

Development of an Aerosol-CVD Technique for the Production of CNTs with Integrated Online Control

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I confirm that the work presented in this dissertation is my own. Where information has been derived from other sources, I confirm that this has been indicated in the dissertation.

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Abstract

This dissertation summarises the study of different aspects of the aerosol-assisted chemical vapour deposition (AACVD) technique for the production of multi-wall carbon nanotubes (MWCNTs). Upscaling the synthesis while retaining the quality of MWCNTs has been a prime objective throughout the work. A key aspect of this work was the study of different growth parameters and their influence on the homogeneity of the products across the reactor. The effect of the precursor composition on the yield and quality of MWCNTs were also investigated. It was shown that the synthesis rate can be significantly (60 – 80 %) increased by tuning the composition of the precursor. Moreover, by optimising the synthesis recipe and using a larger reactor, the synthesis rate and efficiency of the precursor were increased fivefold (up to 14 g/hr) and twice (up to 88 %) respectively. Large area (up to 90 cm²), mm-thick carpets of MWCNTs which were both free-standing and on substrate were produced. The carpets could withstand normal handlings without tearing apart, making them suitable for macroscopic characterisations and applications. By *in-situ* qualitative and quantitative gas analysis of the atmosphere of the reactor, the thermocatalytic cracking behaviour of 25 precursors was investigated and a mechanism for successive formation of different hydrocarbon fragments inside the reactor was proposed. A number of dedicated gas analysis methods and apparatuses such as a probe for zone-by-zone gas analysis of reactor and a heated chamber for preparation of standard gas analysis samples were developed to explore some of the least investigated aspects of the thermocatalytic cracking of precursors. Mapping the reactor revealed that some single-wall and double-wall carbon nanotubes (SWCNTs and DWCNTs) were also produced near the exhaust of the reactor. The SWCNTs were partly covered by fullerene-like species and resembled different forms of carbon nanobuds. In addition, the effect of the electron beam on the interaction of the SWCNTs and the fullerene-like species was studied *in situ* using high-resolution transmission electron microscopy (HRTEM).

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List of publications

- **Published journal articles**

- [1] Rebecca J Nicholls, Jude Britton, Seyyed Shayan Meysami, Antal A. Koós, Nicole Grobert; In-situ engineering of NanoBud geometries, *Chemical Communications*, vol. 49, pp. 10956 – 10958, 2013.
- [2] Seyyed Shayan Meysami, Antal A. Koós, Frank Dillon, Nicole Grobert, Aerosol-assisted chemical vapour deposition synthesis of multi-walled carbon nanotubes: II. An analytical study, *Carbon*, vol. 58, pp. 159 – 169, 2013.
- [3] Seyyed Shayan Meysami, Frank Dillon, Antal A. Koós, Zabeada Aslam, Nicole Grobert, Aerosol-assisted chemical vapour deposition synthesis of multi-walled carbon nanotubes: I. Mapping the reactor, *Carbon*, vol. 58, pp. 151 – 158, 2013.

- **Filed patents**

- [4] Seyyed Shayan Meysami, Nicole Grobert, Device, method and apparatus for the transfer of analytes (publication of patent application), *World Intellectual Property Organization*, WO/2013/030544, 2013.

- **Conference talks**

- [5] Seyyed Shayan Meysami, Antal A. Koós, Frank Dillon, Rebecca J Nicholls, Jude Britton, Nicole Grobert, Development of an Aerosol-CVD Technique for the Production of CNTs with Integrated Online Control (talk), *NanoteC13*, Surrey – United Kingdom, 28-30.8.2013.
- [6] Seyyed Shayan Meysami, Antal A. Koós, Frank Dillon, Nicole Grobert, Development of an aerosol-CVD technique for the production of CNTs with integrated online control, *International workshop on nanocarbon composites*; Valencia – Spain, 4.10.2012.

- **Conference posters**

- [7] Seyyed Shayan Meysami, Antal A. Koós, Frank Dillon, Zabeada Aslam, Nicole Grobert, Aerosol-assisted CVD synthesis of MWCNTs: Mapping the reactor, *International workshop on nanocarbon composites*, Valencia – Spain, 4-5.10.2012.
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- [9] Seyyed Shayan Meysami, Antal A. Koós, Frank Dillon, Nicole Grobert, Gas analysis of an aerosol-assisted CVD reactor for optimising MWCNT synthesis (poster), *NanoteC 12*, Brighton – United Kingdom, 29.8-1.9.2012.

- **Manuscripts submitted / in preparation**

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- [11] Seyyed Shayan Meysami, Antal A. Koós, Nicole Grobert, Quantitative gas analysis of aerosol-assisted chemical vapour deposition synthesis of carbon nanotubes, manuscript in preparation.
- [12] Seyyed Shayan Meysami, Nicole Grobert, Method and apparatus for preparation of standard samples for quantitative gas analysis, manuscript in preparation.

List of abbreviations and symbols

CVD	Chemical vapour deposition
CCVD	Catalytic chemical vapour deposition
AACVD	Aerosol-assisted chemical vapour deposition
SPCVD	Spray pyrolysis chemical vapour deposition
PECVD	Plasma-enhanced chemical vapour deposition
CNTs	Carbon nanotubes
SWCNTs	Single-wall carbon nanotubes
DWCNTs	Double-wall carbon nanotubes
MWCNTs	Multi-wall carbon nanotubes
CNBs	Carbon nanobuds
OM	Optical microscopy
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
ESEM	Environmental scanning electron microscopy
ETEM	Environmental transmission electron microscopy
ESD	Environmental secondary detector
TGA	Thermogravimetric analysis
XRD	X-ray diffraction
EDX	Energy-dispersive X-ray spectroscopy
MS	Mass spectrometry
QMS	Quadrupole mass spectrometry
MBMS	Molecular beam mass spectrometry
GCMS	Gas chromatography–mass spectrometry
TIC	Total ion current (chromatogram)
SIM	Selected ion monitoring (chromatogram)
FID	Flame ionisation detector
QIC	Quartz capillary inlet
TCD	Thermal conductivity detector
LRI	Laser reflection interferometry
RBM	Radial breathing mode (Raman)
PTFE	Polytetrafluoroethylene
m_a	Atomic mass (amu)
D	Density (g/cm ³)
γ	Surface tension (N/m)
η	Viscosity (Pa·s)
ρ	Electrical resistivity (Ω·m)
λ	Thermal conductivity (W/(m·K))
T_m	Melting point (°C)
T_b	Boiling point (°C)
Z	Atomic number
χ	Electronegativity
d_{C–C}	Carbon-carbon distance in graphene lattice (Å)

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Chapter 1. Introduction

1.1. Outline

In recent years, a striking variety of nanomaterials with astonishing properties were reported and a plethora of applications envisaged. However, most of the applications require materials with well-defined and uniform characteristics. In particular, large quantities of uniform carbon nanotubes (CNTs) of high quality are much sought after for the increasing number of CNT applications [1–8]. Aerosol-assisted chemical vapour deposition (AACVD) [9,10] is arguably the most industrially applicable technique for the large scale synthesis of vertically-aligned CNTs as it is suitable for the continuous and simultaneous injection of catalyst and carbon precursor/s [11–44]. Hence, it requires no additional catalyst preparation. Moreover, AACVD is rather versatile and can be used to generate various types of nanotubes, including conventional [11–24,26–30,32,33,35,37,39–43,45–47], doped [14,15,19,25,34,36–38,40,44], metal-filled [31] and metal-coated [25] multi-wall (MWCNTs), double-wall (DWCNTs) [48] and single-wall carbon nanotubes (SWCNTs) [49,50] with minimal need for purification.

Despite its potential and unlike the other counterpart techniques [51], AACVD is not yet deployed for the commercial mass production of MWCNTs. This is perhaps due to the fact that current AACVD setups do not operate continuously [11–20,22–32,34–44]. Moreover, the fabrication of uniform CNTs with predefined properties using the AACVD method remains a primary concern; CNTs are typically mixed with other products such as amorphous carbon [50] and catalyst agglomerates [5] and often exhibit a broad range of diameters, lengths [33] and residual catalyst contents [28].

In this work, the AACVD of MWCNTs has been investigated from different angles. The main objective of the study was to improve the efficiency of the process and the

synthesis rate while retaining the high quality of MWCNTs. After a review of the recent literature in this chapter, the issues related to the inhomogeneity of the products are addressed in chapter two. It is shown how mapping the reactor reveals the reason behind the inhomogeneity of CNTs throughout the reactor. A number of techniques such as electron microscopy, Raman spectroscopy and thermogravimetric analysis (TGA) were used to characterise the products synthesised throughout the reactor. The third chapter covers the topics related to the online monitoring of the reactor and effect of the composition of the precursor on a variety of parameters such as the mass and quality of synthesised products and the conversion yield of the precursor. The third chapter shows why *in-situ* qualitative and quantitative gas analysis is an excellent tool for monitoring the activities of the reactor and how it could be utilised to understand some of the fundamental aspects of the thermocatalytic cracking of precursors down to carbon species required for growth of CNTs. The forth chapter summarises the attempts towards upscaling the AACVD method for synthesising free-standing and on-substrate large area (up to 90 cm²), mm-thick carpets of MWCNTs. The main research outcomes are summarised in chapter five. The proposed future works are also discussed in chapter 5 which include the application of mapping and *in-situ* gas analysis of the AACVD setup in design of advanced reactors for large-scale AACVD of MWCNTs.

The main body of this dissertation (chapters 2 – 4) is adapted from 2 published articles and 2 manuscripts. Each chapter contains dedicated introduction, experimental, results, discussions and conclusions. Figure 1 depicts how different sections of the dissertation are interlinked.

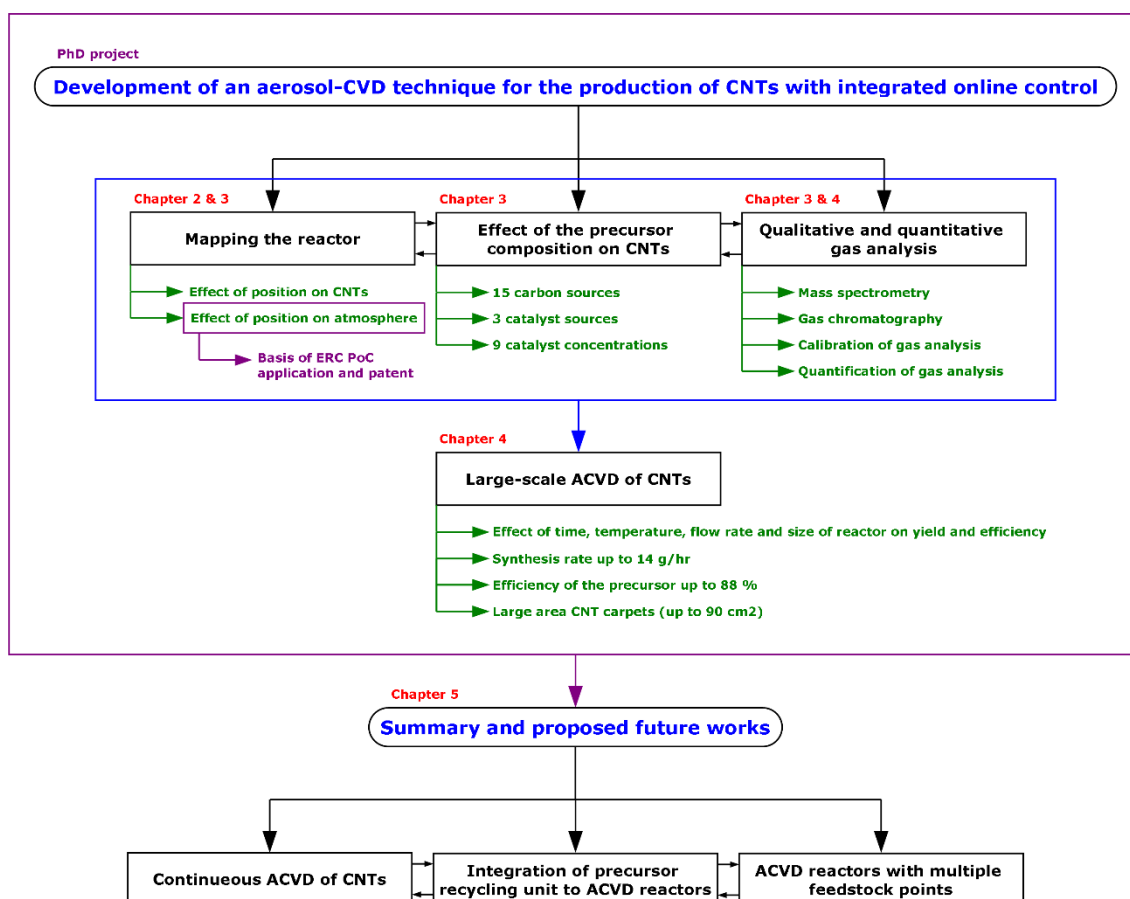


Figure 1. Flowchart of the PhD project and proposed future works.

1.2. Literature review

1.2.1. From Buckminsterfullerene to carbon nanotubes

Carbon is the 6th and 17th most abundant element in the universe and the Earth's crust respectively [52]. It is also one of the main building blocks of the life on earth¹. Table 1 summarises some of the characteristics of carbon.

Table 1. Main characteristics of carbon [52,53].

Origin	Fusion of three helium nuclei	Symbol	C
m_a	12.0107 amu	Z	6
Electronic configuration	$1s^2 2s^2 2p^2$	Natural state	Solid
$D_{\text{diamond}}, D_{\text{graphite}}$	3.5, 2.3 g/cm ³	$T_{m, \text{diamond}}$	~ 3700 °C
$\sigma_{\text{diamond}}, \sigma_{\text{graphite}}$ (parallel to the planes)	$10^{18}, 2.5 - 5 \times 10^{-6} \Omega \cdot m$	$T_{b, \text{diamond}}$	~ 4200 °C
$\lambda_{\text{diamond}}, \lambda_{\text{graphite}}$ (at 25°C)	900 – 2320, 119 – 165 W/(m·K)	Oxidation states	+2, +3, +4
Relative abundance of isotopes	¹² C: 98.89 % ¹³ C: 1.11 %	χ	2.5

Owing to the electronic configuration of carbon, its atomic orbitals can hybridise in a number of ways. The unique characteristics of the bonds between hybridised sp^2 and sp^3 orbitals in carbon explains why it exists in a variety of allotropes and morphologies with completely different structures and properties.

Diamond, graphite, buckminsterfullerene, CNTs and graphene, are the most well-known crystalline allotropes and morphologies of carbon. Unlike the diamond, in which the atomic orbitals undergo sp^3 hybridisation, in graphene and related allotropes such as CNTs, the atomic bonds are formed between the sp^2 orbitals. The honeycomb configuration of atoms in the lattice of graphene and related allotropes originates from

¹ Carbon compounds are extraordinarily numerous, which is perhaps why carbon is the basic element for formation of life's complex molecules. The basic molecules such as the amino acids which define the life are entirely based on carbon and its unique bonding ability to other fundamental life elements. Carbon also plays the central role in one of the most crucial natural cycles which sustains the life, known as the *carbon cycle* [235]: absorption of carbon dioxide by the plants through the photosynthesis, direct and indirect consumption of vegetation by herbivores and carnivores, oxidation and release of carbon dioxide back to the atmosphere.

the 120° angle between the sp^2 orbitals. The mobile electrons in the unhybridised $2p$ orbitals make graphite, as the most naturally-abundant graphene-induced allotrope of carbon, conductive (see table 1).

Buckminsterfullerene was first discovered in 1985 by Kroto *et al.* [54]. They synthesised C_{60} and C_{70} (fullerite) molecules by vaporising a rotating graphite disk under helium atmosphere which acted as a collision media for vaporised materials to cluster in the chamber. They showed that the pressure of helium and the integration time in which the gas and molecules are together, have a substantial effect on the abundance of different molecules detected by a mass spectrometer. Higher pressures of helium was reported to improve the abundance of C_{60} and C_{70} molecules. Figure 2a and 2b show the distribution of clusters with different number of carbon atoms forming at low (< 10 torr) and high (760 torr) pressure of helium respectively. Furthermore, they prolonged the integration of clusters in the reactor by adding a *cup* at the end of the vaporising chamber which resulted in a dramatic increase of the abundance of C_{60} molecules (figure 2c).

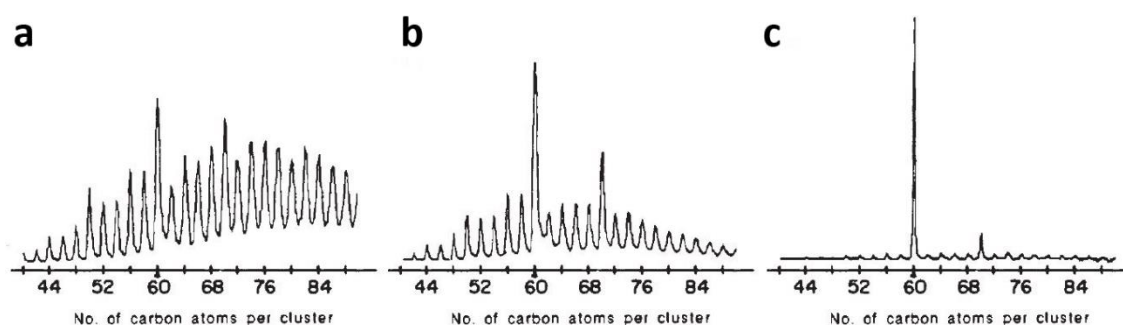


Figure 2. Mass spectrometry (MS) of the effect of the helium pressure and integration time on the abundance of synthesised C_{60} molecules; a) Helium pressure: < 10 torr; b) Helium pressure: 760 torr; c) Using a *cup* to prolong the integration of clusters [54].

This work was particularly outstanding as it presented a rather simple recipe to extract the carbon atoms from an inexpensive source (graphite) and to rearrange them into carbon nanomaterials. Five years later, Krätschmer *et al.* [55] improved the

synthesis yield of fullerite by utilising an arc discharge kit. They substantially increased the production yield and extensively characterised the fullerenes. Figure 3 is one of the earliest transmission electron micrographs of fullerene crystals.

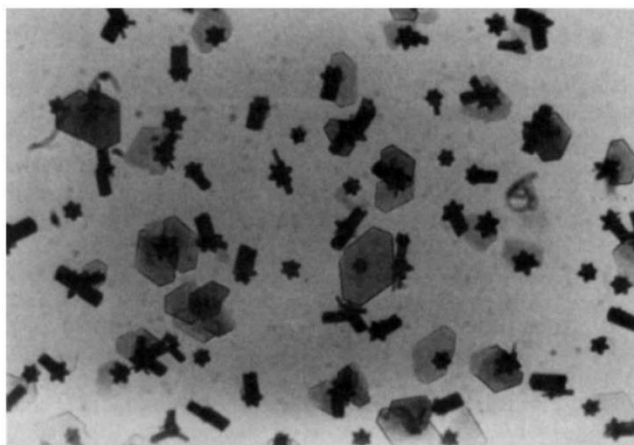


Figure 3. Transmission electron micrograph of C₆₀ crystals [55].

Apart from reporting inexpensive reproducible synthesis recipes, the application of MS in these two articles for confirming the existence and measuring the abundance of fullerene is very important. They are the classic examples of using an online monitoring system for optimising a reactor for synthesis of carbon nanomaterials. Although CNTs do not have distinct molecular masses and are far heavier than C₆₀ and hence cannot be isolated by the current mass filters, the MS remains a powerful method to understand the fundamentals of the growth of CNTs.

In 1991, Iijima reported the structure of CNTs grown in a DC arc discharge carbon vaporiser operating in argon atmosphere [56]. Apart from the amorphous carbon covering the vessel, he observed that the deposit growing on the graphitic negative electrode was rich in what he called ‘helical microtubules of graphitic carbon’. His astonishing micrographs (figure 4a) revealed the *multi-wall* nature of these coaxial tubes. Although he was not the first to synthesise and observe these CNTs, he is widely considered to be the first to describe the structure precisely [57]. Radushkevich and

Lukyanovich's efforts [58] should also be respected for being acutely aware of chemical vapour deposition (CVD) -grown carbon nanotubes and nanofibers and presenting fairly clear transmission electron micrographs (figure 4b, the catalyst particles on the top of the tubes are the signature of the CVD method). Moreover, prior to Iijima's paper, Tibbetts used CVD and synthesised MWCNTs directly on transmission electron microscope (TEM) grid and described the mechanism of the growth [59] (figure 4c). In 1988, Endo reported a CVD process for production of MWCNTs [23]. This article was particularly important as it introduced an inexpensive liquid-precursor CVD method for synthesis of large quantities of MWCNTs. He also presented fascinating high-resolution TEM images (figure 4d) and proposed a mechanism for growth of MWCNTs (figure 4e). In 1989, Baker [60] showed very close structures to CNTs and studied the kinetics and the mechanism of their growth (figure 4f).

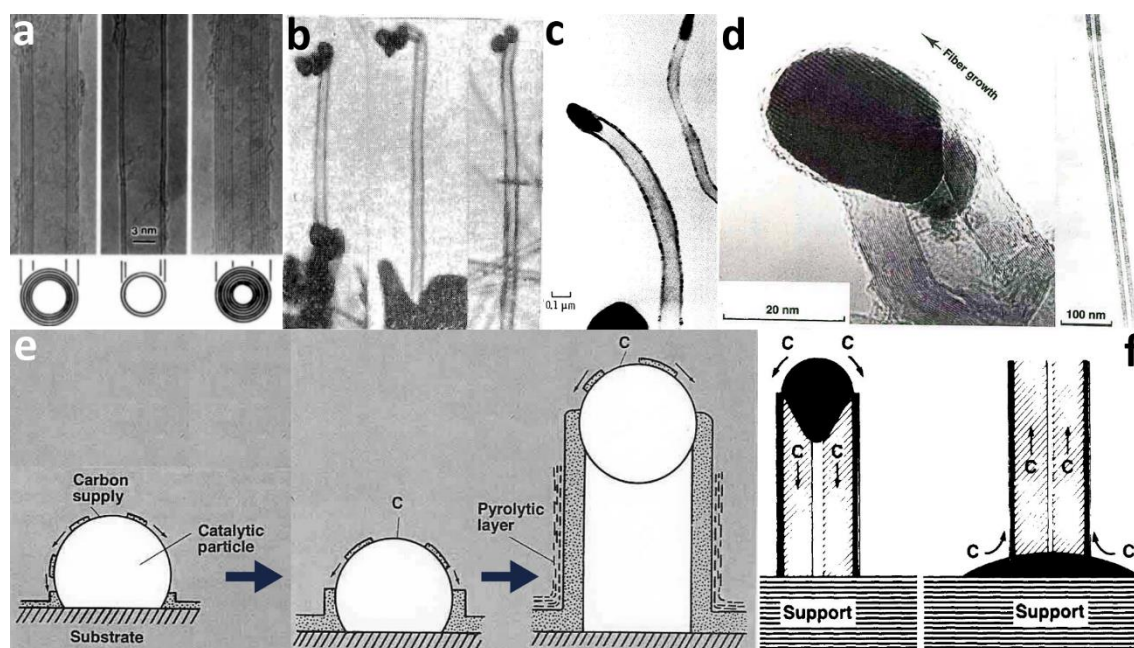


Figure 4. Transmission electron micrograph of a) Arc-discharge MWCNTs [56]; b) CVD MWCNTs [58]; c) CVD MWCNTs directly grown on a TEM grid [59]; d) Liquid-precursor CVD MWCNTs [23]; e) Tip-growth mechanism [23]; f) Tip and base-growth mechanisms [60].

1.2.2. Structure, properties and applications of carbon nanotubes

The lattice structure of graphene can be defined as an infinite two-dimensional set of individually separate points generated by distinct translation operations known as lattice vectors. The vectors connect two crystallographically equivalent points. Any lattice vector can be resolved into two basic non-resolvable vectors known as the unit lattice vectors:

$$\vec{C} = n.\vec{a}_1 + m.\vec{a}_2; \quad (\text{Equation 1})$$

$$|\vec{a}_1| = |\vec{a}_2| = 2 \sqrt{d_{C-C}^2 - \left(d_{C-C}/2\right)^2} = \sqrt{3} d_{C-C} = 2.46 \text{ \AA}; \quad (\text{Equation 2})$$

$$n \text{ \& } m \in \mathbb{Z}; \quad d_{C-C} = 1.42 \text{ \AA} [61].$$

Wherein, $\vec{a}_1$ and $\vec{a}_2$ are the unit lattice vectors, $\vec{C}$ is the lattice vector and d_{C-C} is the carbon-carbon distance in the graphene lattice. Figure 5 depicts a lattice vector in blue and the unit lattice vectors in red and yellow.

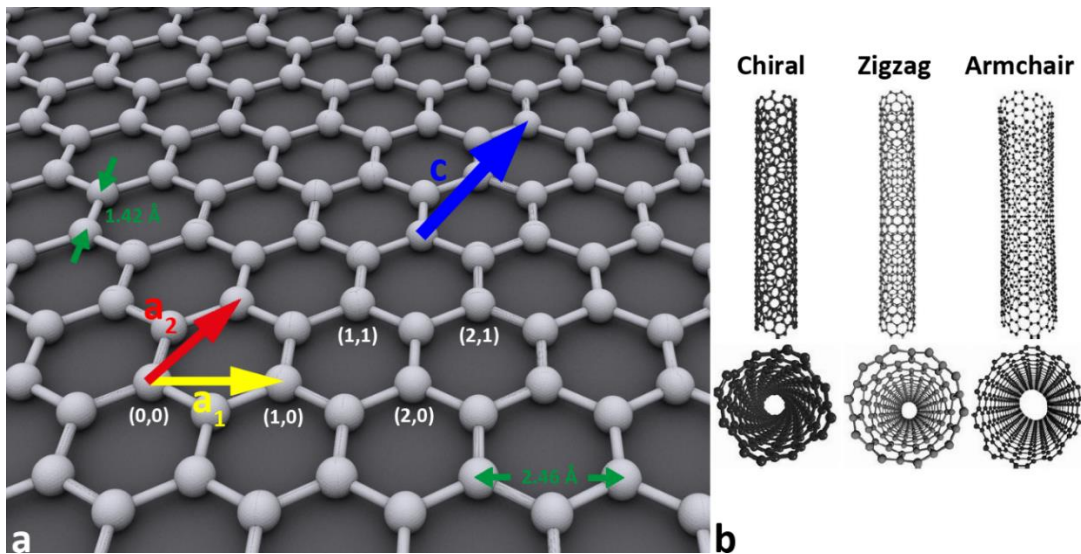


Figure 5. a) Graphene lattice with indexing notation [62], lattice vector ($\vec{C}$), and unit lattice vectors ($\vec{a}_1$ & $\vec{a}_2$); b) Possible chirality of SWCNTs: armchair ($n = m$, $\theta = 30^\circ$), zigzag ($m = 0$, $n > 0$, $\theta = 0^\circ$) and chiral ($0 < |m| < n$, $0 < \theta < 30^\circ$) [63].

A single-wall carbon nanotube (SWCNT) can be considered as a rolled-up sheet of graphene. In other words, if the beginning and the end of a given lattice vector are superimposed, the resulting structure is a SWCNT. Therefore the absolute value of the lattice vector would be the circumference of the tube:

$$|\vec{C}| = 2.46 \sqrt{|n|^2 + nm + |m|^2} \text{ \AA} [64]; \quad (\text{Equation 3})$$

And the diameter of the CNT would be:

$$d_{\text{CNT}} = |\vec{C}| / \pi = 0.78 \sqrt{|n|^2 + nm + |m|^2} \text{ \AA}. \quad (\text{Equation 4})$$

Although an infinite number of lattice vectors can be imagined in a graphene lattice, derived SWCNT structures are finite. Depending on the (n,m) index, only three distinct groups of SWCNT structures could exist: *armchair*, *zigzag* and *chiral* (Figure 5b). *Chiral angle* is a mathematical term which can be used instead of (n,m) index to describe the structure of CNTs and is defined as the angle between the lattice vector $\vec{C}$ and the zigzag direction (parallel to $\vec{a}_1$ in figure 5a):

$$\theta = \tan^{-1} \left[\frac{\sqrt{3} m}{2n + m} \right]; \quad (\text{Equation 5})$$

$$0 \leq |\theta| \leq 30^\circ [65].$$

The chirality dictates the band gap of SWCNTs having a notable effect on their electrical properties [66,67]. The Young's modulus and Poisson's ratio are also controlled by the chirality [68]. Due to the small diameter of SWCNTs (typically < 10 nm), measuring the mechanical properties in a standard and reproducible way remains challenging. The fact that the SWCNTs can have a broad range of defect density and particularly, different chirality angles, introduces another significant amount of uncertainty in experimental measurements. Producing SWCNTs with similar

morphology, defect density and chiral angles using the CVD methods has remained an arduous task in the community for more than a decade.

Carbon NanoBuds (CNBs) are single-wall carbon nanotubes with fullerenes chemisorbed or covalently bonded to their outer surface (figure 6) [69]. They have enhanced field-emission properties [69] and it has been suggested that the fullerenes could act as anchors for SWCNTs in composite materials [70]. Raula *et al.* [71] reported selective functionalisation on the fullerene part of the CNBs and He *et al.* [72] attributed a shift of the radial breathing modes (RBMs) [73,74] in the Raman spectra of CNBs to the covalently bonded fullerenes. The mechanism of the growth of CNBs is unknown and the scale of the production is limited by the very narrow windows of specific experimental parameters required to synthesise them. Moreover, they are often accompanied by SWCNTs. Therefore, it is not surprising that they are not extensively investigated yet.

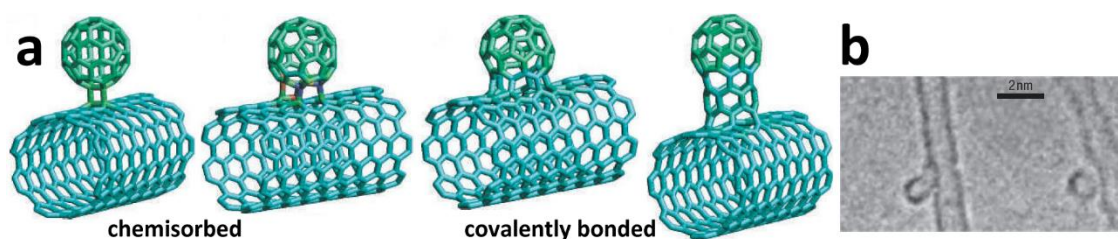


Figure 6. a) Schematics of C₆₀ molecules chemisorbed and covalently bonded to the outer surface of a SWCNTs (carbon Nanobuds) [69]. b) TEM image of two carbon NanoBuds [69].

Depending on the structure, MWCNTs show metallic and semiconducting behaviour [75–78]. Moreover, their mechanical properties have been thoroughly studied [79–82]. The Young's modulus of arc-discharge MWCNTs is around 1 TPa [79,83,84]. However, CVD-grown MWCNTs are far less stiff with a broad range of reported Young's moduli (10-100 GPa [85], 50-350 [79,86]). The large difference between the stiffness of CNTs produced by arc-discharge and CVD methods are due to the

inevitable presence of relatively large number of defects, structural disorders (*e.g.* knees and twists) and inclusions (*e.g.* catalyst particles) in CVD-grown MWCNTs which could not be significantly healed even by annealing the tubes at temperatures as high as 2400 °C [85].

Hence, at first glance, it can be assumed that CVD-grown MWCNTs are as stiff as most of the metals (50 – 300 GPa [87]). However, it is noteworthy that the CVD-grown MWCNT materials (assembly of individual tubes) cannot be understood as real bulk materials and thus their properties are not comparable to other common engineering materials such as metals [88,89]. Although CNTs have astonishing mechanical strength at nano scales, they cannot withstand tensions applied in typical macroscopic engineering applications. In spite of the fact that individual and pure CNT macrostructures such as carpets [90], macrotubes [91] and yarns [92] do not exhibit outstanding mechanical properties at macro scale, they considerably improve the properties of metal [93], ceramic [94] and polymer [95] matrices when used in composites. That is perhaps why CNT-reinforced composites are currently one of the most active topics in the field. Nanotubes toughen the matrices [96,97] by bridging and deflecting the cracks as well as CNT pull out mechanism on the fracture surface [98]. The collapse of CNTs in a matrix during the transfer of external load depends on the catalyst content, purity and defect density of CNTs [99]. Hence, lowering the defect density, residual catalyst content and structural disorders of CNTs could potentially improve the toughness of CNT-reinforced composites [99].

1.2.3. Synthesis of carbon nanotubes

Carbon nanotubes are synthesised through bottom-up/self-assembly approaches. An atomised carbon source can be transformed into CNTs if a number of criteria are met. The individual impact of all the experimental parameters during the growth of CNTs is not fully understood yet. However, the effect of these parameters on the final properties of CNTs and their growth mechanisms are well investigated for nearly all the synthesis methods [57].

As mentioned above, the first step in the synthesis of CNTs is excitation and extraction of carbon atoms from a carbon source. There are three practical methods reported for atomisation of a carbon source for synthesis of CNTs: *arc discharge evaporation*, *laser vaporisation* and *chemical vapour deposition* which will be briefly reviewed in this section.

The arc discharge evaporation technique was reported for production of MWCNTs early in 90s [56]. Figure 7 depicts a typical arc-discharge setup for production of CNTs. The atomisation energy is sourced by an arc discharge which is retained between the anode and cathode throughout the synthesis.

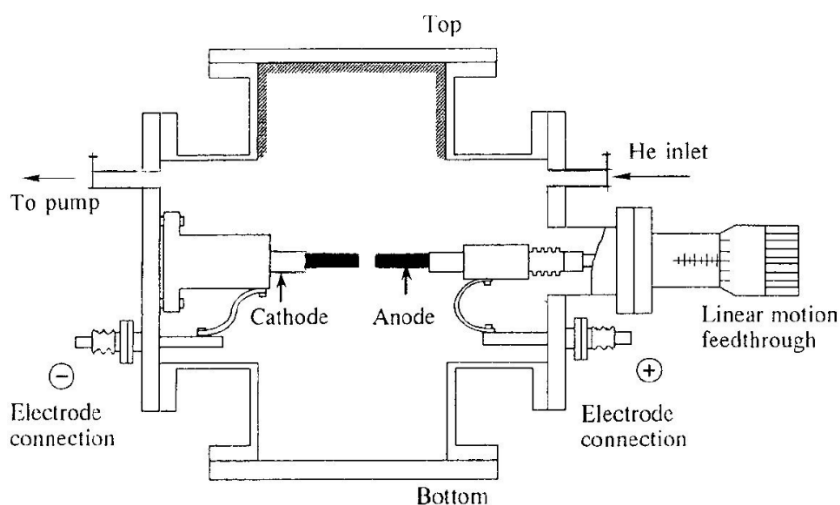


Figure 7. Arc discharge evaporation setup for production of CNTs [57].

The method is based on the high-temperature vaporisation of carbon atoms and formation of a soot-like deposit on the cathode. Different types of tubes including MWCNTs, DWCNTs and SWCNTs have been successfully produced by this approach. Table 2 summarises some of the works in which arc-discharge setups similar to figure 7 were used to produce CNTs.

Table 2. Synthesis of CNTs using arc discharge evaporation technique (catalyst, atmosphere and products).

Type	Catalyst(s)	Atmosphere	Ref.
MWCNTs	Fe, Co, Ni	Air and Ar	[100]
	None	liquid N and deionised H ₂ O	[101]
	Ni, Co, Ti	He	[102]
	None	He	[103]
	Co, S, Pt and C* powder	H	[104]
	Fe ₂ O ₃ , Co ₂ O ₃ , NiO and C powder	N ₂	[105]
	None, Ni and Fe	Deionized H ₂ O, NiSO ₄ , CoSO ₄ , FeSO ₄	[106]
DWCNTs	Iron sulphide, KCl and C powder	H ₂	[107]
	Ni, Co, Fe, S and C powder	Ar and H ₂	[108]
	Fe, Ni, Co and S	H ₂	[109]
SWCNTs	Ni-Co, Co-Y and Ni-Y	He	[110]
	Fe, Ni, Co and C* powder	He	[111]
	Ni/Co/C composite	N ₂	[112]
	None	He	[113]
	Y-Ni alloy (or CaC ₂ /Ni) and C	He	[114]
	Fe ₃ O ₄	H ₂ and Ar	[115]
MW/SWCNTs	None	He and Ar	[116]
	None	H ₂ O	[117]
	Fe	NaCl solution	[118]

*C: graphite

The Effect of the composition of electrodes (*e.g.* presence of catalyst) and the atmosphere of the reactor on the quality of CNTs is the topic of the majority of the works. For instance, water has been shown to improve the quality of tubes [106] and Wang *et al.* [118] reported that a conductive atmosphere (NaCl solution in this case) enhances the homogeneity and stability of the arc. Although this technique is widely known for producing highly-graphitised CNTs (figure 8a), it is unsuitable for mass production. The central part of the arc discharge setup consists of an electrical arc which is generated by transmission of a DC current between two graphite electrodes precisely placed at a certain distance from each other. Most of the power used to generate the arc

is dissipated with water which is used to cool down the whole reactor and in particular the electrodes. Only a fraction of the heat vaporises the graphite and produces a small amount of CNTs. For typical voltages (10 – 35 V) and direct currents (60 – 100 A) [57], a deposit generation rate of 20 – 100 mg/min has been reported which could sustain only for a few minutes [57]. This means that for production of 40 – 200 mg in two minutes, 20 – 100 Whr energy is required. The extreme working temperature ranges (from few to several thousand °C) and the fact that the synthesis cannot be carried out continuously are the main reasons why large-scale producers of CNTs almost exclusively use CVD instead of arc discharge evaporation [119].

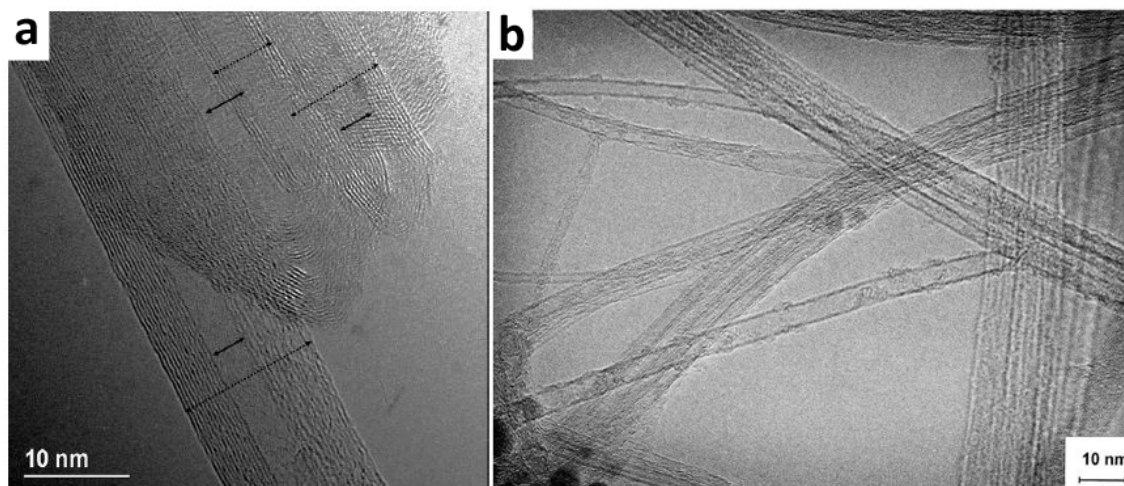


Figure 8. TEM images of a) MWCNTs synthesised by arc discharge evaporation technique [102]; b) Bundles of SWCNTs synthesised by laser vaporisation technique [120].

