

# **Continuous production of Single Walled Carbon Nanotubes by means of a Swirled Fluid Chemical Vapour Deposition Reactor**

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**A dissertation submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, in fulfilment of the requirements for the degree of Master of Science in Engineering.**

**Johannesburg, 2011**

## **Declaration**

I declare that this dissertation is my own unaided work. It is being submitted to the Degree of Master of Science to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

Signed:.....

Date: .....

## Abstract

Research into Carbon Nanotubes and their applications is fast becoming an extremely popular topic and any means to greatly improve the synthesis process has a huge marketability. An investigation was undergone to ascertain whether a Swirled-Fluid Chemical Vapour Deposition reactor could be used to continuously produce single-walled carbon nanotubes (SWCNT) in a feasible manner and, although the process proved successful, the mechanism of the SWCNT synthesis has not been full understood. It was found that the use of a 10% Hydrogen to Argon mixture being passed through a 6.5mol% ferrocene-Xylene solution at 900°C resulted in the presence of Single Walled Carbon Nanotubes attached to Helical Carbon Nanotubes in the product stream exiting the hydro cyclones.

Investigation into the merits provided by the helical structure illustrated the greatly increased likeliness for helical tubes to be lifted from the reactor by the carrier gas giving rise to positive speculation of their possible use in vertical CVD reactors in the future. The increased drag and agglomeration provided by the helical shape provide a possible means by which grown nanotubes can be lifted from a vertical reactor in the future when more control over the products has been achieved. To its disadvantage contrarily, it was also found that the Swirled-Fluid Chemical Vapour Deposition reactor does require further separation of its products as, at present, produced samples still contain large amounts of unwanted material.

## Acknowledgements

The author would just like to acknowledge the assistance of his supervisors, Prof. Sunny Iyuke and Prof. Frank Kavishe, for their excellent supervision and advice, as well as that of Mr. Georgie Mathews who assisted in the running of certain experiments. The financial assistance of the National Research Fund (NRF) and the African Materials Science and Engineering Network (AMSEN) towards the completion of this work is also greatly appreciated.

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## CHAPTER 1 - Introduction

### 1.1 Background and motivation

Until 1980, only three forms of carbon were known, namely graphite, diamond and amorphous carbon. In the 1980s, the discovery of the buckminster fullerene molecule (Scharff, 1998), another allotrope of carbon also known as the 'bucky ball', has led to much research in the field of carbon nanostructures. The later discovery of carbon nanotubes (CNTs) by Sumio Iijima in 1991 was a huge development in the field of nanotechnology (Yamabe, 1995), largely due to their various unique properties. CNTs are allotropes of carbon with a nanostructure that can have a length-to-diameter ratio as large as 28,000,000:1, which is unequalled by any other material (Zheng et al., 2004). The small dimensions, strength and the remarkable physical properties of these structures allow for a very unique material with a whole range of promising applications (Dresselhaus, 2000). Carbon nanotubes are related to graphite, and to use the description given by M. Wilson et al. (2002): When graphene sheets are rolled into a cylinder and their edges seamlessly joined, they form CNTs. Only the tangents of the graphitic planes come into contact with each other, and hence their properties are more like those of a molecule (Wilson et al., 2002). Peigney (2001) states that the "unusual properties of CNTs derive from the curved  $sp^2$  graphene layers by imposing additional quantum confinement and topological constraints in the circumferential direction of the cylinders." CNTs can be classified as single, double and multiple walled based on their physical structure.

The discovery of single-walled carbon nanotubes (SWCNT) proved to be an extremely important development since the structures appeared to be approximate to those of the 'ideal' nanotubes consisting of tubes with walls only one atom thick (Harris, 1999), a discovery previously unseen. To use Paradise et al.'s (2007) description: "Ideal

Nanotubes can be described as a seamless cylinder of rolled up hexagonal networks of carbon atoms.” They also describe possible applications ranging from semiconductors, electronic memory, drive products, and medical delivery systems to uses in plastics such as automobile body panels, paint, tires and as flame retardants in polyethylene and polypropylene.

SWCNTs are a very important variety of carbon nanotube because they possess important electronic properties that the multi-walled carbon nanotube (MWCNT) variants do not possess. Single-walled nanotubes are the most likely candidate for miniaturizing electronics beyond the micro electromechanical scale that is currently the basis of modern electronics (Dekker, 1999). Since SWCNTs can be excellent conductors, they can be of great use in miniaturizing the most basic component of these systems, namely the electric wire. A useful application of SWCNTs is in the development of the first intramolecular field effect transistors (FETs). The production of the first intramolecular logic gate using SWCNT FETs has recently become possible as well (Martel et al., 2001). These discoveries can also be of great use in other related areas such as for the improvement and minimization of biometric security systems.

While the Catalytic Vapour Deposition (CVD) method has been recognised as a major method for synthesizing CNTs, various modified versions of this method have also proved successful. The Swirled Fluid Chemical Vapour Deposition Reactor, which was designed and developed at the University of the Witwatersrand, has been identified to produce CNTs in large quantity on a continuous basis. However, the ability of this reactor to produce single walled carbon nanotubes at specific conditions, and a theory of transport of CNTs in the reactor has not been reported. The present study therefore focuses on the effects of operating conditions on the types of CNTs produced in the reactor and the theory of transport of the nanoparticles present.

## 1.2 Purpose and aims

It shall be investigated whether a feasible process is possible to produce Single Walled Carbon Nanotubes (SWCNTs) continuously in a Swirled Fluid Chemical Vapour Deposition Reactor (SFCVD). With the ever increasing interest in carbon nanotubes, a means to mass produce them in a cost effective manner has a huge marketability. Although the SFCVD reactor at the University of the Witwatersrand has successfully been used to produce SWCNTs previously (Iyuke et al., 2008), the production technique has not been optimised to produce them in a continuous manner.

This shall be investigated by considering different reactor temperatures and conditions. By changing these aspects of SWCNT production, the selectivity and yield of SWCNTs in relation to other nanostructures shall be investigated. Upon finding the optimum conditions for producing single-walled CNTs, different experiment durations shall be implemented to ascertain the feasibility of continuous production by this method.

## 1.3 Scope of research

In this study, the use of a SFCVD reactor for carbon nanotube synthesis shall be investigated by the altering of operating conditions. It shall also be endeavoured to explain the resulting favourable products by the development of a mechanistic theorem if required.

## CHAPTER 2 - Literature Review

### 2.1 Mechanisms of CNT growth

In order to optimize the production of carbon nanotubes, the mechanisms by which they are grown need to be fully understood (Deck et al., 2005). One mechanism based on the processes involved in carbon fibre formation is described by Sinnott et al. (1999), while a more specific mechanism describing carbon nanotubes formation is described by Zhao et al. (2006) whereby carbon diffuses into nanometer-scale catalytic particles. The catalyst particles then realign the carbon atoms on a certain catalytic crystal face with the realigned shape exhibiting a tubular figure. After the formation of C-C chemical bonds, this carbon then precipitates out with a graphitic structure once the solubility limit within the metal is reached. The size and shape of the catalyst can affect whether graphite, carbon filaments or carbon nanotubes are formed. According to Deck et al. (2005), “as more carbon is deposited on the catalyst it will either diffuse into or over the surface of the particle and become incorporated into the graphitic lattice, increasing the tube’s length.” Figure 1.1 below shows how, during formation, the catalyst particles will either remain fixed to the substrate (root growth) or will detach from the surface and stay encapsulated inside the opposite end (tip growth).

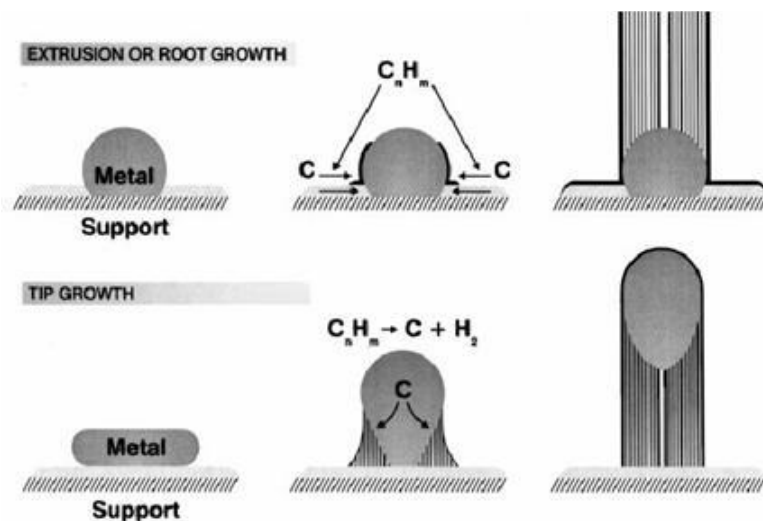


Figure 1.1: Growth mechanisms of carbon nanotubes (Deanan et al, 2003).

Another mechanism is proposed by Zhang et al. (2002) to explain the vapour phase growth of carbon nanotubes. As they describe it, nanotubes nucleate and grow by a tip growth mechanism with metal catalyst particles initially rising with the tube tips as they grow. The particles eventually become fixed in place due to friction between the particles and the tube walls. Deck et al. (2005) expands on this theory to explain the growth of nanotubes by tip growth after which friction had immobilised their catalyst and growth had continued slowly open ended.

## 2.2 Synthesis of carbon nanotubes

At present, three foremost methods exist for synthesis of carbon nanotubes in significant quantities, namely arc discharge, laser ablation and chemical vapour deposition (CVD). Of these, the carbon arc discharge method is most likely the simplest and most common method for producing carbon nanotubes. However, this method does produce a complex mixture of components and as such does require further purification to separate the carbon nanotubes from the mixture. This method creates CNTs through arc-vaporization of two carbon rods placed end to end, separated by approximately 1mm, in an enclosure that is usually filled with inert gas at low pressure (Foley, 2006). A very high temperature is obtained which allows for the sublimation of the carbon, however the growth needs to be interrupted to remove the product from the chamber (Paradise, 2007).

Laser ablation, alternatively, relies on a pulsed laser which vaporizes a graphite target in a high temperature reactor while an inert gas is bled into the chamber. The nanotubes develop on the cooler surfaces of the reactor, as the vaporized carbon condenses. A water-cooled surface may be included in the system to collect the nanotubes (Wilson et al., 2002; Foley, 2006). The method has several advantages, such as high-quality SWCNT production, diameter control, investigation of growth dynamics, and the production of

new materials. High-quality SWCNTs with minimal defects and contaminants, such as amorphous carbon and catalytic metals, have been produced using the laser-furnace method together with purification processes (Ando et al., 2004).

Chemical Vapor Deposition (CVD) is another popular method for producing CNTs in which a hydrocarbon vapor is thermally decomposed in the presence of a metal catalyst (Ando et al., 2004; Sinnot et al., 1999). This usually occurs in two main processing configurations, namely horizontal and vertical. During CVD, a substrate is prepared with a layer of metal catalyst particles, most commonly nickel, cobalt, iron, or a combination (Inami et al, 2007; Ishigami et al, 2008). The substrate is then heated to approximately 700°C or greater. To initiate the growth of nanotubes, two gases are bled into the reactor: a process gas (such as ammonia, nitrogen, hydrogen, etc.) and a carbon-containing gas (such as acetylene, ethylene, ethanol, methane, etc.). Nanotubes grow at the sites of the metal catalyst; the carbon-containing gas is broken apart at the surface of the catalyst particle, and the carbon is transported to the edges of the particle, where it forms the nanotubes (Foley, 2006; Ando et al., 2004).

For a successful CVD process, careful choice of catalyst, carbon source and process/carrier gas must be made. The carrier gas is generally a non-reactive gas that keeps the reactor free from oxygen and provides an inert atmosphere for CNT growth. Argon, hydrogen and nitrogen are most common but other gases such as ammonia and helium have also been used. Qingwen et al. (2004) investigated the effect of carrier gas on the CVD process of cyclohexane and found MWCNTs when argon was used but when hydrogen was used some SWCNTs had formed suggesting that careful choice of carrier gas could affect products formed.

Numerous transition metals have been tested as catalysts for nanotube growth with iron (Fe), cobalt (Co), and nickel (Ni) proving to be the most effective. Research into alloys of two transition metals with each other and with other non-transition metals in order to provide better quality CNTs with lower reaction temperatures is also underway (Lamoureux et al, 2006; Nagaraju et al, 2002; Danafar et al, 2009). The effect of catalyst size can also play a large role in the size of nanotubes produced. Danafar et al (2009) states that there is a consensus in scientific literature that the outer diameter of formed nanotubes is directly correlated to the catalyst particle size. This means that small well-dispersed catalyst particles are more effective as compared to large particles and aggregates.

Carbon feed stocks can also play an important role in nanotube growth in the CVD process. Hernadi et al stated that unsaturated hydrocarbons have much higher yield and deposition rates than saturated gases but also that saturated hydrocarbon gases are favoured for SWCNT growth and unsaturated hydrocarbons for MWCNT growth. Danafar et al (2009) also stated that numerous authors concluded that alcohols are much better carbon sources for SWCNTs than hydrocarbons most likely attributed to the OH- radicals' ability to etch away amorphous carbon deposits. It has even been reported (Yen et al, 2008) that CNTs can be synthesized from solid-stated polymers – polycarbosilane and polyethylene using FBCVD (fluidized bed CVD). It has been found that the best method for high quantity and low cost production of nanotubes is provided through the CVD method (Paradise et al., 2007)

Numerous catalyst techniques exist for the CVD process, each possessing their own advantages and disadvantages. For the floating catalyst technique, a mixture of catalyst and reactants are fed into reactor in the gas phase at an elevated temperature allowing the gas phase catalyst to undergo conversion to nano-sized solid phase active catalyst particles in situ (Danafar et al, 2009). Only once these nano-catalysts adhere to the

reactor surfaces will they possess enough residence time for nanotube growth to occur. Certain disadvantages of this method exist in that particle coalescence can occur and any catalyst particles that were unable to adhere to the reactor walls are swept out of the reactor with the unused reactants and carrier gasses.

