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Synthesis of Large Carbon Nanotubes from Ferrocene: The Chemical Vapour Deposition Technique

[1,2]Clarence S. Yah, [1]Geoffrey S. Simate, [1,3]Kapil Moothi, [1,3]Kwena S. Maphutha and [1,3]Sunny E. Iyuke

[1]School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Private Bag 3, Wits 2050, Johannesburg, South Africa

[2]Biochemistry and Toxicology Section, National Institute for Occupational Health, 25 Hospital Road, Constitutional Hill, Johannesburg 2000, South Africa

[3]DST/NRF Centre of Excellence in Strong Materials, University of the Witwatersrand, Private Bag 3, WITS, South Africa

Corresponding Author: Clarence S. Yah, School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Private Bag 3, Wits 2050, Johannesburg, South Africa Tel: +27 11 7126489 Fax: +27 11 7126465

ABSTRACT

In this study, Carbon Nanotubes (CNTs) were produced through the Chemical Vapour Deposition (CVD) reactor with ferrocene acting as both carbon source and catalyst with argon as the carrier gas. The reaction was carried out at temperatures ranging from 800 to 950°C. Four grams of the ferrocene was placed in a vapouriser at the bottom of the reactor. The system was purged with nitrogen for 20 min to make sure there were no gas leakages as well as free from other gases. The furnace was turned on at the desired temperatures (800-950°C) to produce the CNTs. The CNTs were analysed using the Transmission Electron Microscopy (TEM) and Raman Spectroscopy. The results showed the alignment of multi walled CNTs that ranged between 100 and 1000 nm in length. Furthermore, the CNTs were produced at all the temperatures. However, the optimum temperature for the production of the CNTs was found between 850 and 900°C. The amount of CNTs produced at 800 to 950°C varied from 2.0±0.03 to 2.3±0.34 g at 95% confidence interval with no significant different at $p>0.05$ using the Instat Program version 5.0.1.

Key words: Ferrocene, synthesis, carbon nanotubes, chemical vapour deposition, temperature

INTRODUCTION

With the increasing advancement in nanotechnology (Singh *et al*., 2011) and the need for more durable and flexible materials, Carbon Nanotubes (CNTs) have been identified as one of the most valuable materials due to their unique structural, extraordinary mechanical and electrical properties (Hou *et al*., 2002; Mamba *et al*., 2010; Ngoy *et al*., 2011). These nanostructures may be Multi-Walled Carbon Nanotubes (MWCNTs), Single-Walled Carbon Nanotubes (SWCNTs) and Helical Carbon Nanotubes (HCNTs) (Iyuke *et al*., 2009). Their enormous applications range from polymeric composites, nanomedicine composites to nano-electronic devices (Iyuke and Simate, 2011; Alkhatib *et al*., 2010). These potential applications depend on the low-cost catalyst (ferrocene) which is a readily scalable route to CNTs production (Keller *et al*., 2007; Zambri *et al*., 2011). There are several methods used for the production of carbon nanostructures; the electric arc discharge (Miao *et al*., 2006), laser ablation (Jiang *et al*., 2005), CVD (Iyuke *et al*., 2009; Yah *et al*., 2011; Khavarian *et al*., 2011) and flame synthesis technique (Li *et al*., 2009; Fekri *et al*., 2010). The CVD