Another method mostly devoted but not limited to the production of SWCNTs is laser vaporisation. Similar to the arc discharge, it is based on the excitation of the carbon atoms from a graphitic carbon source up to the atomisation energy level and then rearranging them in a medium, mostly an inert gas. The energy is primarily sourced by laser(s) and optionally a heated furnace. The carbon source can contain catalyst elements. The whole synthesis is carried out in a controlled inert atmosphere and the CNTs are collected on a water-cooled rod. In comparison, the production rate and the

working temperature ranges are less than arc discharge technique. The atomisation apparatus used in this technique is rather expensive to run. Therefore, although a variety of high quality tubes (figure 8b) have been successfully produced by this method, similar to the arc discharge evaporation, it is not considered as an economical method for synthesis of large quantities of CNTs. Figure 9 depicts a typical apparatus and table 3 summarises some of the experimental conditions used by some groups.

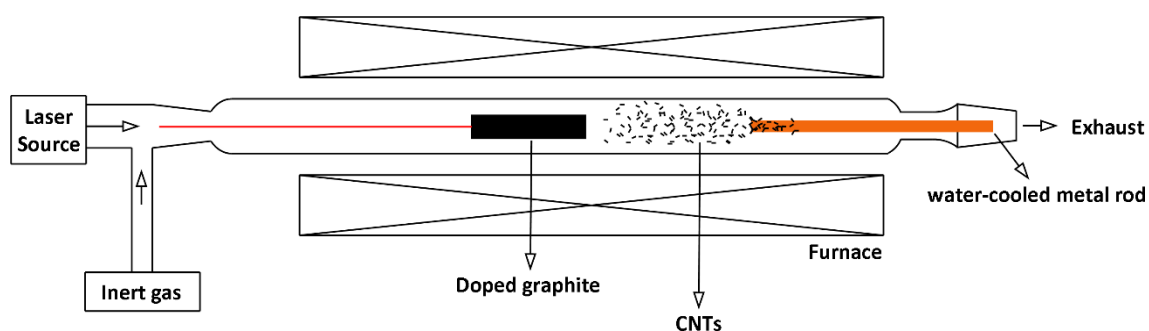


Figure 9. Schematic of a typical laser vaporisation apparatus for synthesis of CNTs.

Table 3. Synthesis of CNTs using laser vaporization technique (synthesised CNTs, laser type, temperature, catalyst and inert atmosphere).

Type	Laser	Reactor T (°C)	Catalyst	Atmosphere	Ref.
SWCNTs	XeCl and Nd:YAG	1000	Ni and Co	Ar	[121]
	CO ₂	ambient	Ni and Y	Ar, N ₂ and He	[122]
	CO ₂	Not mentioned	Co and Ni	Ar	[123]
	Nd:YAG	1150	Co, Ni, FeS	Ar and H ₂	[120]
	CO ₂	1100	Co and Ni	Ar, N ₂	[124]
MWCNTs	Nd:YAG	ambient	Co and Ni	Ar	[125]

Versatility of inexpensive CVD methods for production of CNTs of all types makes them a very good alternative to the synthesis methods mentioned earlier. The numerous amount of works addressing the synthesis, characterisation and application of CVD-grown CNTs reflects this fact. Due to the importance of CVD in general and the fact that this work is about the optimisation of a CVD method for production of MWCNTs, the literature on CVD synthesis of CNTs is reviewed in a separate dedicated section.

1.2.4. Chemical vapour deposition of carbon nanotubes

Vapour deposition refers to the processes wherein gaseous reactant(s) (precursors) meet and react on the surface of a substrate which acts as a reaction template for the synthesis of materials which are different from the precursor(s). A carrier gas with controlled flow rate is normally passed through the reactor to ensure evacuation of gaseous by-products and unreacted precursors. By adjusting the process parameters such as the temperature of the precursor(s) and substrate, partial pressure of the precursor(s) and carrier gas and duration of reaction, the quality of final deposits can be controlled. Therefore, it is a unique method for production of delicate materials such as epitaxial films and nanomaterials. Simply, if the process of adsorption of precursor(s) on the substrate at any stage involves chemical modification of either the substrate or the precursor(s), the process is called *chemical vapour deposition*; otherwise *physical vapour deposition* (PVD). Among these two, CVD can be of particular interest for synthesis of nanomaterials from sources which do not necessarily have the exact chemical composition of the final nanomaterial. Therefore, numerous CVD recipes can be envisaged for growing nanomaterials from a variety of precursors. The versatility of CVD for synthesis of CNTs can be better understood from figure 10 in which different setups with extremely different production scales are shown side-by-side.

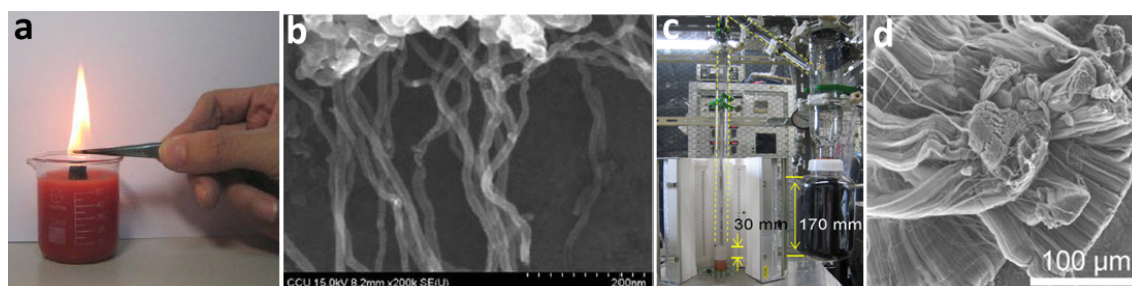


Figure 10. Versatility of CVD for production of CNTs. a) Synthesis of MWCNTs by combustion of a paraffin wax candle [126] with (b) Corresponding scanning electron micrograph; c) Production of

large quantities of MWCNTs in a fluidised-bed reactor [127] with (d) Corresponding scanning electron micrograph.

Most of the CVD processes for synthesis of CNTs are based on the pyrolysis of gaseous hydrocarbons such as alkanes [128–130], alkenes [131–133] and alkynes [134–136]. Heavier hydrocarbons, which are liquid under standard conditions, are often vaporised or atomised before pyrolysis. The liquid precursors are typically atomised using spray injectors or ultrasonic aerosol generators; in which case the methods are normally known as *spray pyrolysis* and *aerosol-assisted chemical vapour deposition* (SPCVD and AACVD) respectively. Atomisation of the liquid precursor in the SPCVD and AACVD setups can be done by nozzles [11,17,22,24,33,43] and nebulisers [10,12–16,18–20,25–28,30–32,34–40,44–46,49,50] which facilitate the control of the precursor feedstock and ensures an effective vaporisation prior to the pyrolysis. The operating temperature is typically around 700 – 1000 °C and MWCNTs are by far the most dominant products. The cracking temperature can be furthermore decreased to 600 – 700 °C using plasma; in which case the method is known as *plasma-enhanced chemical vapour deposition* (PECVD) [137]. Catalysis can significantly increase the pyrolytic conversion of hydrocarbons [39]. Thus, for higher synthesis yields, almost always catalysts are used. That is why the process is more precisely known as *catalytic chemical vapour deposition* (CCVD). Since the size of the catalyst particles define the diameter of CNTs [28,39], they should be less than 100 nm in diameter. The catalyst particles can be introduced inside the reactor by either deposition on the substrate before the synthesis of CNTs or by simultaneous feeding of catalyst source/particles and carbon precursor as in AACVD techniques (see section 1.1). Table 4 summarises some of the reported sources of carbon, catalyst, dopant and operating temperatures in spray pyrolysis and AACVD synthesis of MWCNTs. Benzene derivatives and ferrocene are the most popular carbon and catalyst precursors.

Table 4. Summary of some of the reported sources of carbon, catalyst, dopant and operating temperatures in SPCVD and AACVD synthesis of MWCNTs

Carbon source	Catalyst source	Doping source	Synthesis T (°C)	Product(s)	Ref.
Xylene	Ferrocene	—	675	MWCNTs	[42]
Benzene	Ferrocene	—	850 – 900	MWCNTs	[17]
Benzene	Ferrocene	—	800 & 950	MWCNTs	[24]
Benzene	Ferrocene & nickelocene	—	800	Metal-filled MWCNTs	[31]
Benzene	Ferrocene	—	700 & 900	MWCNTs	[11]
Toluene	Ferrocene	Variety of N-containing hydrocarbons	850	N-MWCNTs	[14]
Toluene	Ferrocene	—	850	MWCNTs	[28]
Toluene	Ferrocene	Triethylborane; benzylamine	800 & 900 – 1100	MWCNTs, N- and B-MWCNTs	[40]
Toluene	Ferrocene	Benzylamine	800, 850 & 900	MWCNTs and N-MWCNTs	[19]
Toluene	Ferrocene	Triphenylsilane, triphenylphosphine & benzylamine	760, 770 & 800	MWCNTs, N-, Si- & P-N-MWCNTs	[15]
Toluene	Ferrocene	—	800	MWCNTs	[30]
Toluene	Ferrocene	—	700 – 760	MWCNTs	[41]
Xylene	Ferrocene	—	850	MWCNTs	[13]
Xylene	Ferrocene	—	820	MWCNTs	[26]
Cyclohexane	Ferrocene	Acetonitrile	700 – 900	MWCNTs & N-MWCNTs	[37]
Tetrahydrofuran	Cobalt nitrate	—	700	MWCNTs	[12]
Pt, Ru or Pd acetylacetonate	Ferrocene	Acetonitrile	800 – 900	Metal-coated N-MCNTs	[25]
—	Tris (acetylacetonato) iron(III)	Acetonitrile, borane pyridine complex	950	B-N-MWCNTs	[34]
—	Ferrocene	Benzylamine	850	N-MWCNTs	[38]
Toluene; cyclohexane	Ferrocene	—	800 & 850	MWCNTs	[18]
Benzene, toluene, xylene, mesitylene & <i>n</i> -hexane	Ferrocene, Cobaltocene and nickelocene	—	800 – 1000	MWCNTs	[16]
Toluene	Ferrocene	—	800 & 850	MWCNTs	[45]
Toluene	Ferrocene	—	850	MWCNTs	[46]
Toluene	Ferrocene	—	800	MWCNTs	[35]
15 hydrocarbons*	Ferrocene	—	800	MWCNTs	[39]
Toluene, Camphor, palm & eucalyptus oil	Ferrocene	—	850	MWCNTs	[27]
Toluene	Ferrocene	—	850	MWCNTs	[21]
Xylene	Ferrocene	—	770	MWCNTs	[47]

* Ethylbenzene, Isopropylbenzene, Toluene, *m*-Xylene, *n*-Butylbenzene, Benzene, Methylcyclohexane, *n*-Heptane, 1,2,4-Trimethylbenzene, *n*-Pentane, Cyclohexane, *n*-Hexane, Cyclohexanone, Diethylbenzene, *n*-Propylbenzene.

The CVD growth mechanism of CNTs is not fully understood yet. However, the vapour-liquid-solid theory developed by Wanger *et al.* [138] and adopted for CNTs by Tibbette [59] appears to be generally accurate. The true physical state of the catalyst particles at the synthesis temperature depends on their size and chemical composition. The melting point of metals are normally suppressed when the size is reduced to nano scale. The melting point of iron nanoparticles with diameter of 10 nm is 900-1000 °C [139]. Moreover, addition of carbon, up to *c.a.* 4 wt%, lowers the melting point of iron by *c.a.* 400 °C (see the iron – iron carbide phase diagram in appendix I). *In-situ* analysis of the deposit during the CVD growth of MWCNTs has shown that iron particles are in fact cementite [38,46,51,140,141]. Hence, one could expect the iron-based nanoparticles to be liquid during the synthesis. However, the activation energies of the CVD growth of MWCNTs measured by Baker *et al.* [142,143] are close to the activation energies of the bulk diffusion of carbon in solid metal particles. These similarities not only suggest that the catalyst particles remain solid during the synthesis but also supports the hypothesis that bulk diffusion of carbon in metal nanoparticles is the rate-determining step. *In-situ* analytical studies have also confirmed the solid state nature of the catalyst particles during the CVD synthesis of MWCNTs [144–147].

The mechanism of SPCVD and AACVD synthesis of CNTs involves multiple steps. Interaction and subsequent cracking of catalyst and carbon sources as well as deposition and coalescence of catalyst particles are important steps which require further investigation. By pyrolysis of metallocenes one can produce MWCNTs even without a hydrocarbon solvent [148–152]. Therefore, it is expected that the carbon atoms required for the SPCVD and AACVD growth of MWCNTs are supplied both by the metallocenes and hydrocarbon solvents. Whether there are separate contributions from metallocenes and hydrocarbon solvents, or the mixture follows a thermocatalytic

cracking route, which is different from the individual components, remains unclear. The study of the interaction of carbon and catalyst sources in liquid and vapour phases, prior to the pyrolysis, not only could explain this uncertainty but also the reason why different hydrocarbons result in different quantities and qualities of MWCNTs.

1.2.5. Online monitoring of chemical vapour deposition of carbon

Herein, *online monitoring* refers to *in-situ* observation of the CVD processes using different analytical methods. Online monitoring is employed to understand the fundamentals of the reactions involved in the process and to provide real-time quality control of products. Depending on which kinetic stage¹ of the CVD is aimed to be monitored online, the analytical method is chosen. For instance, Raman spectroscopy, X-ray diffraction (XRD) and environmental transmission electron microscope (ETEM) can be used to monitor the stages which involve development of the solid phases inside the reactor, whilst gas analysis techniques such as MS and gas chromatography–mass spectrometry (GCMS) can reveal the atomic and molecular interactions in the gas phase. The analytical methods used in this work targeted the kinetic stages where gas phase plays the key role. This is particularly useful for studying the thermal and thermocatalytic conversion of precursors in the synthesis of CNTs. In this section, some of the reports on the online monitoring of CVD reactors are reviewed.

Prior to CNTs, the growth of other allotropes of carbon such as fullerene [54], CVD diamond [153–158] and pyrolytic carbon [159] had been monitored *in-situ*. Figure 11a depicts an example of a diamond CVD reactor with integrated online gas analyser; which in this case is a mass spectrometer with quadrupole mass analyser. As for CVD diamond, there have been a few reports on other types of CVD reactors and gas analysers. Leeds *et al.* [154] utilised a PECVD reactor with integrated molecular beam

¹ For a CVD process, a number of kinetic stages can be imagined: a) Atomisation/vaporisation of the precursor(s); b) Diffusion of precursor(s) into the reactor; c) Adsorption of precursor(s) on the substrate; d) Decomposition of precursor(s) and incorporation into the synthesised product; e) Desorption of by-product(s) and unreacted species to the vapour phase.

mass spectrometer (MBMS) and reported the gas composition of the plasma as a function of microwave power. Since the PECVD is also used for synthesis of CNTs [137], the setup used by Leeds *et al.* [154] (figure 11b) can be considered as a good model for designing a PECVD reactor for synthesis of CNTs with integrated online gas analyser.

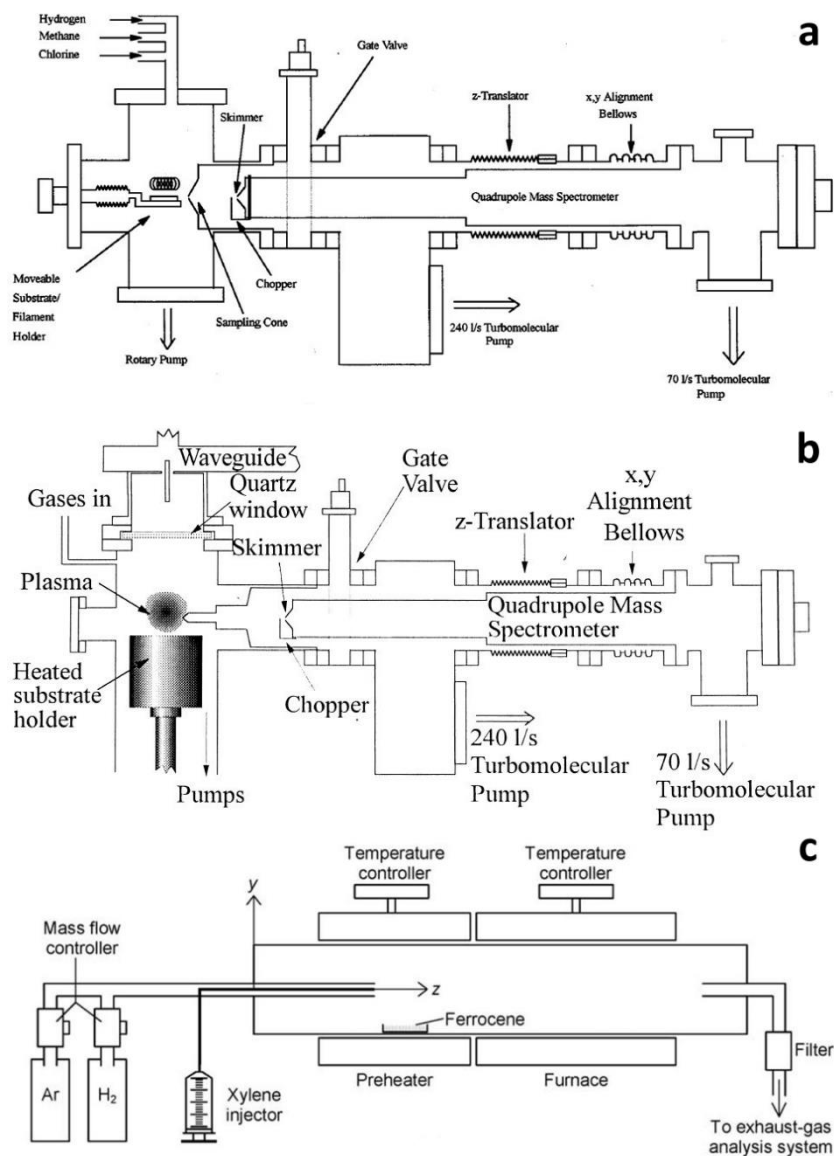


Figure 11. Schematic of a) A diamond CVD reactor with integrated quadrupole MS [153]; b) A diamond PECVD reactor with integrated MBMS [154]; c) SPCVD of MWCNTs using xylene and ferrocene with integrated MS [160].

The sampling inlet in figure 11b consists of a set of orifices connected to a vacuum pump which collect, accelerate, expand, dilute and collimate the analytes (molecules, atoms and radicals) before the ionisation chamber of the MS. The advantage of using this sampling system is that the by expanding through the orifices and succeeding collimation of molecular beam, the analytes are rapidly quenched and transported to the MS. This minimises the condensation and retains the composition of the analytes originally produced by thermocatalytic cracking of the precursor [161,162]. This sampling system seems particularly useful for mapping the gas composition of the CVD reactors for synthesis of CNTs. Rapid transfer of analytes from the reactor might be a way to inhibit any alteration of species as they travel from the sampling point to the analyser.

Raman spectroscopy [163–167] and laser reflection interferometry (LRI) [168] can be used for *in-situ* monitoring of the evolution of the solid phases in a CVD reactor. Mermoux *et al.* [165,166] reported a successful integration of Raman spectroscopy to a diamond PECVD reactor and enhanced the signal using an intensified pulsed laser synchronised with a gated detector. In each cycle, the detector is only responsive to the scattered light when the laser is on. Therefore, the masking effect of the plasma can be avoided [165]. *In-situ* Raman spectroscopy can be particularly helpful for synthesis of CNTs as it can potentially reveal the defect density, doping and secondary growth of CNTs or evolution and deactivation of catalyst layer in AACVD reactors.

Environmental electron microscopy, as one of the most interesting *in-situ* analytical techniques, has improved significantly over the last decade. Environmental transmission electron microscopes (ETEMs) can be equipped with hot stages and gas analysers to simultaneously perform gas analysis and high-resolution microscopy of CVD reactions. Gai *et al.* [169–171] have successfully developed the instrumentation (figure 12) and

performed some case studies on a number of oxides. Charyshkin *et al.* [172] have used an environmental scanning electron microscope (ESEM) to study a diamond CVD reactor. Presence of hot vapours as an unavoidable attribute of CVD processes limits the use of conventional detectors. Instead, environmental secondary detectors (ESD) can be employed [173].

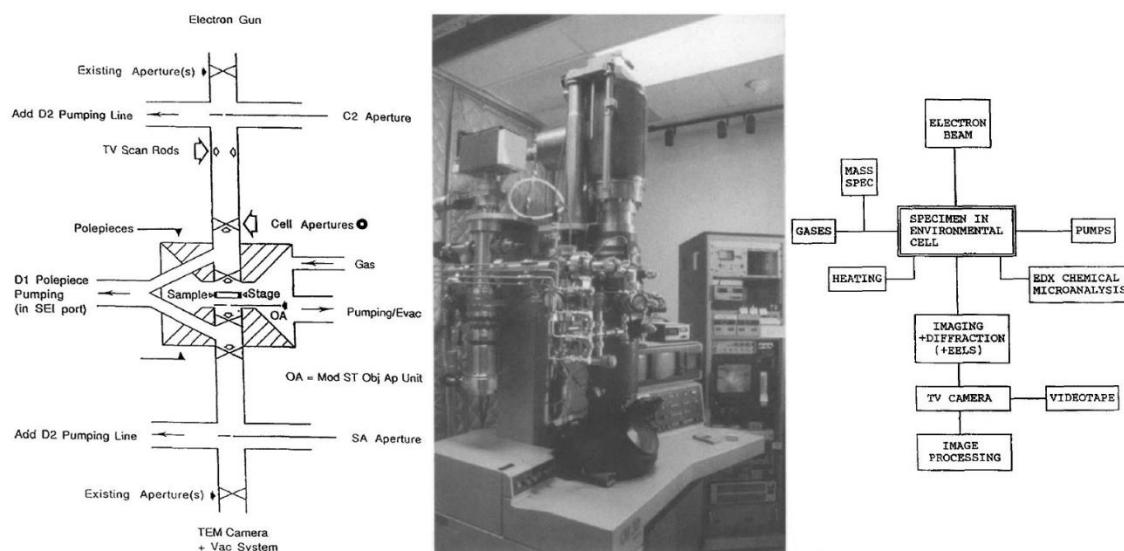


Figure 12. Environmental transmission electron microscope with a hot stage capable of operating at temperatures as high as 1000 °C. A mass spectrometer is connected to the outlet of the stage for simultaneous *in-situ* gas analysis [169–171].

1.2.6. Online monitoring of chemical vapour deposition of carbon nanotubes

Most of the analytical methods reported for online monitoring of CVD reactors for synthesis of CNTs can be categorised into five main groups: a) Gas analysis; b) Environmental electron microscopy; c) Laser-based techniques; d) Electrical analysis and e) X-ray diffraction analysis. This section provides a concise review on these five analytical methods with special focus on *gas analysis* which is used in this work.

Similar to the diamond case, in most of the CVD reactors for synthesis of CNTs with integrated gas analyser [39,160,174–189], an inlet collects the analytes at the exhaust. Figure 11c depicts a typical CVD setup for synthesis of CNTs with integrated gas analyser. Meshot *et al.* [183] used a hot plate CVD apparatus with a pre-heater running on acetylene and reported the gas composition of the reactor as a function of pre-heater and hot plate temperature. Their results show that there is a significant increase of methane abundance when the substrate and preheater are heated. Moreover, some heavier hydrocarbons such as benzene are created during the CVD experiment [181,183]. The article [183] is also well supported by the results of systematic studies on the effect of experimental parameters such as temperature and time on some of the characteristics of CNTs. Therefore, it is one of richest reports on the topic. The work by Kuwana *et al.* [160] is also notable and their experimental approach is quite comparable to the current work. They used xylene/ferrocene precursor and measured the abundance of the main species in the reactor and compared them against the calculated values. It is shown that in the presence of iron nanoparticles at 700 °C, xylene primarily cracks to toluene, benzene and methane which is in agreement with other reports [39]. Tian *et al.* [177] and Kim *et al.* [187] studied the thermocatalytic cracking behaviour of benzene in

the presence of Fe–Co/ γ -Al₂O₃ and Al–Fe–Mo triple catalyst layer respectively and reported the hydrocarbon fragments formed during the synthesis such as CH₄, C₂H₂, C₅H₉, C₆H₉ and C₆H₁₃. Mao *et al.* [174] have also conducted an extensive study on the composition of the plasma in a PECVD reactor for synthesis of MWCNTs. Gas chromatography coupled with different detectors provides another powerful gas analysis technique capable of precise qualification and quantification of the atmosphere of the CVD reactors. The advantage of this technique is the separation of analytes prior to detection. Hence, overlapping fragments in the mass spectra can be avoided. Nessim *et al.* [189] have utilised the same hot plate CVD apparatus reported elsewhere [183] and performed an extensive online gas analysis using a gas chromatograph coupled with three detectors for identification of different classes of analytes. For detection of volatile hydrocarbons such as alkane and aromatic compounds, they used a flame ionization detector (FID) [190]. For detection of light inorganic gases (CO₂, He and H₂), thermal conductivity detector (TCD) was used and polycyclic aromatic hydrocarbons and undefined carbonaceous species were detected using a mass spectrometer. Detection of different classes of analytes by different detectors is a well-established approach in studies of pyrolysis and thermal cracking of hydrocarbons. Froment *et al.* [191–193] have thoroughly explored the topic.

One of the earliest ETEM studies of the CVD growth of CNTs was reported by Helveg *et al.* [144]. They used a Philips CM300 FEG TEM and published a 10-second video, showing the CVD growth of an individual CNT. According to the paper, in a H₂/CH₄ atmosphere at around 500 °C, the nickel nanoparticles constantly deform and are actively mobile. The deformation seems to be a periodic elongation/contraction process. Figure 13 shows a set of recorded frames.

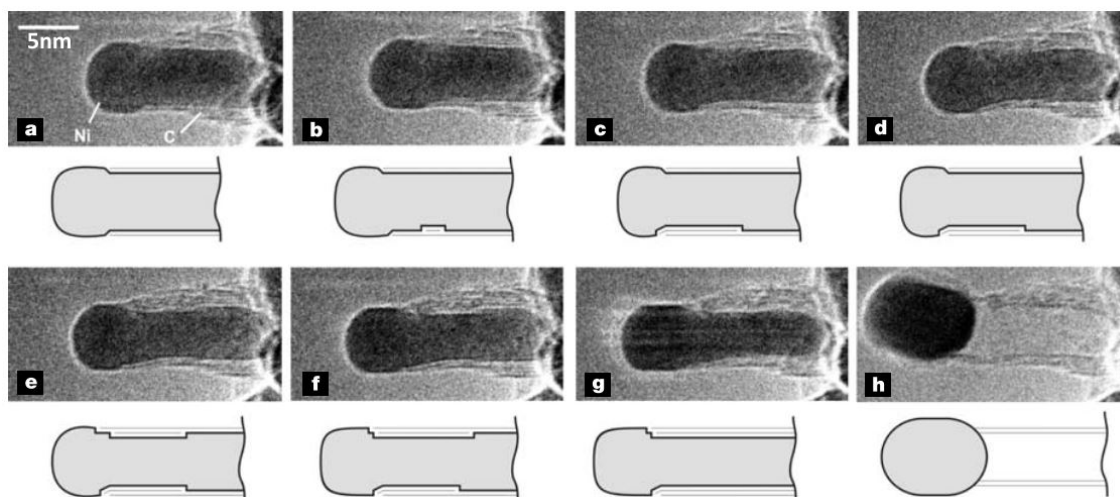


Figure 13. Environmental transmission electron microscopy of CVD tip-growth of a CNT in a H_2/CH_4 atmosphere at around 500 °C. The nickel nanoparticle dissociates from the substrate and deforms [144].

In this setup, the synthesis was carried out under relatively low pressure under a constant emission of electron beam. Therefore, the *in-situ cell* and the conventional CVD reactors cannot be considered the same. However, the article remains a valuable demonstration of CVD growth of CNTs, in action, for the first time. In a similar study by Yoshida *et al.* [145], using acetylene and iron carbide nanoparticles, base-growth of MWCNTs and SWCNTs was reported. The ETEM is currently an active topic for online characterisation of CNTs [141,144,145,147,194–198].

Laser-based analysis of CVD refers to any online characterisation method in which a quality of CNTs is monitored using illumination of a primary laser beam and detection of the secondary beam. Comparing the intensity (in case of reflection) or the wave number (in case of Raman scattering) of the primary and the secondary beams can provide useful information about specific characteristics of CNTs. Geohegan *et al.* [199] and Kim *et al.* [200] have reported similar techniques to measure the growth rate of CNTs based on the intensity of reflected laser beam. The longer the CNTs grow, the less reflectivity is observed. This online monitoring technique can be particularly useful,

if precise thickness of CNT carpets is required. Raman spectroscopy has been also integrated to CVD reactors for *in-situ* observation of the growth and graphitisation of CNTs [201,202].

The growth of individual MWCNT can be also monitored by passing a current through the MWCNTs in a circuit [203] which is an example of *in-situ* detection of the growth of MWCNTs using an electrical analysis technique.

In-situ XRD of the growth of CNTs is a recent reported online analytical technique. The article by Landois *et al.* [140] is particularly important to mention as they integrated an X-ray diffractometer to an AACVD reactor similar to the setup used in this work. Their results show a gradual formation of cementite as a result of thermocatalytic cracking of toluene and ferrocene at 850 °C. The topic is expected to develop in the coming years.

1.3. Conclusions

Different characterisation techniques have been successfully integrated to CVD reactors for synthesis of CNTs. Among them, ETEM and gas analysis are the most popular methods. ETEM has been a primary tool for understanding the mechanism of CVD growth of CNTs since early 2000s. Although this technique has the fundamental advantage of being a *direct observation tool* with minimal requirement for data processing, it cannot be integrated to the conventional CVD reactors. On the other hand, the gas analysers can be mounted easily on almost any type of CVD reactors and can instantly describe the atmosphere. For synthesis of CNTs, the drawback of using gas analysers is that they do not provide direct information from the solid phases *i.e.* CNTs and catalyst particles. However, *in-situ* XRD analysis and Raman spectroscopy are powerful techniques for analysing the solid phases. Therefore, a combination of different *in-situ* techniques is required for precise description of all the aspects of the system.

In-situ gas analysis of AACVD reactors for synthesis of MWCNTs has not been fully explored by the community yet. It is still unclear how *in-situ* gas analysis can be used to actually improve the quality and production rate of the MWCNTs in AACVD reactors. Moreover, a systematic investigation on the effect of different experimental parameters on the atmosphere of AACVD reactors is missing. The hydrocarbons used in AACVD of MWCNTs are normally heavier than ones used in other gas-based CVD techniques. Hence, the mechanisms of thermocatalytic cracking of the precursors in AACVD setups are presumably complex and involve formation of a variety of hydrocarbon fragments. These mechanisms are not fully studied yet and require further investigation.

Chapter 2. Aerosol-assisted chemical vapour deposition of carbon nanotubes

2.1. Introduction

As mentioned in section 1.1, fabrication of uniform CNTs with predefined properties in large quantities using the AACVD methods is currently a challenge in the CNT community. This chapter¹ summarises the results of a study on a widely used AACVD setup whereby two interconnected experimental parameters: *temperature* and *catalyst content* are investigated. The study is aimed at explaining how the variation of the temperature and catalyst concentration across the reactor results in the formation of different nanomaterials. The approach in understanding the system was to simplify it by dividing the reactor into small sections and then characterise the nanomaterials produced with respect to their location within the reactor. This approach allows us firstly to correlate growth parameters and nanotube morphologies/properties and secondly, it helps us to understand the reasons behind the formation of different structures. The majority of previous reports addressing the influence of experimental parameters on the properties of CNTs characterise batches of CNTs collected from specific position inside the reactor (*e.g.* the middle of the reactor where the temperature profile is at a given maximum value (plateau) [13,45]). Alternatively, products grown throughout the reactor are often mixed and sampled randomly for characterisation [40] whilst extensive and position-sensitive characterisation of CNTs from different reactor zones is not available.

¹ Some parts of this chapter are adapted from a published journal article; Meysami *et al.*[35].

2.2. Experimental

CNTs were synthesised using an AACVD system consisting of a piezo-driven aerosol generator (RBI Pyrosol 7901) and a quartz tube (Robson Scientific; 80 cm long; 21 mm inner diameter; 1.5 mm thick with B19/26 socket and cone connections) placed inside a single-zone horizontal tubular furnace (Elite Thermal Systems; 60 cm long; 4 cm inner diameter; N-type (Nicrosil/Nisil) thermocouple; Eurotherm 2416 temperature controller). Prior to the synthesis of CNTs, the temperature profile of the reactor was measured at 800 °C using a K-type (Chromel/Alumel) thermocouple under an argon (BOC zero grade 270050; 99.999% purity) flow rate of 1.000 L/min (Brooks mass flow controller). For the growth of CNTs, the aerosol unit was filled with a precursor solution containing 95 wt.% toluene ($C_6H_5CH_3$; Fluk; 99.7%) and 5 wt.% ferrocene ($C_{10}H_{10}Fe$; Sigma-Aldric; 98%; purified by sublimation at 95 °C) and connected to the quartz tube. Thirteen quartz substrates (UQG Optics; 50 mm long, 10 mm wide and 1 mm thick) were cleaned as described in the following and placed end-to-end inside the quartz tube. Cleaning procedure of the substrates: a) Baking in air at 850 °C for 2 hours; b) Washing with detergent; c) Dipping in hydrofluoric acid (MicroChem; G/0254; 10%) bath for 3 hours; d) Washing with soap and water; e) Annealing in argon at 900 °C for 15 hours; f) Ultrasonic treatment in ethanol for 15 minutes followed by another 15 minutes in acetone; g) Drying at 80 °C for 30 min. Figure 14 depicts a schematic of the experimental setup with the position of the substrates whilst figure 23a shows the corresponding temperature profile of the reactor. Prior to the growth, the aerosol generator chamber was flushed with argon at room temperature. When the reactor reached 800 °C and the temperature stabilised, the aerosol generator was turned on and the amplitude and frequency were optimised to visually gain the densest aerosol which was immediately guided inside the reactor using an argon flow of 1.000 L/min. After 15

minutes, the aerosol generator was switched off, cooled under argon flow, and the substrates were carefully removed for characterisation. Throughout the whole experiment, an acetone bubbler was connected to the end of the quartz tube and before the exhaust to capture the soot and other by-products flying out of the reactor and also to prevent any potential backflow of air.

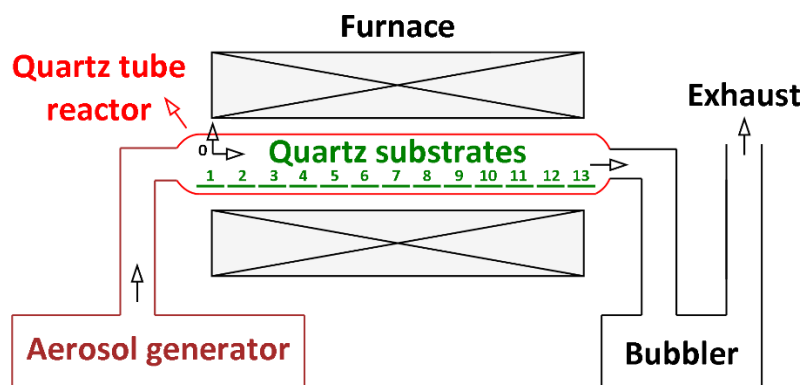


Figure 14. Experimental setup. The entrance where the aerosol enters the reactor is defined as the ‘zero point’; thirteen substrates were placed along the deposition area ranging from -55 to 595 mm. Position of the substrates (beginning, end) in mm: 1: (-55, -5); 2: (-5, 45); 3: (45, 95); 4: (95, 145); 5: (145, 195); 6: (195, 245); 7: (245, 295); 8: (295, 345); 9: (345, 395); 10: (395, 445); 11: (445, 495); 12: (495, 545); 13: (545, 595).

The thickness of the carpet of the CNTs and the growth morphology were investigated using JEOL 840A and 840F SEMs operating at 5 and 10 kV acceleration voltages. Individual nanotubes and their internal structure were studied by JEOL 2000FX, 2010, 4000HR and 2200MCO TEMs operating at 80, 200, 400 kV acceleration voltages. For SEM studies, the CNTs were used as-grown on the substrates. For TEM, few milligrams of deposit was collected from the substrates, dispersed in acetone and sonicated for a minute using an ultrasonic tip. A few droplets of the suspension were dropped on a TEM grid and dried in air for a few minutes. The Raman spectra of the CNTs were obtained using a JY Horiba Labram Aramis imaging confocal Raman microscope with a 532 nm green laser. The Raman samples were prepared by dropping a few droplets from dispersion of samples in acetone on a microscope slide. A

Perkin Elmer Pyris thermogravimetric analyser (TGA) was used to investigate the variation of oxidation behaviour and iron content of the samples at a heating rate of 10 °C/min in air. For each TGA experiment, around 4 mg of sample was scraped from the substrates and directly inserted in the TGA sample cup. To identify the oxidation state of the iron oxide, a Siemens D5000 XRD was used. The non-carbonaceous deposits formed at the entrance (in the direction of the gas flow) of the reactor were analysed using an Oxford Instruments energy-dispersive X-ray spectrometer (EDX) on a JEOL 840A SEM.

2.3. Results and discussions

2.3.1. Structural investigation using electron microscopy

SEM studies of the quartz substrates revealed that depending on the zone, different products formed along the entire length of the reactor (figure 15a – i). For easier comparison of the products, side-view micrographs of the deposit were taken at the same magnification (figure 15j – r). Iron-based particles formed at temperatures as low as 350 °C (*ca.* 20 mm from the beginning of the reactor, defined as the zero point; figure 15a and 16a). The iron was the most dominant original constituent of the deposit (figure 16b; Fe: 64.36 wt.%, O: 29.17 wt.%, C: 6.11 wt.%). According to the mass spectra obtained from the exhaust of the reactor, the synthesis setup is relatively airtight ($C_{\text{oxygen}} \leq 50$ ppm). Therefore the oxygen signal is most probably due to the post-synthesis oxidation. The intensity of silicon peak was below the detection limit in EDX and XRD analyses (see also section 2.3.7).