The fixed bed process, alternatively, utilizes a solid phase catalyst which is placed in boats within the (usually horizontal) reactor after which the gas phase reactant is introduced. The disadvantage of this method is that as more nanotubes are grown, the more of the surface will be covered limiting the diffusion of the carbon source gas to the catalyst particles. A more recent process that is being used is that of the fluidized bed CVD (FBCVD) process whereby larger catalyst particles are suspended above a support by an upward flow of gas in a vertical reactor. This gives the added advantages of excellent heat and mass transfer due to the fluidized bed as well as the catalyst particles being large enough so as to not be swept away with the carrier gas product stream (Danafar et al, 2009). Vahlas et al (2006) also states that the FBCVD process is more efficient for synthesis of large quantities of CNTs.

## **2.3 Applications of carbon nanotubes**

CNTs are the strongest and stiffest materials yet discovered on Earth, in terms of tensile strength and elastic modulus respectively (Foley, 2006). Experimental and theoretical results have shown an elastic modulus of greater than 1 TPa (that of diamond is 1.2 TPa) and have reported strengths 10-100 times higher than the strongest steel at a fraction of the weight (Thoteson, 2001). Table 1.1 below presents some of the Mechanical properties of carbon nanotubes, where the definition of Young's modulus involves the second derivative of the energy with respect to the applied stress/strain. These cylindrical carbon molecules have novel properties that make them potentially useful in many applications in nanotechnology, electronics, optics and other fields of

materials science, as well as potential uses in architectural fields. They exhibit extraordinary strength and unique electrical properties, and are efficient conductors of heat.

**Table 1.1:** Mechanical properties of carbon nanotubes (Yamabe, 1995)

| Material             | Young's modulus (GPa) | Tensile strength (GPa) | Density (g/cm <sup>3</sup> ) |
|----------------------|-----------------------|------------------------|------------------------------|
| Single wall nanotube | 1054                  | 150                    |                              |
| Multi wall nanotube  | 1200                  | 150                    | 2.6                          |
| Steel                | 208                   | 0.4                    | 7.8                          |
| Epoxy                | 3.5                   | 0.005                  | 1.25                         |
| Wood                 | 16                    | 0.008                  | 0.6                          |

Because of their extraordinary attributes, the application of carbon nanotubes in industry is of tremendous potential. Kobayashi et al. (2004) stated: “Carbon nanotubes are self-assembled nanometerscale wires with excellent mechanical, electrical and chemical properties, which are ideal for the wiring material used in nanotechnology.” Some important and interesting applications of nanotubes (Dresselhaus, 2000; Wilson, 2002; Harris, 1999; Foley, 2006; Ando et al., 2004; Paradise et al., 2007) are shown below, although with their amazing electronic and mechanical properties, the field of applications is almost endless:

- Development of electron field emitters for vacuum microelectric devices.
- Individual MWCNTs and SWCNTs can function as nanoprobe for an Atomic Force Microscope (AFM) tip as well as for meteorology and biomedical and chemical investigations.
- MWCNTs as efficient supports in heterogeneous catalysis and as microelectrodes in electrochemical reactions.
- SWCNTs as good media for lithium and hydrogen storage.

- Prototype electron emission devices based on carbon nanotubes including: cathode-ray lighting elements, flat panel display, gas-discharge tubes in telecom networks.
- Energy storage for use in fuel cells, batteries and other electrochemical applications.
- CNTs can be filled with metallic and ceramic materials and act as templates to create nanowires of various compositions and structures.
- Chemical sensors
- Nanotweezers
- Reinforcements in high performance composites
- Catalyst support

## CHAPTER 3 - Experimental Procedure

### *3.1 Materials & Equipment*

Of the methods to produce carbon nanotubes, chemical vapour deposition (CVD) is the most capable of large scale and high efficiency due to its simpler setup and lower operating temperature (Kwok, 2010). This method is also the most easily adapted to a fully continuous process. Although the general CVD process usually makes use of a gaseous carbon source along with the solid metal catalyst, this modification to a continuous process will make use of a liquid carbon source as seen in the work of Kuwana et al. (2005). While their work utilized a semi-batch process of first coating the reactor walls with catalyst, this work shall instead introduce the catalyst particles to the reactor by dissolving them in the liquid carbon source so as to provide a fully continuous feed.

For the experiments, Xylene shall be used as the carbon source, organometallic ferrocene as the catalyst, and Argon gas as the inert carrier gas. Figure 3.1 presents the proposed equipment set-up for the process.

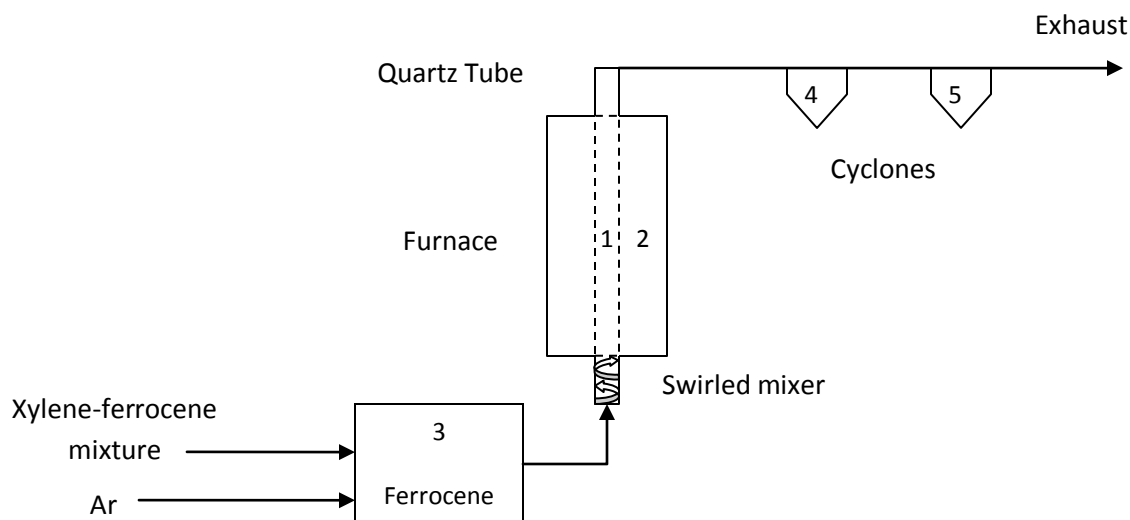


**Figure 3.1:** Equipment configuration for Swirled Fluid Chemical Vapour Deposition (SFCVD) reactor.

Figure 3.1 has previously been described elsewhere (Iyuke, 2008; Iyuke, 2007) but basically consists of a vertical quartz reactor (1) loaded in a tubular furnace (2) operated between 600 – 1000°C. A system of valves and rotameters serve to guide flow of carrier gases (in this case argon, Ar) into the vaporizer (3) after which the gas guides the vaporized catalyst and carbon source through a swirled coiled mixer and into the reactor. After the reactor, the carrier gas guides the newly formed carbon nanoparticles (nanoballs, nanofibres, CNTs, etc) as well as any unreacted feeds from the reactor to be collected in the two cyclones (4,5).

A mantle shall be used to heat the vaporizer above 250°C – ferrocene has a boiling point of 249°C and, depending on the isomer used, xylene has a boiling point of 138.4 - 144.5°C (Lide, 2005). A temperature controller and thermocouple shall be used to regulate the temperature of the furnace. For the initial experiments, a known volume of controlled xylene-ferrocene solution shall be injected into the vaporizer prior to the start of the experiment. Once optimum conditions have been ascertained, then

measures can be taken to improve results and ascertain the feasibility of a continuous process.

### *3.2 Data gathering*

Two cyclones are present after the reactor. Due to the greater density of the carbon compounds relative to that of the carrier gas, Ar, these cyclones result in the separation and collection of the nanoparticles from the gas and provide an easy method for collection. In order to measure the success of the continuous process, these samples will also be compared to samples taken from the reactor walls after the completion of the experiment. This will give a good indication of the feasibility of the continuous process by showing if the product sample is representative of what is formed within the reactor or whether the larger structures are unable to be lifted from the reactor. Further data will also be collected from the analysis of the nanoparticles.

### *3.3 Synthesis and characterization of CNTs*

Before beginning the experimental runs, sufficient care shall be undertaken to ensure that the reactor and vaporizer have both reached the desired temperatures. Once this has occurred, the inert carrier gas, Ar, shall be fed through the reactor for a period of 15 minutes to ensure that all other gases have been flushed from the reactor before the experiment begins. Once this has been completed, the premixed carbon source-catalyst mixture shall be fed slowly into the vaporizer at a rate of approximately 1 ml / minute. This is to allow sufficient time for the solution to be vaporized before entering the reactor. The solution shall be continuously fed into the reactor system for the duration of the experiment, lasting for approximately one hour to establish whether the experiment can continue without the occurrence of blockages or problems in a

continuous fashion. Once the experiment has concluded, the reactor column will be allowed to cool, after which it shall be disassembled and cleaned to prevent interference with consecutive experiments. Each experiment will be repeated once and the results compared to confirm validity and reproducibility.

Upon the completion of experiments, the resulting carbon composites shall be collected from the cyclones and central analysis shall be performed by means of a transmission electron microscope (TEM). By analysing the resulting data, it can be determined what carbon compound structure was formed, namely if carbon nanoballs, nanofibres, helical nanotubes, multi-walled carbon nanotubes or single-walled nanotubes were produced; i.e. the selectivity of the experiment. Depending on the quality of nanotubes produced, other means of analysis will also be utilized such as Raman Spectroscopy. In terms of the continuous production; samples at different times would also give a measure of consistency, i.e. if single-walled CNTs are being produced continuously or only at the start of the process.

## CHAPTER 4 - Results and Discussions

### *4.1 Use of an Argon carrier gas*

#### *4.1.1 Initial experiments with an Argon carrier gas*

Before looking into a fully continuous process, it first needed to be ascertained whether nanotubes could be synthesized using the chosen ferrocene-xylene feed mixture, and secondly, which conditions provided the best synthesis of nanotubes. Initial experiments were performed using a small ratio of ferrocene to xylene (2g per 50ml). Since it was evident fairly soon that this resulted in copious amounts of unreacted feed passing through the reactor at a wide range of temperatures, it was decided that the optimum solubility ratio of catalyst to carbon source be used. Kunadian et al. (2009) found this to be 6.5 mol%, which, by simple calculation, gives 5.271g ferrocene to every 50ml of xylene. For simplicity of measurement and to ensure that all the ferrocene used will dissolve, 5.0g was used giving an acceptable 5% below maximum solution. It was also seen early on that due to the diameter of the reactor column, 6cm, and for effective application of the hydrocyclones, a fairly large carrier gas flow-rate was required. For this reason the maximum flow-rate of gas through the rotameters was used (in the case of Argon this was 650ml/min).

Since it is known that carbon nanotubes have been synthesized in the temperature range from 600°C to over 1000°C (Danafar et al., 2009; Ho et al., 2001; Jung et al., 2001), experimental runs were performed from 600°C upwards in 50°C intervals. At the lower temperatures (700°C and below), no noticeable product was produced and unreacted feed material was observed dripping out the first hydrocyclone. As the temperature was increased, it was evident that as less liquid feed passed through the reactor, smoke was being produced, first orange in colour due to the ferrocene and later darkening to black as 800°C was approached. As it is known that smoke is a solid-gas suspension, this

implies that more of the feed is reacting as the temperature increases. As ferrocene is orange in colour, the orange smoke suggests the presence of unreacted feed in the product but as the temperature increases, more of the feed is broken down into carbon and carbon products giving the smoke the desired black colour.

#### *4.1.2 Use of Argon at the temperatures 800°C and 850°C*

As temperature was increased further to 800 and 850°C, it was observed that although feed material no longer dripped out of the reactor, the produced black smoke was not completely dry of xylene as it immediately collected and adhered to the bottom of the sample container. It was also observed that at both temperatures the product dried with a faintly orange tinge suggesting that not all of the feed material had fully reacted and had taken some of the unreacted material with it. Figures 4.1 (a) and (b) show that while these temperatures are sufficient for the feed material to react and for some small quantities of tubular nanostructures to be produced, the resulting product contains no traces of nanotubes. It is known from the size of the structures found within the reactor that although it is possible that they are large MWCNTs, it is more likely nanofibres that have been produced. Hoenlein et al. (2003) describes nanotubes as having a diameter of 100nm or less so by their description they are not nanotubes at all although the generally accepted range is up to around 200nm.

From these early experiments, it can already be seen that with the chosen feed materials, higher temperatures are favoured. Although no tubular structures are present in the reactor product, visible inspection of the exhaust gases and the presence of tubes within the reactor give indication that further increase in temperature will give an improvement of these results.

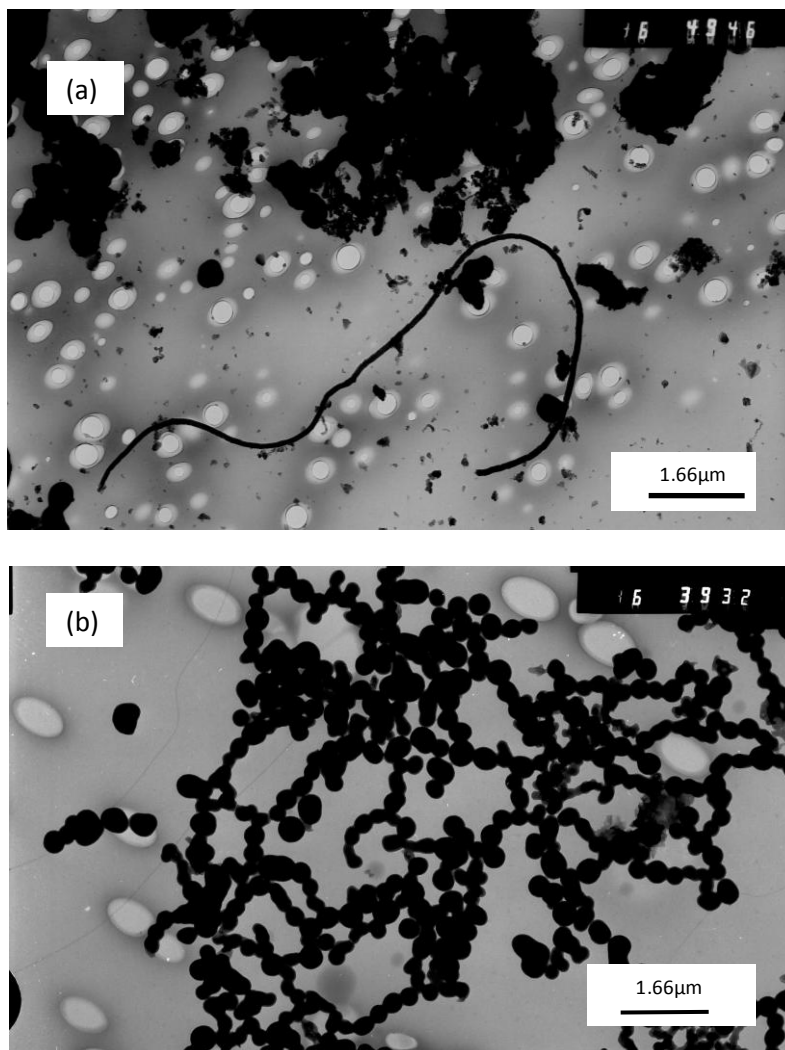


**Figure 4.1:** Transmission Electron Microscope (TEM) images for the experiment performed at 850°C showing that (a) nanotubes are present inside the reactor, while (b) only nanoballs are present in the product, (b).