process has the greatest potential for large scale and continuous production of CNTs because of its low energy input requirements (Iyuke and Mahalik, 2006; Sharma and Lakkad, 2009; Mohamed and Kou, 2011). The lower reaction temperature of this technique is also an added advantage. The CVD production of CNTs uses various sources of carbon with different catalysts and argon as carrier gas (Iyuke and Mahalik, 2006; Sharma and Lakkad, 2009; Iyuke *et al*., 2009). Yu *et al*. (2005) reported the use of an alumina supported Ni-Fe catalyst with syngas as carbon source. Iyuke *et al*. (2009) used ferrocene as catalyst and acetylene as the main carbon source. A review by Philippe *et al*. (2007) described the use of ethylene as carbon source, with Ni/Al_2O_3 catalyst for the production of graphite nanofibres as well as Fe/Al_2O_3 catalyst for the production of MWCNTs. Furthermore, Yuan *et al*. (2001) produced entangled MWCNTs with diameter from 20-60 nm using methane flames and Ni-Cr wire as catalyst. Endo *et al*. (2004) and Kuwana *et al*. (2005) also reported the synthesis of CNTs from xylene as the carbon source and ferrocene as the catalyst in a CVD reactor. Seemingly Khavarian *et al*. (2011) showed the synthesis of CNTs by a Floating Catalyst (FC) CVD method with iron (III) chloride hexahydrate ($FeCl_3.6H_2O$) as catalyst and methane as carbon source. However, it is worthwhile to study the ability of ferrocene to act as a catalyst and low cost source of carbon for CNT production. In the CVD method, temperature is a major parameter affecting the production of CNTs. The current study, therefore, seeks to optimize the temperature for CNT production using thermal decomposition of ferrocene as both a carbon source and catalyst with argon as the carrier gas. Since there is no need for a separate carbon source, the process becomes cheaper. Furthermore, ferrocene itself is cheap and easy to produce (Tanner *et al*., 1995). The aim of this study is to produce CNTs using ferrocene as a catalyst and carbon source in a CVD reactor. This, therefore, eliminates the problem of using various catalysts and different sources of carbon to produce CNTs. This will also pinpoint the likely source of CNT contamination during synthesis.

MATERIALS AND METHODS

Equipment: The equipment used for the experiment is shown in Fig. 1. In brief, the apparatus consists of a vertical furnace that can be operated up to 1200°C. The flow of gases into the glass furnace reactor is aided by a system of valves and rotameters.

Set-up: About 4 g of ferrocene was placed in the vapouriser to be used as the carbon source as well as the catalyst precursor. A layer of quartz wool was placed inside the tube for the product to fall

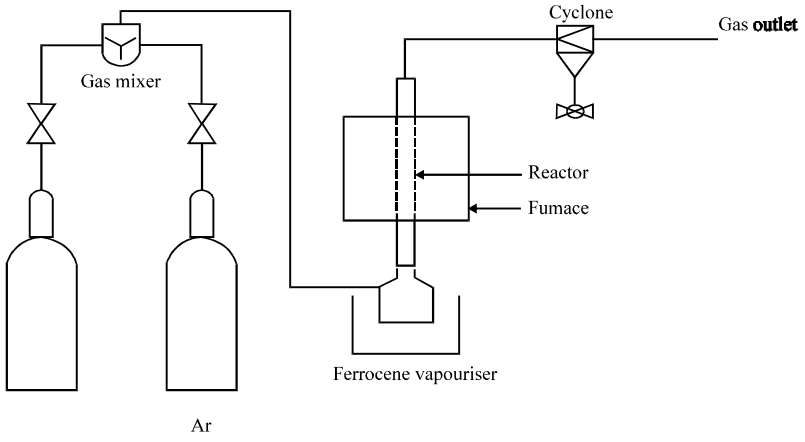

Fig. 1: Chemical vapour deposition reactor

on. A heating cord was wrapped around the exposed parts of the vapouriser at the bottom of the reactor. The purpose of this was to maintain a high temperature so that ferrocene does not crystallise. Once the equipment was connected as shown (Fig. 1), all the connections were sealed with high vacuum grease to ensure that there were no gas leaks. Nitrogen gas was passed through the system for 20 min, to flush out contaminants and to ensure that there were no leakages. Argon was later used to provide an inert atmosphere and to purge unknown gases from the air proof system as well as a carrier gas.