The lowest temperature where individual CNTs and CNT carpet-like structures could be observed in this set-up was around 660 – 670 °C (*ca.* 105 – 110 mm from the zero point; figure. 17b and c).

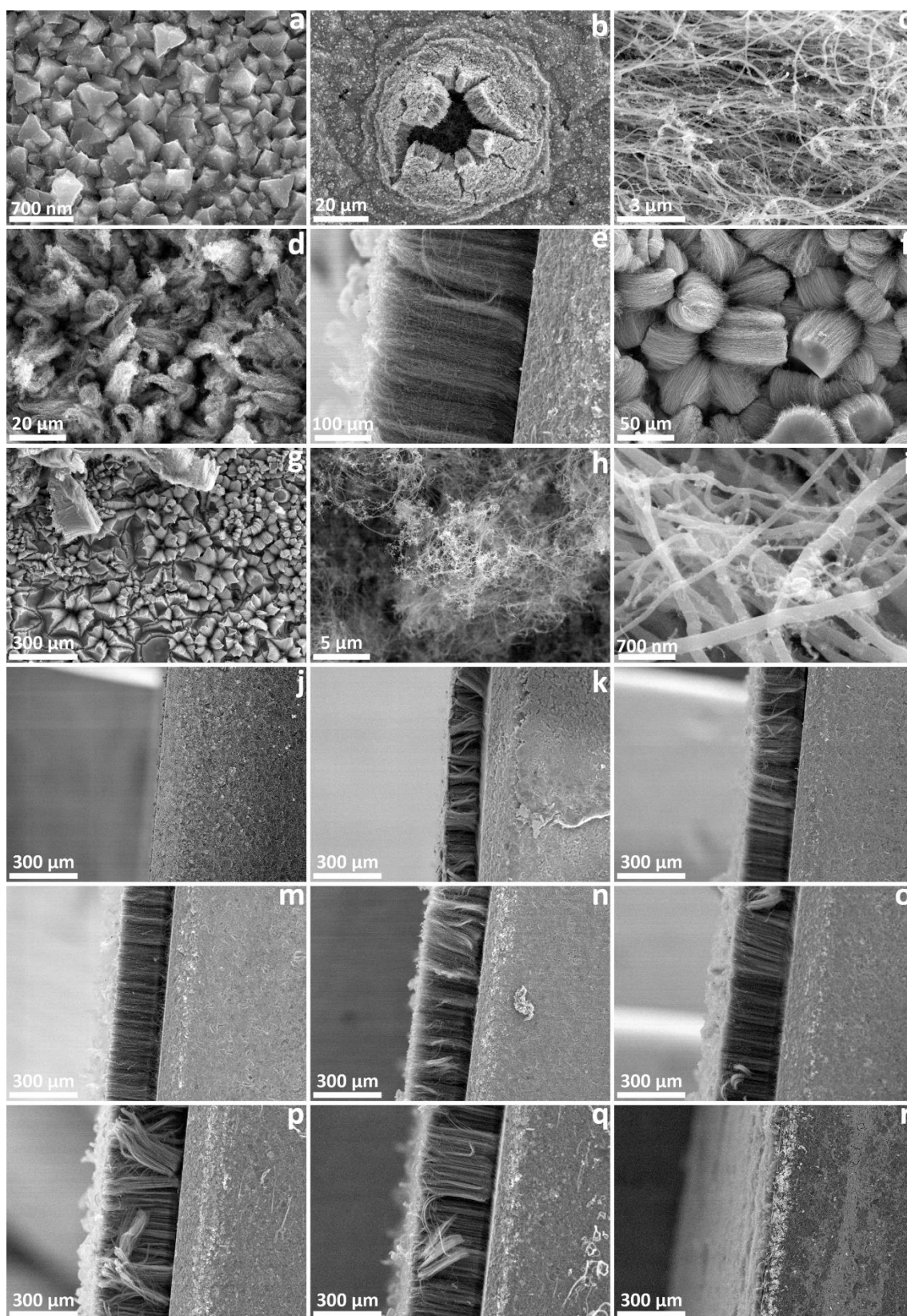


Figure 15. Electron micrograph gallery depicting the products occurring at different locations in the reactor. a) Iron-based crystals (see also the EDX spectrum in figure 16b); b) CNTs with carpet-like structures containing large quantities of catalyst particles; c – g) Typical CNT morphologies; h) CNTs containing amorphous carbon; i) Typical individual CNTs; j – r) Side-view micrographs of

the deposit on the substrates. Corresponding substrate positions inside the reactor: a) 60 mm; b) 115 mm; c) 140 mm; d) 270 mm; e) 340 mm; f) 420 mm; g) 430 mm; h) 530 mm; i) Throughout the reactor; j) 120 mm; k) 170 mm; l) 220 mm; m) 270 mm; n) 320 mm; o) 370 mm; p) 420 mm; q) 470 mm; r) 520 mm.

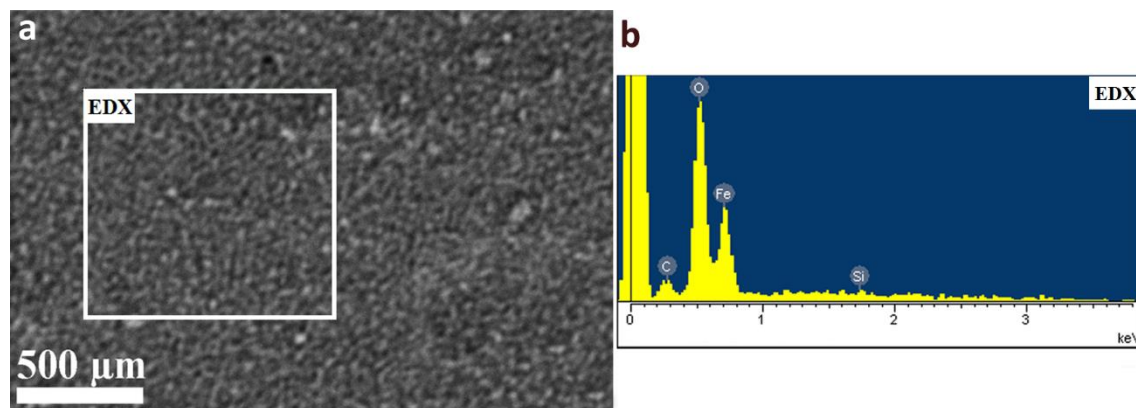


Figure 16. a) Scanning electron micrograph of the substrate located in the first 70 mm of the reactor with corresponding EDX area of examination (see figure 15a for higher magnification); b) EDX spectrum of the deposit on the substrate.

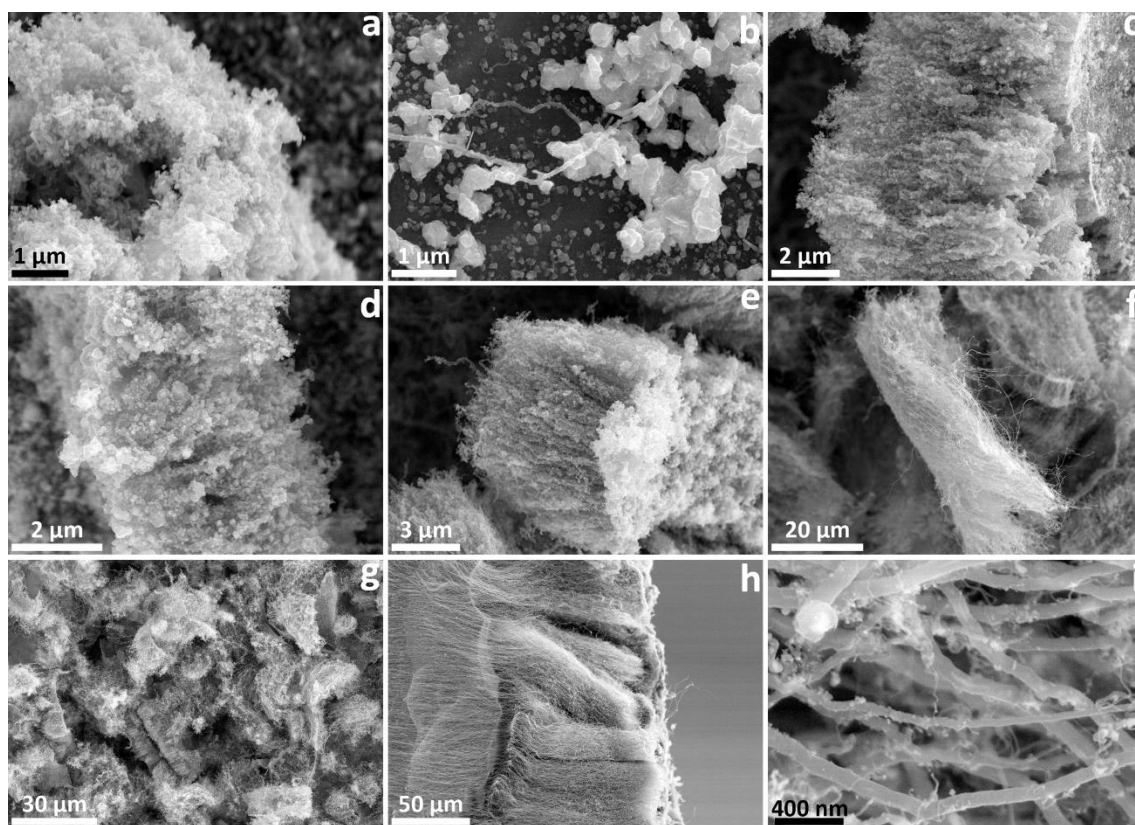


Figure 17. Electron micrographs capturing the critical zone where reaction conditions were suitable for the formation of individual CNTs (a few microns long) and CNT carpets (up to around 100 μm thick): a) Large agglomeration of the catalyst particles; b) One of the few and very short individual CNTs observed at the beginning of the reactor; c – h) Development of the carpets of

CNTs (from a few microns up to *ca.* 100 μm thickness); i) Typical individual MWCNTs. Corresponding positions inside the reactor: a) 100 mm; b) 105 mm; c) 110 mm; d) 112 mm; e) 115 mm; f) 120 mm; g) 130 mm; h – i) 140 mm.

It is important to note that the zone at 105 – 110 mm from the beginning of the reactor appeared to be the critical zone where the transition from the formation of iron-based nanoparticles to the formation of CNTs tends to take place (figure 17). For example, the CNTs that formed near the entrance of the reactor possessed more catalyst particles (figure 15b – c and 17a – e) and were also very short (*ca.* 10 μm). This short length is due to the presence of relatively large catalyst particles and the low thermal content of the precursor (see also discussion in section 2.3.7). Further down the reactor at 110 – 130 mm from the zero point at temperatures of 670 – 700 °C, typical carpets (100 μm thick) could be observed (figure 17h). This means that the critical synthesis parameters for the growth of individual and CNT carpets exist at around 100 mm from the beginning of the reactor. The length and overall morphology of the CNT carpets which formed after this point were more uniform as shown in figure 15d – f and confirmed by TGA results (see section 2.3.7).

Generally, a variety of morphologies of CNT carpet were found. For example, a loose wool-like structure formed on the substrate placed 220 mm from the zero point at around 770 °C (figure 15d) and got denser and more morphologically developed at around 800 °C (320 mm from the zero point; figure 15f). Flower-like carpets were also identified on the last two substrates *i.e.* 495 – 595 mm from the zero point towards the end of the reactor which probably follow a similar formation mechanism as the wool-like structures. The difference is that the flowers grow far apart from each other and the synthesis parameters (potentially time, temperature and abundance of carbon, and catalyst precursor) were not suitable for the flower-like arrangements to merge and fully cover the substrate (figure 18).

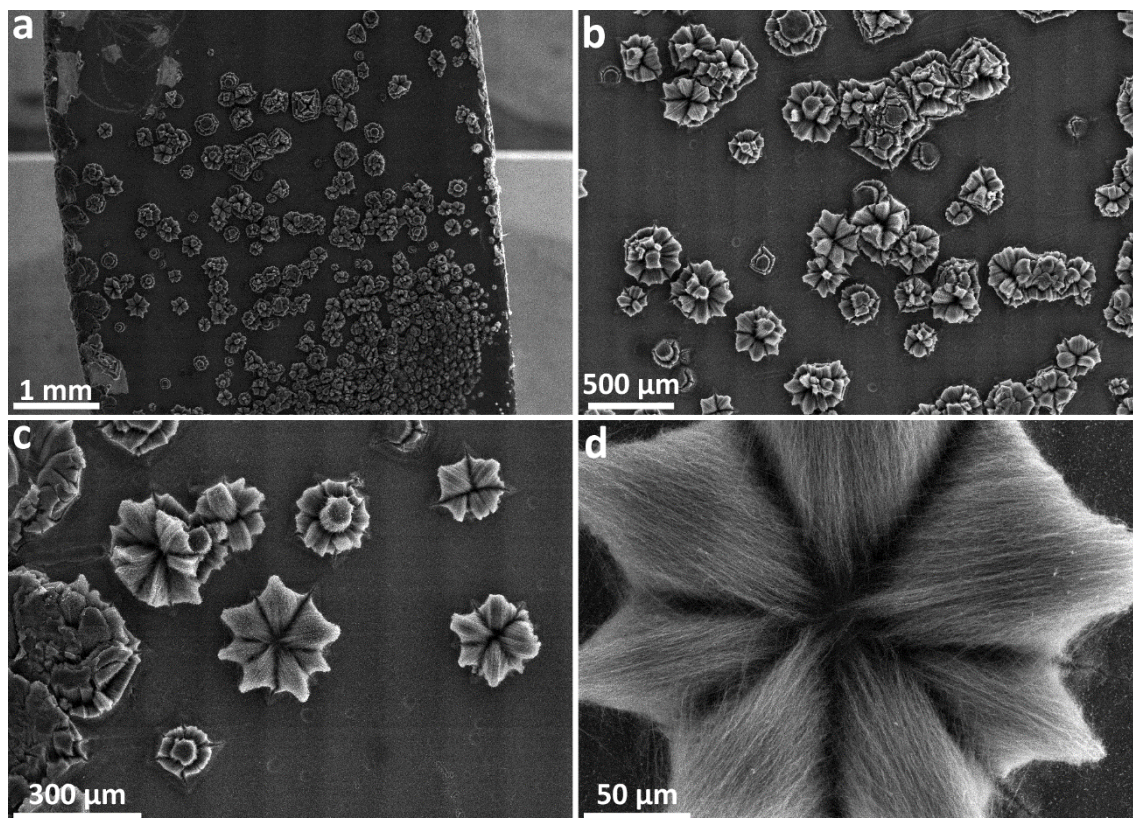


Figure 18. MWCNT flowers with 4 to 7-fold symmetries forming on the last two substrates *i.e.* 495 – 595 mm from the zero point towards the end of the reactor.

Similar flowers with 3 and 4-fold symmetries have been reported by Arab *et al.* [32] using a similar AACVD method. Evidently the bending of the CNTs, which results in these morphologies, only occurs at the top of the carpet and the CNTs were fully aligned from the roots, up to *ca.* 10 μm from the substrate surface (figure 15e and f). However, for thinner carpets with lower densities, the bending could start right from the root (figure 15g). The reason why such bending occurs is thought to be linked with the different growth rates of the CNTs in each bundle. Under the experimental conditions used, the catalyst particles could effectively coalesce to form larger particles. Several locations were found within the entire reactor where such agglomeration occurred. Assuming that the particle size dictates the growth rate of nanotubes [204,205], it is quite possible that such a difference in length and consequently bending exists. The CNTs at the far end of the reactor were accompanied by amorphous carbon (figure 15h)

which is in agreement with the Raman and TGA oxidation resistance data. This trend is most likely due to the sudden decrease of the temperature and abundance of the catalyst particles required for the graphitisation of carbon. SEM micrographs j – r in figure 15 show the evolution of the thickness of the deposit which is discussed in section 2.3.3.

The internal structure of CNTs was investigated by TEM. The majority of products were relatively well-graphitised MWCNTs (figure 19a and b). However, some SWCNTs were observed on the very last substrate (545 – 595 mm from the beginning of the reactor). This is probably due to the size of the catalyst particles. At this point of the reactor, both the quantity of catalyst precursor and the reactor temperature drastically fall and hence some of the nanoparticles retained their initial size and did not agglomerate. As a result, the presence of SWCNTs in this region of reactor is more probable than at any other position (figure 19c – f). Some DWCNTs (figure 19d) were also found which may be explained in a similar manner to the SWCNTs. Apart from nanotubes; some metal encapsulated carbon particles typically found in SWCNT and DWCNT samples could also be observed. High-resolution TEM investigation of the SWCNTs revealed several hollow fullerene-like species with diameters around 1 nm on the walls of SWCNTs (figure 19f), which resemble CNBs (see section 1.2.2).

To investigate the structure of CNBs, the synthesis recipe and sample preparation steps were optimised. In order to minimise the chance of agglomeration of iron nanoparticles, the ferrocene content of the precursor was lowered to 3 wt.%. For capturing the SWCNTs/CNBs, a TEM grid was held by a pair of customised stainless steel X-shape twisters (figure 20) and placed 4 cm after the furnace. The tip of the tweezers was bent to hold the TEM grid at *ca.* 45° angle with respect to the quartz tube. Using this method, potential damage to the delicate SWCNTs and CNBs during the TEM sample preparation was avoided. The walls of the SWCNTs captured on the TEM

grid were straighter with less structural defects compared to the ones scraped from the substrate (figure 21). Aberration-corrected TEM [206] was performed on the SWCNT/CNB sample at 80 kV acceleration voltage in order to reduce the knock-on damage caused by the electron beam. It was confirmed that the SWCNTs are covered by fullerenes of various sizes. It was also observed that the CNBs change with time and the evolution of one particular fullerene (marked by an arrow in figure 22a) is shown in figure 22b – i.

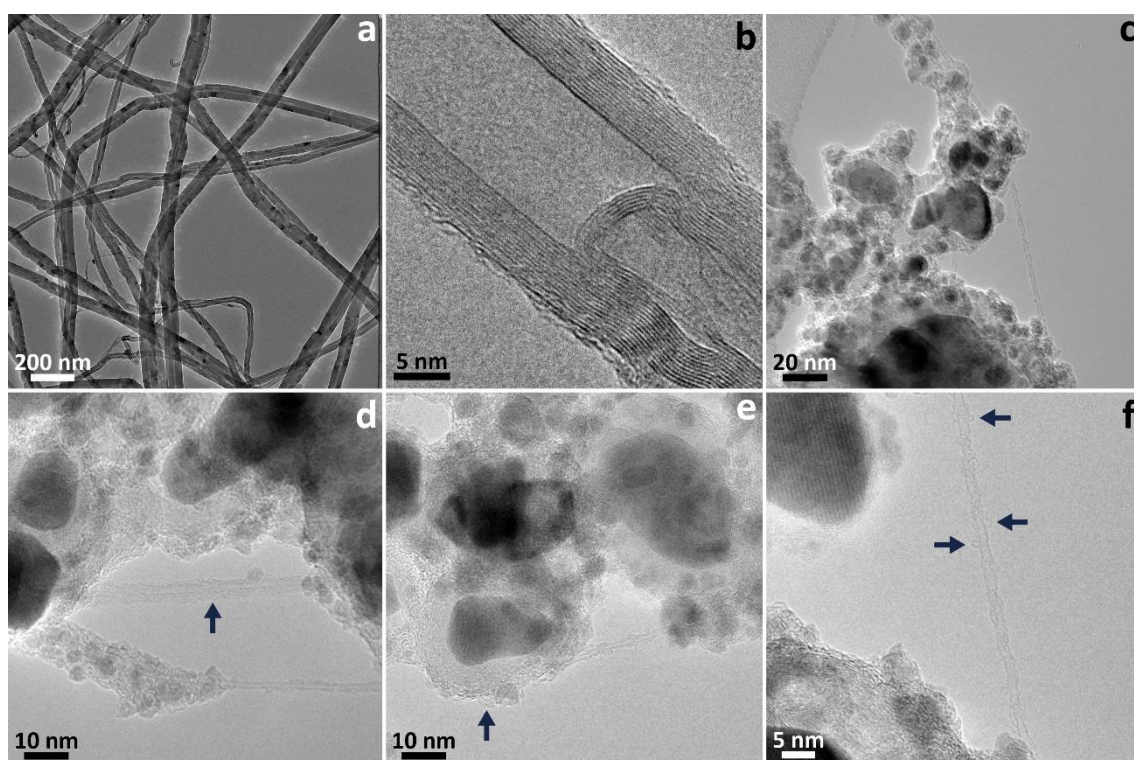


Figure 19. TEM images of a and b) Typical MWCNTs; c – e) SWCNTs (diameter: 1.1 – 1.5 nm), DWCNTs (diameter: 2.6 nm) and metal encapsulated carbon particles (present at 495 – 545 nm from beginning of the reactor; marked by arrows); f) Close-up of a SWCNT with hollow fullerene-like species with diameters around 1 nm (marked by arrows), which resemble CNBs.

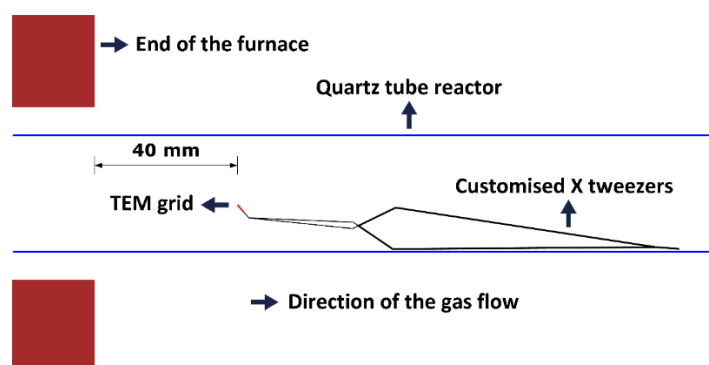


Figure 20. Sketch of a pair of customised stainless steel X-shape twisters holding a TEM grid to capture SWCNTs and CNTBs forming at/flying to 40 mm after the end of the furnace inside the quartz reactor.

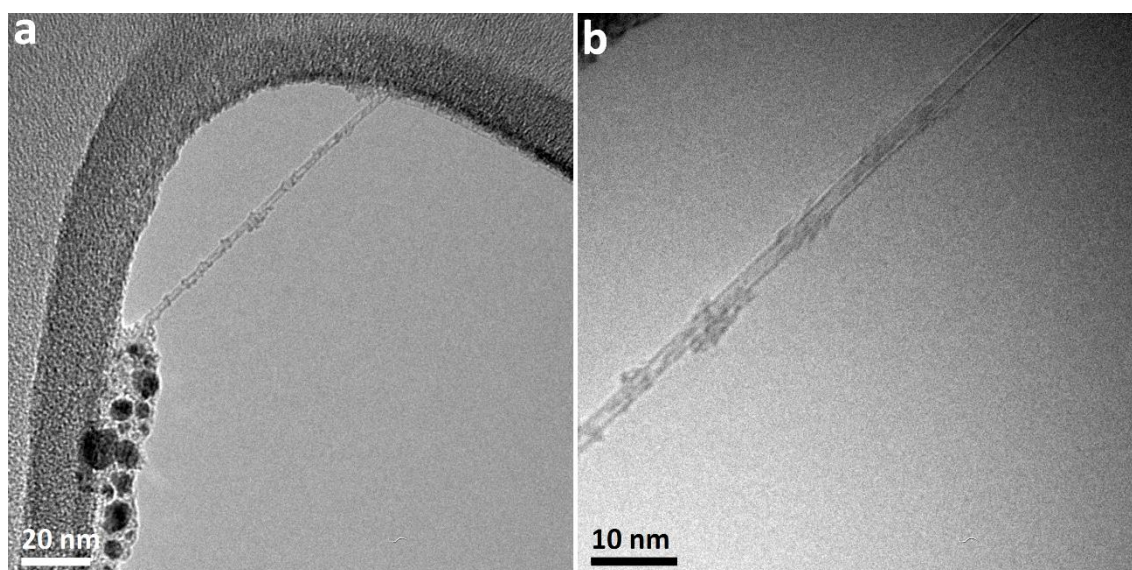


Figure 21. CNBs with outer diameter: 1.5 – 2 nm, captured on a TEM grid using the method described in figure 20.

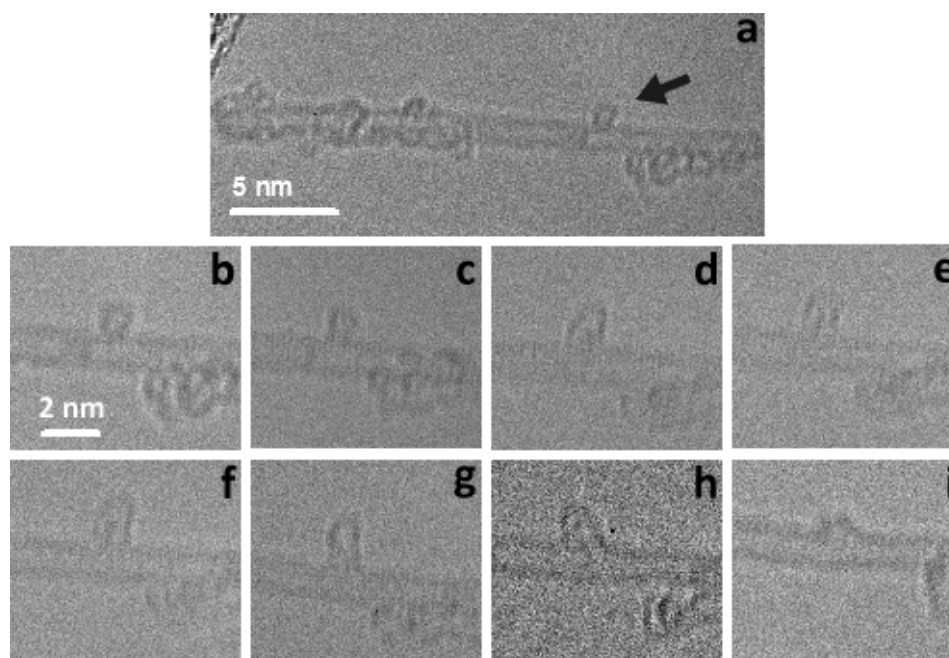


Figure 22. High-resolution TEM gallery of a SWCNT covered by fullerenes of various sizes (CNB) (a) and evolution of a CNB under electron beam at 80 kV acceleration voltage (b – j) [Nicholls *et al.*; manuscript in preparation].

As reported by Füller *et al.* [207], the electron beam deformed the CNB and allowed the fullerene to restructure into a short branch tube (1 – 2 nm long, figure 22g) before collapsing (figure 22i). The carbon atoms contributing to the growth of the fullerene likely came from the nanotube in the immediate vicinity of the fullerene (where the wall has disappeared, figure 22g) but the rest of the nanotube appeared unaffected by the changes and remained straight until the short branch tube started to collapse. An additional supply of carbon could be mobile fullerene fragments or carbon clusters on the surface of the nanotube. The deformation appeared to happen without the presence of catalyst particles.

2.3.2. Mass of deposited products

In order to measure the amount of deposited materials throughout the reactor, each substrate was weighed before and after the synthesis. Figure 23b shows the average mass of the products deposited on each substrate with respect to the temperature profile of the reactor. Four experimental runs were conducted in order to obtain an average value. There were two regions in the reactor where the highest masses were found: 150 – 250 and 400 – 450 mm from the beginning of the reactor. As revealed by the microscopy studies and complemented by EDX (see section 2.3.1) and TGA analyses (see section 2.3.7), a large population of iron-based nanoparticles right at the beginning of the reactor, where the temperature reached $> 350\text{ }^{\circ}\text{C}$ which is sufficient to crack the ferrocene, was observed. The presence of these iron-based particles is the origin of the first peak in figure 23b (first highest mass obtained). In contrast, the second peak is due to the longest CNTs which grew in the second half of the reactor (*ca.* 400 – 450 mm from the beginning of the reactor, *i.e.* zero point). Interestingly, neither of these two peaks was at the centre of the isothermal zone of the reactor, which implies that the highest yield is not obtained in the hottest region of the reactor.

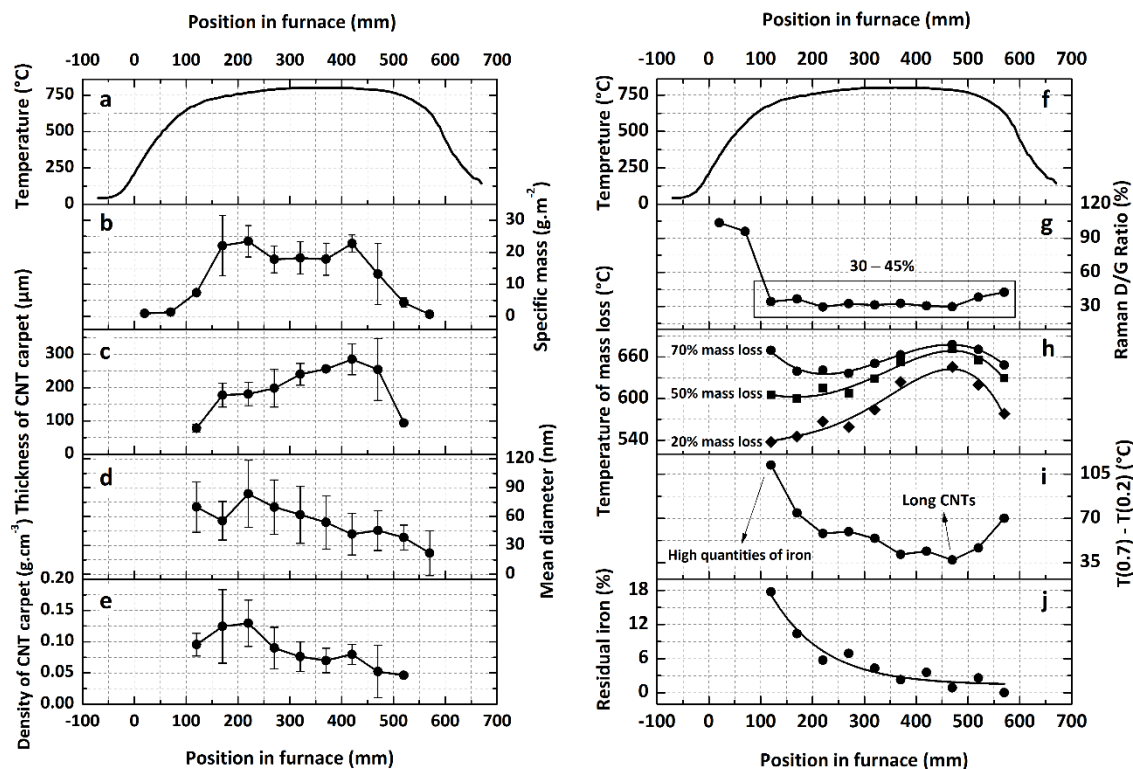


Figure 23. Profiles showing the relationship of the a & f) Temperature of the reactor used for synthesis of CNTs to the b) Yield defined as mass of CNTs per unit of area, c) Thickness which is roughly equal to the length of CNTs forming the CNT carpet, d) Mean diameter of the CNTs, e) Density of the CNT carpet defined as the specific mass divided by the thickness of CNT carpet, g) Ratio between the intensities of Raman D and G-bands (normalised by the intensity of G-band), h) Oxidation resistance of the CNTs (temperature of 20%, 50% and 70% mass loss), i) Uniformity of CNTs (difference between the temperatures at which the CNTs lose 70% and 20% of their initial mass) and j) Iron content of the synthesised product with respect to the position of the substrate inside the reactor.

2.3.3. Length and growth rate of the carbon nanotubes

The thickness of the CNT carpets, which is approximately equal to the length of individual CNTs, was measured by SEM (figure 15j – k). CNT carpets were found to grow in appreciable thickness (*ca.* 200 μm) between 150 – 200 mm from the beginning of the reactor (figure 23c). The length of nanotubes steadily increased to *ca.* 300 μm until 400 – 450 mm from the beginning of the reactor, after which it sharply decreased. It has been reported that the growth rate of nanotubes is substantially influenced by the size of the catalyst particles and there is an optimum particle size which provides the highest diffusion rate for the dissolution of carbon into the catalyst and consequently leads to the longest tubes [204,205]. Hence, in this system, if the length of CNTs is the primary concern, the catalyst particles with optimum size ($13 \pm 6 \text{ nm}^1$) formed between 400 – 450 mm from the beginning of the reactor. The average growth rate of CNTs at this position (*ca.* 20 $\mu\text{m}/\text{min}$) was more than 50% higher than at the beginning of the reactor.

¹ The catalyst particles typically deform during the CVD [144]. Hence, their initial shape and dimensions don not remain the same before and after the synthesis. Here, the *size* of particles are measured from the TEM images. Therefore, it corresponds to the post-synthesis dimensions of the particles. For rod-shaped particles encapsulated inside the CNTs, the diameter (smaller dimension) was used as the *size*. Particles attached to the outer walls of the CNTs were mostly spherical and their diameter was used as the *size*.

2.3.4. Diameter distribution of the carbon nanotubes

In order to obtain the variation of the outer diameter of CNTs, a TEM image analysis of *ca.* 1000 CNTs was performed. Outer diameters were measured using the intensity profile of the micrograph across the randomly-selected CNTs. The variation of the mean outer diameter is shown in figure 23d. It was found that both the outer mean diameter and the outer diameter range (figure 24) of the CNTs decreased as function of distance from the beginning of the reactor. The outer diameter of CNTs is reported to be controlled by the size of the catalyst particles [28]. The decreasing trend of the diameter of CNTs is in agreement with the microscopy observations of the catalyst particles (see section 2.3.1). The relatively large diameter of CNTs formed near the entrance of the reactor can be explained by the observed agglomerates in that zone.

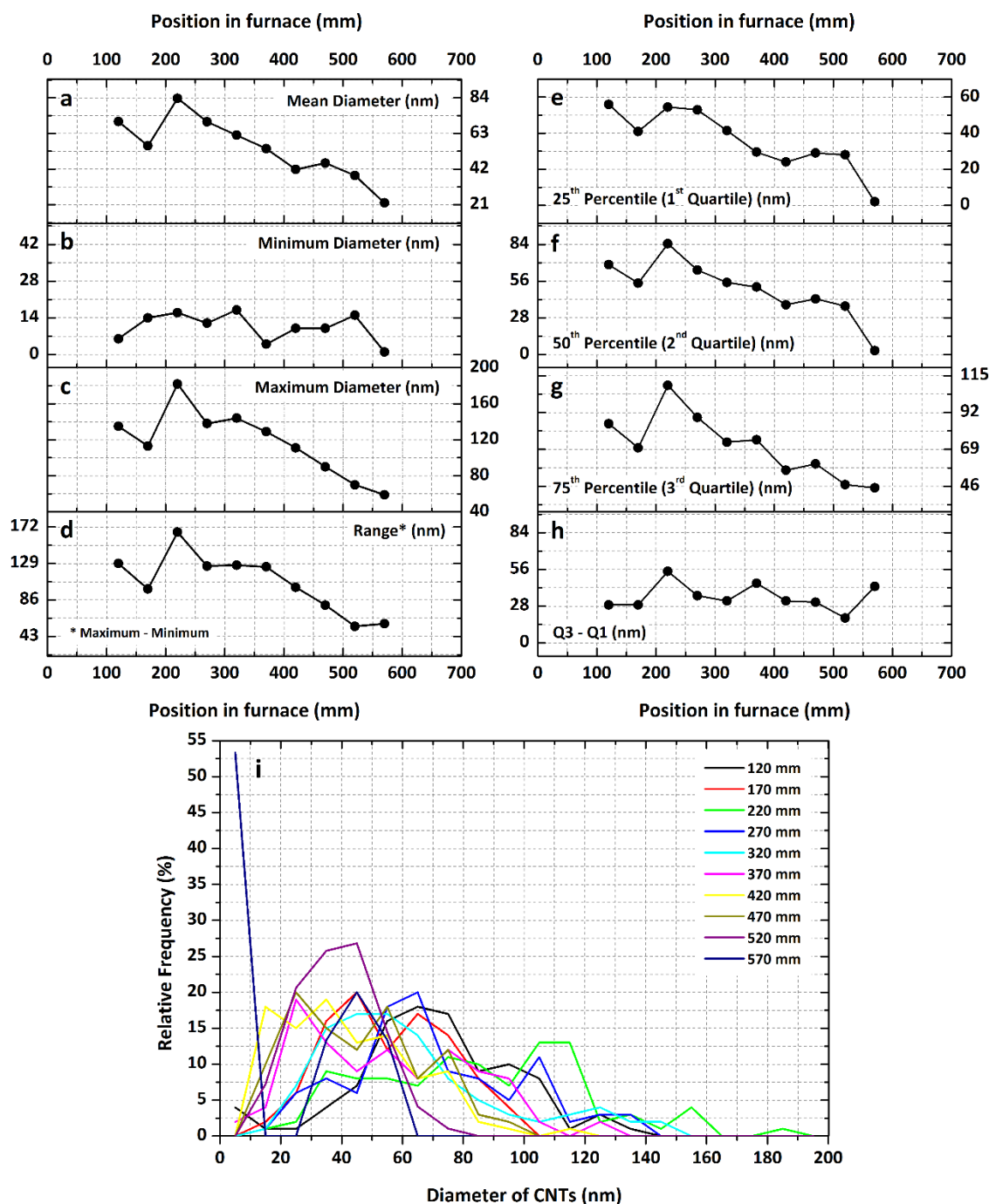


Figure 24. Statistical analysis of the outer diameter of the CNTs. a) Mean outer diameter, b) Minimum outer diameter, c) Maximum outer diameter, d) Range (the difference between the maximum and minimum) of outer diameter, e) 25th percentile (1st quartile) of outer diameter, f) 50th percentile (median) of outer diameter, g) 75th percentile (3rd quartile) of outer diameter and h) Interquartile range (the difference between the 3rd and 1st quartiles) of outer diameter as a function of their position inside the reactor; i) Distribution of the outer diameter of the CNTs synthesised in different positions inside the reactor.

2.3.5. Density of the carbon nanotube carpets

Herein the density of CNT carpets is defined as the specific mass (mass divided by the area of the substrate) divided by the thickness of the CNT deposit (see section 2.3.3). Density in this definition, quantifies how compactly the CNTs have formed on the quartz substrates. The density of the synthesised products, shown in figure 23e, decreases along the reactor which is due to the rapid consumption of the catalyst precursor right at the beginning of the reactor. As is demonstrated in the SEM gallery (figure 15 and 17), the CNTs formed close to the entrance of the reactor contained large quantities of catalyst particles which led to a dense carpet whilst as the precursor got closer to the end of the reactor, the density decreased. It should be noted that, similar to the mass and length profiles, there is a visible peak in the density of the CNT carpets between 400 – 450 mm (figure 23e) which is due to the growth of long, compact and highly aligned carpet of CNTs in this position (figure 15f).