#### *4.1.3 Use of Argon at the temperature of 900°C*

While performing the experiments at 900°C, it was observed that the smoke that was produced appeared to be much lighter than that produced at lower temperatures as well as the collected product having lost the orange tinge seen in previous experiments

from unreacted ferrocene. Analysis of the samples, seen in Figure 3.2, shows the increase in carbon nanotubes observed in the sample from the reactor while nanoballs were collected from the hydrocyclones. It should also be kept in mind that although more nanotubes were present within the reactor, they were still greatly outnumbered by the presence of nanoballs.

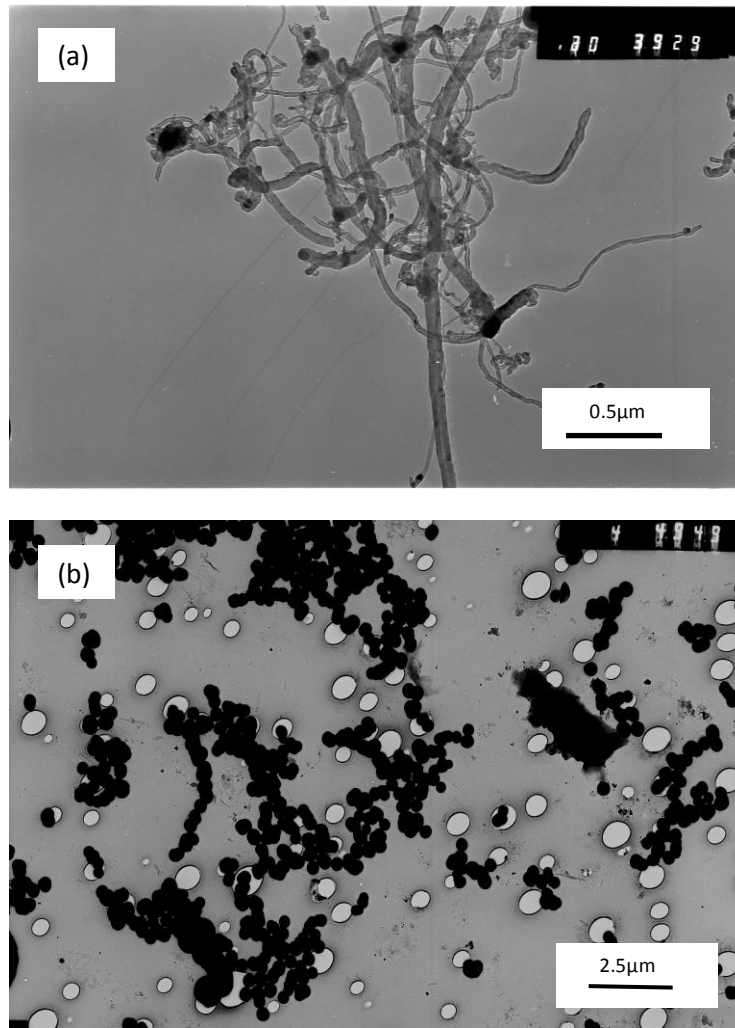


**Figure 4.2:** Samples taken at a temperature of 900°C, showed (a) the existence of nanotubes within the reactor, (b) but only nanoballs in the hydrocyclone product.

#### 4.1.4 Use of Argon at the temperature of 950°C

As shown in Figures 4.3 (a) - (d) at the temperature of 950°C, improved products were observed. Images (a) and (b) illustrate the presence of nanofibres and small numbers of large nanotubes, seen in (a), and the more predominant nanoballs within the reactor. The other two images, namely (c) and (d), show the contents of the product. Although (d) is more representative of the overall product with predominantly nanoballs, image (c) shows that the presence of the occasional rare long nanotube is evident illustrating an immediate improvement on previous experiments.

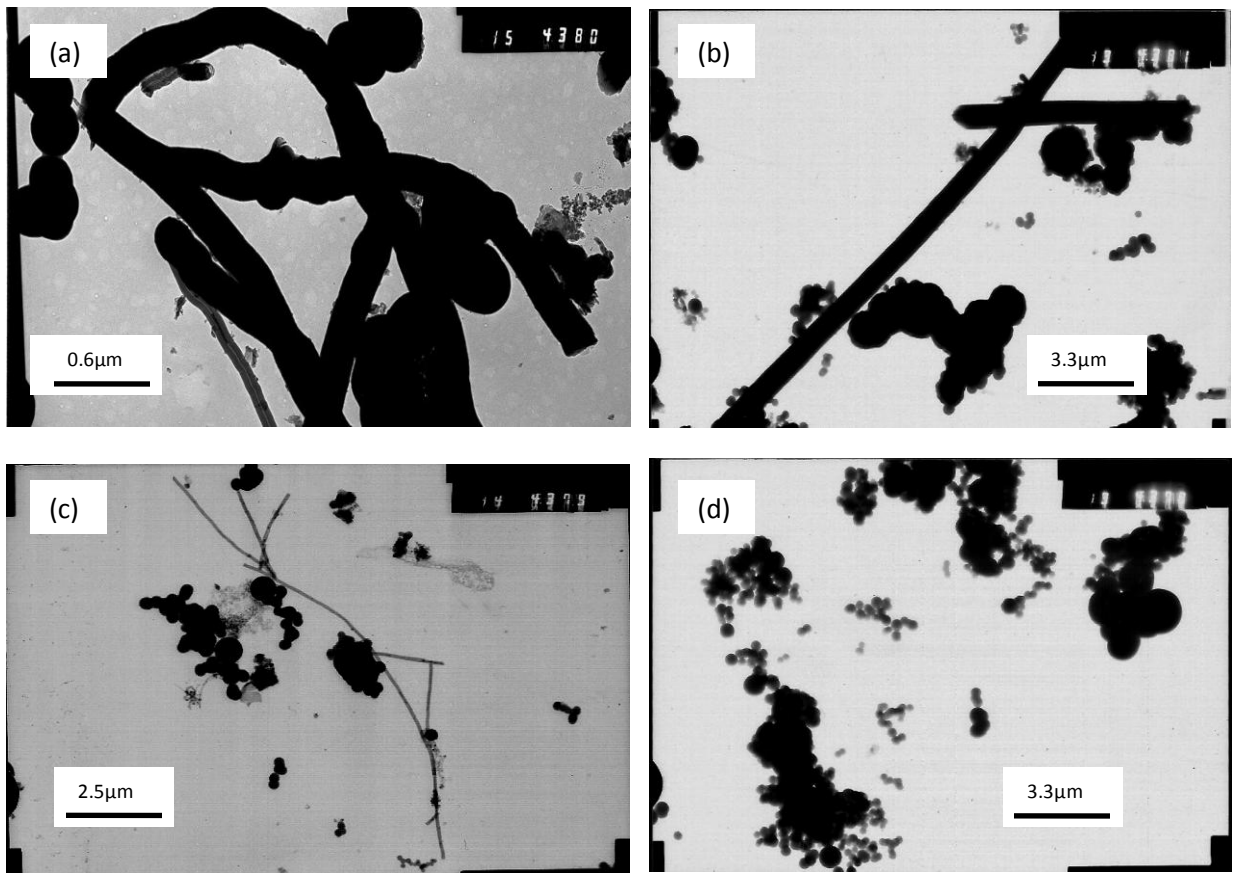


**Figure 4.3:** TEM images of samples taken from (a & b) within the reactor, and (c & d) from the hydrocyclones for the experiments performed at 950°C

#### 4.1.5 Use of Argon at the temperature of 1000°C

At a temperature of 1000°C, the presence of carbon nanotubes in the product has ceased, as shown by Figure 4.4 (b). Samples taken from deposits taken from within the reactor still show the existence of nanotubes within the reactor however, they were found to be shorter in size than previous experiments, as shown in Figure 4.4 (a).

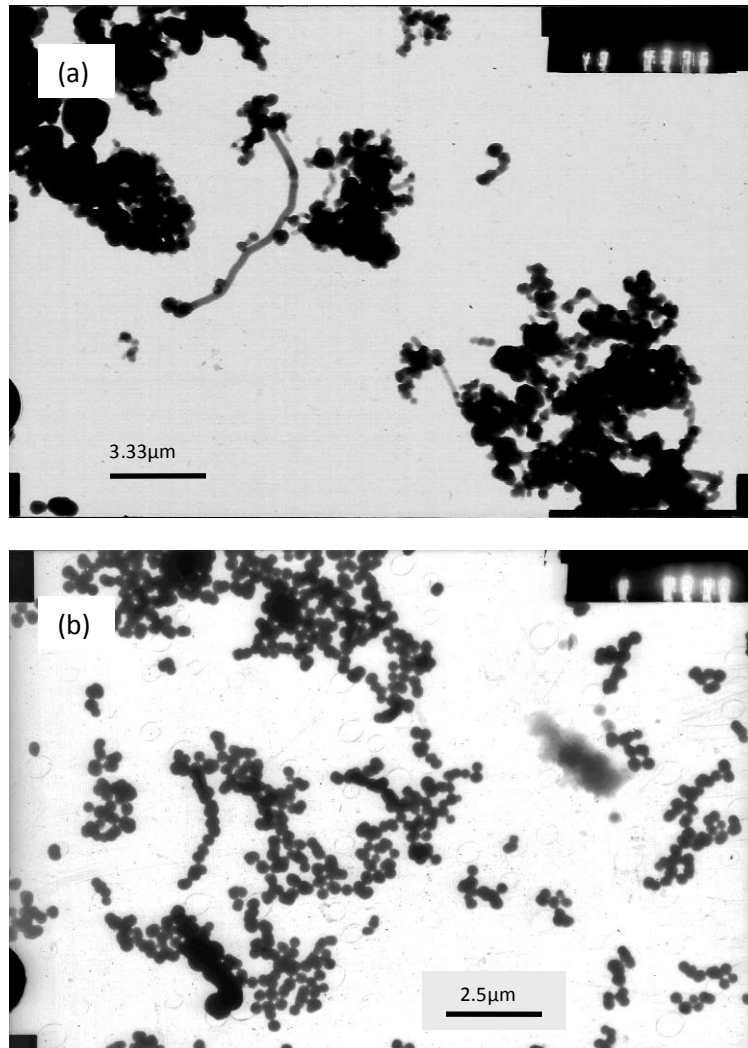


**Figure 4.4:** TEM images for the experiment performed at a temperature of 1000°C. (a) shows the presence of CNTs within the reactor, while (b) confirms only the presence of nanoballs within the product obtained from the hydrocyclones.

#### *4.1.6 Pure Argon as a carrier gas*

From the previous sections, certain aspects concerning the chosen feed stocks are evident. As seen by initial experiments, temperatures 850°C - 950° seemed to give the most favourable results. While 900° seemed to produce more tubes within the reactor, only 950° seemed to give any hope of tubes making it into the product of the cyclones. Raman spectroscopy was also performed on these two samples however it was quickly learned that due to the huge composition of nanoballs and unidentifiable material in the samples in comparison with the nanotubes, it was very unlikely that Raman spectroscopy would provide a means of differentiating single-walled nanotubes unless their concentration increased dramatically. As for results seen at 1000°C, they seem to support the theory that at temperatures around 1000°C pyrolysis of the CNTs themselves begins to occur, as stated and referenced by Danafar et al. (2009), giving a reduction in the carbon nanotubes seen.

#### *4.2 Addition of Acetylene gas*

It has been well documented that carbon nanotubes have been synthesized using acetylene as a carbon source and ferrocene as the metal catalyst in a chemical vapour deposition reactor (Iyuke et al., 2007, Kim et al., 2005). But thus far, no cases of the use of both acetylene and xylene have been found. For this reason, there was some interest on the effect of the addition of acetylene with the argon carrier gas. Experiments were performed at the three most promising temperatures thus far, namely 900, 950 and 1000°C. What was observed at all three temperatures was, instead of the desired thick black smoke that could be settled and analyzed, a lighter grey wispy smoke was produced that, even with excessive time given to settle, remained in a gaseous suspension that would require a Gas Chromatograph (GC) or other gas analyzing systems to identify. Since this work is investigating the best means to synthesize carbon

nanotubes, and it was evident that other reactions were occurring from which other compounds were being produced to give the unwanted grey smoke produced, this production method was soon abandoned and a new process was sought.

### *4.3 Addition of Hydrogen gas*

#### *4.3.1 Initial Experiments*

Since numerous authors (Danafar et al., 2009; Yu et al., 2005) have reported that Hydrogen gas has aided in improving the quality of carbon nanotubes produced, it was thus investigated whether it would bring about the same effect when using the chosen materials and conditions. Consequently, 10% of the Argon feed carrier gas was replaced with H<sub>2</sub> gas and experiments were repeated at the two most promising temperatures, namely 900 and 950°C. Due to the lower density of Hydrogen, this allowed for a slightly higher gas flow rate to be passed through the reactor; approximately 1000 ml/min. To ensure that this was not a too narrow field of focus, an effort to produce CNTs at 850°C was also attempted with little success. As seen in previous experiments, unreacted material was observed passing through the exhaust of the hydrocyclones and little analyzable sample was produced. As for the temperature of 1000°C, it was evident from the results that follow that as the best results are found using a temperature of 900°C, and as the temperature is increased to 950°C the quality of the product was seen to decrease. There was little expectation of improved results found at 1000°C. As stated by Danafar et al. (2009): “not only pyrolysis of carbon sources is generally promoted around 1000°C, but also pyrolysis of the CNTs will begin” meaning that even if more nanotubes are formed, some of the CNTs present in the reactor will decompose and react into other carbon products giving a reduction in quality of product regardless.