Procedure: The furnace was turned on and set to the desired reaction temperature (800, 850, 900 and 950°C). When the reaction temperature was reached, the vapouriser and heating cord were turned on. The catalyst (ferrocene) was evaporated and transported into the reactor by argon gas. This could be seen since the ferrocene was orange in colour. The reaction was allowed to proceed untill all the ferrocene had vapourised. The equipment was then switched off and allowed to cool. The product was collected from the cyclone, quartz wool and also scraped off from the inside of the reactor. The product was analysed with the Transmission Electron Microscope (TEM) (model JOEL 100S). The Raman spectroscopy was also carried out using the Jobin-Yvon T6400 Raman Spectrometer with an Argon ion laser. The analysis was conducted in order to determine whether any nanostructures of carbon were formed using ferrocene as the sole carbon source.

Statistical analysis: The data was performed using the Instat View 5.0.1 (SAS Institute Inc, Cary NC, USA). Statistical significance was based on p-value of 0.05. The mean and standard deviation were analysed as Mean±Standard deviation (X±SD).

RESULTS

The TEM images of the reactor product at the different reaction temperatures are shown in Fig. 2-4. In Fig. 2, it can be seen that a CNT of around 500 nm was produced. Apart from MWCNTs being produced, there was a likely production of other nanostructures such as Carbon Nanofibres (CNFs) or amorphous carbon (data not shown).