2.3.6. Raman spectroscopy of the carbon nanotubes

In Raman spectroscopy, the sample is illuminated by a laser beam and the interaction of the incident photons and the low-frequency modes of the material results in shifts of the energy of the incident photons [208]. The intensities of the energy shifts are recorded to obtain a Raman spectrum. Graphene-induced allotropes of carbon exhibit two first-order modes (Raman peaks) at around 1350 and 1600 cm^{-1} which are commonly referred to as D-band and G-band respectively [73,74]. Originating from the tangential vibration of the carbon atoms on graphitic layers, the G-band is attributed to the sp^2 carbon systems and indicates the graphitisation of the carbon sample being analysed [74]. The D-band is believed to be an indicative of the presence of amorphous carbon in sp^2 carbon systems [74]. The ratio between the intensity of the D-band and G-band (Raman I_D/I_G) is frequently used to quantify the defect density and purity of CNT samples [74]. A second-order band often appears in graphene and CNT samples at around 2700 cm^{-1} known as 2D-band or G'-band. Similar to D-band, G'-band is believed to be sensitive to the defect density in CNTs. Since the G'-band is particularly sensitive to the number of layers in graphite [209], it may also be responsive to the number of walls in CNT samples. Radial breathing mode (RBM) is another Raman mode normally observed in SWCNTs and thin (< 2 nm) MWCNTs [74,210] at low frequencies (< 500 cm^{-1}). RBM is reported to be sensitive to the diameter of SWCNTs [211].

The Raman I_D/I_G of the CNTs grown throughout the reactor are shown in figure 23g (original Raman spectra: figure 25a). The CNTs grown in the first 100 mm of the reactor had the highest Raman I_D/I_G compared to other CNTs grown in other zones and hence were the most defective (Raman $I_D/I_G = 0.95$ to 1.05). Interestingly, whilst the products deposited at 100 and 600 mm were formed at similar temperatures (*ca.* 500 $^{\circ}\text{C}$), their Raman I_D/I_G differed significantly. This behaviour is thought to be linked to

the difference between the temperature of the reactor and temperature of the precursor. The endothermic process of heating, vaporising and thermocatalytic cracking of the precursor in the dynamic atmosphere of a reactor does not happen instantaneously; therefore, the actual temperature of precursor is thought to be lower than the temperature of reactor in the first 100 mm of the reactor which leads to the formation of less structurally-developed products. At 600 mm, the precursor has a higher thermal content and hence more structurally-developed products were formed, as supported by TEM (see section 2.3.1). The CNTs synthesised in the range of 100 – 500 mm showed a similar low [11,12,14,17,19,26,28,40] defect density, *i.e.* Raman I_D/I_G of 0.34 ± 0.04 . No RBM was observed in the Raman spectra obtained from the samples confirming the domination of MWCNTs over potentially-existing SWCNTs. The presence of different shoulder in the D-band of the samples grown at the very beginning (up to 100 mm from the zero point) and end (570 mm from the zero point) of the reactor might originate from different defects and impurities such as excessive catalyst particles and amorphous carbon in two extreme ends of the reactors. The G'-band in Raman spectra of all samples had similar shifts and intensities except for the very first and the last samples. This might indicate that the CNTs grown across the reactor have generally comparable defect density, as suggested by the Raman I_D/I_G . It may also mean that the MWCNTs have alike number of walls.

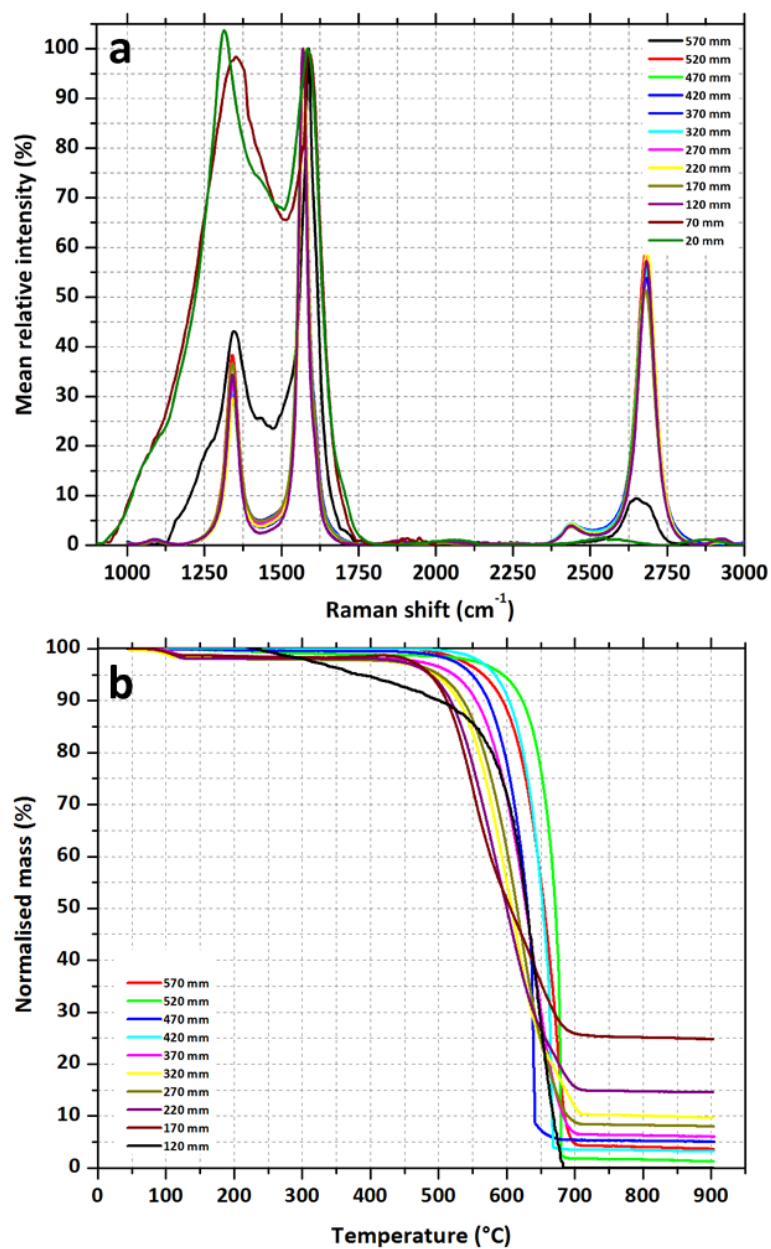


Figure 25. a) Raman spectra and b) TGA graphs of the CNTs grown in different positions inside the reactor.

2.3.7. Thermogravimetric analysis of the carbon nanotubes

The oxidation resistance of the deposited materials was obtained from TGA by observing the temperature at which the samples lose a certain percentage of mass. Figure 23h shows the variation of temperature when 20%, 50% and 70% mass loss occurred throughout the reactor. Original TGA graphs are provided in figure 25b. From the beginning of the reactor up to *ca.* 450 mm, the oxidation resistance of the deposited products (figure 23h) generally improved. However, it should be noted that the first data points on figure 23h can be misleading as they correspond to products with considerable amount of catalyst content. These products may actually even gain mass by oxidising. By comparing figure 23h and 23c it can be observed that the longest nanotubes, formed 400 – 450 mm from the beginning of the reactor, had the highest oxidation resistance whilst the oxidation resistance of CNTs grown at 500 – 600 mm from beginning of the reactor dropped by around 50 °C. This drop in oxidation resistance is due to the presence of less graphitised products at the end of the reactor which is also confirmed by the slight increase of the Raman I_D/I_G at the last data point in figure 23g.

The difference between the temperatures at which the CNTs lose 70% and 20% of their initial mass can be used as an indicator of their uniformity. Inhomogeneous CNTs oxidise at different rates and temperatures. This leads to a large difference between the temperatures at which they lose 70% and 20% of their initial mass. In contrast, more uniform CNTs tend to oxidise at a similar rate over a narrow temperature range (figure 23i). The CNTs which formed between 450 – 500 mm from the beginning of the reactor showed the highest uniformity according to this definition, which is in good agreement with the SEM and TEM data confirming the presence of uniform batches of CNTs with similar morphologies at this region of the reactor (see section 2.3.1). The plateaus at the end of each of the TGA graphs indicate the amount of residual iron oxide after each

experiment. Using XRD (figure 26), the residue was found to be hematite containing 70.8 wt.% iron. Therefore the relative content of the catalyst particles in CNTs alongside the reactor could be calculated. This iron content is shown in figure 23j and demonstrates the sudden consumption of ferrocene and formation of large catalyst agglomerates at the beginning of the reactor with a decreasing trend towards the end of the reactor (see figures 15a and 17a). This results in formation of smaller iron-based nanoparticles as the precursor approaches the end of the reactor, which is in agreement with the decreasing trend of the mean outer diameter of CNTs shown in figure 23d. No obvious peak corresponding to silicon-containing compounds such as FeSiO_3 and SiO_2 was found on the XRD pattern. Therefore, the original catalyst particles are believed to have minimal chemical interaction with the quartz substrate and are relatively free of silicon contamination and mainly composed of iron, carbon and oxygen [46].

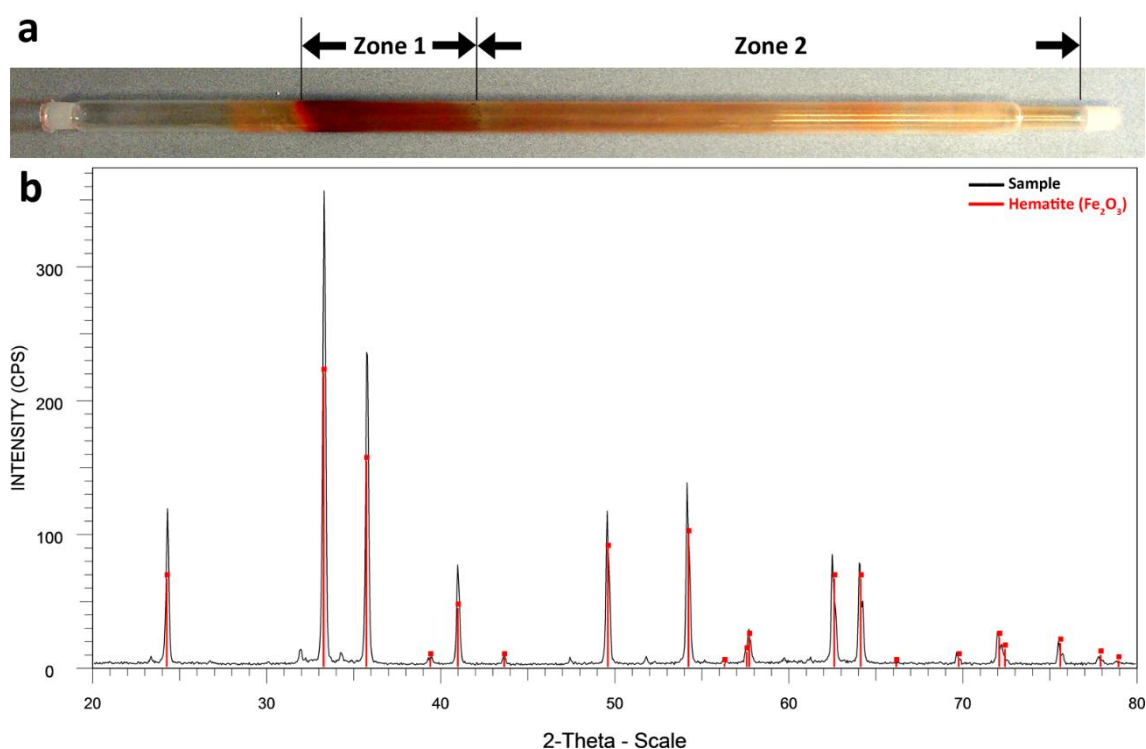


Figure 26. a) Residue after burning the as-grown CNTs inside the quartz reactor at 900 °C (Zone 1: thick opaque layer of oxidised catalyst particles; Zone 2: gradual increase of transparency (decrease of the presence of catalyst particles) towards the end of the reactor); b) XRD pattern of

the residue. It is shown that the residue is almost entirely hematite (Fe_2O_3) containing 70.8 wt.% iron and 29.2 wt.% oxygen.

The significant decrease of the iron content throughout the reactor is probably one of the main reasons for observing inhomogeneity of the properties of the synthesised CNTs. Formation of CNTs with large, small and optimum diameters for the highest growth rate can be explained by the variation of the quantity and consequently the size of catalyst particles. The temperature profile on the other hand largely influences the evolution and characteristics of different product such as the agglomeration of catalyst particles and defect density of the CNTs.

2.4. Conclusions

The AACVD method has high potential for upscaling the production of conventional and chemically modified CNTs. However, the findings showed that the homogenisation of the synthesis parameters in the currently available AACVD reactors should be a crucial step for the design of larger AACVD systems. It was demonstrated that the variation in the deposited materials and CNT characteristics across the synthesis reactor is due to the inhomogeneity of the synthesis parameters; among which the catalyst content of the precursor and temperature had the highest influence. The length and the diameter of the CNTs are evidently controlled by the quantity and size of the catalyst particles. Consequently, the oxidation resistance varies throughout the reactor. Moreover, SEM and TEM of all the samples selected from different zones showed a variety of morphologies of CNT carpets. Small quantities of CNBs, SWCNTs and DWCNTs were observed at the end of the reactor. Using Raman spectroscopy it was found that the defect density of the grown CNTs were relatively constant (less than 8% variation) over a large section of the reactor (85% of the length of the reactor) which is a good indicator of the effectiveness of the method for production of pure and clean CNTs.

Modification of the current way the precursor is introduced in the AACVD reactors could potentially overcome the issues related to the inhomogeneity of products addressed in this chapter. See section 5.2 for the description of the proposed solution.

Chapter 3. Online monitoring of the synthesis of carbon nanotubes

3.1. Introduction

As mentioned in section 1.1, in this work, *in-situ* gas analysis is the method to monitor the AACVD reactor for synthesis of MWCNTs. In order to understand how the atmosphere of the reactor can be monitored and correlated to the characteristics of the synthesised MWCNTs, a variety of experimental parameters of the AACVD can be altered. The composition of the precursor is perhaps one of the most important of all, for a number of reasons. Firstly, unlike other experimental parameters such as *duration* or *flow rate of carrier gas*, using different hydrocarbons as the carbon source would guarantee obvious changes in the gas analysis outcomes. Secondly, if the chosen hydrocarbons have structural similarities and have common thermocatalytically cracked fragments, potential derived theories describing the thermocatalytic cracking behaviour of different classes of hydrocarbons can be better supported with larger number of experimental results. Finally, since the composition of the precursor in AACVD of MWCNTs is relatively less studied compared to other parameters, there is a good chance that different attributes of MWCNTs can be improved by easily altering the composition of the precursor.

Another experimental parameter investigated in this work was the size of the reactor to see how the composition of the atmosphere of AACVD reactors and thermocatalytic cracking behaviour of precursors depend upon the size of the reactor. This will be covered in the next chapter. In this chapter¹, 15 different carbon sources including

¹ Some parts of this chapter are adapted from a published journal article; Meysami *et al.* [39].

benzene derivatives, cyclohexane derivatives and alkanes and 3 different catalyst sources were used to synthesise MWCNTs. The catalyst concentration was also varied from 1 to 15 wt.%. For the analysis of the system, firstly, the conversion yield of all the precursors was measured and their thermocatalytic cracking behaviour inside the reactors was monitored using an integrated mass spectrometer. Secondly, various properties of each batch of MWCNTs including the morphology, residual catalyst content, diameter distribution, defect density, and oxidation resistance were studied. And finally, the potential correlations between the characteristics of the precursors and the properties of their corresponding MWCNT batches were investigated. This chapter also covers the attempts towards mapping the composition of the reactor and calibrating the gas analysis results for quantification. Although the analysis carried out in this, previous and the next chapter target the AACVD synthesis of MWCNTs from different angles (see figure 1), they are all aimed at developing the AACVD for the industrial-scale synthesis of homogeneous, low-defect-density and amorphous-carbon-free MWCNT carpets. Despite the efforts in both academia and manufacturing sectors, this has remained a challenge for a number of years [5].

3.2. Experimental

The exhaust of the AACVD reactor (see section 2.2) was analysed using a Hiden Analytical HPR-20 QIC quadrupole mass spectrometer (QMS) and a PerkinElmer Clarus 580 GC/SQ8S GCMS instrument. Compared to other techniques such as time-of-flight [212] or magnetic sector mass spectrometry [213], QMS provides fast scans and is relatively compact and inexpensive to maintain [214,215]. Therefore, it is widely used for residual gas analysis [216]. The ions in a QMS are normally generated by bombardment of the analytes using an electron beam inside the ion source of the QMS. The ions are separated in the mass filter (mass analyser) of the QMSs. The mass filter is composed of two pairs of metallic rods. One pair of opposite rods have a positive radio frequency (RF) voltage with a superimposed direct current (DC) voltage: $V\cos(\omega t)+U$; wherein $V\cos(\omega t)$ is the RF voltage and U is the DC voltage. The other pair have a negative RF voltage with a superimposed DC voltage: $-(V\cos(\omega t)+U)$. The total applied voltage affects the trajectory of different ions as they travel through the mass filter, depending on their charge and mass values. For given applied RF and DC voltages, only certain ions with a specific mass to charge ratios can pass through the mass filter without colliding with one of rods and getting neutralised. Hence, by varying the RF and DC voltages, the ions with different mass to charge ratios can be filtered and counted by a detector such as a Faraday cup [217] or a secondary electron multiplier [218,219]. A mass spectrum is obtained by plotting the number of ion counts as a function of variations in the applied voltages which can be correlated to the mass to charge ratios [216,220]. Gas chromatography can be used to separate the analytes prior to detection by a mass spectrometer. In gas chromatography, the analytes are passed through a capillary using a mobile phase (normally an inert gas such as helium). Since various analytes interact differently with the stationary phase (a coating inside the

capillary), they elute at different retention times and, hence, can be separated. A gas chromatogram can be obtained by plotting the detected currents (directly related to the ion counts) as a function of time. If the contribution of all the ions and fragments in a scan is used to plot the chromatogram, it is called *total ion current* (TIC) chromatogram. If the current corresponding to only one specific mass is used to plot the chromatogram, it is called *selected-ion monitoring* (SIM) chromatogram. Compared to TIC chromatograms, SIM chromatograms often provide higher sensitivity for detection of analytes with low abundance [220,221].

Figure 27 depicts the AACVD setup with integrated gas analyser.

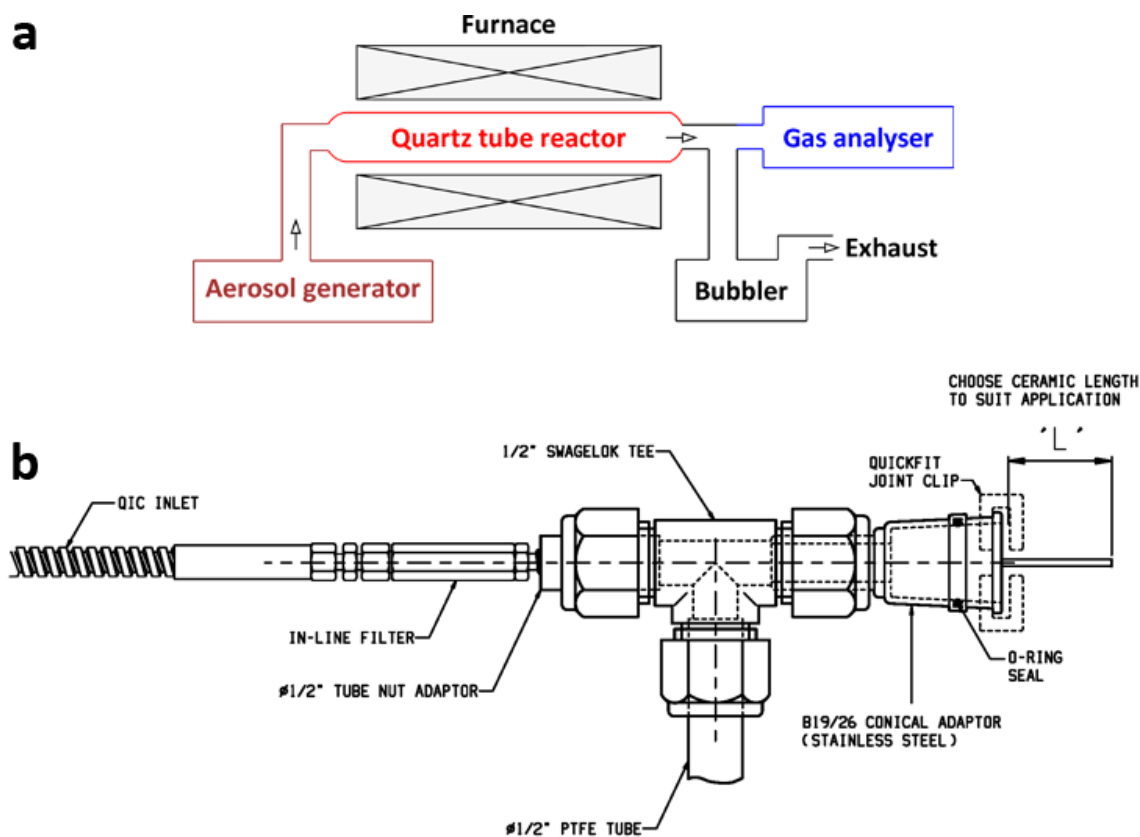


Figure 27. a) AACVD setup with integrated gas analyser at the exhaust; b) The connection assembly between the transfer line of the gas analyser and standard B19/26 quartz cone; manufactured by Hiden Analytical.

The stainless steel B19/26 conical adaptor (socket) was connected to the normal B19/26 quartz cones and sealed with an O-ring inside the socket. A ϕ 1/2" Swagelok tee

splits the flow from the reactor between a $\phi \frac{1}{2}$ " polytetrafluoroethylene (PTFE) tube and the transfer line (quartz capillary inlet (QIC) in figure 27a). The PTFE tube was directly connected to the acetone bubbler. The transfer line was a 2-m-long polyamide coated fused silica capillary, 300 μm inner diameter equipped with an in-line filter to prevent particulates entering and blocking the capillary. To avoid any precipitation of the analytes from the sampling point to the gas analyser, the protecting sheath of the transfer line was constantly heated to *ca.* 150 °C and the whole connection assembly was wrapped with heating tape and aluminium foil and maintained at the same temperature as the protecting sheath. For GCMS studies, the same assembly was used with the exception of the Hiden Analytical QIC which was replaced by a PerkinElmer transfer line and a reducing valve which was placed between the $\phi \frac{1}{2}$ " Swagelok tee and the in-line filter to control the flow of the analytes. The PerkinElmer transfer line was heated to the same temperature as the Hiden Analytical QIC. In order to map the composition of the reactor, an inert heat-resistant probe was required to extend the transfer line into the reactor. For this purpose, 80-cm-long alumina tubes with 800 μm inner diameter were connected to the $\phi \frac{1}{2}$ " tube nut adaptor (see figure 27b).

The heating rate of the GC oven was optimised for separation of benzene derivatives as following: holding the temperature at 30 °C for 2 min, heating to 200 °C in 8.5 min and holding the temperature at 200 °C for 2 min (total GC operation: 12.5 min). The GC was fitted with a Restek fused silica Rtx-5 column (30 m long; 320 μm inner diameter; stationary phase: diphenyl dimethyl polysiloxane, 0.50 μm thick).

In order to quantify the real relative abundance of different analytes coexisting in different phases (liquid/gas), a heated mixing chamber (figure 28) was designed to prepare a set of standard samples. The chamber was filled with known quantities of liquid and gas analytes, enclosed and heated to well above the boiling point of the liquid

analyte. The result was a gaseous mixture of two analytes with known real relative abundance which was then used to quantify the gas analysis results.

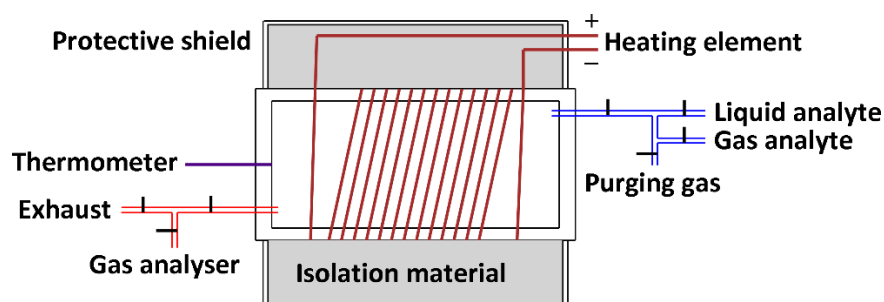


Figure 28. Heated mixing chamber for preparation of standard samples of analytes coexisting in different phases. The standard samples were used for quantitative gas analysis.

For each precursor composition, the gas analysis of the atmosphere of the reactor was carried out by acquiring two sets of mass spectra at room temperature and at 800 °C. At the end of each experiment, the MWCNTs were collected from throughout the reactor and weighed.

The aerosol consumption rate of the precursors was measured by weighing the aerosol captured in a bubbler directly connected to the aerosol generator.

Table 5 lists the carbon and catalyst sources used in this study with their corresponding catalyst source concentrations and synthesis times. The criteria for selection of hydrocarbons were as following: for generation of aerosol, the hydrocarbon should be liquid at the standard conditions; it should not react with ferrocene (only dissolution) and should be cheaper or similarly priced as the commonly used AACVD hydrocarbons such as toluene and xylene (see table 4).

Table 5. Experimental variables for synthesis of MWCNTs: carbon source, catalyst concentration, catalyst source and duration of the experiment.

Variable carbon sources with 5 wt.% ferrocene; synthesis time: 15 min	benzene ($\geq 99\%$), toluene (99.8%), <i>m</i> -xylene ($\geq 98.5\%$), ethylbenzene ($\geq 99\%$), 1,2,4-trimethylbenzene (98%), <i>n</i> -propylbenzene (98%), isopropylbenzene (98%), <i>n</i> -butylbenzene ($\geq 99\%$), diethylbenzene (95%, mixture of different isomers), cyclohexane ($\geq 99\%$), methylcyclohexane (99%), cyclohexanone ($\geq 99.5\%$), <i>n</i> -pentane ($\geq 99\%$), <i>n</i> -hexane ($\geq 99\%$) and <i>n</i> -heptane ($\geq 99\%$). Supplier: Sigma-Aldrich
Variable ferrocene concentrations in toluene; synthesis time: 15 min	0, 1, 3, 5, 7, 9, 11, 13 and 15 wt.%.
Variable catalyst sources in toluene; synthesis time: 15 min	ferrocene 5 wt.%, ferrocene 4.89 wt% + nickelocene 0.11 wt.% and ferrocene 4.89 wt.% + cobaltocene 0.11 wt.% . Supplier: Sigma-Aldrich
Variable synthesis time; precursor: ethylbenzene + 5 wt.% ferrocene	15, 30, 45, 60 and 120 minutes

3.3. Results and discussions

3.3.1. MWCNTs synthesised from different carbon sources

The mass of synthesised MWCNTs, corresponding to different liquid hydrocarbons, is listed in a descending order in table 6. For a better comparison of the precursors, the term *precursor conversion yield* was defined as the mass of synthesised MWCNTs divided by the amount of precursor consumed. The most efficient precursor is the one which has the highest conversion yield and gives the largest quantity of MWCNTs. In this sense, and as can be seen from table 6, although methylcyclohexane had the highest conversion yield ($\sim 50\%$), it did not result in large quantities of MWCNTs (~ 400 mg in 15 min). In contrast, ethylbenzene and isopropylbenzene had the second and third highest conversion yields (38% and 27%, respectively) and produced significantly large amount of MWCNTs (950 mg and 700 mg in 15 min, respectively). The mass of MWCNTs synthesised from ethylbenzene under the specific synthesis condition used in this study was 60% and 80% higher than those synthesised from toluene and *m*-xylene, respectively. The conversion yield of ethylbenzene was also around 80% higher than both toluene and *m*-xylene. Other precursors only generated less than half of the quantity obtained from ethylbenzene. Therefore, ethylbenzene and isopropylbenzene are the most efficient carbon sources amongst all the studied hydrocarbons. Neither the molar mass nor the boiling temperature of the hydrocarbons showed a significant trend with regard to the mass of synthesised MWCNTs (table 7). The consumption rate of each precursor is provided in table 6. All benzene derivatives had very similar aerosol consumption rate of around 10 g/hr. Owing to the difference in viscosity, density and surface tension, the consumption rate of the cyclohexane derivatives and alkanes (table 7) were significantly different from the benzene derivatives.

Table 6. Characteristics of different precursors and properties of their corresponding synthesised MWCNTs. Synthesis time: 15 min.

Carbon source (+ 5 wt% ferrocene)	Total mass of MWCNTs (mg)	Characteristics of precursor		Properties of MWCNTs						
		Precursor conversion yield (%)	Precursor consumption rate (g/hr)	Outer diameter (nm)	Raman I _D /I _G	TGA T _{20%} (°C)	TGA T _{50%} (°C)	TGA T _{70%} (°C)	TGA T _{70%} - T _{20%} (°C)	Iron concentration (wt.%)
Ethylbenzene 	954 ± 175	38.2 ± 8.5	10 ± 1.3	45.1 ± 24.3	0.327	597	640	654	58	1.8
Isopropylbenzene 	699 ± 159	27.4 ± 6.6	10.2 ± 0.8	58.8 ± 26.6	0.290	610	650	673	63	2.8
Toluene 	591 ± 141	21.2 ± 5.9	11.15 ± 0.6	38.3 ± 13.4	0.290	575	622	644	69	5.9
<i>m</i> -Xylene 	531 ± 42	20.8 ± 3.6	10.2 ± 1.6	40.4 ± 20.4	0.286	581	616	630	49	3.3
<i>n</i> -Butylbenzene 	466 ± 54	16.6 ± 2.4	11.19 ± 1	57.0 ± 26.8	0.322	573	615	638	64	3.0
Benzene 	403 ± 51	16.6 ± 2.2	9.7 ± 0.4	47.5 ± 22.2	0.292	581	621	632	51	4.4
Methylcyclohexane 	392 ± 183	50.6 ± 23.8	3.1 ± 0.1	43.1 ± 20.8	0.345	607	649	672	66	1.1
<i>n</i> -Heptane 	392 ± 263	14.3 ± 9.6	10.95 ± 0.5	33.5 ± 17.2	0.414	562	606	630	68	4.1
1,2,4-Trimethylbenzene 	309 ± 78	13.2 ± 3.3	9.35 ± 0.2	52.1 ± 22.6	0.307	558	594	624	66	4.3
<i>n</i> -Pentane 	302 ± 196	< 1*	~ 250 *	40.3 ± 18.3	0.349	595	641	665	70	1.3
Cyclohexane 	204 ± 11	6.5 ± 0.8	12.45 ± 1.3	47.4 ± 23.5	0.384	583	633	663	80	5.0
<i>n</i> -Hexane 	131 ± 59	< 1*	~ 100 *	39.2 ± 14.7	0.401	555	606	637	82	7.5
Cyclohexanone 	125 ± 49	9.6 ± 3.8	5.2 ± 0	48.0 ± 25.6	0.429	548	585	608	60	5.6
Diethylbenzene 	60 ± 37	1.9 ± 1.2	12.9 ± 2.9	57.5 ± 21.4	0.309	570	608	624	55	3.7
<i>n</i> -Propylbenzene 	57 ± 21	2.1 ± 0.8	10.9 ± 0.8	37.4 ± 12.2	0.542	512	574	620	108	10.9

* Due to the low boiling point of *n*-pentane and *n*-hexane, the data acquisition was highly dependent on the measurement temperature. This introduced a relatively large uncertainty in the measurement.

Table 7. Some of the physical properties of hydrocarbons used in this work [222,223].

Carbon source	M (g/mol)	T _b (°C)	D at 20 °C (g/mL)	γ at 20 °C (mN/m)	η at 20 °C (mPa·s)	Solubility of Ferrocene*
Ethylbenzene	106.17	136	0.867	28.745	0.669	Good
Isopropylbenzene	120.19	153	0.864	27.685	0.791	Good
Toluene	92.14	110.6	0.865	27.9275	0.623	Good
<i>m</i> -Xylene	106.17	136	0.868	28.47	0.617	Good
<i>n</i> -Butylbenzene	134.22	183	0.86	28.7175	1.035	Good
Benzene	78.11	80	0.874	27.5634	0.649	Good
Methylcyclohexane	98.19	101	0.77	23.285	0.734	Good
<i>n</i> -Heptane	100.20	98	0.684	19.65	0.416	Poor
1,2,4-Trimethylbenzene	120.19	168	0.876	29.1975	0.894	Good
<i>n</i> -Pentane	72.15	36	0.626	15.4475	0.237	Poor
Cyclohexane	84.16	81	0.779	24.65	0.98	Good
<i>n</i> -Hexane	86.18	69	0.659	17.885	0.313	Poor
Cyclohexanone	84.16	81	0.947	34.565	2.453	Unstable
Diethylbenzene	134.22	181	0.87	~30	0.749	Good
<i>n</i> -Propylbenzene	120.19	159	0.862	28.4425	0.8	Good

* 5 wt.% at room temperature. The solubility was evaluated visually. A *good* solubility means that after a few minutes, no solid particle was observed in the solution. A *poor* solubility means that the saturation limit was less than 5 wt.% ferrocene at room temperature. An *unstable* solubility means that some new particles appeared in the solution after complete dissolution of 5 wt.% ferrocene.

The hydrocarbons were all found to dissolve 5 wt.% ferrocene at room temperature with the exception of the alkanes. This, combined with the fact that particularly *n*-pentane and *n*-hexane have low boiling points and therefore leave a significant deposit of crystallised ferrocene on the walls of the aerosol unit, make alkanes unsuitable carbon sources for large-scale synthesis of MWCNTs using the AACVD method. The mixtures of cyclohexanone and ferrocene were unstable and precipitated form in the solutions after a few hours.

The quantity of synthesised MWCNTs could be increased by prolonging the synthesis to 2 hr. As can be seen from the SEM images in figure 29, 1.5-mm-thick carpet of highly aligned MWCNTs was obtained after 2 hr of synthesis. Figure 29g and h show how the yield and the length of MWCNTs synthesised from ethylbenzene depend upon the synthesis time.

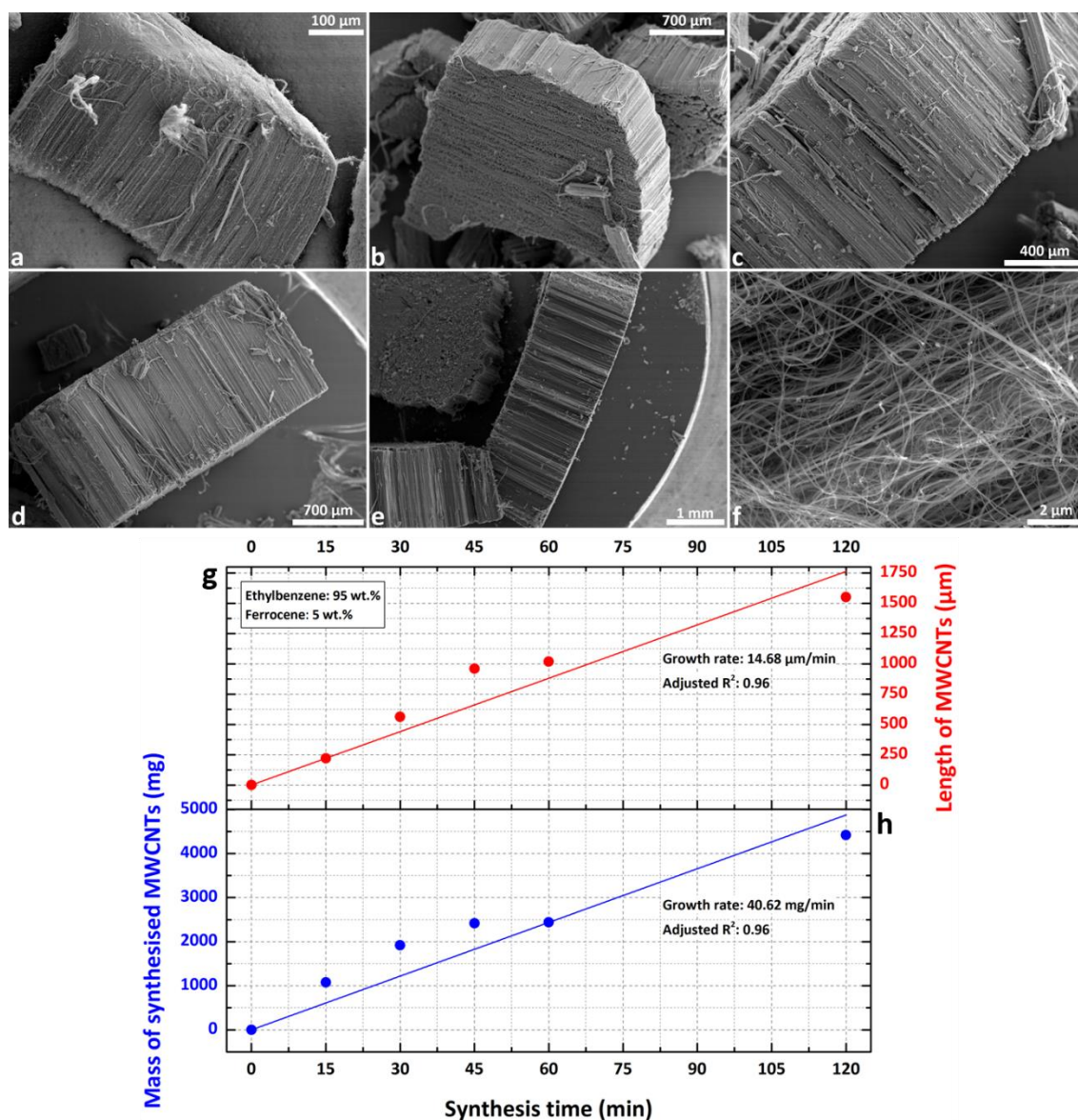


Figure 29. SEM images of carpets of vertically aligned MWCNTs synthesised for a) 15 min; b) 30 min; c) 45 min; d) 1 hr and e) 2 hr from ethylbenzene and 5 wt.% ferrocene at 800 °C with argon flow rate of 1 L/min; f) High magnification SEM image of the typical MWCNTs; g) Length and h) Mass of synthesised MWCNTs as a function of synthesis time. The average growth rate after 2 hr was 62 mg/min (14.68 μm/min).

TEM was used to compare the structure of the individual MWCNTs. Figure 30 depicts a gallery of TEM images of the MWCNTs synthesised from different hydrocarbons.