#### *4.3.2 Use of Hydrogen and Argon at 900°C*

After the addition of H<sub>2</sub> gas to the Argon gas feed, it was noticed that experimental runs produced visibly better results, i.e. thicker and more smoke was produced. The liquid feed was supplied to the system at gradual rate of approximately 2ml/min to allow it to vaporize easily in the vaporizer. An analysis of the sample collected from the walls of the reactor column is presented in Figure 4.5. What was observed is a large increase in the observable nanotubes in comparison with previous experiments. While large quantities of carbon nanoballs are still present, a definite improvement is still evident in the fact that the nanotubes found are far smaller in diameter and larger in number than seen in previous experiments, immediately justifying the use of Hydrogen gas. By observation, there is even the presence of nanotubes with a diameter below 50nm.

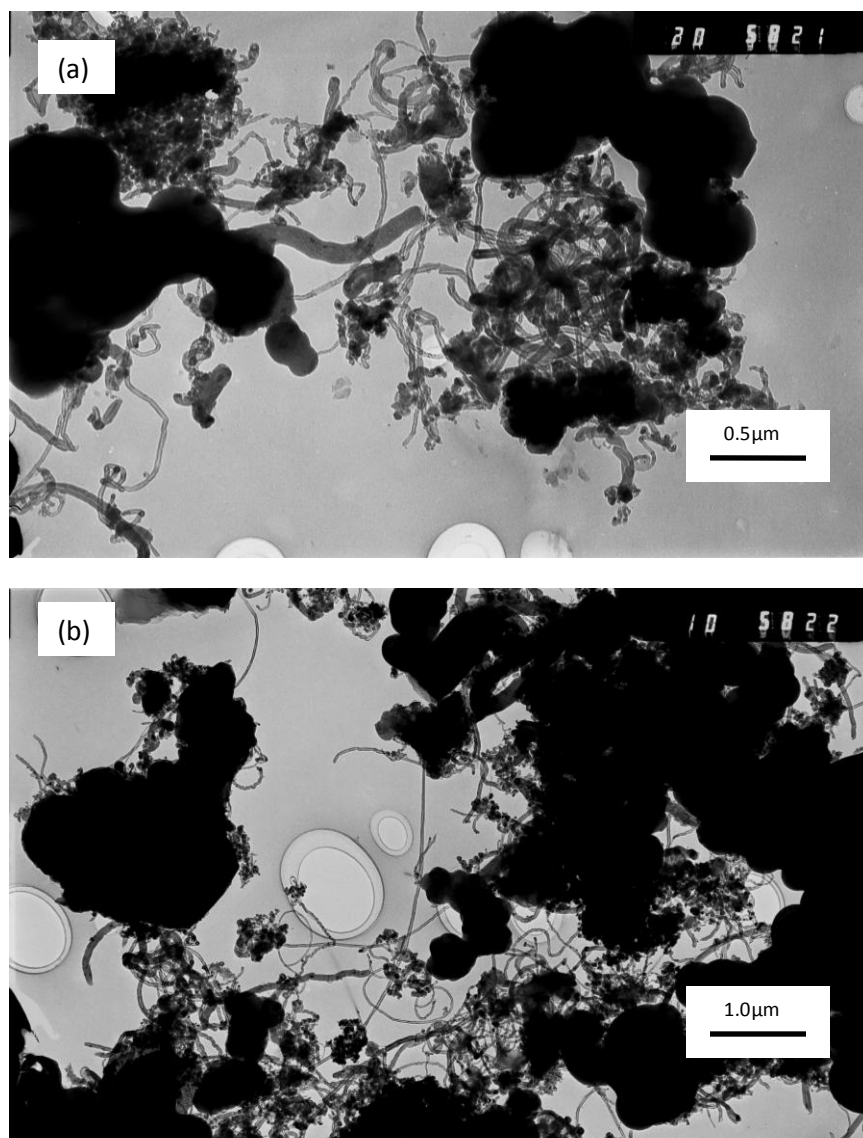


**Figure 4.5:** Transmission Electron Microscope images illustrating the vastly increased numbers of large and small carbon nanotubes found within the reactor.

As Hydrogen gas was used in the hope that more nanotubes would be produced and of smaller diameter in order to get single-walled tubes, the contents of the product was most eagerly anticipated. Figure 4.6 shows the TEM analysis of the collected sample where an unusual phenomenon is observed. In addition to the rare occurrence of nanotubes in the product, for the first time helical nanostructures are also visible. When observing across the sample, it was also noticed that almost all the straight carbon nanotubes found seem to be attached in some way or another to a section of helical nanotubes of approximately equal diameter.

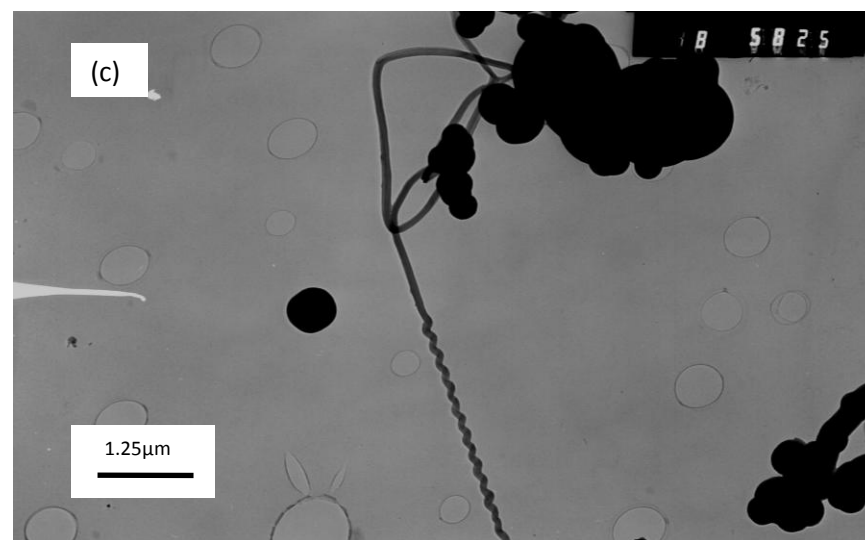
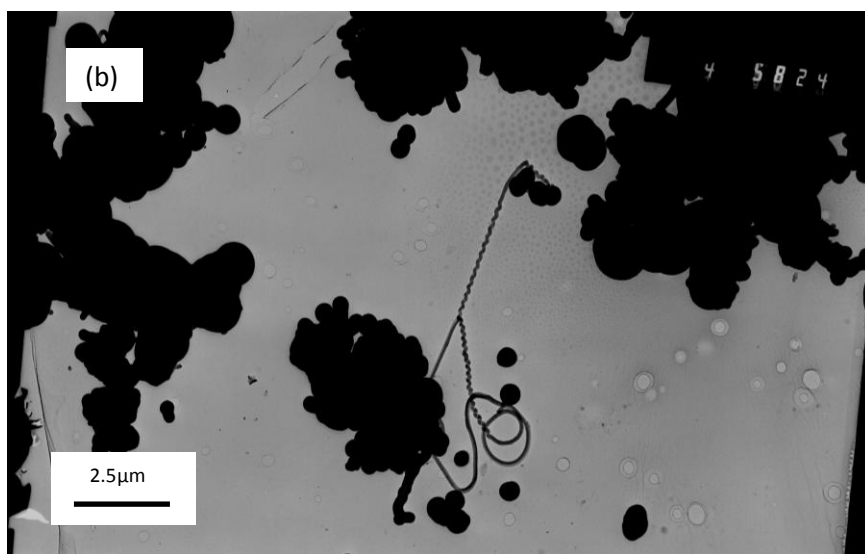
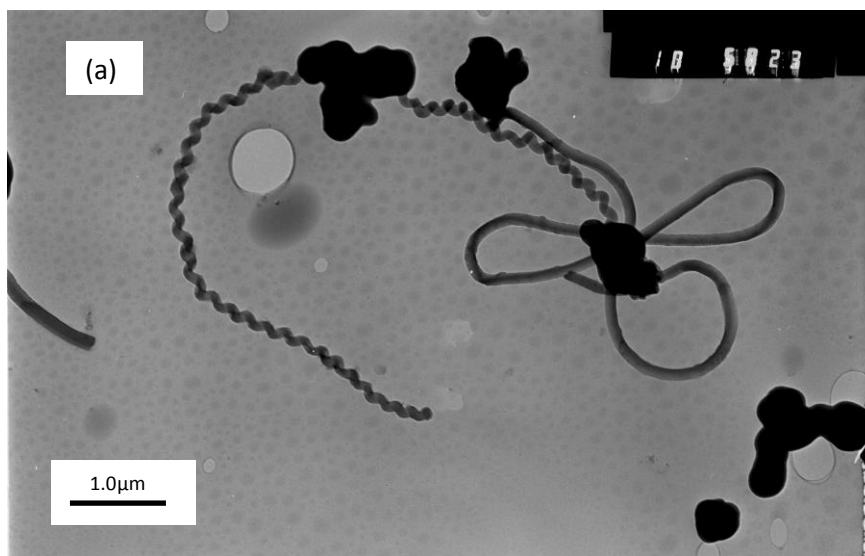


**Figure 4.6:** Three TEM images showing the presence of helical nanotubes grown from SWCNTs at 900°C.

#### *4.3.3 Use of Hydrogen and Argon at 950°C*

The same conditions and procedure was followed using a reactor temperature of 950°C with similar high expectations. Initially, results looked very promising. While previous experimental products all possessed a slightly sticky quality that required some of the settled product to be scraped from the collecting flasks and never allowed for an accurate quantitative measurement of product, this experiment produced an extremely dry settled product that allowed for nearly all of the settled product to be collected with ease and measured, giving a measured weight of 0.53g. To give a comparison to the amount of material that collects within the reactor, as much as possible was collected and remarkably more than usual had been formed on the reactor walls in this experiment. The collected sample was weighed to be about 6.08g, in contrast to previous experiments where about 1.5g had formed.

An analysis of the sample collected from the reactor are presented in Figures 4.7, illustrates the vast number of carbon nanotubes formed, similar to those seen when using a temperature of 900°C. What is noticeable, however, is the vast number of different tubes present with varied diameters, especially visible in Figure 4.7 (c).

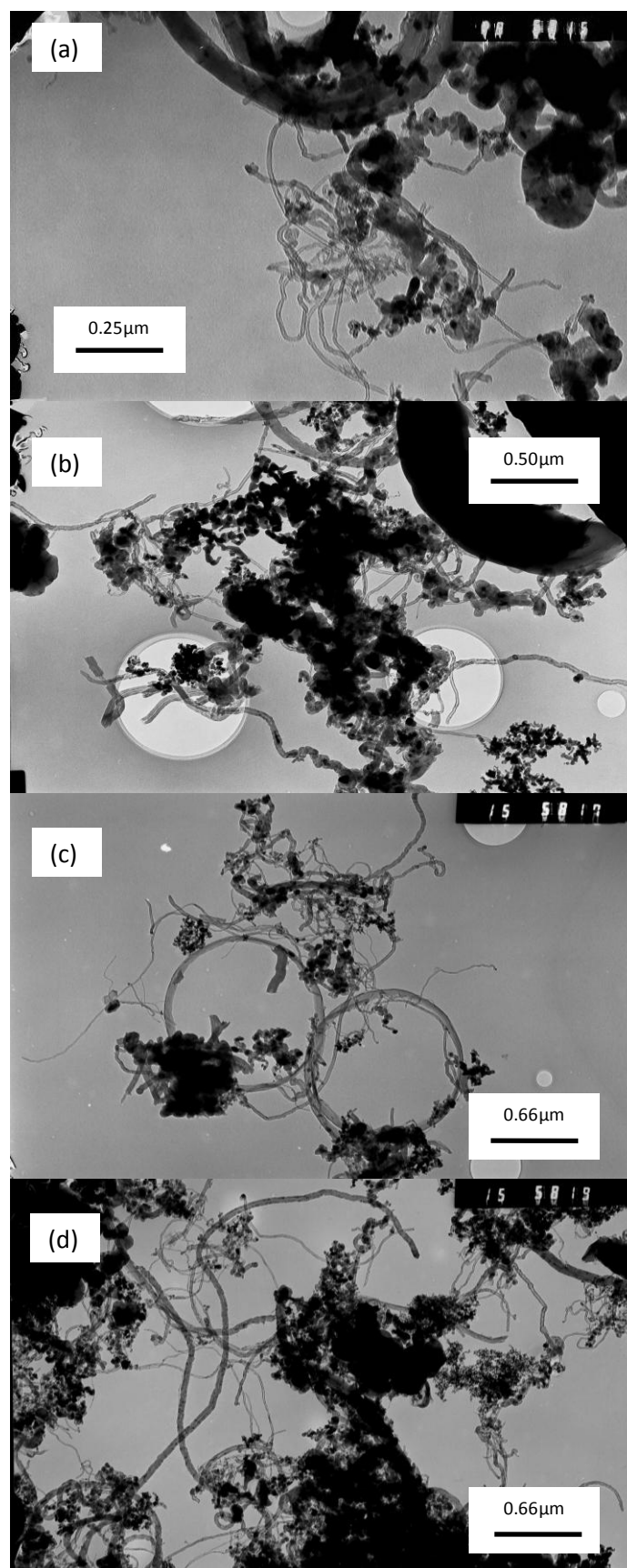


**Figure 4.7:** TEM images of samples for the experiment performed at 950°C using H<sub>2</sub> and Argon gases (a – d).

As these results proved to be very similar to those seen using  $\text{H}_2$  gas at  $900^\circ\text{C}$ , it just had to be seen whether the same success would be found with the presence of tubular structures in the collected sample at the cyclones. Figure 4.8 shows the analysis of the product illustrating that nothing but nanoballs managed to pass through the reactor to the hydrocyclones.