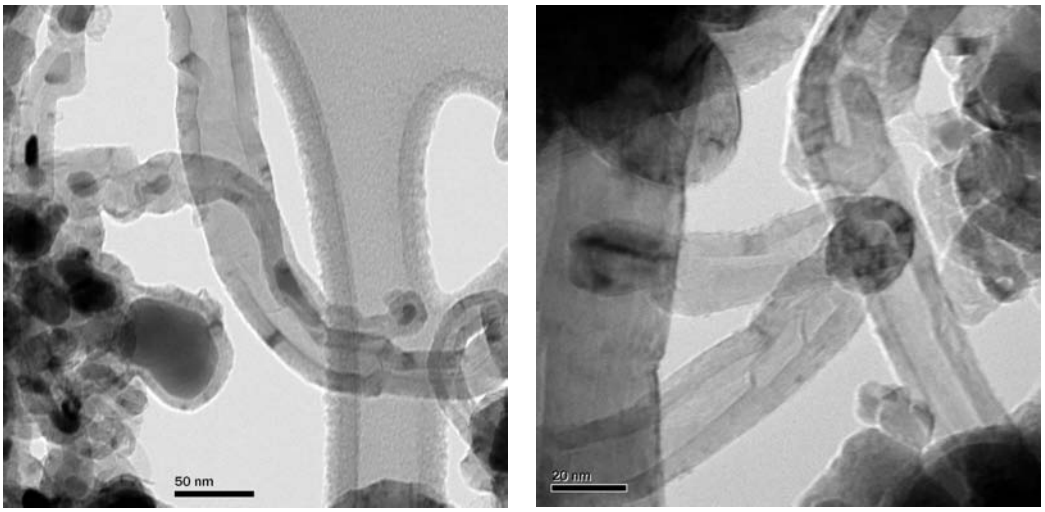

Fig. 2: TEM image of the reactor product at 800°C

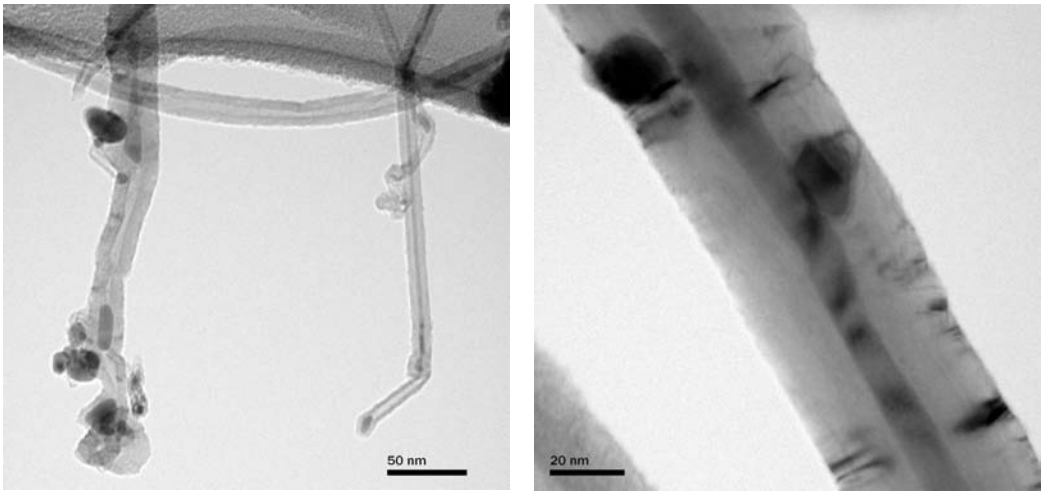

Fig. 3: TEM image of the reactor product at 850°C

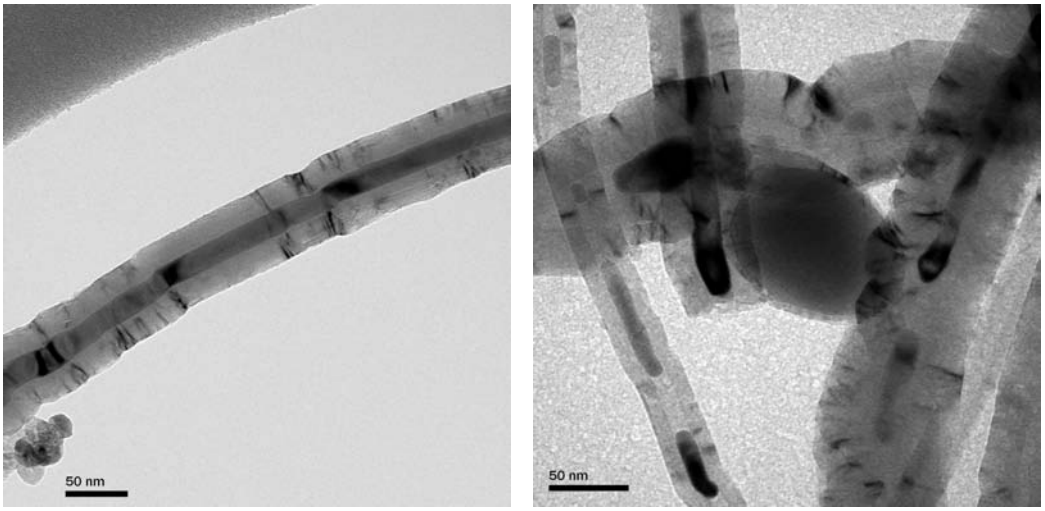

Fig. 4: TEM image of the reactor product 900°C

Figure 3 clearly shows one CNT of about 900 nm long, with a shorter one of around 400 nm and possible CNFs. These CNTs ranged between 500 and 1000 nm in length.

Figure 4 shows CNFs and a few short CNTs, ranging between 100 and 300 nm.

Figure 5 shows a CNT having a length of approximately 1.5 μm, with shorter CNTs also present. Catalyst particles can be seen within the hollow tubes of the CNTs. The Raman spectra (Fig. 6-10) show that CNTs with essentially similar properties are produced at the temperatures of 800, 850, 900 and 950°C using ferrocene. This confirms the TEM images shown in Fig. 2-5. Most of the CNTs produced using ferrocene are not agglomerated and entangled with each other. Such CNTs are ideal for integration into devices i.e., CNT-based Field Effect Transistors (FET), etc.