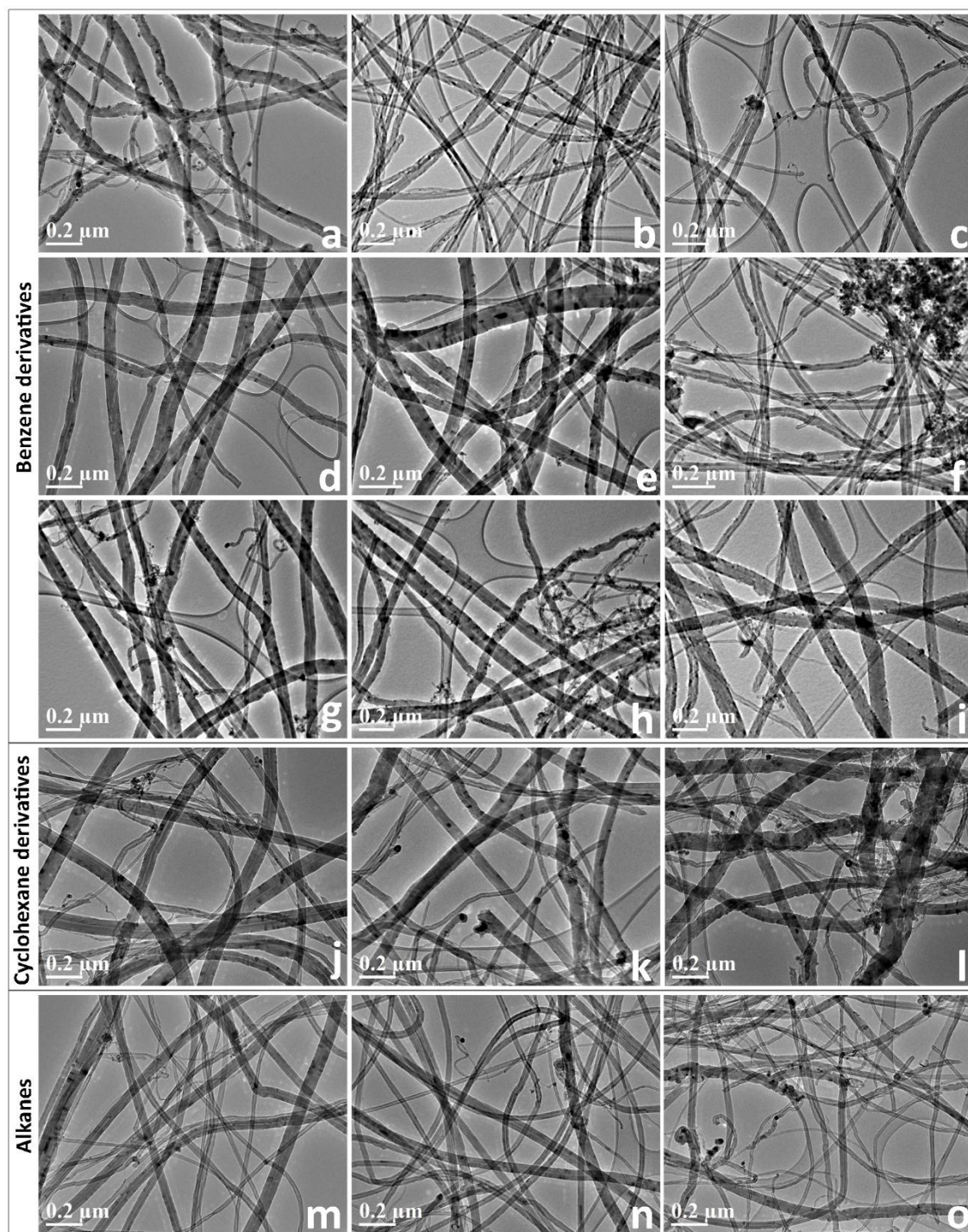


Figure 30. TEM image gallery comparing the structure of the individual MWCNTs synthesised from a) Benzene; b) Toluene; c) *m*-Xylene; d) Ethylbenzene; e) 1,2,4-Trimethylbenzene; f) *n*-Propylbenzene; g) Isopropylbenzene; h) *n*-Butylbenzene; i) Diethylbenzene; j) Cyclohexane; k) Methylcyclohexane; l) Cyclohexanone; m) *n*-Pentane; n) *n*-Hexane and o) *n*-Heptane. The TEM images are categorised in three sections depending on the class of corresponding hydrocarbons: benzene derivatives, cyclohexane derivatives and alkanes.

Based on the TEM results, with the exception of the sample obtained from *n*-propylbenzene, all the MWCNT samples were relatively clean with insignificant amount of amorphous carbon. The outer diameter of MWCNTs was measured (table 6) and it was shown that the mean outer diameter of MWCNT samples ranges from 34 nm (*n*-hexane) to 58 nm (isopropylbenzene). The MWCNTs synthesised from isopropylbenzene, diethylbenzene and *n*-butylbenzene exhibited the largest mean outer diameter (57 – 60 nm) of all samples; while toluene, *m*-xylene, *n*-propylbenzene, and the alkanes resulted in relatively thin MWCNTs (33 – 40 nm). The homogeneity of the outer diameter of MWCNTs can be quantified by the standard deviation. In this sense, the batches with large mean outer diameter such as the ones synthesised from isopropylbenzene had bigger variations in diameter while the batches with small mean outer diameter such as the ones synthesised from toluene, had less variations in diameter. This dependency is shown in figure 31a. The similarity of the relative standard deviation (standard deviation divided by mean) of the outer diameter of the MWCNTs in all the batches (0.3 – 0.55, figure 31b) suggests that normalised variation of the outer diameter of MWCNTs, was nearly independent of the carbon source.

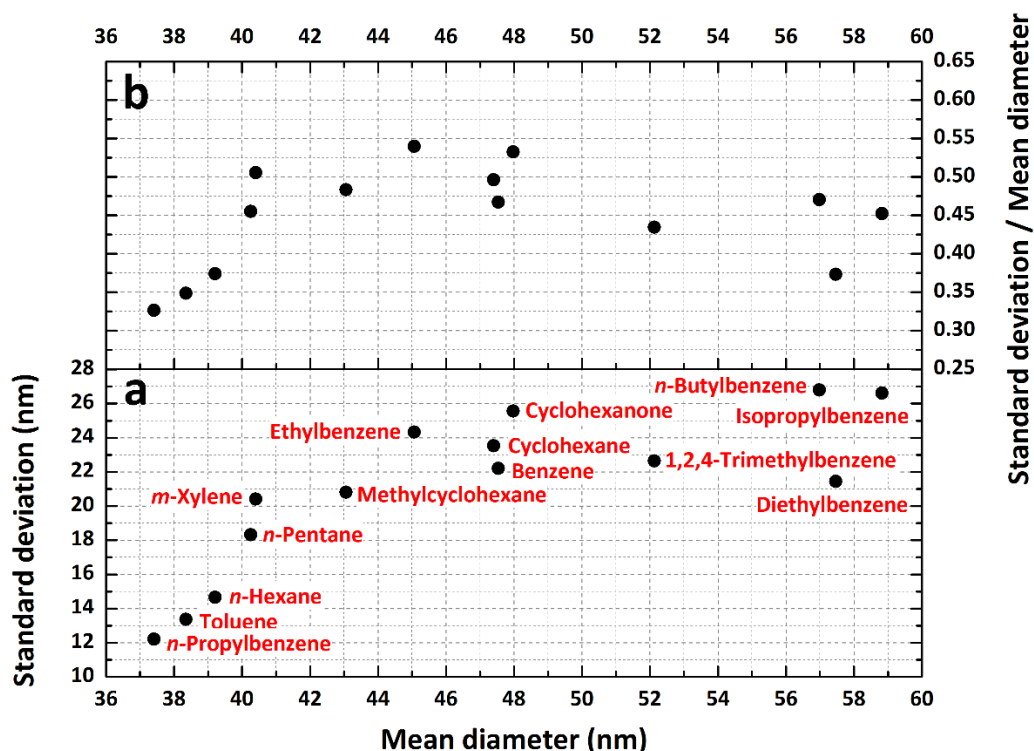


Figure 31. a) The dependency of the standard deviation on the mean outer diameter of MWCNTs synthesised from different hydrocarbons; b) Similarity of the relative standard deviation (standard deviation divided by mean) of the outer diameter of MWCNTs synthesised from different hydrocarbons (variation between 0.3 and 0.55).

Qualitative characteristics of different samples including the Raman I_D/I_G , TGA-derived oxidation resistance (temperature at which a sample loses 20%, 50% and 70% of its initial mass), and the residual iron content of MWCNTs are provided in table 6 (see the original TGA graphs and Raman spectra in figure 32). The difference between the temperatures at which a MWCNT sample loses 20% and 70% of its initial mass is shown by parameter $T_{70\%} - T_{20\%}$. As described in the previous chapter, this parameter is mathematically equivalent to the slope of the falling part of the TGA graphs (figure 32b) and quantifies the structural homogeneity of the samples. Already small differences between the temperature of 20% mass loss and temperature of 70% mass loss (≤ 70 °C) can mean a structurally homogeneous batch of nanotubes. There is a clear trend between the Raman I_D/I_G with TGA-derived oxidation resistance ($T_{50\%}$) and structural homogeneity ($T_{70\%} - T_{20\%}$). The MWCNTs synthesised from most of the

benzene derivatives had generally low defect density (Raman $I_D/I_G \approx 0.3$) [11,12,14,17,26,28,40,41], high oxidation resistance ($T_{50\%} > 600$ °C) [14,18,19,40] and good structural homogeneity ($T_{70\%} - T_{20\%} \approx 50 - 70$ °C). This is probably due to the good interaction and dissolution of ferrocene in these hydrocarbons. In contrast, samples such as the ones obtained from *n*-propylbenzene or *n*-hexane had high defect density (Raman $I_D/I_G > 0.4$), low oxidation resistance ($T_{50\%} \approx 500 - 550$ °C) and poor structural homogeneity ($T_{70\%} - T_{20\%} > 80$ °C). There was no significant correlation between the oxidation resistance of the MWCNTs and their mean outer diameter.

The majority of samples had less than 5 wt.% residual iron, with the exception of *n*-propylbenzene (~10 wt.%) which was expected from the TEM studies revealing the presence of agglomerates of iron-containing particles (figure 30f). The MWCNTs synthesised from ethylbenzene and isopropylbenzene had significantly lower content of residual iron particles (1.8 and 2.8 wt.%, respectively) compared to the ones obtained from toluene (5.9 wt.%). The method of calculation of the residual iron content of MWCNTs was the same as in the previous chapter.

MWCNTs synthesised from isopropylbenzene had a very low defect density (Raman $I_D/I_G = 0.29$) and a very good oxidation resistance (temperature of 50% mass loss = 650 °C). This high quality, along with the fact that isopropylbenzene had the second highest synthesis rate while being the cheapest of all, make isopropylbenzene a good carbon source for cost-effective large-scale synthesis of high quality MWCNTs using the AACVD method.

Similar to toluene, ethylbenzene and isopropylbenzene are both irritating to the respiratory system and harmful, if inhaled. However, these hydrocarbons are considered less toxic than benzene [224].

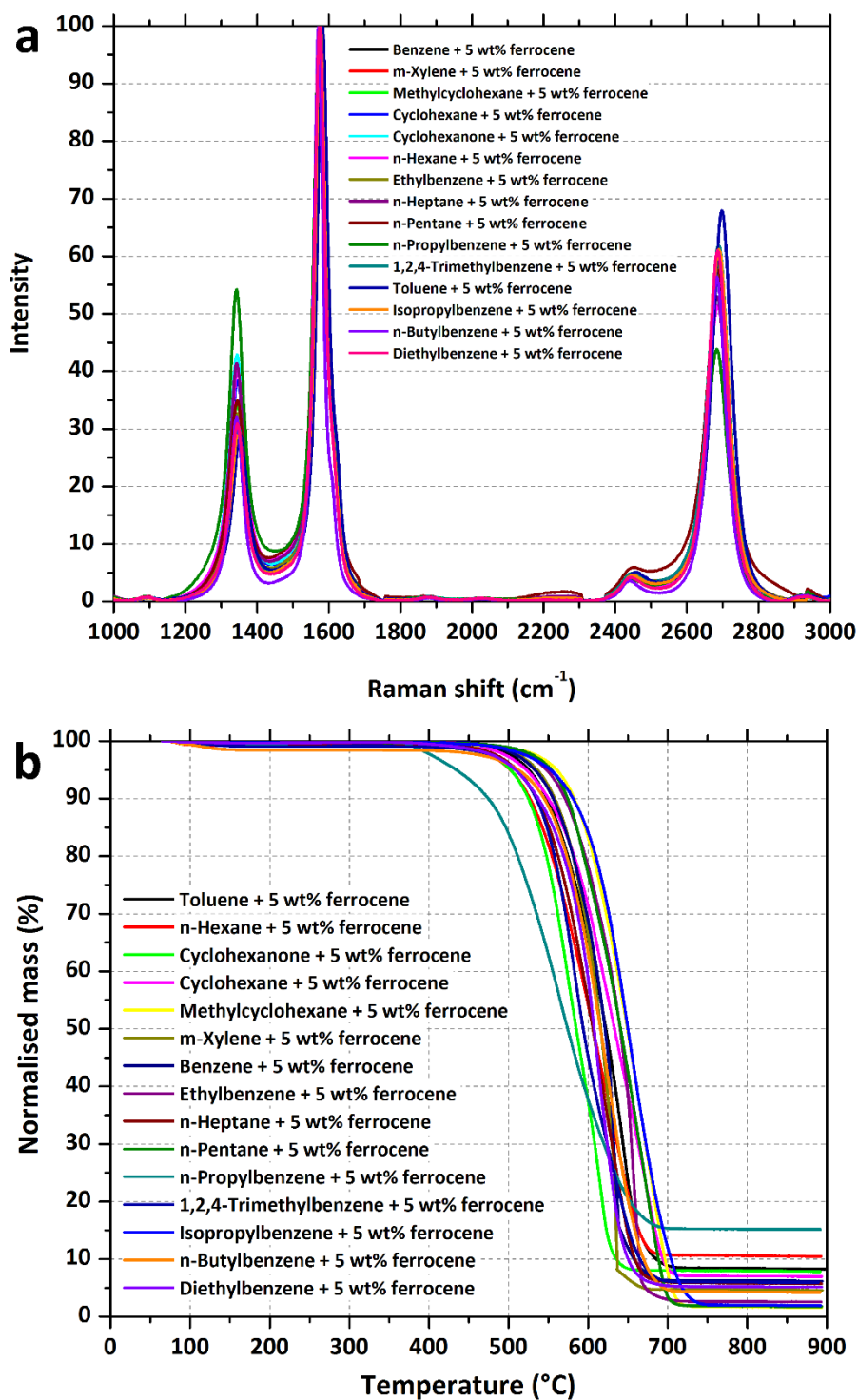


Figure 32. a) Raman spectra and b) TGA graphs of the MWCNTs synthesised from different carbon sources.

3.3.2. MWCNTs synthesised from different catalyst contents and sources

In this section, a number of precursors composed of toluene with variable ferrocene concentrations are compared (table 5). The study was carried out in order to identify the impact of the ferrocene concentration in toluene, on the yield and other previously discussed properties of MWCNTs. Toluene was chosen, as it is currently the most widely used carbon source in the AACVD methods (see table 4). As in the previous section, it is shown that altering the composition can be an easy approach for tuning the properties of MWCNTs.

At room temperature, pure toluene can easily dissolve up to 13 wt.% ferrocene. This solubility can be raised to around 15 wt.% if the solution is kept warm (40 – 60 °C) and sonicated. Figure 33 shows the dependence of different properties of MWCNTs on the ferrocene concentration in toluene. Increasing the ferrocene concentration in the precursor solution can improve the yield. Interestingly, ferrocene concentration had no impact on the defect density as shown by Raman. However, samples obtained from the solutions with higher ferrocene concentrations, possessed higher concentrations of residual catalyst nanoparticles on or inside the MWCNTs (Figure 33e and TEM gallery: figure 34a – h) and exhibited lower oxidation resistances ($T_{50\%} < 600$ °C). This decrease in the oxidation resistance of the MWCNTs is attributable to their residual iron content which can catalyse the oxidation reaction [225,226]. Therefore, low oxidation resistance is not necessarily due to a poor structure, low graphitisation or thin diameter, but can also originate from the excessive residual catalyst content of CNTs.

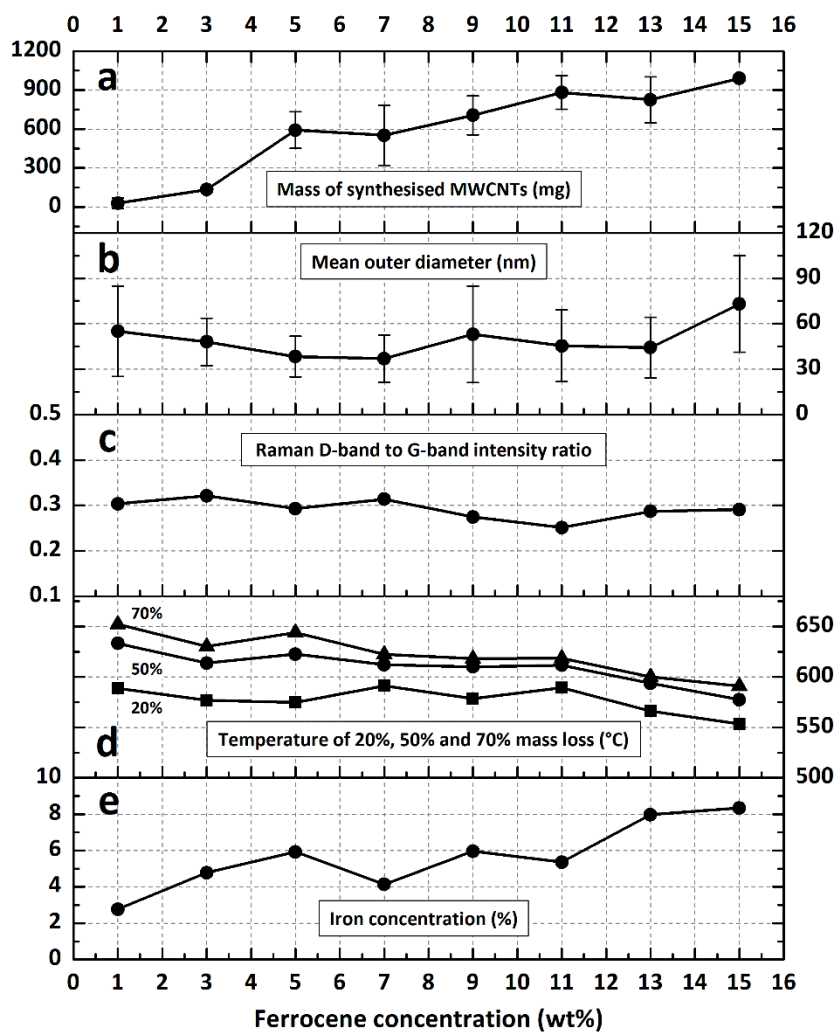


Figure 33. Graphs depicting the variation of different parameters of MWCNTs vs. the ferrocene concentration in the precursor: a) Mass; b) Mean outer diameter; c) Raman I_D/I_G ; d) Oxidation resistance (temperature of 20%, 50% and 70% mass loss) and e) Residual iron content of MWCNTs. Synthesis time: 15 minutes. The uncertainty of data on graphs c, d and e was less than 5%.

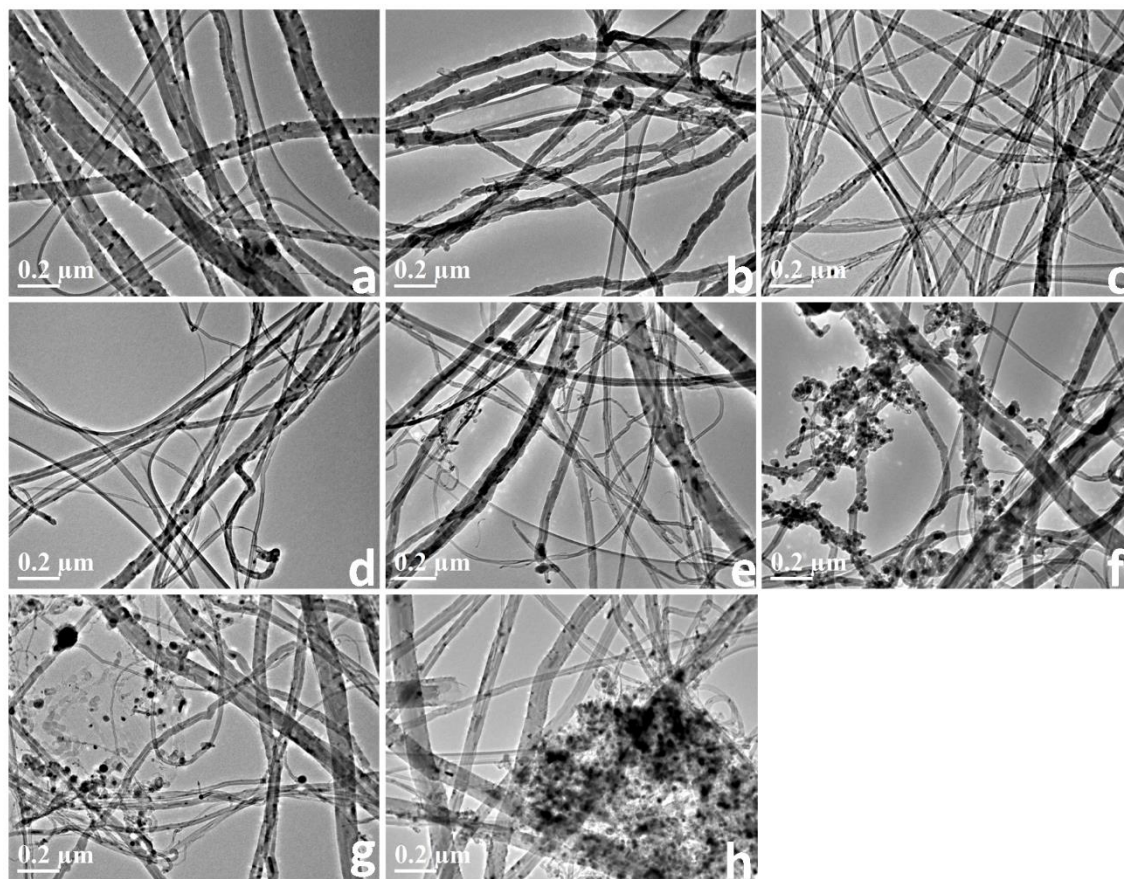


Figure 34. TEM gallery for the comparison of the structure of the individual MWCNTs and the concentration of the residual catalyst nanoparticles synthesised from toluene with various ferrocene concentrations: a) 1 wt.%; b) 3 wt.%; c) 5 wt.%; d) 7 wt.%; e) 9 wt.% f) 11 wt.%; g) 13 wt.% and h) 15 wt.%.

The mean outer diameter of MWCNT samples mostly varied between 30 and 60 nm with an average standard deviation of *ca.* 22 nm. The exception was the batches synthesised from the precursor containing 15 wt.% ferrocene which had mean outer diameter of more than 70 nm.

Clean carpets of vertically aligned MWCNTs were obtained from all precursors with the exception of solutions containing 1 wt.% ferrocene which resulted in randomly-oriented MWCNTs.

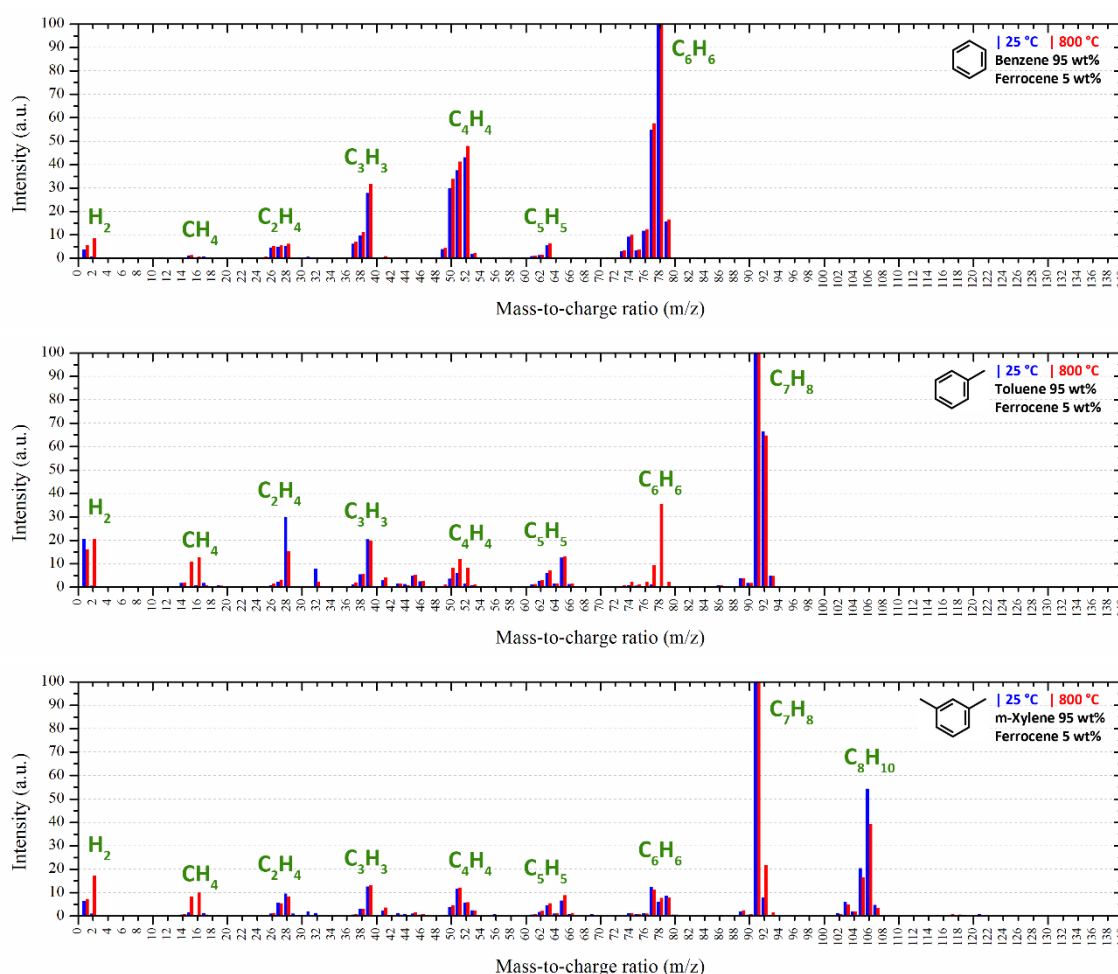
Figure 34 is a gallery of TEM images of products synthesised from toluene with variable ferrocene contents (1 – 15 wt.%) and shows that all the samples contained

MWCNTs. Agglomerates of iron-containing nanoparticles are visible in the samples synthesised from the precursors containing 11 wt.% ferrocene and more, due to the excessive abundance of synthesised iron inside the reactor. It seems that some of the agglomerates did not fully contribute to the catalytic growth of MWCNTs as they were larger than a micron. The relatively high concentrations of iron-based particles on or inside the MWCNTs can be potentially useful for catalytic applications in which the MWCNTs would act as a scaffold for iron-based nanoparticles as catalysts [227].

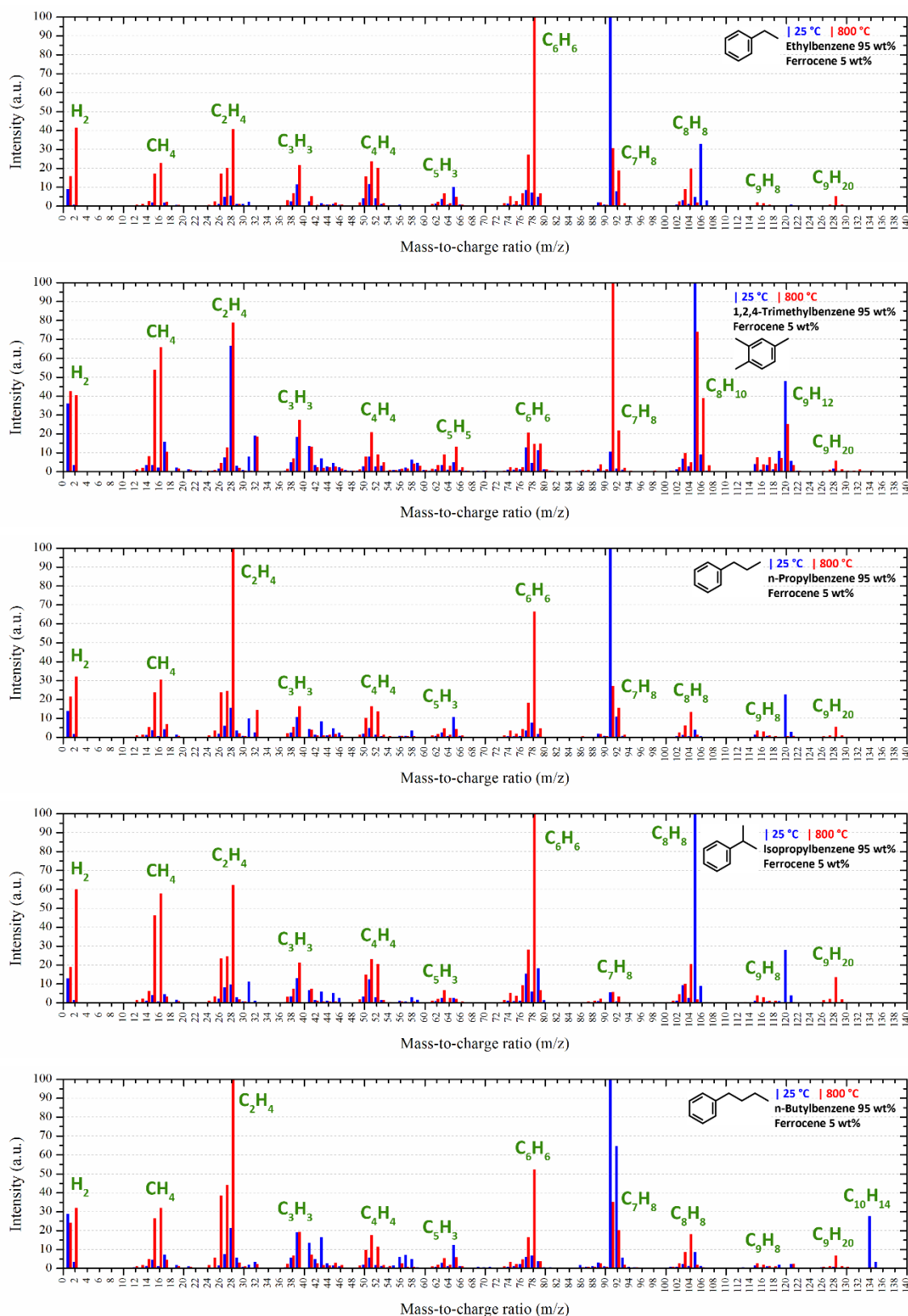
In order to investigate the effect of catalyst source on the synthesis yield and properties of MWCNTs, three different mixtures of catalyst sources were compared (table 5). The yield and the quality of MWCNTs could not be improved by using nickelocene or cobaltocene in the precursor. These metallocenes have far less solubility in benzene derivatives (*ca.* 0.05 [22] – 0.1 wt.%) and are considerably more expensive than ferrocene. Hence, they are not suitable catalyst sources for large scale synthesis of MWCNTs using AACVD method. This is also suggested by the fact that ferrocene is by far the most popular catalyst source in SPCVD and AACVD setups for synthesis of MWCNTs (table 4).

3.3.3. Qualitative gas analysis of the reactor: different carbon sources

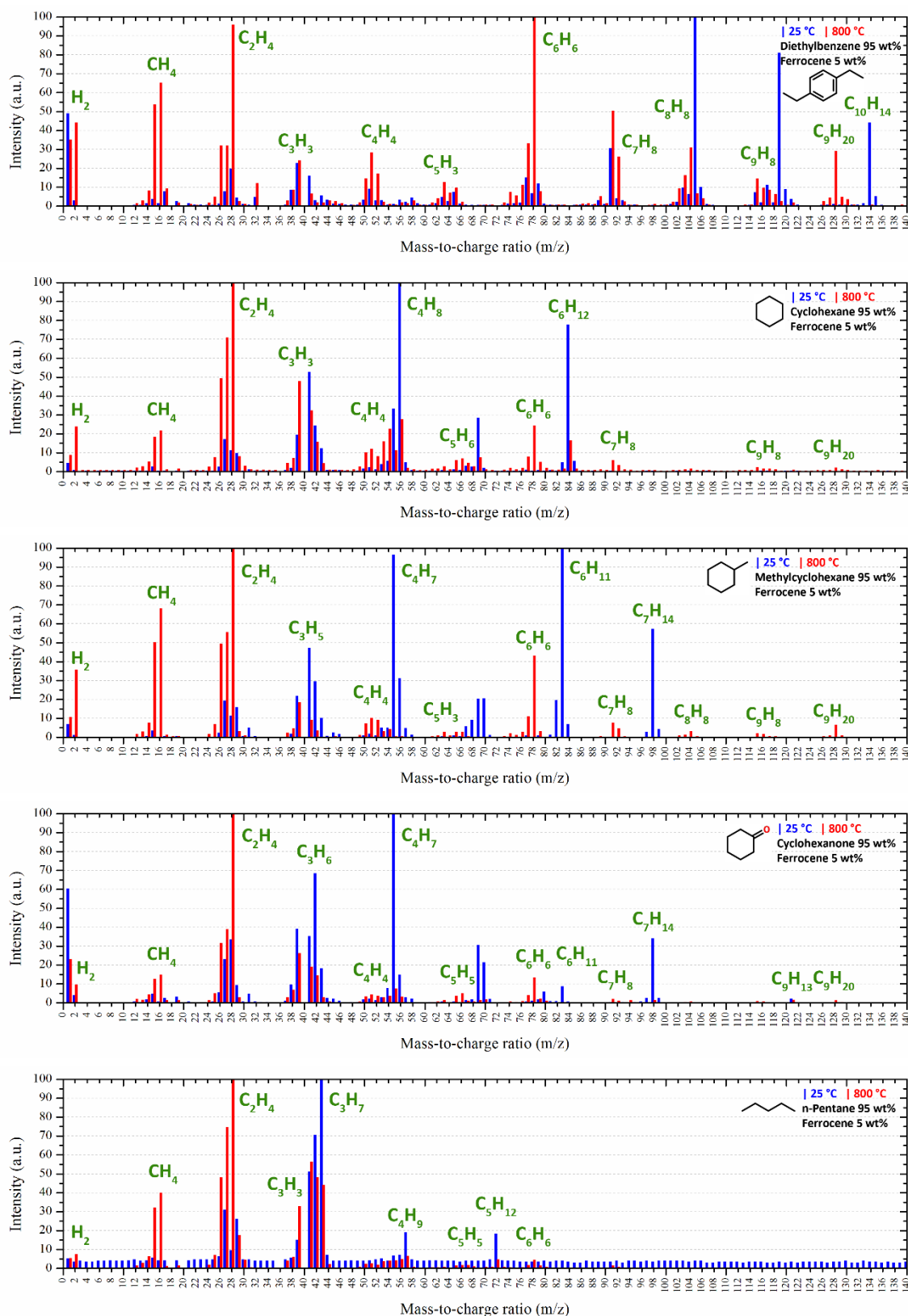
An extensive spectrometry study was carried out to understand the thermocatalytic cracking behaviour of all the hydrocarbons to observe, to what extent, the attributes of synthesised MWCNTs depend upon the way their corresponding precursors crack down. In this and the next two sections, the results of the online mass spectrometry of the reactor are discussed. Figure 35 shows the mass spectra acquired from the reactor when different hydrocarbons with 5 wt.% ferrocene were used as the precursor. Each graph contains two spectra; one from the reactor at the room temperature (in blue) and one acquired at the synthesis temperature (in red).



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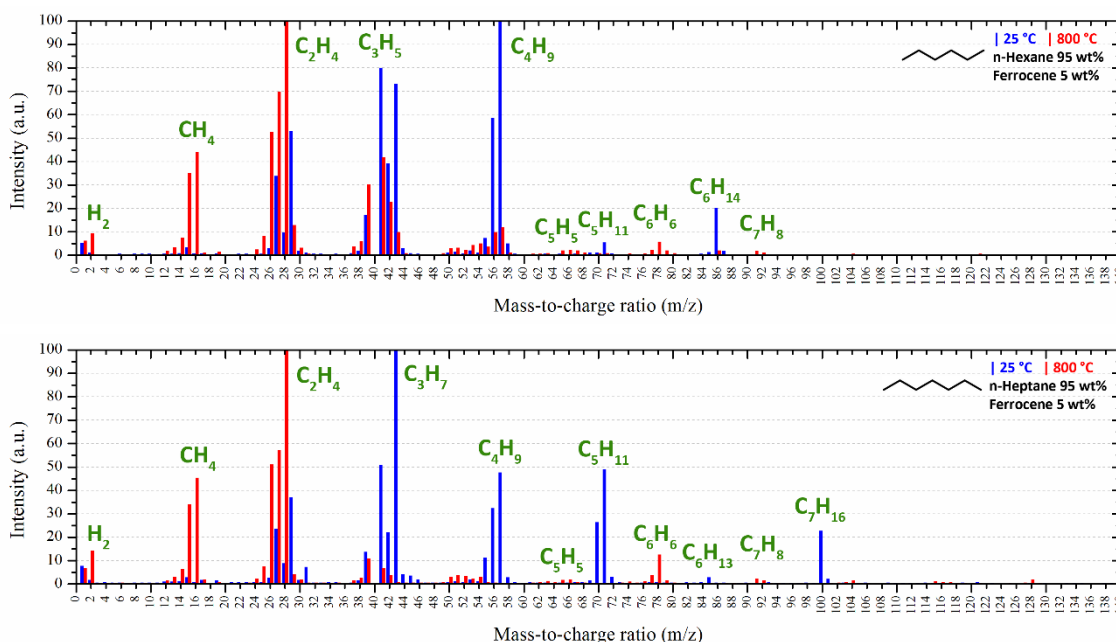


Figure 35. Online qualitative gas analysis of the atmosphere of the AACVD reactor using the following carbon sources in order of appearance in the figure: benzene, toluene, *m*-xylene, ethylbenzene, 1,2,4-trimethylbenzene, *n*-propylbenzene, isopropylbenzene, *n*-butylbenzene, diethylbenzene, cyclohexane, methylcyclohexane, cyclohexanone, *n*-pentane, *n*-hexane and *n*-heptane. All the hydrocarbons were mixed with 5 wt.% ferrocene. Each graph contains two mass spectra acquired at the room temperature (blue) and at the synthesis temperature (red).