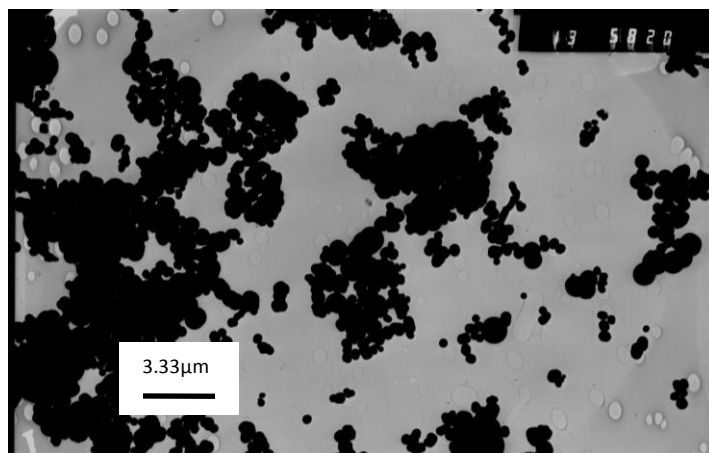


**Figure 4.8:** Analysis of cyclone product for the experiment performed at  $950^\circ\text{C}$  using  $\text{H}_2$  gas

## ***4.4 Discussion of Results***

### ***4.4.1 Analysis of Results***

In order to properly compare the results seen in Figures 4.5 (b) and 3.6 (a) as shown together in Figure 4.9, both these images were taken at the same magnification giving a clear comparison of the results. It is immediately evident that the helical and straight nanotubes found in the product are of a much larger diameter than those found within the reactor. This suggests that the mechanism by which the tubes are transported out of the reactor is one of air friction whereby the larger tubes, as they possess a larger surface per weight, provide a larger surface for friction to act, lifting the tubes from the reactor. This is further theorised in Section 4.4.2. The presence of helical tubes also suggests the existence of SWCNTs

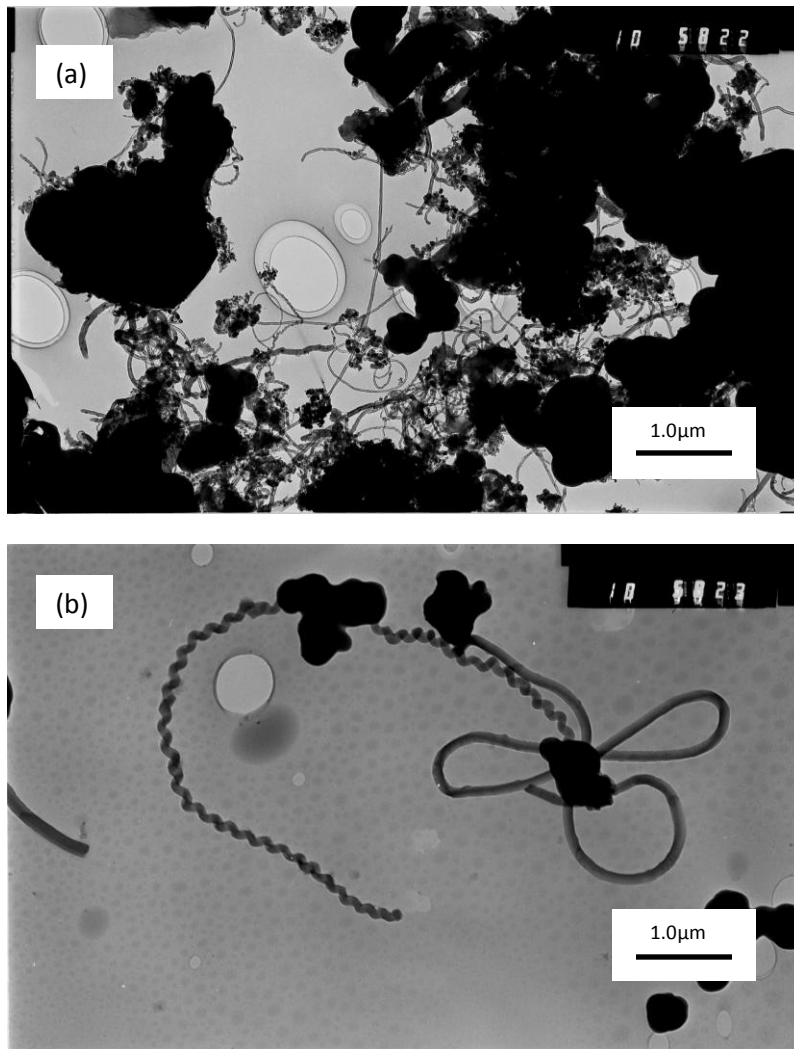


**Figure 4.9:** Comparison of images taken from within the reactor (a) and the product (b) at the same magnification for the temperature of 900°C.

#### 4.4.2 Effect of shape and size on air resistance

##### 4.4.2.1 Analysis of Forces

Since this work makes use of a vertical reactor with carrier gas passing upward through the reactor column in order to carry the product from the reactor to the hydrocyclones where it can be collected, the primary mechanism by which the product is lifted is one

of drag caused by air friction. Figure 4.10 below shows the basic forces acting on an object within the reactor.

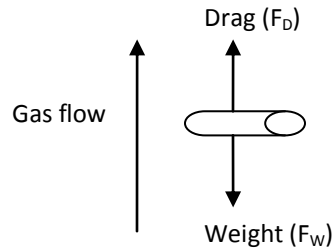


**Figure 4.10:** Simplified force diagram for an object within the reactor.

The weight of the object,  $F_w$ , applies a downward force and is defined as:

$$F_w = mg \quad (4.1)$$

where  $m$  represents the mass of the object and  $g$  represents gravitational acceleration, namely  $9.81\text{m/s}^2$ . The upward moving gas also pushes on the object causing an upward drag force,  $F_D$ , caused by the frictional resistance of the gas passing around the object. For relatively small objects that are roughly spherical in shape, it can be assumed that the drag force is proportional to the velocity giving:

$$F_D = bv \quad (4.2)$$

where  $v$  is the velocity of the falling object relative to the flow of gas, measured in units of m/s and  $b$  is a constant of proportionality called the drag coefficient with units of kg/s. This type of drag force is called viscous drag. For objects that are not spherical in shape, Newton drag needs to be considered (Bisquert, 1991) where instead the drag force is described by:

$$F_D = \frac{1}{2} C_D \rho A v^2 \quad (4.3)$$

Where  $\rho$  = mass density of the fluid/gas in kg/m<sup>3</sup>

$u$  = the velocity of the object relative to the fluid in m/s

$A$  = the reference area in m<sup>2</sup>

$C_D$  = the dimensionless drag coefficient

What these three equations show is that in order for any object to be lifted out the top of the reactor, the force acting on the object due to drag has to exceed the force due to gravity. Therefore, by Equation 4.3, for nanotubes to be easily lifted from the reactor, three main factors can be considered, namely gas density, gas velocity and the object's frontal surface area. For these experiments very little can be changed in terms of gas density as the gases were particularly chosen to be an inert carrier gas, Argon, along with Hydrogen to give the best possible opportunity for nanotube production. As for gas velocity, the reactor is already utilizing maximum gas flow and any modification to increase gas flow will most likely result in the feed passing through the reactor with too little time to react and form products. With these two factors remaining reasonably constant; the remaining factors are the drag coefficient and reference area. The larger either of these factors, the more likely the object is to be lifted by the gas out of the reactor.

The drag coefficient,  $C_D$ , is generally not constant for a given body shape. Streamlined objects such as spheres possess low values for  $C_D$  (well below 1) while unstreamlined objects can have coefficients of 1 and greater (Hoerner, 1965). In general, the drag coefficient is always associated with a particular surface area (McCormick, 1979). Even when considering different orientations of both helical and cylindrical tubes, a helix is far less streamlined than a cylinder in the same orientation. The loops of the helix provide a larger surface area per tube length resulting in a larger drag coefficient than that of a cylindrical tube.

To properly compare the drag forces it is also necessary to look at the orthographically projected reference areas of a cylinder and helix, as seen in Figure 4.11. Since actual elongated tubes in suspension are prone to constantly change orientation as well as being liable to bend, spin or tumble, it is extremely difficult to calculate the reference areas for all possible circumstances. For this reason, the area comparisons investigated include the orientations where the maximum and minimum reference areas occur, namely where the tubes are oriented parallel to the direction of gas flow, giving the smallest area, and where the tubes are oriented perpendicular to the direction of the gas flow.

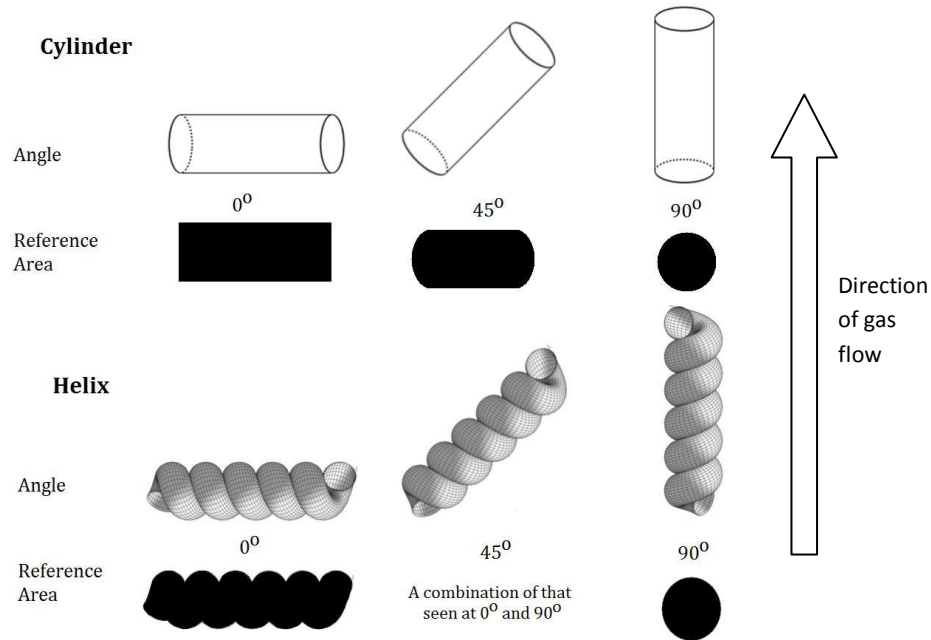


**Figure 4.11:** A comparison of orthographically projected reference areas for helices and cylinders at different orientations relative to flow of gas.

#### 4.4.2.2 Calculation of reference areas

Before mathematically comparing the reference areas of the cylindrical and helical tubes it is necessary to have a clearly defined set of nomenclature:

$A^{par}$  = Reference area for tubes parallel to direction of gas flow

$A^{perp}$  = Reference area for tubes perpendicular to direction of gas flow

$r_t$  = Tube radius

$r_h$  = Helix radius

$L$  = Length of tube

$p$  = Pitch: length of one rotation/coil of the helix

$\theta$  = Angle of rotation in the x-y plane for a helix extending in the z-direction

For a cylindrical tube parallel to the direction of gaseous flow, the orthographically projected area is just a circle of radius  $r_t$ , and thus the area is calculated as:

$$A_{cylinder}^{par} = \pi r_t^2 \quad (4.4)$$

Should the tube be orientated perpendicular to the direction of flow, the resulting reference area is that of an elongated rectangle giving an area of:

$$A_{cylinder}^{perp} = 2r_t L \quad (4.5)$$

For a helical tube, the reference areas are a bit more complicated. In the instance where the tube is aligned with direction of gas flow, the resulting reference area can either take the shape of a circle or of a ring, i.e. a circle with a central smaller circle removed. This is dependent on whether the tube radius is smaller than the helix radius or not. This gives for the helix:

$$A_{helix}^{par} = \pi(r_t + r_h)^2 \quad \text{for } r_t \geq r_h \quad (4.6)$$

$$A_{helix}^{par} = \pi(r_t + r_h)^2 - \pi(r_h - r_t)^2 \quad \text{for } r_t < r_h \quad (4.7)$$
$$= 4\pi r_t r_h$$

The resulting area for a helical tube perpendicular to flow direction gives a far more complex shape. Changes in both  $r_t$  and  $r_h$  can largely affect the given area and as such a more complex mathematical analysis is required. When mathematically analyzing the behaviour of a helix tube, it is necessary to start by observing the behaviour of the helical core. It is known that helices follow certain mathematical parameters (Mancosu, 2010), namely:

$$x = r_h \cos \theta \quad (4.8)$$

$$y = r_h \sin \theta \quad (4.9)$$

$$z = c\theta \quad (4.10)$$

for  $\theta \in [0, 2\pi]$  where  $r_h$  is the radius of the helix and  $c$  is a constant conversion factor giving the vertical separation of the helix's loops, also equal to  $p(2\pi)^{-1}$ . A visual representation of the orientation of the parameters can be seen in Figure 12a below.

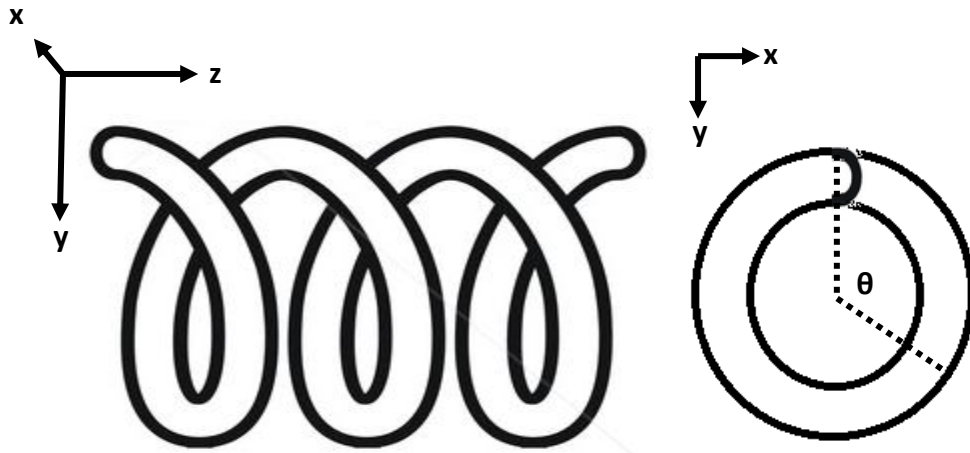


**Figure 12a:** Visual representation of assigned mathematical parameters for calculation.

When finding the reference area, it is necessary to find the area between the top and bottom edges of the resulting shape when plotting either  $x$  or  $y$  against  $z$ . Figure 4.12b below depicts an example of a possible helix possessing a large tube radius compared to helix radius and a fairly wide distance between peaks. This was generated using Excel to plot the developed equations.