The peaks around 1580 cm^{-1}, G-band (Fig. 6-10) corresponds to an E2g mode of graphite and is related to the vibration of sp^2-bonded carbon atoms in a two dimensional hexagonal lattice, such

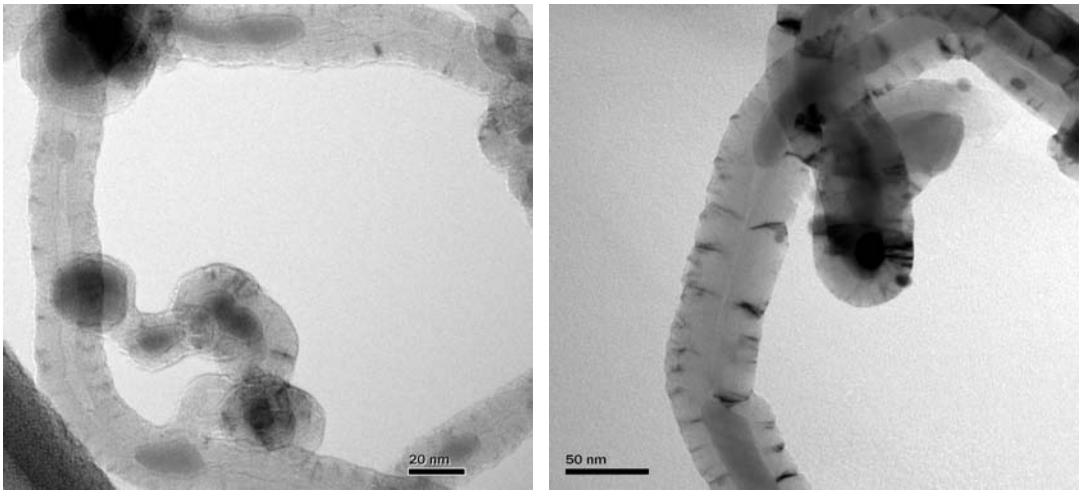

Fig. 5: TEM image of the reactor sample at 950°C

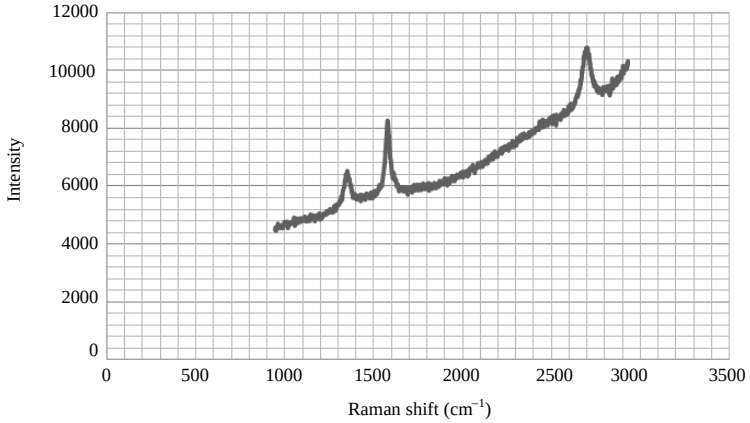

Fig. 6: Raman Shift of the product at 800°C

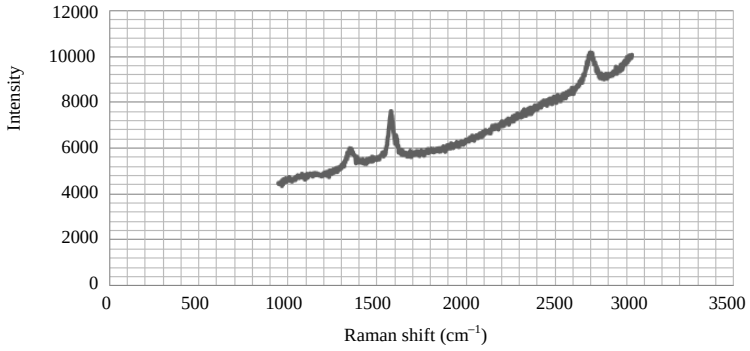

Fig. 7: Raman Shift of the product at 850°C

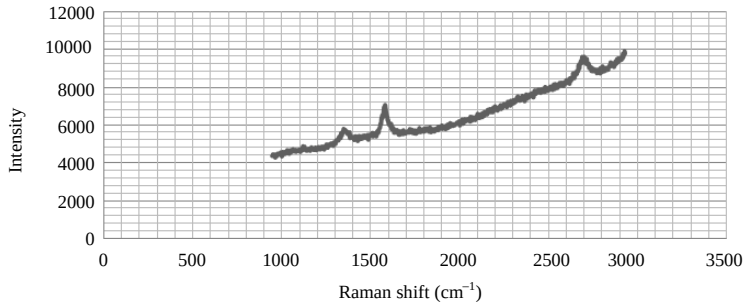

Fig. 8: Raman shift of the product at 900°C

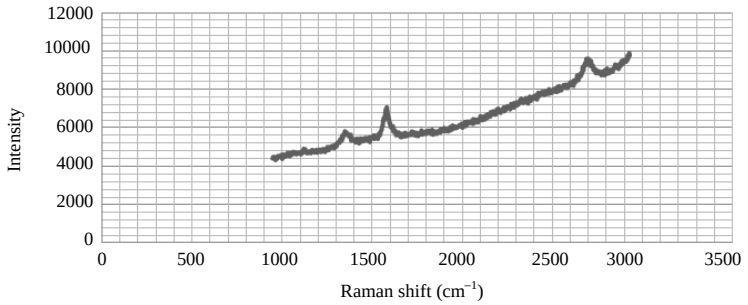

Fig. 9: Raman shift of the product at 950°C