The fragments identified in the mass spectra, originate from two different phenomena: thermocatalytic cracking inside the reactor and ionisation-induced cracking inside the ion source of the mass spectrometer. The acquisition of mass spectra at low and high temperature has this advantage that by comparing the spectrum acquired at the synthesis temperature with the spectrum acquired at the room temperature, one can exclude the ionisation-induced cracking. On the other hand, as can be seen from the spectra, the thermocatalytic cracking sequence of the hydrocarbons involves the creation of certain intermediate fragments. The main intermediate fragments created during the thermocatalytic cracking of different hydrocarbons are summarised in table 8 and the ones that are common to all the hydrocarbons are underlined.

Table 8. Some of the main intermediate fragments created during the thermocatalytic cracking of different hydrocarbons and the intensities of three selected fragments: $m/z = 16$, 28 and 78 at room temperature: I_{25} and at synthesis temperature: I_{800} . The intensities are normalised with respect to the base peak of the corresponding precursor. The possible formulas for the main intermediate fragments are provided below the table.

Carbon source (+ 5 wt% ferrocene)	Main intermediate fragments (m/z)	$m/z = 16$		$m/z = 28$		$m/z = 78$	
		I_{25}	I_{800}	I_{25}	I_{800}	I_{25}	I_{800}
Ethylbenzene	<u>2</u> , <u>16</u> , <u>28</u> , 39, 52, 63, <u>78</u> , 92, 104, 116, 128	0.33	22.73	5.47	40.62	7.22	100
Isopropylbenzene	<u>2</u> , <u>16</u> , <u>28</u> , 39, 52, 63, <u>78</u> , 92, 104, 116, 128	0.67	57.85	9.79	62.38	6.03	100
Toluene	<u>2</u> , <u>16</u> , <u>28</u> , 39, 52, 65, <u>78</u>	0.87	12.75	29.87	15.39	0.22	35.37
<i>m</i> -Xylene	<u>2</u> , <u>16</u> , <u>28</u> , 39, 52, 65, <u>78</u> , 92	0.37	9.99	9.58	8.35	6.09	7.72
<i>n</i> -Butylbenzene	<u>2</u> , <u>16</u> , <u>28</u> , 39, 52, 63, <u>78</u> , 104, 116, 128	1.11	31.92	21.43	100	6.70	52.16
Benzene	<u>2</u> , <u>16</u> , <u>28</u> , 39, 52, 65	0.20	0.64	5.31	6.13	100	100
Methylcyclohexane	<u>2</u> , <u>16</u> , <u>28</u> , 39, 52, 65, <u>78</u> , 92, 104, 116, 128	0.33	68.16	11.23	100	0.22	43.29
<i>n</i> -Heptane	<u>2</u> , <u>16</u> , <u>28</u> , 39, 52, 65, <u>78</u> , 92	0.87	45.30	8.91	100	0.69	12.58
1,2,4-Trimethylbenzene	<u>2</u> , <u>16</u> , <u>28</u> , 39, 52, 65, <u>78</u> , 92, 106, 128	2.15	65.71	66.65	78.76	4.66	14.52
<i>n</i> -Pentane	<u>2</u> , <u>16</u> , <u>28</u> , 39, <u>78</u>	4.37	39.94	9.53	100	3.58	4.39
Cyclohexane	<u>2</u> , <u>16</u> , <u>28</u> , 39, 56, 66, <u>78</u> , 84, 92	0.49	21.86	11.38	100	0.54	24.24
<i>n</i> -Hexane	<u>2</u> , <u>16</u> , <u>28</u> , 41, 56, 66, <u>78</u>	0.77	44.09	9.60	100	0.43	5.77
Cyclohexanone	<u>2</u> , <u>16</u> , <u>28</u> , 39, 56, 65, <u>78</u>	0.75	14.94	33.59	100	1.07	13.30
Diethylbenzene	<u>2</u> , <u>16</u> , <u>28</u> , <u>78</u> , 92, 102, 116, 128, 152	1.41	65.19	19.79	95.95	6.82	100
<i>n</i> -Propylbenzene	<u>2</u> , <u>16</u> , <u>28</u> , 39, 52, 65, <u>78</u> , 92, 104, 116, 128	0.61	30.37	15.61	100	7.64	66.46

Possible formulas for the main intermediate fragments:

2: H_2 16: CH_4 28: C_2H_4 39: C_3H_3 41: C_3H_5 52: C_4H_4 53: C_4H_5 56: C_4H_8 63: C_5H_3 65: C_5H_5 66: C_5H_6
 78: C_6H_6 84: C_6H_{12} 92: C_7H_8 104: C_8H_8 106: C_8H_{10} 116: C_9H_8 120: C_9H_{12} 128: C_9H_{20} 152: $C_{10}H_{32}$

In order to compare the thermocatalytic cracking of different hydrocarbons, the intensities of few common intermediate fragments can be compared. To simplify, three main common fragments were selected: peaks at $m/z = 16$, 28 and 78 representing methane, ethane and benzene, respectively. As can be seen from table 8, heating up the reactor resulted in a significant increase of the abundance of these selected fragments. This increase of intensity represents the magnitude of the thermocatalytic cracking of the hydrocarbons.

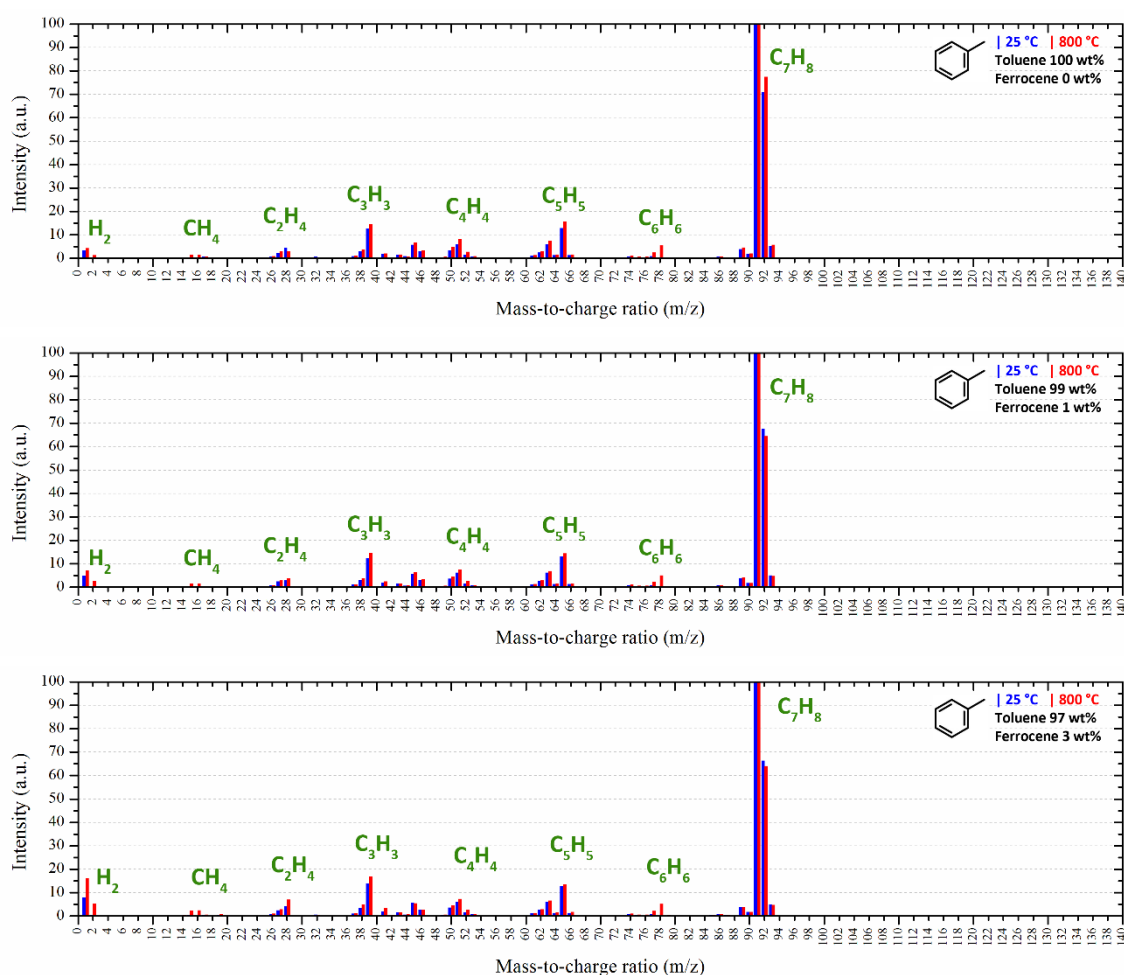
The massive increase of the abundance of methane ($I_{25} \rightarrow I_{800}$ at $m/z = 16$) shows that, all the hydrocarbons effectively cracked down to methane with the exception of

benzene which underwent a relatively low molecular conversion (mass spectra of benzene at the room temperature and at 800 °C were almost identical: figure 35). All other hydrocarbons transformed to benzene to some extent inside the reactor. This reflects the high structural stability of benzene. The precise mechanism of this transformation from various hydrocarbons to benzene, however, is not fully understood but might involve recombination of fragments and radicals. Similar observation has been reported in CVD reactors for synthesis of MWCNTs using acetylene [181,183]. Moreover, this transformation appears to be significantly higher for toluene and methylbenzene while it seems to be less common in the case of *n*-pentane.

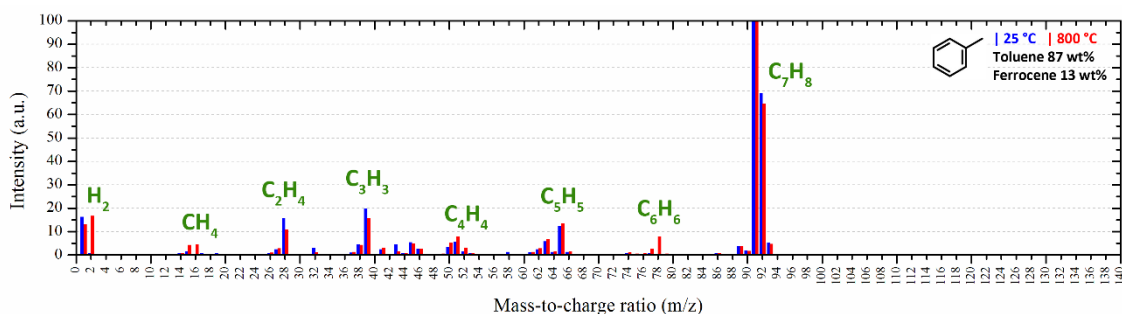
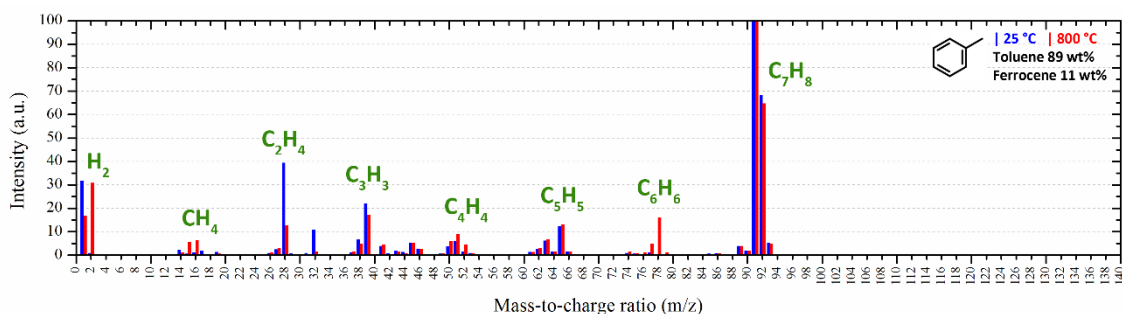
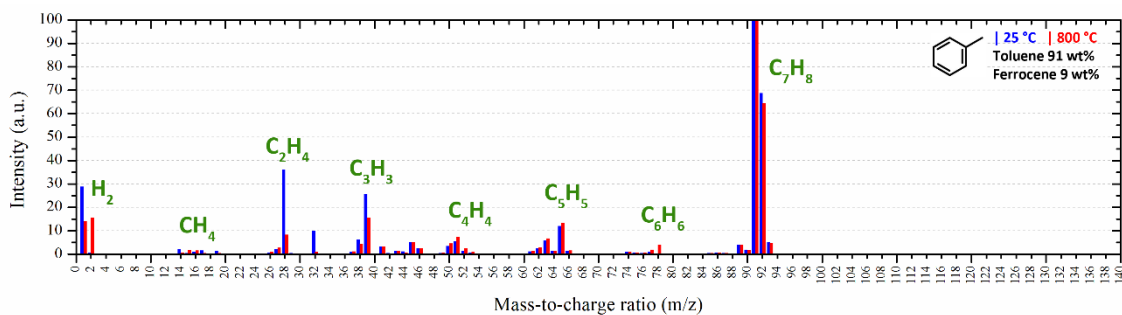
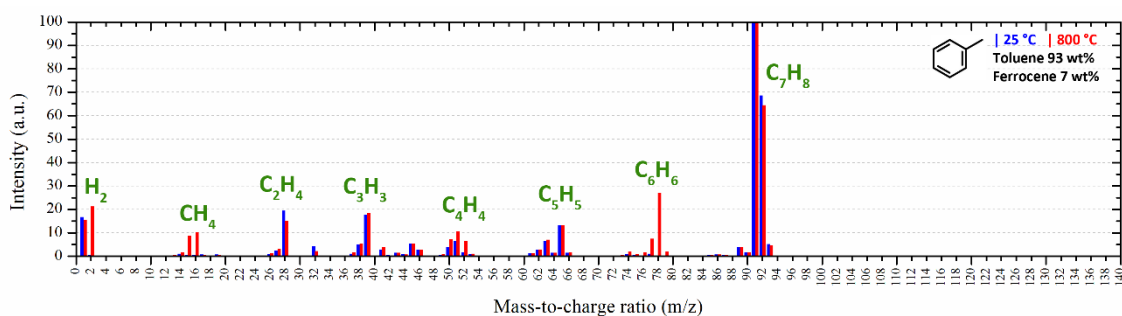
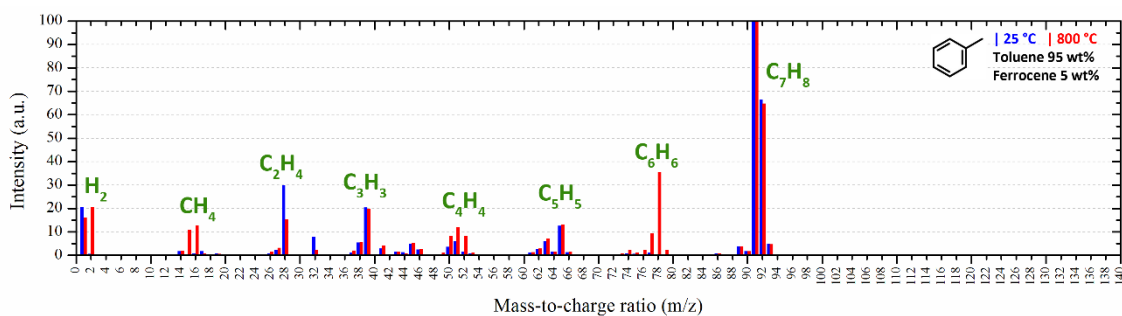
As discussed in Section 3.3.1, methylcyclohexane showed the highest conversion yield (~ 50%). On the other hand, the increase of the abundance of methylcyclohexane's fragments ($m/z = 16, 28$ and 78) suggests a massive thermocatalytic cracking in the reactor which might explain the relatively high conversion yield obtained from this hydrocarbon. However, this trend is not always valid. For instance, table 8 predicts that *n*-propylbenzene should give a higher conversion yield than benzene which is not the case (table 6). This means that a hydrocarbon which undergoes high thermocatalytic cracking, does not necessarily yield large quantities of MWCNTs. Therefore, the effectiveness of a hydrocarbon in AACVD synthesis of MWCNTs is most probably dictated by other factors as well, such as its interaction with the catalyst source or the size of the catalyst particles it leads to.

3.3.4. Qualitative gas analysis of the reactor: different catalyst contents

In this section, thermocatalytic cracking behaviour of toluene with different concentrations of ferrocene is presented and discussed. Similar to section 3.3.3, for each experiment, two spectra were acquired from the atmosphere of the reactor: one at the room temperature and one at 800 °C. Figure 36 shows the mass spectra acquired from the reactor when different concentrations of ferrocene were used in toluene.



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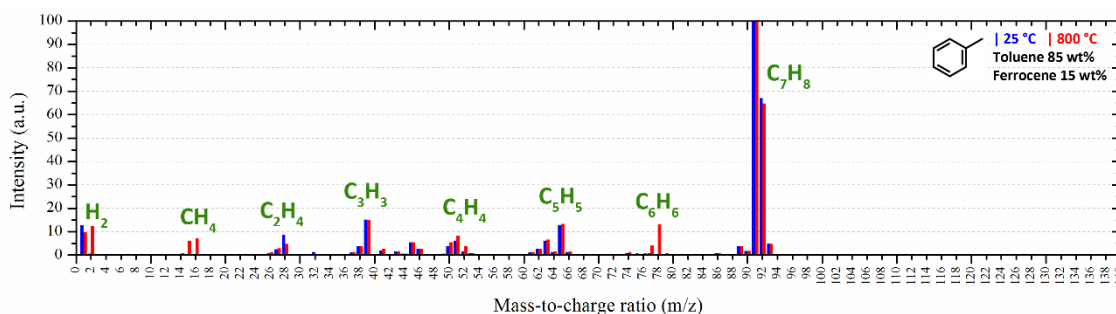


Figure 36. Online qualitative gas analysis of the atmosphere of the AACVD reactor using toluene with the following concentrations of ferrocene in order of appearance in the figure: 0, 1, 3, 5, 7, 9, 11, 13 and 15 wt.%. Each graph contains two mass spectra acquired at the room temperature (blue) and at the synthesis temperature (red).

Table 9 summarises the intensity of the most abundant fragments at the room temperature and at 800 °C for different precursor compositions (toluene with variable ferrocene concentrations).

Table 9. Summary of the mass spectrometry of the atmosphere of the reactor using toluene with different concentrations of ferrocene: intensity of the most significant intermediate fragments at the room temperature (I_{25}) and at 800 °C (I_{800}). The intensities are normalised with respect to the base peak of toluene.

Ferrocene concentration (in toluene)	m/z = 2		m/z = 15		m/z = 16		m/z = 52		m/z = 77		m/z = 78	
	I_{25}	I_{800}	I_{25}	I_{800}	I_{25}	I_{800}	I_{25}	I_{800}	I_{25}	I_{800}	I_{25}	I_{800}
0	0.44	1.32	0.34	1.48	0.17	1.50	1.47	2.79	0.85	2.40	0.11	5.51
1	0.44	2.70	0.38	1.43	0.12	1.45	1.55	2.63	0.88	2.22	0.14	5.07
3	0.48	5.31	0.41	2.26	0.15	2.50	1.54	2.60	0.90	2.14	0.14	5.13
5	0.68	20.73	0.44	10.81	1.14	12.68	1.53	8.39	0.98	9.56	0.23	36.13
7	0.60	21.29	0.49	8.74	0.48	10.17	1.69	6.66	1.00	7.39	0.39	27.07
9	0.71	15.58	0.46	1.70	0.97	1.63	1.50	2.39	0.95	1.86	0.27	3.96
11	0.90	30.80	0.61	5.56	1.11	6.24	1.59	4.64	1.00	4.80	0.32	16.21
13	0.73	16.78	1.48	4.24	0.40	4.58	1.49	3.15	0.87	2.81	0.16	7.94
15	0.63	12.36	0.46	6.10	0.21	7.05	1.56	3.93	0.90	4.00	0.18	13.05

Once again, the most significant intermediate fragments (H_2 , CH_3 , CH_4 , C_4H_4 , C_6H_5 and C_6H_6) were used to compare the thermocatalytic cracking of different precursors. These intermediate fragments can explain the thermal ($C_{\text{ferrocene}} = 0$ wt.%) and

thermocatalytic ($1 \text{ wt.\%} \leq C_{\text{ferrocene}} \leq 15 \text{ wt.\%}$) cracking mechanism of toluene for the growth of MWCNTs:

Inside the reactor, toluene molecules fragment down to form benzene rings and methyl radicals. From this point onward, we can assume that the majority of the benzene molecules remain unchanged because the benzene radicals (C_6H_5) had a relatively low abundance in the system. Consequently, the methane molecules and methyl radicals are responsible for the formation of MWCNTs.

By focusing on the characteristic benzene peak, it can be seen that the precursor containing 5 wt.% ferrocene underwent the highest thermocatalytic cracking (normalised intensity of benzene peak at 800 °C is around 36). Likewise the case of different hydrocarbons (section 3.3.3), the yield is not governed by the magnitude of the thermal and/or thermocatalytic conversion.

There seems to be a trade-off between the solvation¹ of ferrocene in toluene and the thermal and/or thermocatalytic conversion of precursor containing more than 5-7 wt% ferrocene. The reason why such a trade-off occurs is not very clear. However, it might be due to the catalyst size distribution achieved from different ferrocene contents in toluene. The growth rate of the CNTs is believed to be affected by their diameter (section 2.3.3). As shown in figure 33b, the precursors containing 5 and 7 wt% ferrocene lead to MWCNTs with the smallest mean diameters: 38 ± 13 and 37 ± 16 nm respectively. These mean diameter values are very close to the optimum mean diameter of MWCNTs with the highest growth rate in the AACVD conditions used for the study: *ca.* 40 nm (section 2.3.3). As mentioned earlier in section 2.3.4, the size of the catalyst

¹ Any stabilising interaction of a solute and the solvent or a similar interaction of solvent with groups of an insoluble material. Such interactions generally involve electrostatic forces and van der Waals forces, as well as chemically more specific effects such as hydrogen bond formation [236].

particles dictates the diameter of MWCNTs. On the other hand, the abundance of catalyst particles rises by increasing the ferrocene content of the precursor (figure 33e). Hence, it is possible that ferrocene contents beyond 5-7 wt% result in more catalyst agglomerates which are not optimally sized to effectively crack the precursor.

3.3.5. Qualitative gas analysis of the reactor: different catalyst sources

In this section, thermocatalytic cracking behaviour of toluene with different catalyst sources is presented and discussed. The same gas analysis approach presented in previous two section is used. Figure 37 shows the mass spectra acquired from the reactor when different catalyst sources were used in toluene.

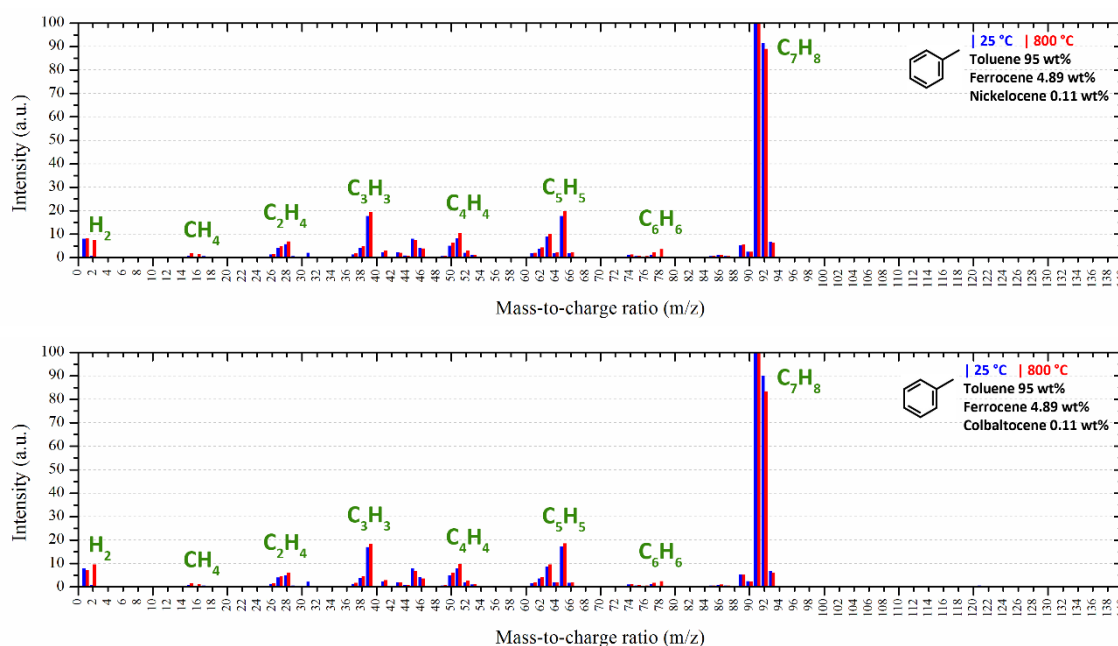


Figure 37. Online qualitative gas analysis of the atmosphere of the AACVD reactor using toluene with the following catalyst sources in order of appearance in the figure: ferrocene 5 wt.%, ferrocene 4.89 wt.% + nickelocene 0.11 wt.% and ferrocene 4.89 wt.% + cobaltocene 0.11 wt.%. Each graph contains two mass spectra acquired at the room temperature (blue) and at the synthesis temperature (red).

By comparing the spectra in figure 36 and 37 it can be concluded that addition of 0.11 wt.% (maximum solubility) of nickelocene or cobaltocene does not alter the thermocatalytic cracking behaviour of toluene / ferrocene mixture. The spectra are very similar to the ones obtained from toluene and ferrocene only (see section 3.3.4).

3.3.6. Quantitative gas analysis of the reactor

An alternative way to increase the efficiency, with minimal modification of the AACVD reactor, is to collect, filter, adjust the composition and reuse the hydrocarbon by-products at the end of the reactor. Since these hydrocarbon by-products are mostly liquid benzene derivatives (see figures 35 – 37 and tables 8 and 9), they can be selectively collected and filtered in a distillation chamber similar to the ‘cooler’ used by Terrones *et al.* Once the precise composition of the distilled hydrocarbons is known, catalyst source and fresh carbon source can be added to the solution in the precursor reservoir to retain the optimum composition of the precursor. This process ensures a more efficacious use of the feedstock. Figure 38, schematically depicts a possible industrial AACVD setup with integrated recycling unit.

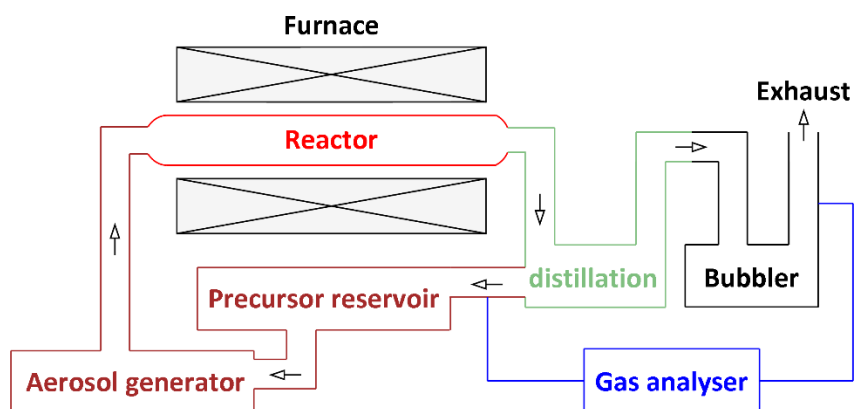


Figure 38. A possible industrial AACVD setup with integrated precursor recycling unit (distillation chamber) and gas analyser.

The workability of such a process strongly depends upon the precise qualitative and quantitative gas analysis of the exhaust of the reactor. In this section, using the gas analysis methods and devices described in section 3.2, the exhaust of the AACVD reactor was analysed quantitatively and the composition of the main liquid hydrocarbon by-products was determined. Moreover, the relative abundance of methane in the

exhaust, as one of the key molecules (see section 3.3.4) in the synthesis of carbon nanotubes was estimated with regard to the liquid hydrocarbon by-products.

The mass spectra and TIC chromatograms of the exhaust of the AACVD reactor are shown in figure 39a and 39b respectively. For comparison, each figure consists of the results of the gas analysis, both with furnace kept at the room temperature (25 °C, in blue) and at the reaction temperature (800 °C, in red). The peaks on the mass spectra were normalised to the base peak of the most abundant analyte and marked with the corresponding mass-to-charge ratio values. The peaks on the TIC chromatograms were detected from the SIM chromatograms and marked with the corresponding eluting analytes. The experiments were carried out using ethylbenzene with 5 wt.% ferrocene as it was the most efficient precursor composition for synthesis of clean vertically aligned MWCNTs (see section 3.3.1).

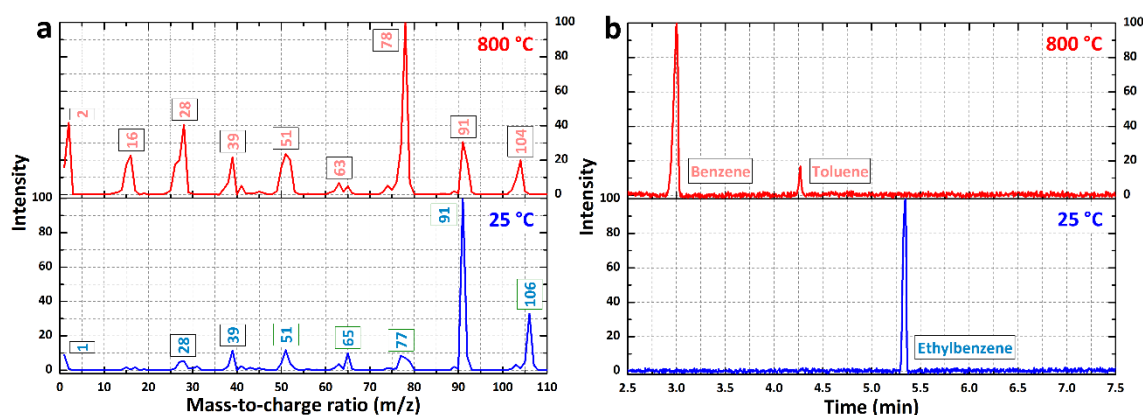


Figure 39. a) Mass spectra and b) TIC chromatograms of the exhaust of the AACVD reactor at the room temperature (25 °C, in blue) and at the reaction temperature (800 °C).

The molecular ion peak of ethylbenzene ($m/z = 106$, C_8H_{10}) on the blue mass spectrum was replaced by a fragment peak ($m/z = 104$, C_8H_8) on the red mass spectrum. Therefore, it can be assumed that inside of the reactor, ethylbenzene completely cracks to smaller fragments. This was also confirmed by the absence of any eluting analyte after 5.34 minutes on the red TIC chromatogram (5.34 minutes is the expected retention

time for the elution of molecular ethylbenzene under the chromatography conditions deployed in this study; see the blue TIC chromatogram for the expected retention time of ethylbenzene). Instead, after 5.75 minutes, the same fragment which was observed on the red mass spectrum ($m/z = 104$, C_8H_8) appeared on the SIM chromatogram.

Based on the comparison of the blue and red graphs in figure 39a and b, the products of the thermocatalytic cracking of ethylbenzene in the AACVD setup are mostly toluene ($m/z = 91$), benzene ($m/z = 78$), ethene ($m/z = 28$), methane ($m/z = 16$) and hydrogen ($m/z = 2$). The abundance of the rest of the fragments in the system was relatively low. This was suggested by the insignificant difference of the intensities of the following peaks on the blue and red mass spectra: $m/z = 63$, 51, and 39.

Interestingly, the exhaust gas contained no ferrocene detectable by the gas analysers which suggests an effective decomposition of ferrocene inside the reactor.

Unlike other hydrocarbon by-products such as ethene, both benzene and toluene are in liquid form under the standard conditions and are efficient carbon sources for AACVD synthesis of MWCNTs (see section 3.3.1 and table 4). Hence, they are the most important hydrocarbon by-products in an AACVD reactor operating with ethylbenzene. It is, therefore, necessary to quantitatively analyse the mixture of benzene and toluene at the exhaust of the reactor which as mentioned earlier in this section, is a prerequisite for feeding them back into the precursor reservoir. On the other hand, since methane is regarded as a key component in AACVD synthesis of MWCNTs (see section 3.3.4), it is interesting to see how much methane leaves the reactor without actually contributing to the synthesis of MWCNTs. In order to determine the ratio of benzene and toluene, standard solutions were prepared and analysed under the same chromatography conditions used for the gas analysis of the reactor. Standard mixtures of benzene and methane were also prepared using the heated mixing chamber described

in section 3.2 and analysed with the mass spectrometer. Figure 40a is the calibration graph for the benzene/toluene solutions, in which the data points on the vertical axis are calculated as following:

$$\text{Abundance of benzene peak in gas chromatogram (GC)} = \frac{S_{\text{benzene peak}}}{S_{\text{benzene peak}} + S_{\text{toluene peak}}} \times 100$$

(Equation 6)

Wherein S_i is the area of i peak in the TIC chromatogram.

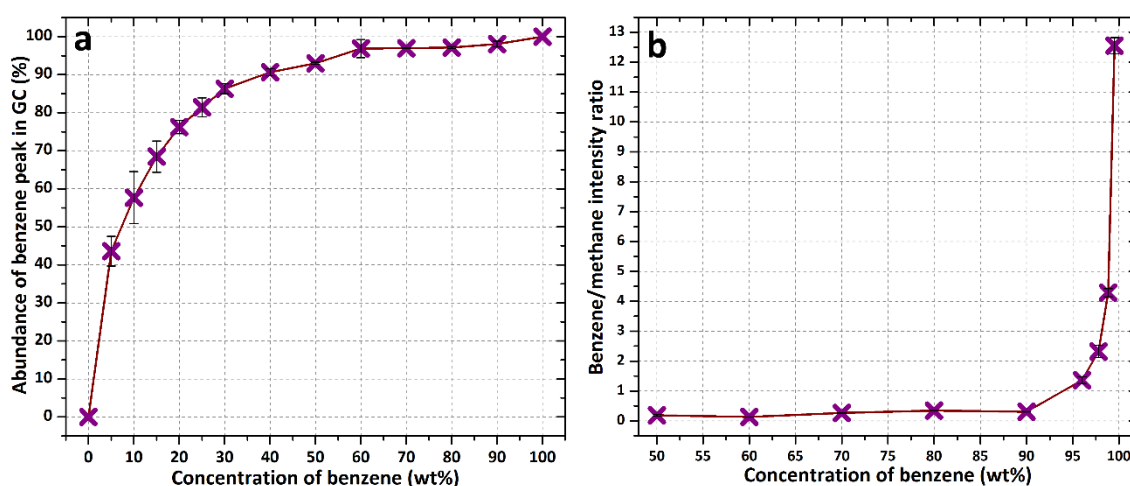


Figure 40. a) The GC calibration graph for the benzene/toluene standard solutions: relative area of benzene peak in the TIC chromatogram as a function of the real concentration of benzene in the standard solution; b) MS calibration graph for the benzene/methane standard mixture: intensity ratio of benzene peak ($m/z = 78$) and methane peak ($m/z = 16$) as a function of the real concentration of benzene in the standard mixture.

Using the equation 6, the relative abundance of the benzene peak in the TIC chromatogram acquired from the reactor at 800 °C was 90.4 ± 1.7 % (see the red TIC chromatogram in figure 39b). By interpolating this abundance in the calibration graph 40a, the composition of the liquid hydrocarbon by-products at the exhaust of the reactor can be determined:

$$C_{\text{Benzene}}: 40 \pm 1 \text{ wt.}\%; C_{\text{Toluene}}: 60 \pm 1 \text{ wt.}\%. \quad (\text{Equation 7})$$

Figure 40b is the calibration graph for the benzene/methane mixtures, in which the data points on the vertical axis are the ratios between the intensity of benzene and methane peaks in the mass spectra.

The ratio between the intensity of benzene and methane peaks in the mass spectrum acquired from the reactor at 800 °C was 4.4 ± 0.2 (see the red mass spectrum in figure 39a). By interpolating this ratio in the calibration graph 40b, the real relative abundance of unbroken methane which leaves the reactor can be obtained compared to the abundance of benzene:

$$C_{\text{Methane}}/C_{\text{Benzene}}: 1-1.5\%. \quad (\text{Equation 8})$$

This ratio suggests that there is an insignificant amount of methane at the exhaust of the reactor.

In conclusion, the exhaust of the AACVD reactor operating with ethylbenzene and ferrocene was mostly composed of benzene (40 wt.%) and toluene (60 wt.%). By distillation of this hydrocarbon mixture and addition of a few wt.% ferrocene, it can be used as a precursor for further synthesis of MWCNTs in the AACVD reactor. The actual development and use of a precursor recycling unit based on the results of the quantitative gas analysis of the exhaust of the AACVD reactor is a part of the proposed set future works discussed in section 5.2.

3.3.7. Mapping the composition of the reactor

In order to investigate the correlation between the inhomogeneity of products throughout the reactor (see chapter 2) and the local composition of the atmosphere, it is necessary to sample the atmosphere of the reactor zone by zone. This is a particularly challenging task as it involves developing a dedicated probe capable of sampling the atmosphere without interfering with the CVD reaction and without altering the composition of the analytes from the sampling point to the analyser. This section addresses the methodology and attempts towards mapping the composition of the reactor. It also covers the difficulties associated with the development and deployment of a probe fulfilling the conditions mentioned above.

The simplest form of a probe is a capillary tube connected to the end of the transfer line of the gas analyser. Dealing with highly reactive hydrocarbons at high temperatures (800 – 900 °C), it is necessary to select an inert material. Ceramics are possibly the best choice since the metals are likely to interfere with the CVD reaction (catalysis and corrosion) Figure 27b demonstrates how an alumina capillary can extend the transfer line inside of the reactor. The collection and transfer of the analytes inside the probe rely on the negative pressure created by the vacuum pumps of the analyser.

The primary results revealed that the probe could successfully sample the atmosphere from a desired position inside the reactor without any blockage of the probe or major interference with the growth of MWCNTs. However, the gas analysis showed that the composition of a particular zone inside the reactor depends on whether the probe is introduced from the end (exhaust) of the reactor or the beginning (precursor entrance). In other words the length of the probe which was exposed to the heat of the reactor had a significant effect on the recorded spectra. This means that the thermocatalytic cracking

of analytes continued to occur even inside of the probe. Therefore, the gas which was sampled at the end of the probe was not the same observed by the gas analyser. Table 10 compares the relative abundance of benzene and methane collected from 8 cm from the beginning of the reactor when the alumina probe was introduced from the beginning of the reactor (exposed length to the heat: 8 cm) and when it was introduced from the end of the reactor (exposed length to the heat: 52 cm).

Table 10. Comparison of the relative abundance of methane and benzene collected from 8 cm from the beginning of the reactor when the alumina probe was introduced from either the beginning (8 cm exposure to the heat) or end (52 cm exposure to the heat) of the reactor. The abundance values are relative to the base peak (toluene).