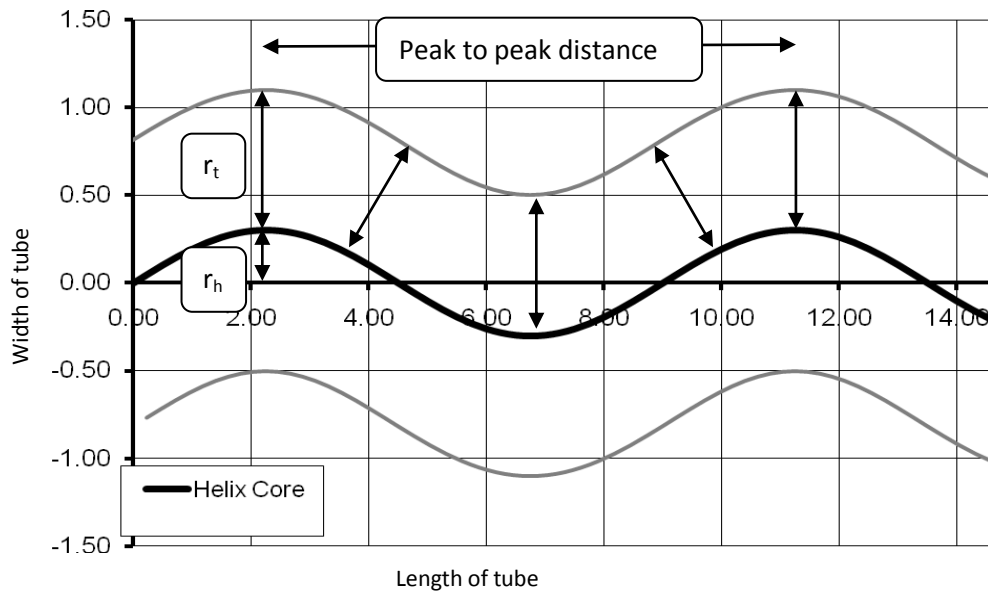


**Figure 4.12b:** Labelled example of a possible helix.

In order to find the area of a complete tube of variable length, the best approach is to find the area between the top and bottom edges of one coil of the represented helical tube and multiply it by the number of coils in the complete length. The number of coils can be easily found from the tube length and length of a single coil. While the core of the represented helix may follow a sine or cosine shape, it is important to remember that the upper and lower edges do not. Being that it is still a tube, the tube itself is one tube radius from the core. Hence, in terms of the represented figure, at all points along the core curve, two points will exist one tube radius away perpendicular to the gradient of the core.

Since it is already known that  $y$  is a function of  $\theta$  [Equation 4.9], the gradient (in radians),  $\psi$ , at any point on the core can be found from the differential:

$$\psi = f(\theta) = \tan^{-1} \frac{dy}{d\theta} = \tan^{-1} \left( \frac{d}{d\theta} r_h \sin \theta \right) = \tan^{-1} (r_h \cos \theta) \quad (4.11)$$

This gives, for any point along the core, a perpendicular angle,  $\psi_p$ , in radians of:

$$\psi_p = \psi + \frac{\pi}{2} = f(\theta) \quad (4.12)$$

It is also known:

$$z = \frac{p\theta}{2\pi} = f(\theta) \quad (4.13)$$

In order to obtain curves for the top and bottom edges, it is possible to plot points one tube radius above and below the core on a plot of  $y$  versus  $z$  using:

$$y_{edges} = y \pm r_t \sin \psi_p \quad (4.14)$$

$$z_{edges} = z \pm r_t \cos \psi_p \quad (4.15)$$

This allows the edges to be described as sets of co-ordinates, the values of which remain dependant on  $\theta$ :

$$Edges = f(\theta) = (z_{edges}(\theta), y_{edges}(\theta)) \quad (4.16)$$

Where:

$$y_{edges} = r_h \sin \theta \pm r_t \sin \left[ \tan^{-1}(r_h \cos \theta) + \frac{\pi}{2} \right]$$

$$z_{edges} = r_h \sin \theta \pm r_t \cos \left[ \tan^{-1}(r_h \cos \theta) + \frac{\pi}{2} \right]$$

Initially it was hoped that since the equations for the co-ordinates are both functions of  $\theta$ , they could be combined into a single equation for the top edge and another single equation for the bottom edge. This would provide a means to determine the reference area of the helix by the difference of the differentials. It was soon determined that while this approach may provide adequate results for simple helix representations such as those seen in Figure 4.12b, it is not suitable for calculating the reference area for more complex helices where the closeness of the the loops results in the presence of a visible overlap. A graphical depiction of this (generated in Excel) can be seen in Figure 4.13.

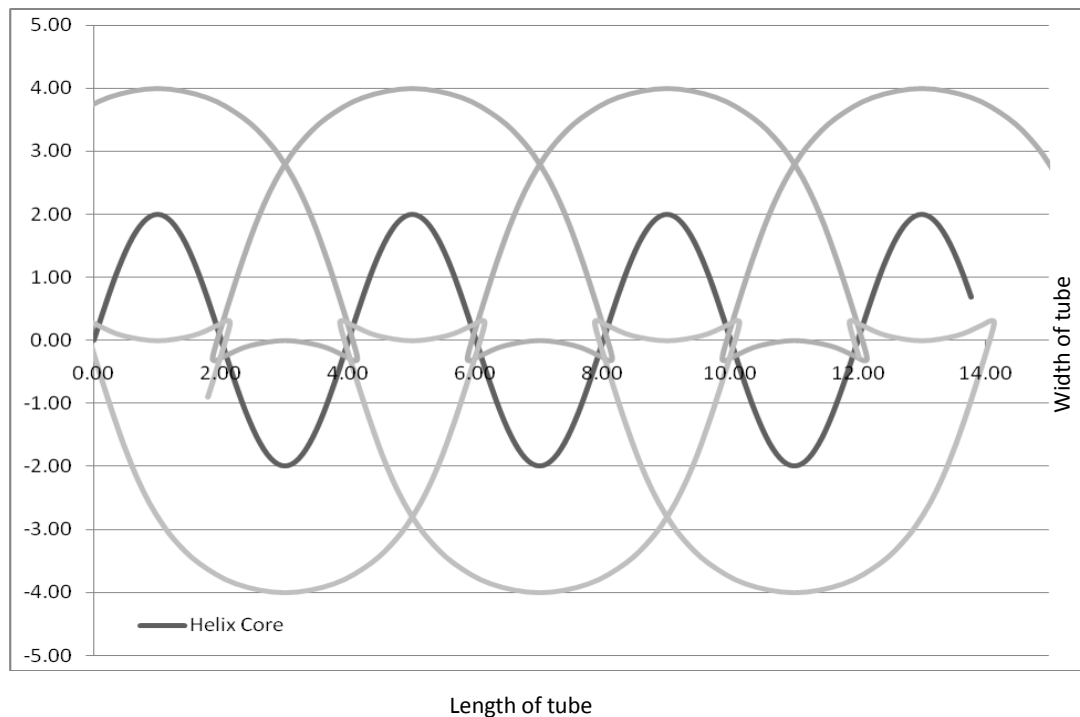


**Figure 4.13:** Graphical representation of a complex reference area resulting from visible overlaps of loops.

Since this resulting overlap results in vast inaccuracies with the traditional methods of integration to find the underlying area, graphical methods are required. As the graphs are created by plotting new points relative to initial points on the core, by increasing the initial number of points it is possible to increase the accuracy by which the edges are plotted. By applying Boolean logic algebra to the resulting points in Excel, it is possible to exclude the points present in the overlap and leave only those in the uppermost edge. This basically means that Excel is utilized to graphically determine which of the points that are calculated to be on the outer edge are physically present on that outer edge and to eliminate all the points which result in the overlap. To simplify calculations, the same principles can be used to leave only the points present for one coil, as depicted in Figure 4.14.

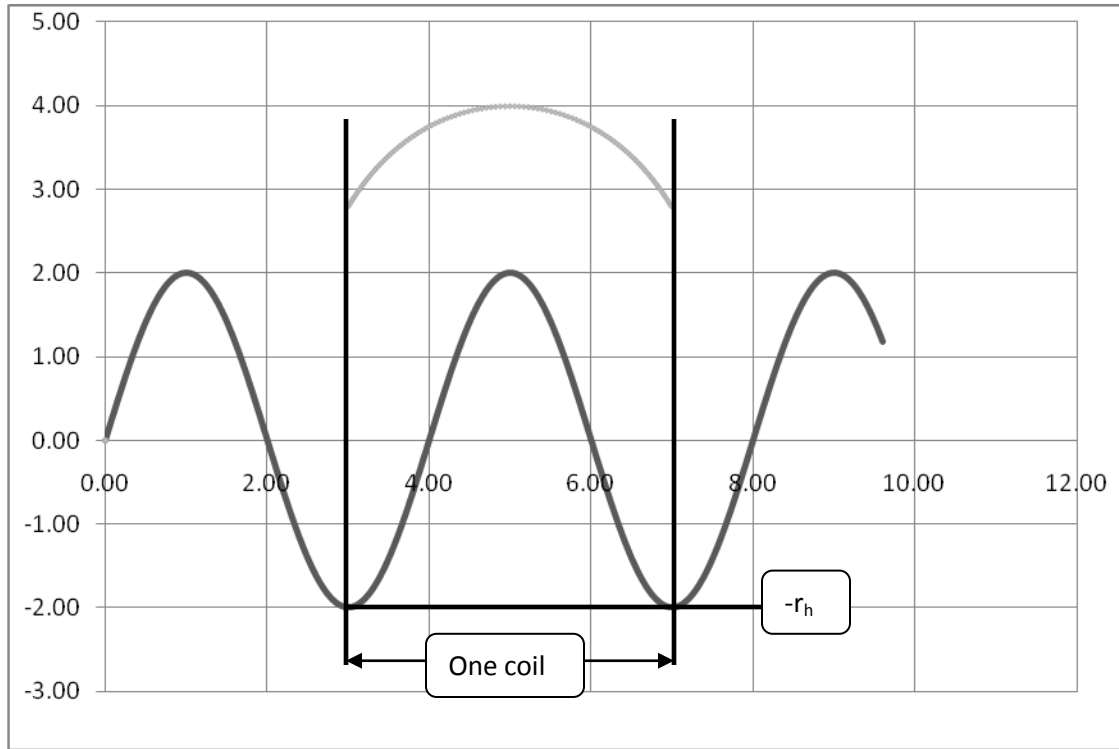


**Figure 4.14:** The application of Boolean algebra to leave a single edge for one coil.

Once the unnecessary points have been eliminated, it is possible to find the area by graphical methods. It is known that the lowest possible point on the graph is negative  $r_h$ . Thus the area can be found from the difference in areas of the top edge and the core to this base. To find the area below the collection of points, summation of a number of vertical bars provided by consecutive points can be performed. In mathematical terms, this is given by, for  $k$  points:

$$Area = \sum_i^{k-1} \left( \frac{Y_i + Y_{i+1}}{2} - (-r_h) \right) (Z_{i+1} - Z_i) \quad (4.17)$$

where  $(Y_i, Z_i)$  represents the Cartesian co-ordinates for each point,  $i$ , on the graph.

Once the area below the core has been subtracted from the area beneath the top edge, it can be doubled to provide the reference area per coil. This can be done due to the rotational symmetry of the helix, a consequence of which, for each coil, the area below the core line shall be equal to the area above. While this method may not provide the accuracy that differentiation could, were it possible, it is clear that as the number of defined point's increases, the accuracy of the result nears that of differentiation. As such, by using a high number of points it is possible, with reasonably high accuracy, to calculate the reference area for any given helix.

#### *4.4.3 Growth mechanism of Single Walled CNTs to Helical CNTs*

While Section 4.4.2 shows how the helical shape can contribute to the upward force offered by the extra drag, it does not provide an explanation for the presence of helical nanotubes in the first place. To quote Sharma et al. (2009): "The non-straight, spiral shape twisted filaments or tubes are generated from asymmetrical shaped catalyst particle. Due to this asymmetry of catalyst the carbon atoms traverse across different diffusion path lengths relative to the symmetry axis." What this basically means is that as certain carbon molecules may take a longer time to diffuse into the catalyst particle on one side of the catalyst than the other, the nanotube begins to form faster on one side giving rise to the twisted helical shape. As Li et al. (2010) described: "The difference in diffusion through surface and bulk of a catalyst particle results in the difference of precipitation rates among the precipitation facets".

It is believed that multiple possible means whereby the catalyst particle can change shape are possible. One of these methods is a result of catalyst particles deforming due to local poisoning of certain areas of the particle (Amelinckx et al., 1994). This results in differences in catalytic activity over the particle with reaction time, consequently resulting in carbon nanotubes with various shapes such as a helix. This implies that the

catalyst particles within the reactor can change in shape when exposed to enough heat. This heat provides the necessary energy required to overcome the high elastic energy inherent in the catalyst, and allows for deformation to occur. As this deformation is random, it is not guaranteed that the resulting shape will give rise to the formation of helical nanotubes which explains the small concentration of helical nanotubes present in the samples. Another possible explanation for the change in catalyst particle shape is the possible presence of weak points on certain catalyst particles. With the flow of gas particles as well as the unreacted material and particles being lifted by the gas, it is a reasonable assumption that the exposed catalyst particle at the end of a growing nanotube could experience an impact from flowing material which could cause the particle to break at any weak points present. It is also possible that while carbon precipitates out of the catalyst particle, any smaller pieces of the catalyst could break off the larger catalyst particle while the nanotube grows. Figure 4.15 illustrates the change in growth of the nanotube after part of the catalyst particle has broken away. Any of these explanations give an explanation for the existence of straight tubes becoming helical tubes without the observation of a catalyst particle at the junction. It also accounts for the small concentration of helical tubes seen as only certain shapes provide the correct surfaces for helical nanotubes to form.