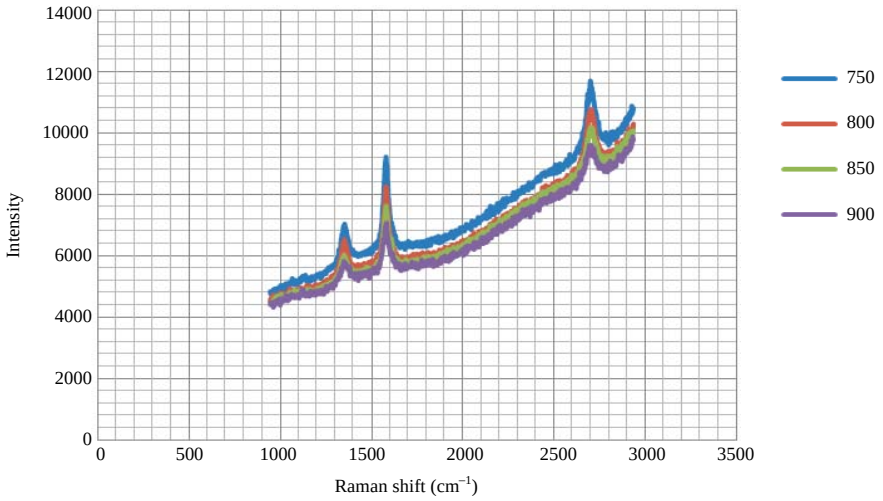

Fig. 10: Raman shifts for the Products formed at different temperature

as in a graphitic layer (Tuinstra and Koenig, 1970). Nanotubes with concentric multi-walled layers of hexagonal carbon lattice display the same vibration (Kasuya *et al*., 1997). The D-band, in the region of 1350 cm^{-1}, is associated with the presence of defects in the hexagonal graphitic layers (Lou *et al*., 2003). The ratio of the G-band to D-band intensities provides an indication of the quality of the sample. These ratios for each product sample are shown in Table 1.