	Relative abundance of methane ($m/z = 16$)	Relative abundance of Benzene ($m/z = 78$)
8 cm exposure of probe in the reactor	0.51	0.50%
52 cm exposure of probe in the reactor	2.87%	2.00%

The observation described above invalidated the results of a systematic mapping of the atmosphere of the AACVD reactor using the alumina probe. The next step was to develop a probe which retains the composition of the analytes once collected. This can be potentially done if the probe is kept at a certain temperature which is low enough to avoid thermocatalytic cracking but high enough to prevent condensation. Therefore, the temperature of the ideal probe must be controllable. The fact that such a probe should fit and operate in a reactor heated to several hundred °C and not interfere with the CVD reaction imposed a great degree of limitation in term of materials selection and design.

For this purpose, a multi-layer quartz probe was designed and filed for a patent [228]. Figure 41 depicts the construction of the probe.

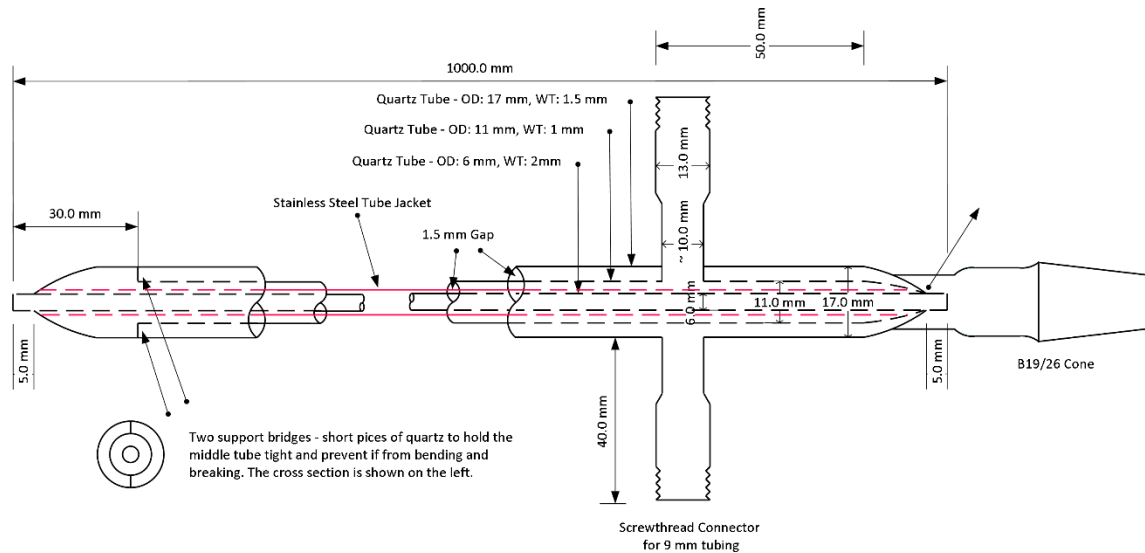


Figure 41. Schematic of the dedicated probe designed for mapping the composition of the high temperature reactors [228].

The full specification of the probe is provided in the appendix II. Briefly, the probe is composed of three coaxial quartz tubes. The outer and middle tubes are cooled with counter currents of an inter gas such as nitrogen. The flow prevents the transfer of heat from the furnace to the inner tube, through conduction and convection.

Even after a few upgrades, the prototypes were still unable to fully isolate the analytes from the intensive radiation of the reactor and the probe requires further modifications. The development of the probe including the protection against the radiation is out of the scope of this PhD project and is the subject of a new project (postdoctoral research assistantship in *in-situ* diagnostics, nanomaterials manufacturing and up-scaling) in the Department of Materials at University of Oxford funded by the European Research Council (Proof of Concept).

3.4. Conclusions

Utilising different liquid precursors and catalyst concentrations in the AACVD method is an easy one-step way of tuning the attributes of MWCNTs. For instance, by using ethylbenzene or isopropylbenzene instead of commonly used toluene or xylene, the total mass of synthesised nanotubes can be improved by more than 60%. Being as hazardous as toluene but not significantly more expensive, ethylbenzene is possibly the best candidate for the large-scale synthesis of vertically aligned MWCNTs. Heavier hydrocarbons such as *n*-propylbenzene, *n*-butylbenzene or diethylbenzene did not result in higher synthesis rates or quality.

It was observed that the interaction of the catalyst and the hydrocarbon in the precursor, the precursor conversion rate and thermocatalytic cracking behaviour are not the same for all the hydrocarbons. These and possibly other factors are the reasons behind the differences in the properties of MWCNTs synthesised from various hydrocarbons.

The qualitative gas analysis of the AACVD reactor revealed the thermocatalytic cracking mechanism of different precursors. It was shown that most of the precursors form considerable amounts of benzene rings inside the reactor. These rings are extremely stable and undergo little further fragmentation. Hence, the majority of individual carbon atoms are synthesised from the hydrocarbons such as methane, ethane and their radicals.

By quantitative gas analysis of the reactor operating with ethylbenzene, it was shown that the liquid by-products at the exhaust of the reactor are mainly composed of *ca.* 40 wt.% benzene and 60 wt.% toluene. These two hydrocarbons themselves, are very good carbon precursors and can be relatively easily re-cycled into the precursor reservoir.

This can significantly increase the efficiency of the whole process without any requirement for major modification of the reactor. Moreover, it was shown that methane as one of the key molecules in growth of carbon nanotubes has an insignificant abundance at the exhaust.

Chapter 4. Upscaling the synthesis of carbon nanotubes

4.1. Introduction

As mentioned earlier, the ultimate goal of this work is to develop the AACVD method for industrial large-scale production of MWCNs. In the previous chapter, it was discussed how optimising the precursor composition and integrating a precursor recycling unit controlled with *in-situ* gas analysers could improve the efficiency of the process. In this chapter an 8.5-litre AACVD reactor was utilised and the effect of different experimental parameters such as the size of the reactor, temperature, time and flow rate of the carrier gas on the efficiency of the catalytic conversion of the precursor and various properties of MWCNTs such as the mass, length, outer diameter, defect density, oxidation resistance and catalyst concentration were investigated. An optimised recipe was demonstrated for synthesis of free-standing and on-substrate large-area (9×10 cm), mm-thick carpets of vertically aligned MWCNTs which are suitable for characterisations and applications from nano to macro scale. Moreover, the atmosphere of the large reactor was analysed and compared to the atmosphere of the conventional reactor which was discussed in the previous chapter, to see how the size of the reactor influences the thermocatalytic cracking behaviour of precursors.

4.2. Experimental

A similar AACVD setup described in section 2.2 was used here. However, in some of the experiments a larger quartz tube (Robson Scientific; 120 cm long; 9.5 cm inner diameter; 1.5 mm thick with B19/26 socket and cone connections) was inserted in a three-zone horizontal tubular furnace (Elite Thermal Systems; 120 cm long; 10 cm inner diameter) and used for synthesis. Where required, two aerosol generator units were connected to the quartz tube reactor using a Y-shaped quartz adaptor and operated simultaneously to increase the precursor input rate. A mixture of ethylbenzene with 5 wt.% ferrocene was used as the precursor in all the experiments for the same reason as mentioned in section 3.3.6. Table 11 summarises the experimental parameters used in order to improve the yield of the synthesis.

Table 11. List of the experimental parameters with corresponding samples. Reactor size (0.2 and 8.5 L); synthesis temperature: 800 and 850 °C; synthesis time: 15, 30, 45, 60, 120 and 240 min; argon flow rate: 1, 2, 2.5 and 5 L/min.

Reactor size: length / inner diameter (cm); volume (L)	Sample	Synthesis temperature (°C)	Synthesis time (min)	Argon flow rate (L/min)	Precursor consumption rate (g/hr)
60 / 2.1; 0.2	1	800	15	1.0	10.0
	2	800	30	1.0	10.0
	3	800	45	1.0	10.0
	4	800	60	1.0	10.0
	5	800	120	1.0	10.0
	6	800	120	2.5	27.4
	7	850	120	1.0	10.0
	8	850	120	2.5	27.4
120 / 9.5; 8.5	9	800	120	1.0	12.0
	10	850	120	1.0	12.0
	11	850	120	2.5	32.9
	12	850	120	2 × 2.5	54.8
	13	850	240	2 × 1.0	20.0

Apart from the characterisation methods described in section 2.2, optical microscopy (OM) was used to investigate the morphology of MWCNTs. For OM studies, free-standing as-synthesised carpets of MWCNTs were used.

In order to grow large area, mm-thick carpets of MWCNTs, silicon wafers (Sibert Instruments; IC prime grade; $90 \times 100 \text{ mm} \times 625 \text{ }\mu\text{m}$; orientation: (100); n-type; surface roughness: $< 5 \text{ }\text{\AA}$) were inserted inside the large reactor.

4.3. Results and discussions

4.3.1. Mass of synthesised MWCNTs and precursor conversion yield

The mass of synthesised MWCNTs and the precursor conversion yield (mass of synthesised MWCNTs divided by the mass of consumed precursor) in different experiments are provided in table 12.

Table 12. Catalytic conversion yield of precursor, mass of synthesised MWCNTs and morphological information (outer diameter and thickness of the carpets) of synthesised MWCNTs. in different experiments. See table 11 for the synthesis parameters corresponding to each sample.

Sample	Total mass of MWCNTs (g)	Precursor conversion yield (%)	Outer diameter (nm)	1 st quartile OD (nm)	Median OD (nm)	3 rd quartile OD (nm)	Maximum carpet thickness (μm)
1	0.95	43.2	45.1 ± 24.3	25.5	40.0	56.1	310
2	1.92	38.4	33.6 ± 16.1	24.3	30.4	38.9	670
3	2.41	32.1	35.2 ± 22.2	21.6	29.2	41.0	1050
4	2.44	24.4	37.2 ± 22.3	19.6	31.9	53.4	1350
5	4.42	22.1	76.0 ± 37.8	41.6	72.4	106.5	1550
6	4.95	9.0	39.7 ± 26.9	19.8	29.3	55.4	1400
7	2.54	12.7	39.9 ± 20.9	21.9	39.5	49.9	2280
8	5.48	10.0	84.9 ± 42.6	50.2	84.5	106.7	2450
9	21.1	87.9	44.3 ± 25.4	26.2	36.9	54.6	1190
10	5.6	23.3	48.2 ± 24.9	28.0	42.6	63.2	1430
11	6.8	10.3	35.7 ± 16.1	25.0	32.0	40.4	1430
12	28	26	43.6 ± 21.8	29.0	38.1	56.4	860
13	25	31	33.2 ± 15.2	21.8	30.4	39.3	2680

As can be seen from the first five rows in table 12, increasing the synthesis time from 15 min up to 2 hr while keeping the rest of the parameters constant (temperature: 800 °C, argon flow rate: 1 L/min) increased the quantity of synthesised MWCNTs, but also led to a significant loss of the precursor conversion yield (from 43.2% to 22.1%). The loss of the precursor conversion yield was probably due to the more coverage of substrate (quartz tube) and lack of new nucleation sites in prolonged experiments. The

increasing length of MWCNTs in prolonged experiments could also limit the effective penetration of precursor fragments through the carpet of MWCNTs to the substrate and, therefore, lower the precursor conversion yield. By comparing the 5th and 6th samples, it is also observed that increasing the argon flow rate from 1 to 2.5 L/min while keeping the other parameters constant (temperature: 800 °C, time: 2 hr) had little impact on the growth rate, but reduced the precursor conversion yield to less than a half (from 22.1% to 9.0%). Higher flow rates normally result in lower precursor resting times inside the reactor which might explain the loss of precursor conversion yield from 22.1% to 9.0% (sample 5 and 6). Comparing the 5th and 7th samples shows that rising the temperature by 50 °C while keeping the rest of parameters unchanged (argon flow rate: 1 L/min, time: 2 hr) dropped the efficiency of the catalytic conversion of precursor by 10% (from 22.1% to 12.7%) and the mass of synthesised MWCNTs by *ca.* 40% (from 4.42 to 2.54 g). The conversion yield of the precursor for producing the 8th sample was 10.0% which revealed that simultaneous increase of the temperature and flow rate from the base parameters (temperature: 800 °C, argon flow rate: 1 L/min) resulted in less conversion yield of the precursor. Therefore, in the case of small reactor, although the mass of synthesised MWCNTs could be considerably improved (5.8 times) by increasing the time, temperature and flow rate of the carrier gas, the conversion yield of the precursor could not be improved beyond 43.2%. The maximum growth rate achieved in the small reactor was 2.74 g/hr (sample 8).

By running the large reactor at 800 °C with argon flow rate of 1 L/min for 2 hr, more than 20 g of MWCNTs was obtained which was nearly five times the maximum amount produced in the small reactor under the same experimental conditions (compare the 5th and 9th samples in table 12). The precursor conversion yield was also significantly enhanced to more than 80%. This was most probably due to higher efficiency of the

large reactor in cracking the hydrocarbons down to carbon species required for the growth of MWCNTs.

Unexpectedly, operating the large reactor at 850 °C was not as efficient as at 800 °C and the amount of MWCNTs produced was similar to the quantity achieved in the small reactor (compare the 8th, 10th and 11th samples in table 12). On the other hand, the last two rows in table 12 show that when the large reactor was fuelled by two aerosol generator units under optimised experimental conditions, the efficiency was acceptably high (26% and 31% for the 12th and 13th samples respectively) even at high temperature (850 °C), long synthesis times (2 and 4 hr) and high argon flow rates (2 and 5 L/min). The mass of synthesised MWCNTs was ultimately increased to 28 g by operating the large reactor at 850° C with two aerosol generators units and total argon flow rate of 5 L/min.

The maximum synthesis rate of MWCNTs in the large reactor was 14 g/hr which was more than five times the maximum rate achieved in the small reactor (2.74 g/hr). Comparison of the 12th and 13th samples suggests that in the large reactor, using higher argon flow rates (equivalent to more precursor input) had a better improving effect on the mass of MWCNTs rather than longer synthesis times. However, in the small reactor, synthesis time seems to be the parameter with the highest impact. This can be due to the significant difference between the deposition areas in the two reactors. In the small reactor, the coverage of the quartz tube occurs faster than in the large reactor. Therefore, the number of nucleation sites drops more rapidly in the small reactor and the negative impact of the time on the precursor conversion yield is expected to be more pronounced in the small reactor.

4.3.2. Large-area, mm-thick carpets of carbon nanotubes

One of the benefits of synthesising MWCNTs in the larger reactor was the possibility of using large silicon wafers (9×10 cm) as the CVD substrates. The wafer was placed at 30 cm from the beginning of the reactor and was almost fully covered with a continuous 2-mm-thick carpet of vertically aligned MWCNTs. The carpets were easily removable from both the wafer and the quartz reactor. The free-standing carpets were sturdy and could withstand tensions and compressions during normal handling. The density of the carpets were similar to the ones synthesised using the regular reactor (figure 22e) Figure 42 shows the continuous 2-mm-thick carpet of vertically aligned MWCNTs on the silicon wafer and free-standing carpets (thickness: 1 – 2 mm).

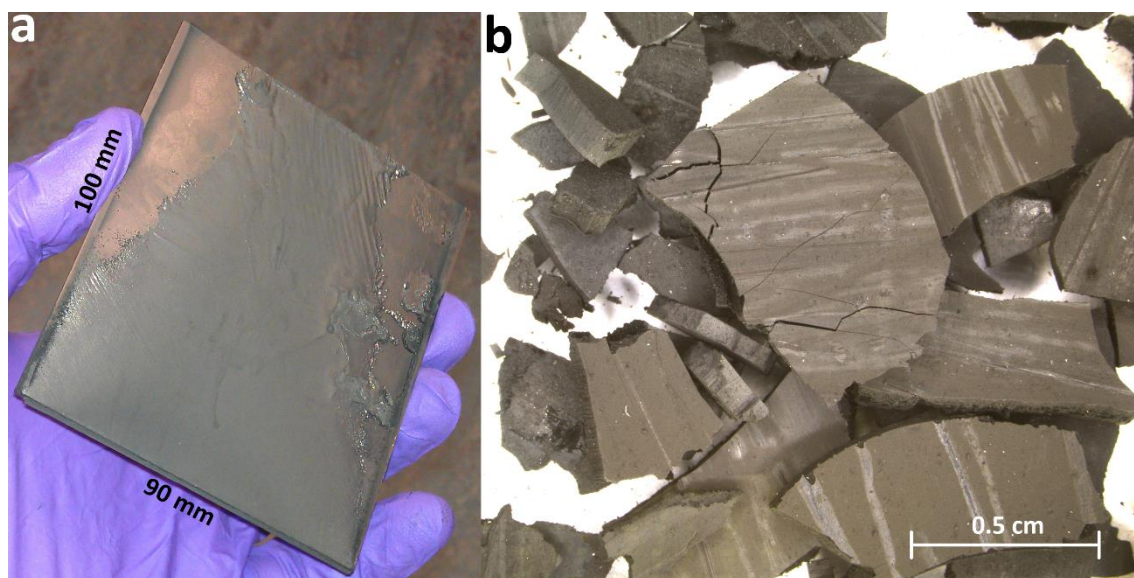


Figure 42. a) Continuous 2-mm-thick carpet of vertically aligned MWCNTs on large (9×10 cm) silicon wafer; b) Free-standing carpets of vertically aligned MWCNTs (thickness: 1 – 2 mm).

4.3.3. Structural investigation using electron microscopy

Figure 43 is a gallery of electron micrographs of different samples. The mean and quartile values of the outer diameter and the length (maximum thickness of carpet) of the MWCNTs are provided in table 12.

All the samples contained carpets of vertically aligned MWCNTs. The MWCNTs synthesised for up to an hour in the small reactor at 800 °C, generally had lower structural disorders than the ones synthesised for two hours in the same reactor and at the same temperature. This suggests that for synthesising straight and clean MWCNTs, synthesis time is limited to one hour when a small reactor is used at 800 °C. In contrast, MWCNTs produced from the large reactor had comparable appearance to the ones synthesised for up to an hour using the small reactor, regardless of temperature. This means that in a large reactor, synthesis time within the range of other experimental parameters used in this work, is not a limiting factor for producing straight and clean MWCNTs.

The 5th and 8th samples contained MWCNTs with significantly large diameter (around twice) compared to the rest of the samples (mean diameter: 76 and 85 nm respectively). This might be due to the formation of graphitic and amorphous carbon layers around the already-grown tubes during the synthesis of these two sample. TEM image of the 8th sample in figure 43 shows some MWCNTs exposed out of what look like *carbon sheaths*. The mean outer diameter of the MWCNTs in the rest of the samples were between 33 and 45 nm.

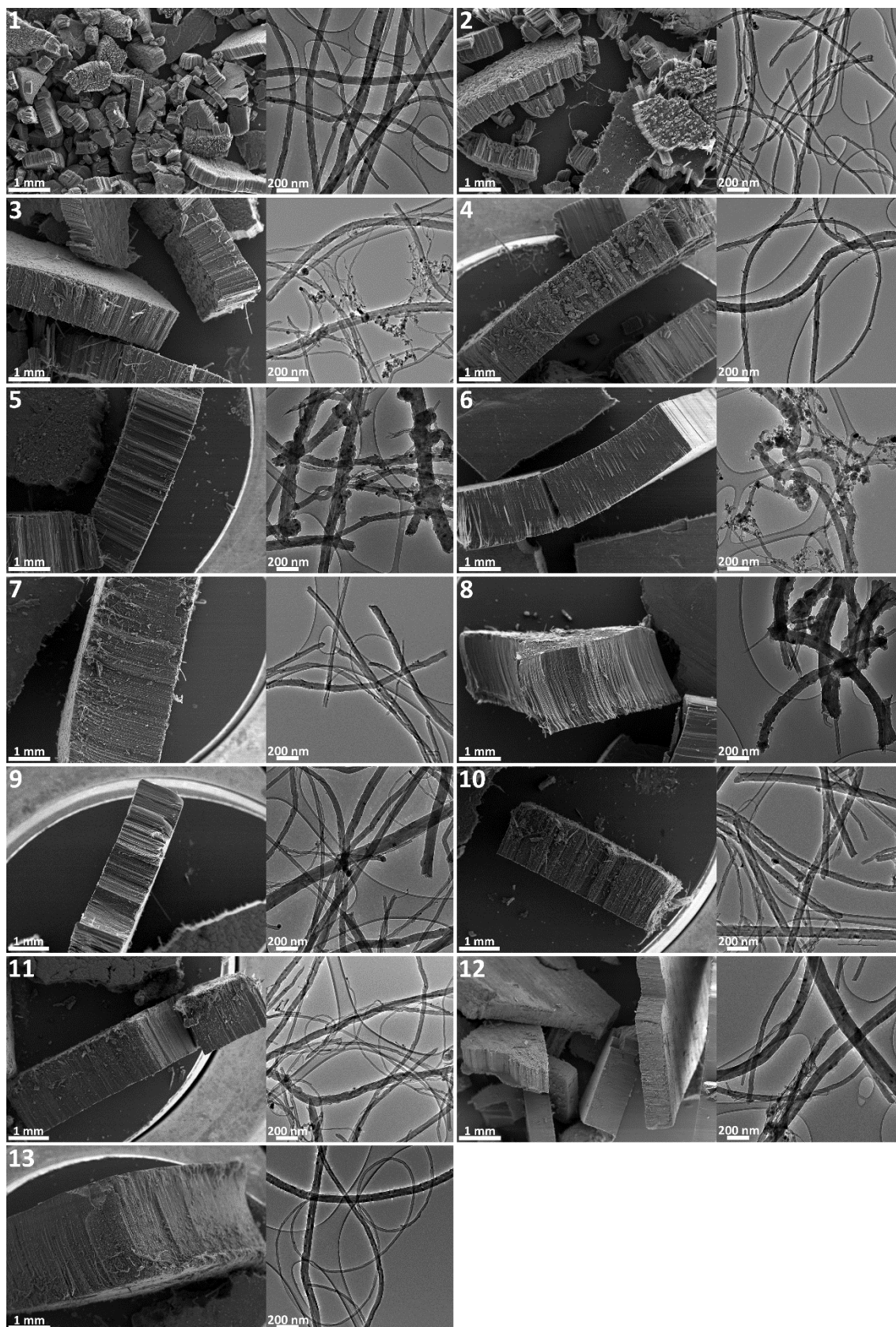


Figure 43. Scanning and transmission electron micrographs of different samples. See table 11 for the synthesis parameters corresponding to each sample.

Both samples synthesised in the small reactor at 850 °C for two hours contained MWCNTs longer than 2 mm. For synthesising similarly-long MWCNTs in the large reactor, it was necessary to increase the synthesis time up to four hours. This is perhaps due to the significantly larger number of nucleation sites (uncovered area of the substrate) in the large reactor. In the small reactor, shortly after the start of the synthesis (*ca.* 10 min) the reactor is almost entirely covered with the MWCNT deposit. Therefore, supplied precursor is more likely to contribute to the further growth of an already-existing nanotube rather than nucleating a new one. Hence, the growth rate of MWCNTs in the small reactor was considerably higher than in the large reactor (compare the samples 5 with 9, 7 with 10 and 8 with 11).

The longest MWCNTs (*ca.* 2.6 mm long) with the smallest mean outer diameter (33 nm) were obtained using the large reactor operating at 850 °C for 4 hours with a total argon flow rate of 2 L/min (sample 13).

4.3.4. Raman spectroscopy of the carbon nanotubes

In order to compare the quality of synthesised MWCNTs, Raman spectroscopy was used. Table 13 summarises the Raman I_D/I_G and G'-band to G-band intensity ratios (I_G/I_G). The original Raman spectra are provided in figure 44a.

Table 13. Raman I_D/I_G and I_G/I_G values; TGA $T_{20\%}$, $T_{50\%}$ and $T_{70\%}$ (temperatures of 20%, 50% and 70% mass loss); TGA $T_{80\%} - T_{20\%}$ (difference between the temperatures at which the samples lose 20% and 70% of their initial mass) and concentration of the residual catalyst of different samples. See table 11 for the synthesis parameters corresponding to each sample.

Sample	Raman I_D/I_G	Raman I_G/I_G	TGA $T_{20\%}$ (°C)	TGA $T_{50\%}$ (°C)	TGA $T_{70\%}$ (°C)	TGA $T_{70\%} - T_{20\%}$ (°C)	Concentration of the residual catalyst (wt%)
1	0.327	0.582	597	640	654	58	1.85
2	0.325	0.595	593	626	645	52	2.16
3	0.352	0.569	601	630	646	45	1.71
4	0.410	0.561	574	600	615	41	2.90
5	0.384	0.552	586	622	655	69	2.42
6	0.484	0.512	552	577	596	44	5.87
7	0.318	0.599	574	613	661	88	2.93
8	0.289	0.551	571	595	618	47	3.61
9	0.368	0.500	615	646	663	48	1.29
10	0.385	0.421	610	641	658	48	1.37
11	0.315	0.529	595	626	653	58	1.83
12	0.519	0.481	574	608	645	70	2.25
13	0.310	0.561	592	616	641	49	2.02

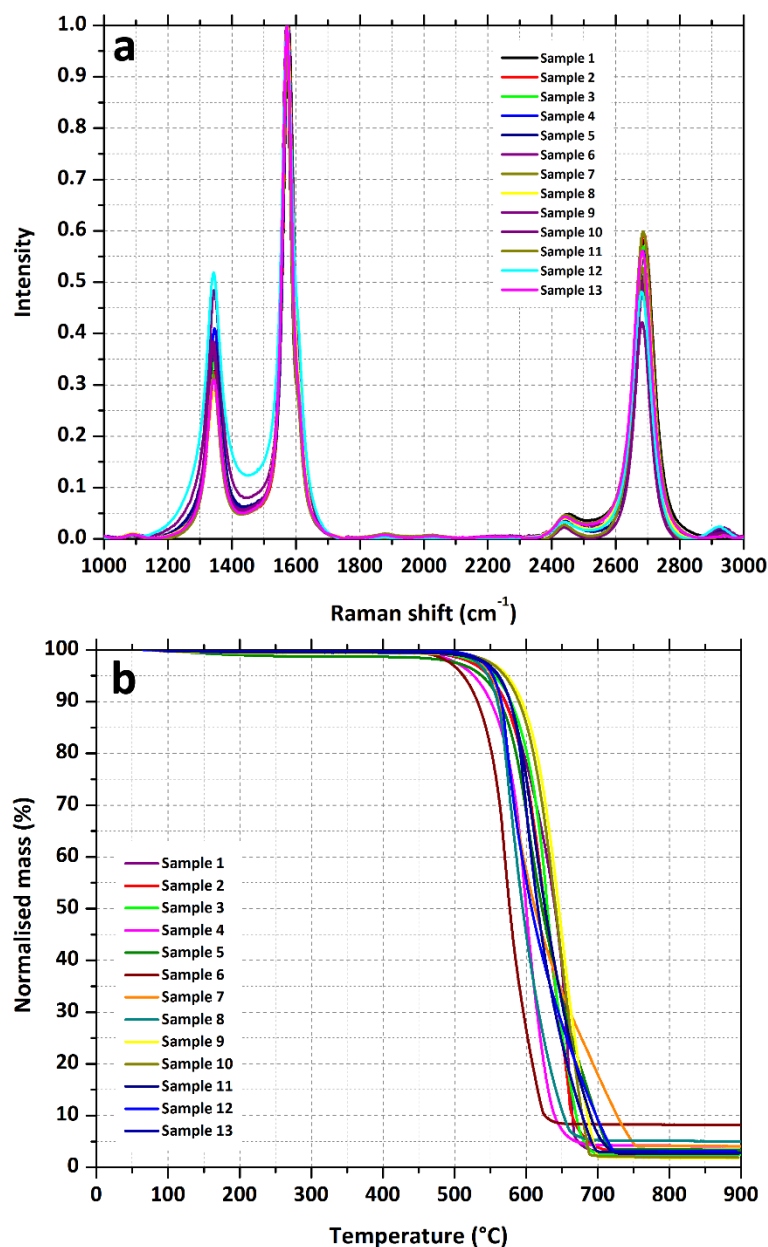


Figure 44. a) Raman spectra and b) TGA graphs of different MWCNT samples. See table 11 for the synthesis parameters corresponding to each sample.

As can be seen from the Raman data, most of the samples had low (section 2.3.6) defect density ($I_D/I_G = 0.3 - 0.5$). The Raman I_G/I_G of samples did not follow a clear trend with respect to their Raman I_D/I_G . However, the variation of the Raman I_G/I_G in most of the samples ($0.5 - 0.6$) was smaller than the variation of their Raman I_D/I_G ($0.3 - 0.5$). The interpretation of Raman I_G/I_G ratio is still a subject of debate [229], but has been attributed to the concentration of radiation-induced [229] and chemically-induced

[230] defects and impurities [231] in MWCNTs. Among the samples produced in the small reactor, the ones synthesised at 850 °C had the lowest defect density (7th sample: 0.318 and 8th sample: 0.289) which may be due to the more graphitisation of carbon at 850 °C compared to 800 °C. By comparing the Raman I_D/I_G of samples 1 to 5, it can be seen that prolonging the synthesis time has a negative impact on the quality of MWCNT synthesised in the small reactor (Raman I_D/I_G has an increasing trend as a function of synthesis time). This might be linked to the rising concentration of amorphous carbon and catalyst impurities as a function of synthesis time which is also suggested by the microscopy (see section 4.3.3) and TGA (see section 4.3.5). Higher argon flow rates, which normally result in more precursor input, had a similar negative impact on the quality of MWCNTs synthesised in the small reactor at 800 °C. By comparing the 5th and 6th samples it is obvious that rising the argon flow rate from 1 to 2.5 L/min (precursor consumption rate from 10 to 27.4 g/hr) while keeping the rest of the parameters constant, increases the Raman I_D/I_G from 0.384 to 0.484. This trend is not valid at 850 °C. As mentioned earlier, both samples synthesised at 850 °C had low Raman I_D/I_G , regardless of the argon flow rate.

Using a larger reactor had an insignificant effect on the defect density of MWCNTs (compare the samples 5 with 9, 7 with 10 and 8 with 11). The Raman I_D/I_G of the MWCNT samples synthesised in the large reactor mostly varied between 0.30 and 0.38 with exception of the sample synthesised with total argon flow rate of 5 L/min (sample 12, Raman I_D/I_G = 0.519). This was probably due to the turbulence caused by the excessively large argon flow rate which increased the amount of deposited soot and amorphous carbon on the surface of MWCNT carpets. It is possible that the turbulence carried some of the amorphous carbon forming near the exhaust of the reactor (see chapter 1) back to the zones from which the MWCNTs were collected. The sample

synthesised for 4 hours at 850 °C using total argon flow rate of 2 L/min had the lowest defect density (sample 13, Raman $I_D/I_G = 0.310$) among the samples produced in the large reactor.

4.3.5. Thermogravimetric analysis of the carbon nanotubes

The results of the TGA of the samples are listed in table 13. Most of the samples exhibited high oxidation resistance ($T_{50\%} \geq 600\text{ }^{\circ}\text{C}$; see table 6 for comparison). Increasing the synthesis time from 15 min up to 1 hr lowered the oxidation resistance of MWCNTs ($T_{50\%}$ is reduced from 640 to 600 $^{\circ}\text{C}$) similar to the trend of the Raman I_D/I_G . As mentioned in the previous section, this was probably due to the increasing concentration of the amorphous carbon particularly at the end of the reactor (see also section 2.3.6). It seems that continuing the synthesis for another hour led to formation of tubes and fibres (sample 5 in figure 43) which were nearly twice as thick as most of the other nanotube samples (mean outer diameter = 76 nm) and hence exhibit higher oxidation resistance. Since the Raman I_D/I_G was relatively high (0.384), it is unlikely that the high oxidation resistance of the 5th sample is due to its high graphitisation.

The MWCNTs synthesised in the small reactor at 800 $^{\circ}\text{C}$ for 2 hours with argon flow rate of 2.5 L/min had the lowest oxidation resistance ($T_{50\%} = 577\text{ }^{\circ}\text{C}$) which is in agreement with the Raman spectroscopy results (Raman $I_D/I_G = 0.484$). Therefore, it is suggested that for producing quality MWCNTs in the small reactor for prolonged synthesis times (2 hours) with argon flow rate of 2.5 L/min, a temperature of 850 $^{\circ}\text{C}$ should be used.

The oxidation resistance of all the samples synthesised in the large reactor were acceptably high ($T_{50\%} = 608 - 646\text{ }^{\circ}\text{C}$). The samples produced in the large reactor using only one ultrasonic generator had generally higher oxidation resistance than the ones produced using two ultrasonic generators. This is probably due to the fact that a single ultrasonic generator introduces lower amount of ferrocene inside the reactor compared to two ultrasonic generators. As a results, MWCNTs in the samples 9, 10 and 11

contained less residual catalyst particles than MWCNTs in the samples 12 and 13 (see table 13). Therefore, they had a higher oxidation resistance (see section 3.3.2 for description of correlation between the residual catalyst content and oxidation resistance of MWCNTs).

All the MWCNT samples synthesised in both reactors had good structural homogeneity ($TGA\ T_{70\%} - T_{20\%} \leq 70\ ^\circ C$) with the exception of the 7th sample. This sample had particularly low defect density, high oxidation resistance and contained straight and well-aligned MWCNTs with moderate concentration of catalyst particles (see table 13 and figure 43). However, a close look at the corresponding original TGA graph in figure 44b reveals that beyond 650 °C, the 7th sample had the highest oxidation resistance. This means that compared to the other samples, the 7th sample contained a higher population of MWCNTs burning beyond 650 °C. Therefore, this sample contained a wider range of MWCNTs with different oxidation resistance which is reflected in the corresponding high $TGA\ T_{70\%} - T_{20\%}$ value ($\approx 90\ ^\circ C$).

The concentration of the residual catalyst particles in most of the samples varied between 1 and 4 wt.%. The 6th sample had excessive concentration of iron-based particles (5.87 wt.%) which is visible in the corresponding TEM image in figure 43 and also suggested by the relatively high Raman I_D/I_G (0.484). The excessive concentration of the residual catalyst particles in the 6th sample could explain its low oxidation resistance ($T_{50\%} = 577\ ^\circ C$). Since the same precursor composition was used in all the experiments, the deviation of the concentration of the residual catalyst particles in the 6th sample is not quite clear (see figure 33e) but might be linked to the cracking behaviours of ferrocene in different synthesis times, temperatures and flow rates of argon.

4.3.6. Effect of the size of the reactor on the composition of the atmosphere

In this section, the results of the gas analysis of the atmosphere of the small and the large reactors are compared. This comparison could potentially explain to what extent the size of the reactor has an impact on the thermocatalytic cracking behaviour of the precursor. The *in-situ* gas analysis is particularly important in large reactors as they are generally more expensive to run.

Figure 45 provides the results of the mass spectrometry of the atmosphere of the small and large reactors. Each graph contains the mass spectra acquired at the room temperature (blue) and at 800 °C (red).

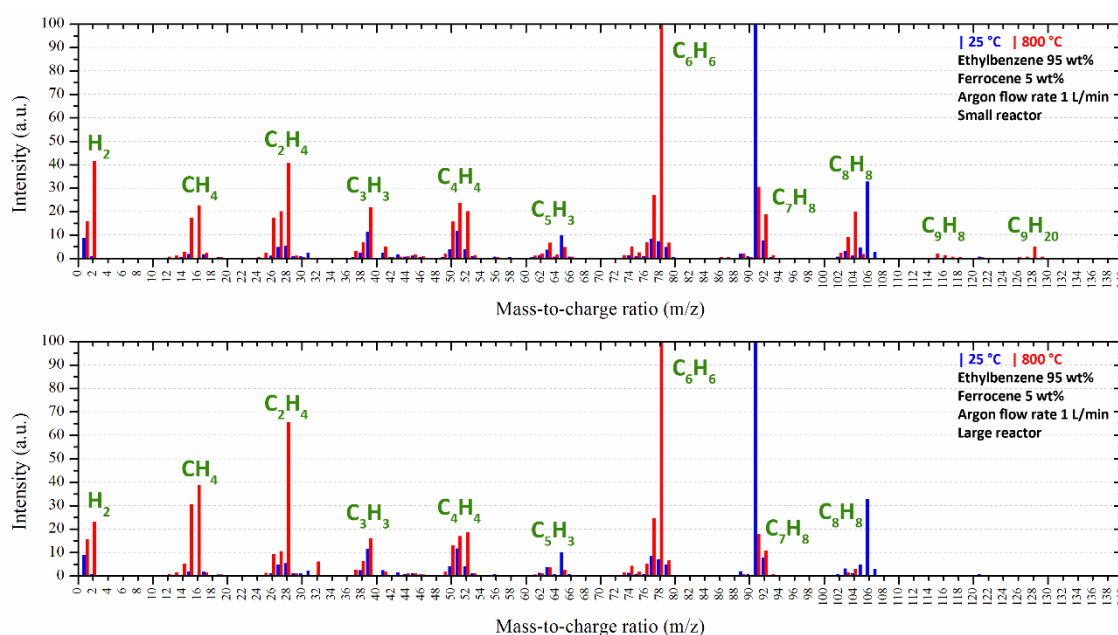


Figure 45. Mass spectrometry of the atmosphere of the small and the large reactors. Each graph contains two mass spectra acquired at the room temperature (blue) and at the synthesis temperature (red).

A quick comparison of the two graphs shows that the main intermediate fragments of ethylbenzene in the large reactor are the same as in the small reactor (see table 8).

Toluene and benzene are the main hydrocarbon by-products in both reactors (see section 3.3.6).

Interestingly, lighter hydrocarbons such as methane ($m/z = 16$) and ethene ($m/z = 28$) are significantly more abundant in the large reactor; while heavier fragments such as toluene and ethylbenzene radicals ($m/z = 102 - 105$) are less abundant. This generally means a higher efficiency of the thermocatalytic cracking of ethylbenzene in the large reactor compared to the small reactor. However, as discussed in 3.3.3, an efficient thermocatalytic cracking of precursor does not necessarily always guarantee a high yield of MWCNTs.

4.4. Conclusions

The production of vertically aligned MWCNTs can be scaled up using bigger AACVD reactors. By optimising the synthesis parameters, both the synthesis rate of MWCNTs and the catalytic conversion yield were improved nearly five times and twice respectively. By inserting a silicon wafer inside the large reactor, continuous large area (9×10 cm), mm-thick carpets of MWCNTs were produced. It was shown that such large carpets can be produced inexpensively with the same if not better quality than the ones produced in small lab-scale reactors.

The mass spectrometry of the atmosphere of the large reactor showed that ethylbenzene follows the same thermocatalytic cracking route as in the small reactor. Toluene and benzene were the most important hydrocarbon by-products in both reactors and should be ideally recycled back to the precursor reservoir (see sections 3.3.6 and 5.2). The abundance of the light hydrocarbons such as methane and ethene in the large reactor was higher than in the small reactor which is probably an indication of a higher efficiency of the larger reactor in thermocatalytic cracking of precursors.

