechanism number one.
6.7 Conclusion

The effect of hydrogen on xylene decomposition in the CVD reactor to produce CNTs has been experimentally studied. The SEM, TEM, and HRTEM images show that hydrogen concentration inside the CVD reactor influenced the nature and quality of the synthesized materials. Absence of hydrogen resulted in soot or carbon black synthesis instead of CNTs. Increasing hydrogen concentration resulted in the appearance of CNTs among the synthesized materials, and the percentage of CNTs increased among the synthesized carbon materials. The quality of these CNTs is improved by increasing the hydrogen concentration.

The differences between the two-step and the single-step method were studied. This study indicated an improvement in the quality of carbon materials synthesized by this method especially for the carbon fibers. There was also a very slight increase in the quantity of the collected carbon materials produced by the two-step method although it takes more time for the catalyst preparation step.
CHAPTER SEVEN

CONCLUSION

The effect of hydrogen on xylene decomposition in the CVD reactor to produce CNTs has been experimentally studied. The SEM, TEM, and HRTEM images show that hydrogen concentration inside the CVD reactor influenced the nature and quality of the synthesized materials. Absence of hydrogen resulted in soot or carbon black synthesis instead of CNTs. Increasing hydrogen concentration resulted in the appearance of CNTs among the synthesized materials, and the percentage of CNTs increased among the synthesized carbon materials. The quality of these CNTs is improved by increasing the hydrogen concentration.

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Using our scale model CVD reactor, an experimental study has been done to measure the major gas species concentrations inside a CVD reactor for xylene decomposition at temperatures 600–1200°C. The temperatures were measured along the reactor center at the same location, as the sampling probe was located. This study showed that the CH\(_4\) and C\(_2\)H\(_x\) concentrations increased.
along the reactor heating zone, and this increase is related to temperature and is much higher at higher temperatures 1000°C and above. The increase in (Ar+H₂) concentration is relatively small compared with those for CH₄ and C₂Hₓ.

The temperature profiles for axial and radial measurements are in agreement with the theoretical profiles for laminar flow in a hot wall tube. The radial measurements for species concentrations did not show much difference.

The following conclusions were made. The overall rate constant for the gas-phase reaction was calculated based on the measured species concentration data using the Benson and Shaw reaction mechanism [157]. Despite the fact that the Benson and Shaw mechanism is based on relatively short residence time (order of 1 s) and our result is based on longer residence time (order of 100 s), our study showed that the Benson and Shaw mechanism could be used in the temperature range lower than 800°C.

Further studies are needed to measure the concentrations of xylene, toluene, and benzene vapors inside the CVD reactor at different locations for better understanding to the gas-phase reaction mechanism of xylene decomposition in the CVD reactor.
Appendices

Appendix A: Symbols (List of Abbreviation)

CVD : Chemical vapor deposition
CNTs : Carbon nanotubes
PAN : Polyacrylonitrile
CFs : Carbon fibers
GW : Graphite whisker
VGCFs : Vapor grown carbon fibers
HOPG : Highly oriented pyrolytic graphite
SWNTs : Single-walled carbon nanotubes
MWNTs : Multi wall carbon nanotubes
SEM : Scanning electron microscopy
STM : Scanning tunneling microscopy
EELS : Electron energy loss spectroscopy
VGCNFs : Vapor grown carbon nanofibers
DWNTs : Dingle-walled carbon nanotubes
DMAc : Dimethyl acetamide
PPy : Polypyrrole
FETs : Field-Effect Transistors
SETs : Single-Electron Transistors
DET : Direct electron transfer
HA : Anti-Hemagglutinin
slm : Slug per minute
HAB : Height above the burner
TGA : Thermo gravimetric analysis
PE-CVD : Plasma enhanced chemical vapor deposition
RTP : Rapid thermal processing
MPCVD : Microwave plasma chemical vapor deposition
GC : Gas Chromatograph
ANOVA : Analyses of Variable
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