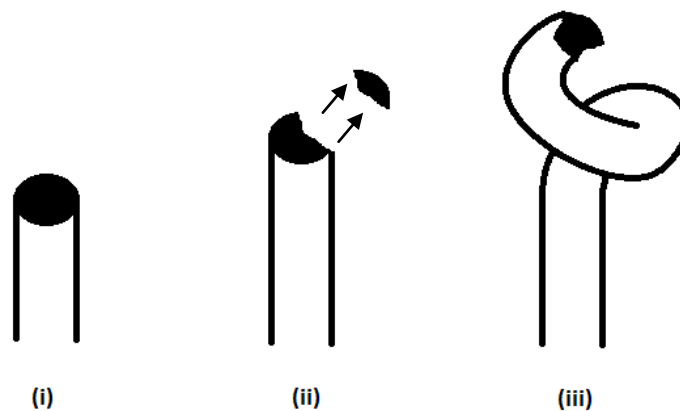


**Figure 4.15:** Change in tube growth from cylindrical to helical.

Another aspect to be considered is growth mechanism of the carbon nanotubes within the reactor. If the general assumption of growth is followed, namely, first the metal catalyst adheres to a substrate (in this case the reactor walls) after which carbon diffuses into the catalyst particle and carbon nanotubes begin to form in either a root growth or tip growth manner (as explained in Section 2), then it can also be assumed that the change from straight to helical tubes seen in the results is more likely to occur with tip growth. As the nanotube grows away from the reactor wall, it is exposed to more of the high temperature gas flowing through the reactor which means that catalyst particles would be more exposed to impact from other particles as well as to more carbon particles with which to promote nanotube growth. This means that under the circumstances that the catalyst particle should deform due to temperature, it will still be provided with carbon atoms from which the helical nanotubes can grow. This also allows for the presumption that if a catalyst particle does change shape and form a helical nanotube, the helical nanotube will be more exposed to gas flow and therefore more likely to be lifted from the reactor.

#### 4.4.4 Comparison of helical and straight tubes

In order to properly compare the drag forces acting on different tubes within the reactor, it was necessary to investigate the orthographically projected reference areas provided by these tubes. Since the product contains multiple straight and helical tubes of differing length and radius, a comparison of equal length tubes shall be made in order to ascertain the effect the helix shape has on the reference area. For comparative purposes, dimensionless numbers have been chosen arbitrarily, using different ratios of  $r_h : r_t$  to illustrate the different helical shapes' effect on reference area, as well as the effect of the pitch height (distance between corresponding peaks of the helix coil),  $p$ . A dimensionless length of 100 was used for calculation purposes. Table 4.1 below compares the calculated reference areas for different tube dimension inputs.

**Table 4.1:** Comparison of calculated reference areas for helical and cylindrical tubes for different tube dimensions.

| $(p, r_h, r_t)$  | <i>Orientation</i> | <i>Cylindrical Tube</i> | <i>Helical Tube</i> |
|------------------|--------------------|-------------------------|---------------------|
| <b>(4,2,1)</b>   | Parallel           | 3.14                    | 25.13               |
|                  | Perpendicular      | 200                     | 431.63              |
| <b>(4,1,1)</b>   | Parallel           | 3.14                    | 12.57               |
|                  | Perpendicular      | 200                     | 284.52              |
| <b>(4,0.5,1)</b> | Parallel           | 3.14                    | 7.07                |
|                  | Perpendicular      | 200                     | 225.08              |
| <b>(1,1,1)</b>   | Parallel           | 3.14                    | 12.57               |
|                  | Perpendicular      | 200                     | 379.55              |

What is evident from Table 4.1 above is the fact that, regardless of the structure of the helical tube, the resulting orthographically projected area of a helical tube is always larger than that of a straight tube for both orientations (parallel and perpendicular to the direction of flow), and as such, it can reasonably be assumed that this shall remain the case for other orientations as well. This coupled with the fact that the more streamlined structure of a straight tube shall also result in a lower drag coefficient, explicitly suggest that the helical shape results in a noticeably higher drag force and as such, are far more likely to be lifted from the reactor.

#### 4.4.5 Transport considerations for helical and straight tubes in the reactor

The problem that arises with long tubes is that although they possess a large frontal surface area along the face of their length, it is not true for forces acting parallel to their

length. This only becomes a problem when it is considered that falling objects tend to move and shift according to the flow of gas. For example, if a tube is slightly curved, the drag force will be larger on the end more perpendicular to the flow causing a larger torque than the end slightly more aligned to the path of flow. What this means is that, while sufficient force to lift the tube may be present while the tube is horizontal, when the tube shifts to a vertical alignment it may drop more than it was lifted.

The same cannot be said of the helical nanotubes. Although they too possess a far larger frontal area perpendicular to their length than parallel to it, their shape gives far more drag per length at any angle than a straight tube especially when considering gas flow parallel to the length of the tube. With each twist of the helix a new surface offering resistance is exposed that is not otherwise offering resistance with the straight tube, shown in Figure 4.16. It is assumed that this explains why almost no purely straight nanotubes are seen in the product for the experiment at 900°C with hydrogen. Almost all straight nanotubes seen were attached in some way to a section of helical tubes giving far more drag. This, in turn, provides enough of an upward force to counteract the tubes weight and lift the tubes from the reactor.

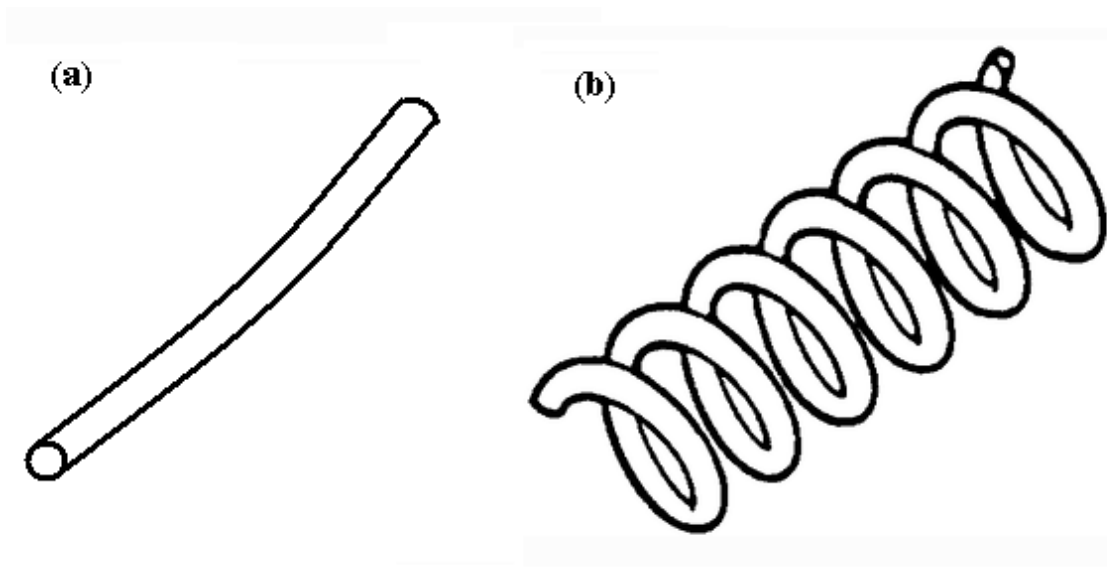


**Figure 4.16:** Comparison of a straight tube to a helical tube.

Another aspect to be considered is whether or not nanotubes behave the same as larger cylinders as gas flows past them since their size compared to the gas molecules is far smaller than that of a macro scale cylinder to any gas flow. Tang et. al. (2006) investigated the drag on a nanotube in uniform liquid argon flow and what they found was that the calculated results for the drag force are different from what one would expect from continuum mechanics. Their work comprised of calculating the drag coefficient from Molecular Dynamics (MD) simulations and comparing it to an empirical equation based on experiments using macro scale cylinders. What was found, surprisingly, was that for a low inlet velocity, the calculated drag from the empirical equation was much smaller than that from MD simulation. At higher flow velocities, the opposite was seen with the simulated drag from MD dropping faster and falling below the empirical result. This was attributed to slippage of the argon atoms on the nanotube at large velocities and confirmed by performing finite element method simulations of flow past a cylinder using continuum approach for the same dimensional similitude. Although this work made use of a liquid Argon flow, it provides a good premise to assume that even with a gas, at higher flow-rates, the drag on a straight carbon nanotubes will be lower than that expected by empirical calculations due to their small size.

Although the actual drag experienced may be lower than calculations predict, this is equally true for all particles at the nanoscale. The same quantum mechanical effects influencing straight CNTs would also affect helical CNTs and other nano particles. While Tang et al.'s (2006) evidence shows that drag experienced in the nanodimensional regime is lower than that calculated from continuum mechanics; their work also suggest that this decreased drag is proportional to the gas velocity present and hence it can be assumed that similarly sized particles of different shapes will still behave similarly in relation to each other when present in the same gas flow. What this inherently means is that when comparing straight and helical tubes, the defining difference is still a result of frontal surface area, and although the actual drag experienced by the particles may be

less than that calculated, the drag force can still be used as a possible explanation for the increased concentration of helical nanotubes in the hydrocyclone product.

Possibly one of the most important things to consider when investigating the effect of the helical shape is that of grouping. Coalescence is far more likely with irregular shapes and helical nanotubes provide far more points whereby other tubes can get hooked or stuck than their straight counterparts. Add to this the increased interaction of particles within the reactor due to the swirling action provided by the reactor's design. The resulting clump or cluster of nanotubes would possess a far higher area by which the flowing gas could provide drag by which it would be far more easily lifted from the reactor. This would also help explain the lack of helical nanotubes present within samples taken from reactor walls after the completion of experiments.

Consideration can also be given to the technical dimensions of the reactor and the connecting tubes. Since the tubes connecting the reactor to the hydro-cyclones are approximately half the diameter of the reactor column itself, the gas velocity will increase four-fold once the tube is reached meaning that, should the proposed drag theory be true, all nanotubes produced that are lifted up to near the top of the reactor are more likely to be collected in the hydro-cyclones as the drag provided by the increased velocity would more easily lift them from the reactor.

## CHAPTER 5 - Conclusions and Recommendations

### 5.1 Conclusions

The continuous production of single-walled carbon nanotubes is still a fairly new field of research and a feasible method of a completely continuous production is yet to be proven due to their adhesion to the reactor and pipe walls. In order to attempt a continuous process using the swirled-fluid chemical vapour deposition reactor, a means to introduce the solid catalyst to the system continuously needed to be found. A solution was found by first dissolving the ferrocene catalyst in a liquid carbon source, namely xylene. Initial experiments using a pure argon carrier gas soon showed that little chance of success existed for temperatures under 800°C but use of 950°C seemed to give reasonable results and most promising for improvement.

Upon the addition of 10% hydrogen to the gas feed, a great improvement was seen in Transmission Electron Microscope (TEM) images of the product samples and samples taken from within the reactor. Although all samples contained far larger quantities of nanotubes and unidentifiable material; at 950°C a wide variety of carbon nanotubes of varied diameter were seen to be present within the reactor although none were found within the cyclone. At a temperature of 900°C however, tubes of varied diameter were once again found within the reactor itself but in this case the product sample contained trace quantities of helical nanotubes with an approximate diameter below 100nm, but far larger than some of the tubes that remained in the reactor.

A look into the physics and possible mechanism by which carbon nanotubes are lifted upward out of the reactor column gave some possible rationalization for this. It is theorized that with their near incredibly small weight at such small dimensions, the

main lifting force is generated by drag against the frontal surface area of the tube in line with the flow of gas. This also implies that this drag force will be larger for structures with larger frontal surface areas ie. larger tubes. The helix structure provided by helical nanotubes similarly gives far larger drag per length due to the increased cross-sectional area provided at any orientation with the helix shape. Added to this is the increased agglomeration effect provided by the helical shape. With the far greater lift force acting on helical nanotubes, they are more easily lifted from the reactor explaining the presence of helical nanotubes in the product but not the reactor.

An analysis of the results provided by this work suggests that use of this swirled-fluid CVD reactor for continuous production of single-walled nanotubes is possible. Although, by comparison, far less research has been performed on investigating the growth mechanism by which helical nanotubes are produced, it is possible that their unique structural properties provide a means by which Single Walled Carbon Nanotubes can be removed from the Swirled Fluid Chemical Vapour Deposition Reactor. More research is still required to produce purer samples and to effectively separate products but this work confirms the possibility of SWCNT production.

## 5.2 Recommendations

Research into the uses of Single Carbon Nanotubes is both diverse and extensive. While some applications, such as their use in electrical circuitry, may require large amounts of long, straight SWCNTs, many other uses do not possess these requirements. With further research, the SFCVD reactor could be used to produce straight and helical SWCNTs for a variety of applications although it is recommended that the process be coupled with the use of an Ultra-Centrifuge in order to better separate the products. Further investigation into the effects of varying the operating conditions on chain length, diameter and growth dynamics as well as optimization of the vaporizer and its

effects on the resulting product could provide invaluable means for improving process synthesis and optimization. While it is possible that further research into this work's method of SWCNT production could indeed improve the quality of the hydro cyclone products, the continuous feed of catalyst particles into the reactor indicates the necessity to separate the particles from the product in order for them to be recycled back into the process and hence reduce costs.

For applications requiring high purity long chain SWCNTs, it is recommended that other possible production methods be investigated as well and compared. As continuous production of nanotubes is still a fairly new process, research would have to be done into comparing the costs of the other more expensive methods which give highly pure samples to the use of the cheaper SFCVD reactor which may require expensive purification and separation.

## CHAPTER 6 - References

- Ando Y, Zhao X, Sugai T, Kumar M. *Growing Carbon Nanotubes*. Materials Today (October 2004), ISSN:1369 7021.
- Amelinckx, S.; Zhang, X.B.; Bernaerts, D.; Zhang, X.F.; Ivanov, V.; B.Nagy, J. *A formation mechanism for catalytically grown helix-shaped graphite nanotubes*. *Science* **1994**, 265, 635-639.
- Bisquert J, Ramirez P, Barbero AJ, Mafe S. *Eur. J. Phys.* **12** 249 doi: 10.1088/0143-0807/12/6/001. 1991.
- Collins PG, Avouris P. *Nanotubes for Electronics*. Scientific American: 67, 68, and 69. December 2000.
- Danafar F, Fakhru'l-Razi A, Salleh MAM, Biak DRA. *Fluidized bed catalytic chemical vapor deposition synthesis of carbon nanotubes – A review*. Chemical Engineering Journal 155 (2009) 37-48.
- Daenen M, de Fouw RD, Hamers B, Janssen PGA, Schouteden K, Veld MAJ. *The Wonderous World of Carbon Nanotubes*. Eindhoven University of Technology. (2003).
- Deck CP, Vecchio K. *Growth mechanism of vapour phase CVD-grown multi-walled carbon nanotubes*. Carbon 42 (2005) 2608-2617.
- Dekker C. *Carbon nanotubes as molecular quantum wires* (PDF). *Physics Today* **52** (5): 22–28. May 1999.
- Dresselhaus MS, Dresselhaus G, Avouris P, Eds. *Carbon Nanotubes: Synthesis, Structure, Properties, and Applications*. Springer-Verlag Berlin Heidelberg, TA455.C3 C38, 2000.
- Foley M. *Carbon Nanotubes: What are CNTs*. Carbon Nanotubes, September 2006.