The average production of the CNTs varied from 2.0±0.03 to 2.3±0.34 g at 95% confidence interval. The highest production was found at 900°C. There was no significant difference

Table 1: Ratio of G-band to D-band intensities for products formed at different temperatures

Temperature (°C)	I_G/I_D	Amount of CNT produced (g) (X±SD)
800	1.265	2.0±0.03
850	1.270	2.2±0.12
900	1.216	2.3±0.34
950	1.250	2.1±0.16

I_G: G- Band, I_D: D-Band, (X±SD): Mean±Standard deviation

(i.e., p>0.05) in the amount of CNTs produced at the various temperatures used. Although ferrocene is vapourised at lower temperatures, the maximum yield was found between 850 and 900°C.

DISCUSSION

Figure 2-5 shows the synthesis of CNTs at temperatures ranging from 800-950°C. This is due to the fact that ferrocene is a relatively volatile organo-metallic compound with excellent vapourisation above 400°C (Barreiro *et al*., 2006). At 500 to 650°C the ferrocene completely decomposes as shown in Eq. 1 (Barreiro *et al*., 2006):

$$Fe(C_5H_5)_2\ Fe+H_2+CH_4+C_5H_6+..... \quad (1)$$

Previously, this was supported by the findings of Lewis and Smith (1984) when they found that ferrocene could be consumed through reactions with radicals during the decomposition of ferrocene to unimolecular gas-phase as shown in Eq. 2:

$$Fe(C_5H_5)_2\ Fe+2C_5H_5 \quad (2)$$

Furthermore, Hou *et al*. (2002) reported the pyrolysis of pure ferrocene at 580-700°C resulting in spherical iron nanoparticles with diameters in the order of 10 nm. In addition, Kuwana and Saito (2005) reported the production of iron nanoparticles at 973 K (700°C) from ferrocene using the CVD technique. However, this was different from the results obtained in this study, where MWCNTs dominated instead of the spherical and aggregated nanoparticles. Hou *et al*. (2002) argued that the inability to produce CNTs in the process was due to the low carbon/iron ratio in pure ferrocene. In the present study, iron to carbon ratio in ferrocene was 30 to 75%. Furthermore, a report by Barreiro *et al*. (2006) has shown that when ferrocene is present at the reaction zone, iron clusters and reactive carbon are produced at the gaseous phase. Barreiro *et al*. (2006) claim this could result in the production of Single-Walled Carbon Nanotubes (SWCNTs). With the current work, higher temperatures were used (800 to 950°C), resulting in the production of MWCNTs. The study showed the highest amount of CNTs at 900°C, although there was no significant difference (i.e., p>0.05) in the amount produced within the temperature range used. This was similar to the report by Barreiro *et al*. (2006) where it was found that MWCNTs were produced between 750 and 900°C using ferrocene as sole carbon source and argon as carrier gas. In present study, it was noticed that at higher temperatures (800-950°C), there was less adherence of the product to the walls of the reactor such that more of the product could be collected from the cyclone. Therefore, if the process had to be scaled up for industrial production or for continuous production, higher temperatures would be recommended for ease of product collection.

Figure 6-10 revealed G-band peaks which supports the production of MCWNTs. In other words, in the Raman spectra, the D-band, G-band and G'-band occur at wavelengths (Raman shifts) which are characteristic of CNTs. If the intensities of the G-band and D-band are similar, a high number of structural defects are present. The calculated I_D/I_G ratios for all the temperatures were close to 1. This could be due to the presence of MWCNT. In the range 850 to 900°C, the Raman intensities decreased with an increase in temperature. The decrease in intensities was as a result of an increase in the number of defects in the samples (Liu *et al.*, 2008). This could imply that more MWCNTs are formed at higher temperatures.

CONCLUSION AND RECOMMENDATIONS

The carbon nanotubes were produced at the temperature range of 800 to 950°C. The ferrocene acted as both catalyst and carbon source for the production of CNTs. There was no significant difference (i.e., $p>0.05$) in the amount of CNTs produced in all the temperature studied. Although, at 900 to 950°C reaction temperatures, there were fewer adherences of the CNTs at the walls of the reactor as compared to the 800 to 850°C. Therefore, for industrial processes, 900 to 950°C are preferable to CNT production.

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