- Harris PJF. *Carbon Nanotubes and Related Structures*. Cambridge University Press, 1999. TA455.C3H37 1999.
- Hernadi K, Fonseca A, Nagy JB, Siska A, Kiricsi I. *Production of nanotubes by the catalytic decomposition of different carbon- containing compounds*. Appl. Catal. A 199 (2000) 245-255.
- Hoenlein W, Kreupl F, Duesberg GS, Graham AP, Liebau M, Seidel R, Unger E. *Carbon Nanotubes for Microelectronics: status and future prospects*. Materials Science & Engineering C 23:663 (2003).
- Hoerner, S. F. *Fluid-Dynamic Drag*. Hoerner Fluid Dynamics, Brick Town, N. J., USA. 1965.
- Ho GW, Wee ATS, Lin J, Tjiu WC. *Synthesis of well-aligned multiwalled carbon nanotubes on Ni catalyst using radio frequency plasma-enhanced chemical vapour deposition*. Thin Solid Films 388 (2001) 73-77.
- Iijima S. *Growth of Carbon Nanotubes*. Materials Science and Engineering. B19 (1993) 172-180.
- Inami N, Mohamed A, Shikoh E, Fujiwara A. *Synthesis-condition dependence of carbon nanotube growth by alcohol catalytic chemical vapor deposition method*. Sci. Technol. Adv. Mater. 8 (2007) 292.
- Ishigami N, Ago H, Imamoto K, Tsuji M, Iakoubovskii K, Miname N. *Crystal Plane Dependent Growth of Aligned Single-Walled Carbon Nanotubes on Sapphire*. J. Am. Chem. Soc. **130** (30): 9918–9924. 2008.
- Iyuke SE. *A Process for Production of Carbon Nanotubes*. World Intellectual Property Organization, International Bureau, WO 2007/026213 A1, 2007.
- Iyuke SE, Mamvura TA, Liu K, Meyyappan M, Varadan VK. *Process synthesis and optimisation for the production of a clean, large quantity of single-walled carbon nanotubes*, 2008.

- Jung M, Eun KY, Lee JK, Baik YJ, Lee KR, Park JW. *Growth of carbon nanotubes by chemical vapour deposition*. Diamond and Related Materials 10 (2001) 1235-1240.
- Kim KE, Kim KJ, Jung WS, Bae SY, Park J, Choi J, Choo J. *Investigation on the temperature-dependant growth rate of carbon nanotubes using chemical vapour deposition of ferrocene and acetylene*. Chemical Physics Letters 401 (2005) 459-464.
- Kobayashi Y, Nakashima H, Takagi D, Homma Y. *CVD growth of single-walled carbon nanotubes using size-controlled nanoparticles catalyst*. Thin Solid Films 464-465 (2004) 286-289.
- Kukovecz A, Konya Z, Najaraju N, Willems I, Tamasi A, Fonseca A, Nagy JB, Kiricsi I. *Catalytic synthesis of carbon nanotubes over Co, Fe and Ni containing conventional and sol-gel silica-alumina*. Phys. Chem. Phys. 2 (2000) 3071-3076.
- Kunadian I, Andrews R, Qian D, Menguc MP. *Growth kinetics of MWCNTs synthesized by a continuous-feed CVD method*. Carbon 47 (2009) 384-395.
- Kuwana K, Endo H, Saito K, Qian D, Andrews R, Grulke EA. *Catalyst deactivation in CVD synthesis of carbon nanotubes*. Carbon 43 (2005) 253-260.
- Kwok CTM, Reizman BJ, Agnew DE, Sandhu GS, Weistroffer J, Strano MS, Seebauer EG. *Temperature and time dependence study of single-walled carbon nanotube growth by catalytic chemical vapour deposition*. Carbon 48 (2010) 1279-1288.
- Lamoureux E, Serp Ph., Kihn Y, Kalck Ph.. *New efficient Fe<sub>2</sub>O<sub>3</sub> and Fe Mo supported OMCVD catalyst for single wall carbon nanotubes growth*. Catal. Commun. 7 (2006) 604-609.
- Lee WY, Lin J, Gu L, Leou KC, Tsai CH. *CVD catalytic growth of single-walled carbon nanotubes with a selective diameter distribution*. Diamond & Related Materials 17 (2008) 66-71.

- Lide DR, ed. *CRC Handbook of Chemistry and Physics*, Internet Version 2005, <http://www.hbcpnetbase.com>. CRC Press, Boca Raton, FL, 2005 (Accessed February 2009).
- Li DW, Pan LJ, Liu KP, Yu NS. *Relationship Between Geometric Structures of Catalyst Particles and Growth of Carbon Nanocoils*. Chemical Vapor Deposition 2010, 16, 166-169.
- Li F, Zou X, Wang M, Cheng J, Zhang H, Ren P, Zhu G. *Influence of the Shape and Size of Catalyst on the Morphology of Carbon Sub-microfibers*. 2008 2<sup>nd</sup> IEEE International Nanoelectronics Conference (INEC 2008).
- Mancosu, P, Arana A. *Descartes and the cylindrical helix*. Historia Mathematica Volume 37, Issue 3. August 2010, p403-427.
- Martel, R.; Derycke, V., Lavoie, C., Appenzeller, J., Chan, K.K., Tersoff, J. and Avouris, P. *Ambipolar Electrical Transport in Semiconducting Single-Wall Carbon Nanotubes*. Physical Review Letters **87** (25): 256805. December 2001.
- May WR. *Solubility of Ferrocene in Organic Solvents*, SFA International, Houston , TX, April 2009.
- McCormick, Barnes W. *Aerodynamics, Aeronautics, and Flight Mechanics*. p. 24, John Wiley & Sons, Inc., New York, ISBN 0-471-03032-5. 1979.
- Nagaraju N, Fonseca A, Konya Z, Nagy JB, Mol J. *Alumina and silica supported metal catalyst for the production of carbon nanotubes*. Catal. A-Chem. 181 (2002) 57-62.
- Oida S, Sakai A, Nakatsuka O, Ogawa M, Zaima S. *Effect of alcohol sources on synthesis of single-walled carbon nanotubes*. Applied Surfaces Science 254 (2008) 7697-7702.
- Paradise M, Goswami T. *Carbon Nanotubes – Production and industrial applications*. Materials and Design 28 (2007) 1477-1489.

- Peigney A, Coquay P, Flahaut E, Vandenberghe RE, De Grave E, Laurent C. *A study of the formation of single- and double-walled carbon nanotubes by a CVD*. Journal of Physical Chemistry. B 105 (2001) 699-710.
- Qian W, Liu T, Wei F, Wang Z, Luo G, Yu H, Li Z. *The evaluation of the gross defects of carbon nanotubes in a continuous CVD process*. Carbon 41 (2003) 2613-2617.
- Qingwen L, Hao Y, Jin Z, Zhongfan L. *Effect of hydrocarbons precursors on the formation of carbon nanotubes in chemical vapour deposition*. Carbon 42 (2004) 829-835.
- Scharff P. *New Carbon materials for research and technology*. Carbon 1998; 36 (5-6):481-6.
- Sharma SP, Lakkad SC. *Morphology study of carbon nanospecies grown on carbon fibers by thermal CVD technique*. Surface & Coatings Technology 203 (2009) 1329–1335. 2009.
- Sinnot SB, Andrews R, Qian D, Rao AM, Mao Z, Dickey EC. *Model of carbon nanotube growth through chemical vapour deposition*. Chem. Phys. Lett. 1999; 315:25-30.
- Tang W, Advani SG. *Drag on a nanotube in uniform liquid argon flow*. The Journal of Chemical Physics **125**: 174706. November 2006.
- Thoteson E, Ren Z, Chou T. *Advances in the science and technology of carbon Nanotubes and their composites: a review*. Compos. Sci. Technol. 2001; 64(13):1899-912.
- Vahlas C, Caussat B, Serp Ph., Angelopoulos GN. *Principles and applications of CVD powder technology*. Mater. Sci. Eng. R53 (2006) 1-72.
- Wang Z, Jia D, Liu S, Zhang M. *Direct growth of carbon nanotube junctions by switching source gases in a continuous chemical vapour deposition*. Materials Letters 62 (2008) 3288-3290.
- Wilson M, Kannangara K, Smith G, Simmons M, Raguse B. *Nanotechnology: Basic Science and Emerging Technologies*. Chapman and Hall, ISBN 1-58488-39-1, 2002.

- Yamabe T. *Recent development of carbon nanotubes*. Synthetic Met. 1995:1511-8.
- Yen YW, Huang MD, Lin FJ. *Synthesize carbon nanotubes by a novel method using chemical vapour deposition-fluidized bed reactor from solid-stated polymers*. Diamond Relat. Mater. 17 (2008) 567-570.
- Yu Z, Chen D, Totdal B, Zhao T, Dai Y, Yuan W, Holmen A. *Catalytic engineering of carbon nanotube production*. Applied Catalysis A: General 279 (2005) 223-233.
- Zhang X, Cao A, Wei B, Li Y, Wei J, Xu C. *Rapid growth of well-aligned carbon nanotube arrays*. Chem. Phys. Lett. 2002; 362:285-90.
- Zhao N, He C, Jiang A, Li J, Li Y. *Fabrication and growth mechanism of carbon nanotubes by catalytic chemical vapour deposition*. Materials Letters 60 (2006) 159 – 163. 2006.
- Zheng LX, O'Connell MJ, Doorn SK, Liao SZ, Zhou YH, Akhadvov EA, Hoffbauer MA, Roop BJ, Jia QX, Dye RC, Peterson DE, Huang SM, Liu J, Zhu YT. *Ultralong Single-Wall Carbon Nanotubes*. Nano letters **3**. pp. 673–676. 2004.

## CHAPTER 7 – Appendices

### Appendix A – Gas corrections

When using gases other than air through a rotameter that is calibrated for air flow, it is necessary to calibrate the rotameter for the gases being used in order to get accurate flow readings. As different gases possess different densities, it is essential to calibrate the rotameter to account for this:

$$q_G^{\circ} = q_A^{\circ} \sqrt{\frac{\rho_A^{\circ}}{\rho_G^{\circ}}} \quad (\text{A.1})$$

Where  $q_G^{\circ}$ ,  $q_A^{\circ}$ ,  $\rho_A^{\circ}$  and  $\rho_G^{\circ}$  are the standard gas flow reading, air flow reading, air density, and gas density at standard conditions respectively. Table A.1 below gives the correction factors for all the gases used during experiments. Adjustments also need to be made to take into account the change in pressure as the experiments were performed in Johannesburg (approximately 1694m above sea-level):

$$q_G' = q_G^{\circ} \sqrt{\frac{P}{760\text{mmHg}}} \quad (\text{A.2})$$

Where  $q_G'$  is the gas flow corrected for pressure,  $P$ . Since barometric pressure decreases with altitude, at 1694m there is an approximate pressure of 82.5kPa giving a pressure correction factor of 0.9 to be used.

**Table A.1:** Gas Correction Factors for gases used in this work.

| <u>Gas</u> | <u>Correction Factor</u> |
|------------|--------------------------|
| Air        | 1                        |
| Argon      | 0.85                     |
| Acetylene  | 1.04                     |
| Hydrogen   | 3.61                     |

## Appendix B – Hazard and Operability Study (Hazop)

In order to prevent injury while producing the CNTs, the following protocol will be followed for each experiment:

- Due to release of toxic vapours, respirator masks shall be worn at all times when preparing and working with samples.
- Laboratory coats and gloves shall also be worn at all times as a precautionary measure in accordance with the Material Safety Data Sheets (MSDS) for certain materials used as well as to prevent sample contamination.
- Due to the flammability of xylene liquid, a fire extinguisher shall be present nearby at all times as well as gas detection devices nearby as a safety measure against the buildup of toxic gases.
- To help prevent process line blockage, process steps shall be used to achieve a continuous CVD process.

A Hazard and Operability (HAZOP) study was also conducted, the results of which are presented in Table B.1 below.

**Table B.1:** HAZOP performed for continuous CVD process.

| Item | Deviation                         | Cause                              | Consequences or implications                              | Indication or protection                                   |
|------|-----------------------------------|------------------------------------|-----------------------------------------------------------|------------------------------------------------------------|
| 1    | No Argon flow into the reactor    | Blockage in pipe<br>Cylinder empty | Insufficient removal of nanoparticles – blockage          | Check cylinder levels and flow before starting experiments |
| 2    | Reduced gas flow into the reactor | Leakage                            | Introduction of O <sub>2</sub> into the reactor which can | Ensure all connections are completely sealed and leak-free |

|   |                                            |                                                         |                                                                             |                                                                                                               |
|---|--------------------------------------------|---------------------------------------------------------|-----------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------|
|   |                                            |                                                         | lead to fire                                                                |                                                                                                               |
| 3 | No flow of feed or catalyst into vaporizer | Pump set incorrectly<br>Blockage                        | No/Reduced production of carbon nanotubes                                   | Only observable after examination of products                                                                 |
| 4 | Insufficient temperature in vaporizer      | Heater set incorrectly<br>Insufficient insulation       | Reduced nanotube production                                                 | Presence of noticeable quantities of catalyst or feed in process products                                     |
| 5 | Excessive gas flow into the reactor        | Excessive Ar flow chosen                                | Low production rates due to decreased residence time                        | Presence of catalyst and feed in products<br>Reduce Ar flow                                                   |
| 6 | No flow of materials out of reactor        | Build up of products in reactor                         | Pressure build up<br>Equipment failure                                      | Pressure gauges can indicate pressure build up so that the experiment can be stopped and the blockage cleared |
| 7 | Low temperature in the reactor             | Faults occurring in the furnace thermocouple/controller | Possible formation of unwanted side-products<br>Reduced nanotube production | Observable on examination of products<br>Check the operability of the temperature controllers                 |
| 8 | Excessive pressure within the reactor      | Blockage<br>Closed valves                               | Possible leaking from the reactor<br>Ignition of leaking material           | Ensure connections are tightly sealed and product is visible from the reactor                                 |