It is suggested that further development of AACVD should be focused on modifying the current *batch* style of production towards a more industrially-favourable *continuous* processes. This can enormously enlarge the production rate and avoid inefficiencies associated with batch processes such as frequent heating and cooling the reactor.

Chapter 5. Summary and future of research

5.1. Summary of research

In this work, different aspects of the AACVD technique for production of CNTs were studied. By mapping an AACVD reactor, it was first shown that the technique is quite effective for the production of a variety of CNTs with numerous morphologies. MWCNTs were by far the most dominant product throughout the reactor. Some of the characteristics of the MWCNTs such as the length, outer diameter, oxidation resistance and residual catalyst content varied as a function of the position inside the reactor. Agglomerates of iron-containing nanoparticles, DWCNTs and SWCNTs were also present in specific zones of the reactor. A closer look at the SWCNTs revealed that they are partially covered with some fullerene-like species and their interaction with the walls of the SWCNTs under electron beam were studied *in situ* using high-resolution TEM.

It was suggested that formation of a variety of carbon nanomaterials inside the reactor was due to the inhomogeneity of the synthesise parameters throughout the reactor; among which the temperature and catalyst content had the highest influence.

The effect of the composition of the precursor on the synthesis yield and different characteristics of MWCNTs was another major part of the work. Different hydrocarbons, catalyst sources and catalyst concentrations were used and the corresponding synthesised MWCNTs were characterised. In term of synthesis yield, ethylbenzene and isopropylbenzene were found to be *ca.* 60 to 80 % more efficient than other commonly-used hydrocarbons such as xylene, toluene and benzene. Moreover, characteristics of MWCNTs such as the morphology and defect density can be tuned by simply choosing the right hydrocarbon. Similarly, the catalyst source and concentration

can be altered to meet the application-defined requirements such as the concentration of the residual catalyst content.

It was shown how *in-situ* gas analysis of the atmosphere of the reactor as an effective online monitoring tool can be used to observe the operation of AACVD reactors. The reported mass spectra and gas chromatograms could be used as reference finger prints to predict the properties of the final products. The gas analysis also revealed some of the fundamental aspects of the thermocatalytic cracking of different hydrocarbons for production of MWCNTs. The most important fragments of each precursor were identified and the cracking mechanism of some of the hydrocarbons was discussed.

By qualitative and quantitative gas analysis of the AACVD reactor running on ethylbenzene, the composition of the liquid hydrocarbon by-products was identified. A good knowledge of the composition is particularly useful since the liquid hydrocarbons by-products can be potentially distilled at the exhaust of the reactor, mixed with catalyst precursor and recycled back to the precursor reservoir. This method can significantly increase the efficiency of the synthesis and minimise the scape of the carcinogenic hydrocarbons from the exhaust to the atmosphere.

The conversion yield and mass of synthesised MWCNTs were considerably improved using a larger reactor. By optimising the precursor input rate, temperature and time, clean batches of vertically aligned MWCNTs with low defect density and minimum catalyst impurities were produced with growth rate of up to 14 g/hr.

The reported recipes including the optimised composition of the precursor and the method of recycling the liquid hydrocarbon by-products at the exhaust the reactor can be used to upscale the method for industrial production of continuous large-area, few-mm-thick carpets of vertically aligned MWCNTs.

5.2. Future of aerosol-assisted chemical vapour deposition of carbon nanotubes

There are still a few technical challenges which need attention to further increase the efficiency of the method. None of the current AACVD setups, including the ones used in this work, can operate continuously. Therefore, for removing the synthesised CNTs, it is almost always necessary to disassemble the setup. Since the CVD-grown CNTs normally oxidise at temperatures beyond 400 – 600 °C, they should be inevitably cooled below the mentioned range before any exposure to the air. Cooling down the furnace and/or reactor is a serious issue if the energy consumption is concerned. Hence, it is suggested that the design and manufacturing of a continuous AACVD reactor should be the focus of future research. In an ideal continuous AACVD reactor, the only constituents heated and cooled are the precursors, CNTs and the carrier gas. A probe could collect and transfer the deposit from inside the heated zone to a cold collection point. For continuous production of vertically aligned MWCNTs on substrates, the substrates could be preheated with the exhaust gases and continuously fed into the reactor and cooled gradually by the counter currents used to preheat the blank substrates.

There are several experimental parameters involved in AACVD synthesis of MWCNTs. Chemistry and temperature of the precursor; size distribution and concentration of the liquid particles in the aerosol; precursor input; chemistry, flow rate, pressure and temperature of the carrier gas; geometry of the aerosol generator and the reactor; size and composition of the reactor; temperature profile, heating and cooling rates of furnace are among the parameters which affect the quality and quantity of synthesised MWCNTs. Understanding the mutual or collective effect of independent

experimental parameters requires a large number of systematic experiments (*full factorial design*). Moreover, considering the fact that it is often necessary to check the reproducibility of AACVD synthesis experiments, full factorial design of experiments is infeasible. Alternatively, the most important subset of the full factorial design can be selected (*fractional factorial design*) [232,233]. The selection of the subset can be based upon the *hierarchical ordering principle* which prioritises the importance of the low-order interactions [233]. The interaction of the most important parameters of AACVD such as the chemistry of the precursor, synthesis temperature and the flow rate of the carrier gas should be studied using a fractional factorial design of experiments.

As discussed in chapter 3 and 4, there is a considerable loss of unreacted hydrocarbons from the exhaust of current AACVD reactors. Cost and environmental considerations necessitate the development and use of a hydrocarbon recycling unit to capture and reintroduce the unreacted carbon sources to the precursor reservoir. Hydrogen, as a major by-product of CVD reactors for synthesis of CNTs, could also be separated.

Modification of the current way the catalyst is introduced inside the AACVD tubular reactors can potentially homogenise the catalyst content across the reactor. Multiple feedstock entrance points or using reactors with bigger diameters can enhance the travel of the catalyst source deeper inside the reactor and might solve the issue. Figure 46 depicts a possible setup with multiple feedstock points. The substrate could be mobile to have a continuous production of homogeneous MWCNTs.

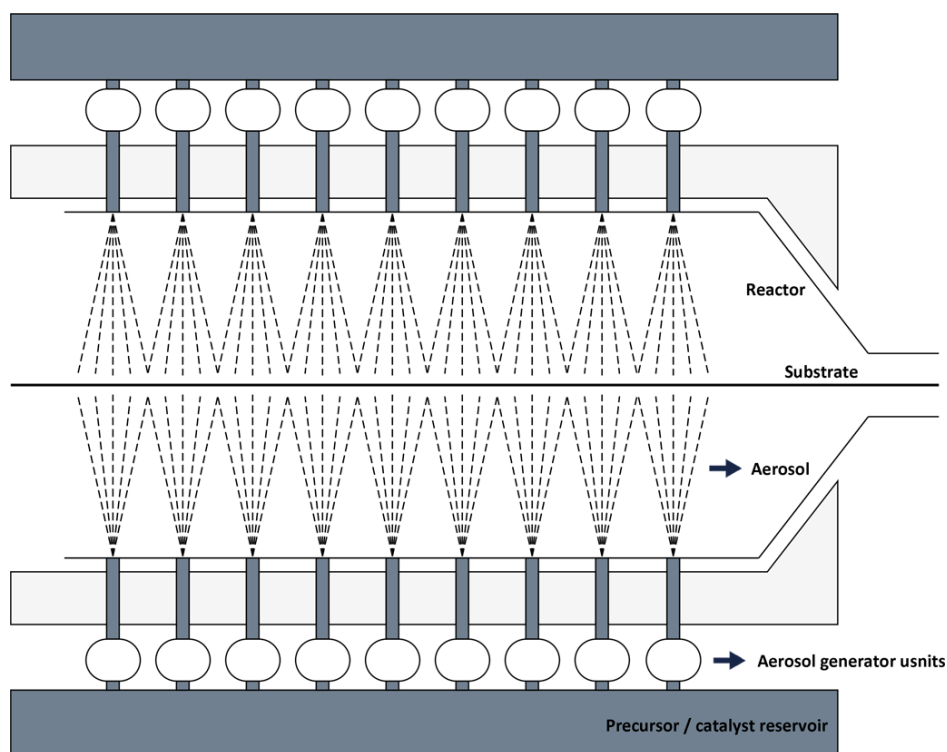


Figure 46. Schematic of a suggested AACVD reactor with multiple feedstock points for large-scale production of MCNTs.

Another aspect of AACVD method which requires further attention is the aerosol itself. Currently, there is no practical control over the size distribution of the liquid droplets in the aerosols of different hydrocarbons. A homogeneous aerosol cannot be generated and maintained, unless it is fully characterised online. Hence, more fundamental research should be carried out to develop techniques for real-time characterisation of aerosols and to manufacture aerosol generators with higher efficiencies and more control.

Further development of the probe [228] described in section 3.3.7 is one of the key parts of this PhD project which is planned to be continued in the Department of Materials at University of Oxford within a project funded by the European Research Council (Proof of Concept). A potential solution could be inserting a thin stainless steel jacket between the layers of the probe to reduce the radiation. The jacket can be constantly cooled down by a liquid coolant. Moreover, acceleration and collimation of

the analytes as in MBMS (see section 1.2.5) could possibly prohibit or limit the alteration of the analytes.

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Appendices

Appendix I. Iron – iron carbide phase diagram

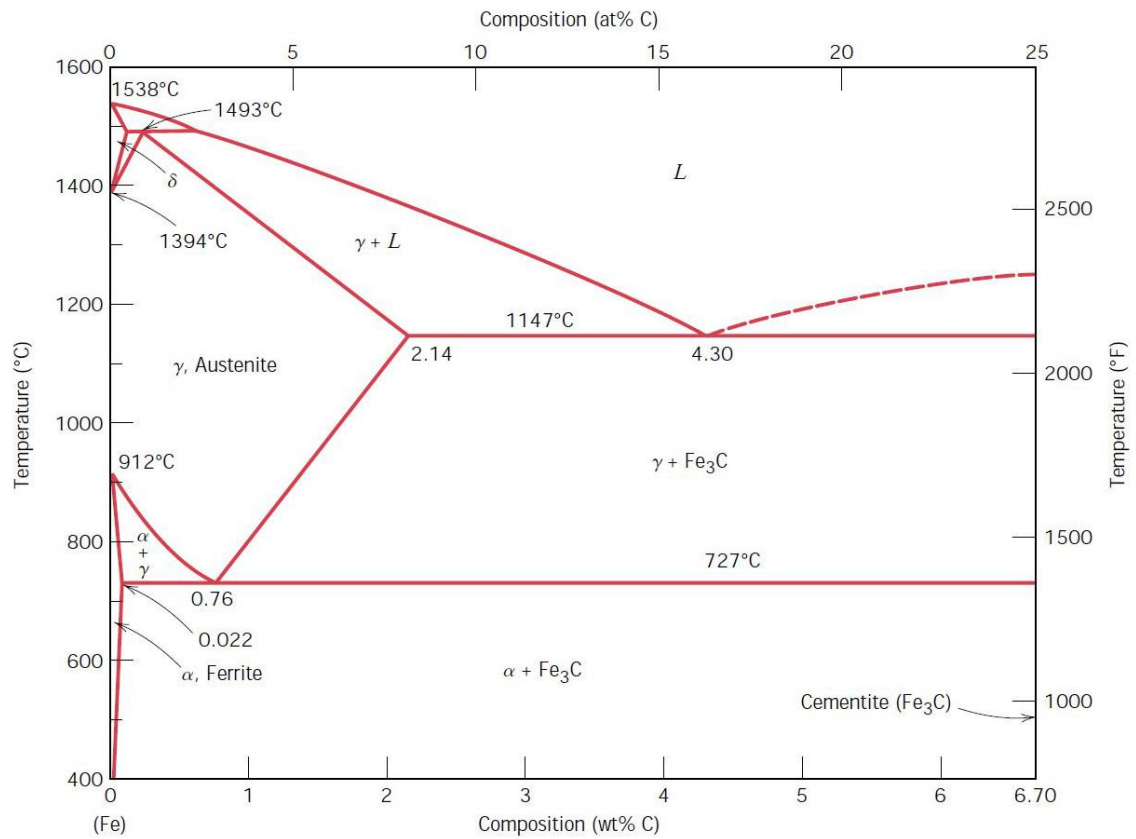


Figure 47. Iron – iron carbide phase diagram [234].

Appendix II. Analytical probe

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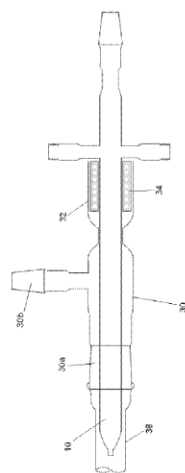


Fig. 3

(57) Abstract: According to the present invention, there is provided a device for transferring an analyte from a reaction chamber to a detector, which detector is capable of detecting said analyte. The device comprises a tubular member having a first end adapted to receive a sample containing said analyte within said reaction chamber and a second end adapted to communicate with a sample inlet of said detector; and a jacket for regulating the temperature of sample passing through the tubular member, wherein said jacket is disposed about at least a portion of the tubular member. Methods of using the device, and apparatus comprising the device, are also provided. The device may be used to transfer an analyte from a reaction chamber to a detector during the course of a chemical reaction, such that the reaction can be monitored in situ.

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DEVICE, METHOD AND APPARATUS FOR
THE TRANSFER OF ANALYTES

Field of the Invention

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The present invention relates to a device for transferring an analyte from a reaction chamber to a detector. Methods of using the device, and apparatus comprising the device, are also provided. The device may be used to transfer an analyte from a reaction chamber to a detector during the course of a chemical reaction, such that the reaction can be monitored *in situ*.

10

Background to the Invention

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For a variety of reasons, it is often desirable to monitor the state of a chemical reaction *in situ*. Information regarding the state of a chemical reaction can be useful for determining the extent to which the reaction has progressed, for quality control (e.g. by analysing the reaction products and adjusting one or more parameters to encourage formation of the desired reaction product), and for determining the intermediates that are formed during a reaction.

20

Nanomaterials, such as carbon nanotubes, are of great interest due to their mechanical and electrical properties. The electrical properties of nanotubes, which can behave as metals or as semiconductors, depend on their morphology, in particular on their diameter and their chirality. It has been found that the electrical properties of nanotubes may be tuned by the incorporation of heteroatoms in the lattice. Boron and nitrogen are typically used, due to their similarity in atomic size with carbon and their ability to function as p-type and n-type dopants, respectively. However, it is notoriously difficult to control the synthesis of nanotubes, and in particular to achieve product uniformity on a large scale.

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The details of the mechanism by which nanotubes form, and the influence of different parameters on nanotube formation, are not well understood. Typically, studies of nanotube growth rely on *post-mortem* studies of the products, which provide little information on the reactions taking place during nanotube formation. Consequently, it

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has not been possible to establish a complete growth mechanism. *In situ* monitoring of the growth process is therefore desirable from a point of view of providing information on the mechanism by which nanomaterials form.

- 5 In order to monitor a chemical reaction *in situ*, it is usually necessary to obtain, during the course of the reaction, a sample containing one or more analytes which provide information regarding the state of the reaction. However, in order for the analyte(s) to be detected, they must normally be transferred from the reaction chamber to a suitable detector. A device commonly referred to as a "transfer line" may be used for such a
- 10 purpose. Capillary transfer lines are an example of such a device. However, a number of problems are associated with the use of capillary transfer lines which reduce the accuracy of the information obtained. For instance, where the reaction is conducted at high temperature, the capillary can be heated to such an extent that the sample continues to undergo reaction as it passes through the capillary. Conversely, capillary
- 15 transfer lines may also be prone to rapid cooling as a result of heat exchange with the surroundings, which can result in the sample being deposited onto the tube by condensation. Moreover, when a metal device is used, the capillary can act as a catalyst, thereby affecting the composition of the sample. Flexible transfer lines made of fused silica are also known. However, such transfer lines also suffer from many of the
- 20 same limitations as capillary transfer lines and, moreover, cannot be introduced into high temperature reaction chambers. For instance, many transfer lines comprise a coating which is sensitive to high temperatures and therefore cannot be introduced into high temperature reaction chambers.
- 25 Accordingly, there exists a need for a device for transferring a sample containing an analyte from a reaction chamber to a detector, which device allows a sample to be obtained at a desired location within the reaction chamber and transferred to the detector whilst substantially preserving the composition of the sample. In particular, there exists a need for a device which can be used to monitor the formation of nanomaterials *in situ*.

30

Summary of the Invention

According to an aspect of the invention, there is provided a device for transferring an

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analyte from a reaction chamber to a detector, which detector is capable of detecting said analyte, wherein the device comprises:

5 a tubular member having a first end adapted to receive a sample containing said analyte within said reaction chamber and a second end adapted to communicate with a sample inlet of said detector; and

a jacket for regulating the temperature of sample passing through the tubular member, wherein said jacket is disposed about at least a portion of the tubular member.

10 According to another aspect of the invention, there is provided a method of detecting an analyte present in a reaction chamber, which method comprises:

obtaining a sample containing said analyte from within said reaction chamber;

transferring at least a portion of said sample to a detector; and

detecting said analyte using said detector;

15 wherein said steps of obtaining and transferring are performed using a device comprising:

a tubular member through which said sample is passed from said reaction chamber to said detector, wherein said tubular member comprises a first end which receives said sample within said reaction chamber and a second end which is in communication with a sample inlet of said detector; and

20 a jacket which regulates the temperature of the sample passing through the tubular member, wherein said jacket is disposed about at least a portion of the tubular member.

25 According to a further aspect of the invention, there is provided an apparatus for detecting an analyte present in a reaction chamber, wherein the apparatus comprises a detector capable of detecting said analyte and a device for transferring said analyte from said reaction chamber to said detector, wherein the device is a device of the present invention.

30 A device of the present invention may be advantageous for a number of different reasons. For instance, the present device is adapted to receive a sample within the reaction chamber, and therefore may allow accurate and location-specific information regarding the inside of the reaction chamber to be obtained. In particular, a device of the

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present invention may be used to obtain samples from a variety of different positions within the chamber, thereby allowing the reaction chamber to be profiled and/or optimised. Moreover, a device of the present invention comprises a jacket disposed about at least a portion of the tubular member, which jacket advantageously allows the temperature of sample passing through the tubular member to be regulated. Regulating the temperature of the sample as it passes through tubular member may minimise any physical or chemical changes to the sample during transfer from the reaction chamber to the detector. For example, the device may minimise further reaction or condensation of the sample during the transfer process, or reduce the occurrence of unwanted thermal and thermocatalytic decomposition reactions (e.g. pyrolysis and cracking). Consequently, when the sample is analysed, the information obtained may provide a more accurate indication of the state of the reaction within the reaction chamber.

Description of Various Embodiments

The present invention provides a device which is suitable for transferring an analyte from a reaction chamber to a detector. A device of the present invention comprises a tubular member having a first end adapted to receive a sample containing said analyte within the reaction chamber and a second end adapted to communicate with a sample inlet of the detector. The tubular member is generally a hollow, elongate member through which the sample or a portion thereof may be transferred from the reaction chamber to the detector. The tubular member may have a variety of cross-sections, but is preferably a cylindrical member, and more preferably a right circular cylindrical member. The tubular member may be made of a flexible or a substantially rigid material. The dimensions of the tubular member may vary depending on e.g. the nature of the analyte being detected, and the type of reaction chamber and the detector being used. By way of illustration, and without limitation, the tubular member may have a length from the first end to the second end of from about 0.5 m to about 3 m, from about 0.75 m to about 1.5 m, or about 1 m; and/or may have a diameter of from about 0.2 cm to about 1 cm, about 0.4 cm to about 0.8 cm, or about 0.6 cm.

The tubular member comprises a first end which is adapted to receive a sample containing the analyte within the reaction chamber. Thus, since the first end of the

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tubular member will be placed within the reaction chamber during use, at least the first end of the tubular member, and preferably the entire tubular member, preferably comprises a material which is capable of withstanding the physical and chemical conditions that occur during the reaction chamber during use. The tubular member is preferably made of a material that is substantially chemically inert under the conditions of use. In this regard, the use of a material that will not catalyse a reaction of the sample and/or that is resistant to corrosive samples may be preferred. The material is preferably resistant to the extreme temperatures and/or pressures which are commonly encountered in furnaces and other high temperature reaction chambers.

10

In an embodiment, the tubular member is fabricated from a ceramic material (e.g. a glass) and/or a metallic material (e.g. stainless steel). The use of ceramic materials over metallic materials may be preferred particularly when the sample is susceptible to thermocatalytic decomposition, as such processes can be catalysed by metals.

15

Preferably, the tubular member, or at least a portion of the tubular member that is to be exposed to the chamber environment, comprises a glass such as a borosilicate glass or a quartz glass. In a particularly preferred embodiment, the tubular member comprises a quartz glass. Quartz glasses can generally withstand the high temperatures and pressures that are encountered in high temperature reaction chambers. In an embodiment, the tubular member comprises a radiation resistant coating. In a particular embodiment, at least a portion of the external surface of the tubular member comprises a radiation resistant coating.

20

The device preferably tapers towards the first end of the tubular member. This feature may facilitate insertion of the first end of the tubular member into the reaction chamber and may allow greater control and accuracy when manipulating the device in the reaction chamber. Preferably the device is adapted to receive a sample from a variety of different locations within the reaction chamber, so that e.g. the state of a reaction at different locations within the reaction chamber can be monitored. This can be particularly advantageous for studying the level of homogeneity of products in different locations within the reaction chamber. In an embodiment, the reaction chamber comprises an elongate tubular chamber and the device is adapted to receive a sample at a plurality of different positions along the length of the chamber.

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Movement of the tubular member within the reaction chamber may be controlled manually or by automation. In a particular embodiment, movement of the tubular member within the reaction chamber is controlled by automation, *e.g.* by robotics. Thus, for instance, the device may comprise one or more motorised units or other actuators, which allow movement of the tubular member to be controlled in one, two or three dimensions. Movement may be controlled using a suitably programmed computer.

In use, the sample may be received and passed through the tubular member by diffusion. In an embodiment, the pressure in the reaction chamber is higher than the pressure in the detector such that a pressure gradient is provided which acts as a driving force for transfer of the sample through the tubular member.

A device of the present invention may be used in conjunction with a variety of different reaction chambers. The device may be used with any chamber in which the materials are exposed to extreme temperatures. For example, the reaction chamber may be a chemical or physical vapour deposition reactor; an industrial drying, baking or roasting oven; or a refrigerator. The reaction chamber may be an analytical furnace. Particularly where the formation of carbon nanomaterials, *e.g.* carbon nanotubes, is desired, the reaction chamber may be a chemical vapour deposition reactor. The chamber may be of any conventional design (*e.g.* laboratory or industrial), and may be of any shape and size (*e.g.* tubular, cylindrical, spherical or cuboid). By way of illustration, and without limitation, the reaction chamber may have a length of from about 0.5 m to about 20 m, from about 0.75 m to about 10 m, or from about 1 m to about 5 m.

One of the benefits of the device of the present invention is that it may be used with a reaction chamber operating under a wide range of temperatures and a wide range of pressures. In an embodiment, the temperature within the reaction chamber is from about -100 °C to about 1500 °C, *e.g.* from about 0 °C to about 1500 °C, *e.g.* from about 200 °C to about 1250 °C, *e.g.* from about 400 °C to about 1000 °C. In an embodiment, the temperature within the reaction chamber is from about 400 °C to about 1500 °C. In an embodiment, the temperature within the reaction chamber is from about -100 °C to about 150 °C. In an embodiment, the pressure within the reaction chamber is from about 1.33

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$\times 10^{-5}$ Pa to about 1.01×10^7 Pa, from about 1.33×10^{-4} Pa to about 1.01×10^6 Pa, or from about 1.33×10^{-3} Pa to about 1.01×10^5 Pa.

One or more samples may be obtained from the reaction chamber prior to, during and/or after the reaction. The or each sample may comprise one or more components selected from *e.g.* reactants, intermediates and products of the reaction. The nature of the sample obtained from the reaction chamber will depend upon the reaction being monitored. Thus, the sample may comprise a solid, a liquid, a gas, or a mixture thereof. The sample may be a liquid suspension or an aerosol, in which case a filter-vaporiser extension is preferably used with the device. The sampler may collect solids as suspensions of particles, such as smoke. The sample may comprise particles having a size of less than 1 mm, less than 100 μm , less than 10 μm , less than 1 μm or less than 100 nm. The sample may comprise one or more compounds selected from organic compounds, inorganic compounds, and mixtures thereof.

The device is particularly useful for monitoring a reaction involving nanomaterials such as carbon nanomaterials which, as explained above, are difficult to monitor *in situ*. Thus, in a preferred embodiment, the sample comprises a nanomaterial, such as a carbon-containing nanomaterial. The carbon nanomaterial may be doped with one or more heteroatoms, such as boron or nitrogen. The nanomaterial may be a fullerene (*e.g.* a carbon nanotube or a spherical fullerene, *e.g.* a C_{60} , C_{70} , C_{76} , C_{84} , C_{90} or C_{94} spherical fullerene), a layered material (*e.g.* a two-dimensional material such as graphene), a nanowire, a nanoparticle or a nanocluster.

The tubular member also has a second end which is adapted for communication with a detector. The detector is capable of detecting one or more analytes present in the sample, and may provide useful information regarding the state of the reaction. The detector may be or may form part of an analyser, which may permit qualitative and/or quantitative analysis of the analyte(s). In an embodiment, the detector is a mass spectrometer (*e.g.* a tandem mass spectrometer; MS-MS), a gas chromatograph, or a mass spectrometer-gas chromatograph. Alternatively, the detector may be a gas analyser, such as a galvanic gas analyser, an industrial combustion analyser, or an emission analyser. An analyser may be used which comprises one, two or more

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detectors. For instance, a mass spectrometer may have one, two or more detectors for different purposes, *e.g.*, with different detection limits and precisions. In an embodiment, the tubular member is adapted for communication with a plurality of detectors. For example, the tubular member may be a branched tubular member comprising a plurality
5 of ends each adapted for communication with a detector. In this way, one or more samples may be obtained and passed to a number of different detectors simultaneously.

The device may comprise a capillary disposed within the tubular member, through which capillary at least a portion of the sample is introduced into the sample inlet of the
10 detector. As a result, the build up of deposits towards the second end of the tubular member may be minimised. The capillary will generally be disposed at the second end of the tubular member and preferably extends into the tubular member. By way of illustration, the capillary may extend at least 1%, at least 3%, at least 5%, or at least 10% of the length of the tubular member as measured from the second end to the first end of
15 the tubular member. The capillary may comprise a ceramic material (*e.g.* alumina, or a glass such as fused silica), a metallic material (*e.g.* stainless steel), or a combination thereof.

The device may comprise an adaptor for connecting said second end of the tubular
20 member to a sample inlet of the detector. The adaptor may comprise a first end adapted for placement in or about the second end of the tubular member, and a second end which connects to a sample inlet of the detector. It may be preferable for the first end of the adaptor to be fabricated from the same or a similar material to the material from which the tubular member is fabricated. Thus, where the tubular member is fabricated
25 from a ceramic material (*e.g.* a glass such as a borosilicate glass or a quartz glass), it may be preferable for the first end of the adaptor to be fabricated from a ceramic material, and more preferably from the same material as that from which the tubular member is made. The second end of the adaptor may be fabricated from the same material as the first end of the adaptor, or from a different material. In an embodiment,
30 the first end of the adaptor is fabricated from a ceramic material (*e.g.* a glass such as a borosilicate glass or a quartz glass) and the second end of the adaptor is fabricated from a metallic material (*e.g.* stainless steel). The adaptor may be removable from the device,

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so that it can be easily cleaned and/or so that different adaptors can be fitted to the device depending on the type of detector being used.

5 The device also comprises a jacket for regulating the temperature of the sample as it passes through the tubular member, which jacket is disposed about at least a portion of the tubular member. The jacket may comprise any suitable heating or cooling means operative to regulate the temperature of sample passing through the tubular member. In an embodiment, the jacket covers at least 50%, at least 60%, at least 70%, at least 80%, at least 90%, or substantially all of the external surface area of the tubular member. The greater the proportion of the tubular member that is covered by the jacket, the more effective the jacket may be at regulating the temperature of sample passing through the tubular member.

15 In a preferred embodiment, the jacket comprises an inlet and an outlet for a fluid, and is adapted for fluid flow therethrough. In this case, the jacket is preferably fully sealed with respect to the tubular member so as to ensure that fluid present in the jacket does not mix with sample present in the tubular member or its surroundings. In a preferred embodiment, the fluid inlet and the fluid outlet are positioned at the same end of the jacket. Particularly where the fluid inlet and outlet protrude from the device, the inlet and outlet are preferably positioned towards the second end of the tubular member, rather towards the first end. Such an arrangement may allow a greater proportion of the device to be inserted into the reaction chamber, and also assist with manoeuvring the device within the reaction chamber. For similar reasons, the jacket preferably tapers towards the first end of the tubular member.

25 The jacket may be disposed about the tubular member such that a channel is formed between an inner surface of the jacket and an outer surface of the tubular member, through which passage a fluid can be passed. The tubular member and the jacket may each be substantially cylindrical, in which case they may be arranged in a substantially concentric arrangement. In a preferred embodiment, fluid flows through at least a portion of the jacket in a counter-current relationship with sample passing through the tubular member. This may be achieved using a jacket comprising one or more internal tubular members, which partition the interior space of the jacket into two or more channels which

are in fluid communication with one another. Thus, for instance, the jacket may comprise an internal tubular member which partitions the interior space of the jacket such that: an inner channel is formed between an inner surface of the internal tubular member and an outer surface of the tubular member through which the sample passes; and an outer channel is formed between an inner surface of the wall of the jacket and an outer surface of the internal tubular member. In this case, the fluid inlet and outlet of the jacket may be situated towards the second end of the transfer line, with the fluid inlet located on the inner channel and the fluid outlet located on the outer channel, and the inner and outer channels may meet towards the first end of the transfer line, the channels together forming a substantially U-shaped channel through which the fluid passes. The use of such an arrangement may enhance the insulation provided by the jacket, and thus facilitate the attainment of a constant temperature within the tubular member.

The fluid or fluids flowing through the jacket may each be a liquid or a gas. Preferred fluids may vary according to the level of temperature regulation that is required. Where the fluid is to be used at relatively low temperatures (e.g. lower than about 400 °C, e.g. lower than about 300 °C), liquids may be preferred over gases due to their higher heat capacity. Water may be preferred when the fluid is to be used at a low temperature (e.g. less than about 100 °C), and where a high flow rate is required. Oils may be preferred when the fluid is at a higher temperature (e.g. between about 100 °C and about 400 °C), and when a slow flow rate is acceptable. Preferred gases include air and inert gases such as nitrogen, argon and helium. Since the efficiency of cooling or heating between inert gases does not greatly differ, the choice of gas may be based on cost and availability. In this regard, the use of helium may be preferred. The desired flow rate of the fluid may vary depending on the degree of temperature regulation that is required. By way of illustration, the fluid may flow through the jacket with a flow rate of from about 0.01 L/min to about 100 L/min, from about 0.1 L/min to about 10 L/min, or about 1 L/min.

The temperature of the fluid is selected so as to regulate the temperature of the sample as it passes through the tubular member. By way of illustration, and without limitation, the temperature of the fluid may be such that the temperature of the sample as it passes through the tubular member is from about -100 °C to about 500 °C, from about 0 °C to about 400 °C, or from about 100 °C to about 300 °C. The temperature of the fluid in the

jacket may be lower than the temperature in the reaction chamber, *e.g.* so as to minimise further reaction of the sample as it passes through the tubular member to the detector. For example, the temperature of the sample passing through the tubular member may be from about 50 °C to about 600 °C, from about 100 °C to about 550 °C, from about 150 °C to about 500 °C, or from about 200 °C to about 450 °C lower than the temperature in the reaction chamber. Alternatively, the temperature of the fluid in the jacket may be higher than the temperature in the chamber, *e.g.* so as to minimise condensation of the sample. For example, the temperature of the fluid may be such that the temperature of the sample as it passes through the tubular member is from about 10 °C to about 500 °C, from about 50 °C to about 400 °C, or from about 100 °C to about 300 °C higher than the temperature in the reaction chamber. In a preferred embodiment, the temperature of the fluid is between the temperature of the reaction chamber and the temperature of the detector. For instance, where the reaction chamber is hotter than the detector, the temperature in the tubular member may be lower than that in the reaction chamber so as to minimise further reaction of the sample, yet greater than the temperature in the detector so as to minimise condensation of the sample. Similarly, where the chamber is cooler than the detector, the temperature in the tubular member may be higher than that in the reaction chamber so as to minimise condensation of the sample, yet lower than the temperature in the detector so as to minimise degradation of the sample.

Like the tubular member, the jacket is preferably fabricated from a material that is substantially chemically inert with respect to the sample under the conditions of use. In this regard, the use of a material that will not act as a catalyst for the reaction and/or that is resistant to corrosive analytes is again preferred. The jacket may be fabricated from a ceramic material (*e.g.* a glass) and/or a metallic material (*e.g.* stainless steel). Preferably, the jacket comprises a glass. In a particularly preferred embodiment, the jacket comprises a borosilicate glass or a quartz glass. In an embodiment, both the tubular member and the jacket are fabricated from a ceramic material, *e.g.* a glass such as a borosilicate glass or a quartz glass. The tubular member and the jacket may be fabricated as a single piece or as separate pieces. In an embodiment, the tubular member is removable from the jacket. This may allow the tubular member to be replaced with a new member or to be removed, cleaned and subsequently replaced.

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Particularly at high temperatures, e.g. at temperatures greater than 500 °C, radiation may be a significant route for heat transfer. Thus, in an embodiment, the jacket further comprises a radiation resistant coating. This coating may serve to prevent heating of the device by the surroundings, or to prevent heat from being lost to the surroundings.

- 5 Examples of suitable materials for use in radiation resistant coatings include metallic coatings, particularly metallic coating with a high thermal stability. For instance, a preferred coating comprises platinum.

- 10 The device may comprise various other features. For instance, in one embodiment, the device further comprises an exhaust system for removing excess gas and analytes that have not entered tubular member. Alternatively or additionally, the device may further comprise a handle to assist with manoeuvring the device within the reaction chamber. In an embodiment, the device comprises means for fluid recirculation, which reclaims the fluid from the jacket, regulates its temperature and/or adjusts its flow rate, before
15 returning the fluid to the jacket.

The present invention will now be described with reference to the accompanying drawings, in which:

- 20 Figure 1 is a cut-away view of a device of the present invention;
Figure 2 depicts a cross section of the device of Figure 1;
Figures 3 and 4 depict an exhaust system for use with the device of Figure 1; and
Figure 5 depicts an adaptor for connecting the device of Figure 1 to a detector.
- 25 Figure 1 illustrates a device in accordance with the present invention. The device 10 comprises an elongate tubular member 12 having a first end 12a and a second end 12b. A jacket 14 having a fluid inlet 14a and a fluid outlet 14b is disposed about the tubular member 12. The jacket comprises an internal tubular member 20 and an outer wall 22. The device tapers towards the first end 12a of the tubular member to assist with the
30 introduction of the first end of the device into a reaction chamber. The device further comprises a joint 18 disposed about the second end of the tubular member 12. A cross section of the device is shown in Figure 2, from which it can be seen that the tubular member 12, the internal tubular member 20 of the jacket, and the outer wall 22 of the

jacket are arranged in a substantially concentric configuration. It can also be seen that outer wall 22 of the jacket is attached to the internal tubular member of the jacket by bridges 24.

- 5 In use, the first end 12a of tubular member is inserted within the reaction chamber (not shown) and the second end 12b is connected via joint 18 to the sample inlet of a detector (not shown). A sample containing one or more analytes of interest (*e.g.* a reactant, intermediate or product) is received within the reaction chamber at said first end of the tubular member. The sample may be received in the first end of the tubular member 12 by applying a pressure differential across the reaction chamber and the detector. The sample then passes from said first end 12a of the tubular member 12 to the second end 12b, and to a sample inlet of the detector. The temperature of the sample as it passes along the tubular member 12 is regulated using jacket 14, which contains a fluid (*e.g.* water or air) of a desired temperature. The fluid flows through the fluid inlet 14a into the channel formed between the outer surface of the tubular member 12 and the inner surface of the internal tubular member 20 of the jacket 14. The fluid flows along this channel towards the first end 12a of the tubular member 12, such that the fluid flows counter-currently to the direction of the sample passing through the tubular member 12. The fluid then flows back along the channel formed between the outer surface of the internal tubular member 20 and the inner surface of the outer wall 22 of the jacket, before exiting the jacket through fluid outlet 14b. The fluid may heat or cool the sample relative to the temperature of the reaction chamber, *e.g.* so as to minimise further reaction of the sample as it passes along the tubular member 12.
- 25 Figure 3 depicts the device 10 of Figures 1 and 2 present in an exhaust system 30. The exhaust system may be used to remove unwanted matter, *e.g.* precursors, products or carrier gas from the reaction chamber, and may be particularly useful where *e.g.* only a small amount of analyte is required. The illustrated exhaust system 30 comprises an exhaust inlet 30a and an exhaust outlet 30b. The exhaust inlet 30a is shown engaging with reaction chamber 38. The exhaust system 30 may also serve to support the transfer device 10. As shown in Figure 3, the exhaust system 30 has a supporting end 32 containing a supporting tube 34 in which the transfer device 10 is supported. Figure 4

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shows the exhaust system without the transfer device 10 present therein, as well as the supporting tube 34.

Figure 5 shows an adaptor 40 for connecting the transfer device 10 shown in Figure 1 to a detector (not shown). The adaptor comprises a first end 40a and a second end 40b. The first end 40a may be made of the same material(s) used for fabrication of the device 10 (preferably a glass, more preferably a borosilicate or a quartz glass) and is adapted to be placed about the joint 18 of the device 10. The second end 40b is adapted to connect to a sample inlet of a detector (not shown). The cone-socket configuration of the first end 40a of the adaptor 40 and the joint 18 of the device 10 helps to efficiently connect the adaptor 40 and device 10 in a sealed manner, whilst still allowing the adaptor 40 and device 10 to be separated for cleaning, replacement and/or repair.

A device of the present invention may allow for more accurate monitoring of a chemical reaction *in situ*. By way of illustration, a transfer device of the type shown in the Figures has been used to monitor the synthesis of multiwalled carbon nanotubes (MWCNTs) by catalytic chemical vapour deposition (CCVD). The device was used to deliver an analyte (a precursor composition) from a reaction furnace at around 800 °C for analysis in a mass spectrometer. The use of the device resulted in more accurate mass spectra with less relative abundance for peaks corresponding to the lighter hydrocarbons. Thus, the device increased the precision of the qualitative and quantitative detection of precursor composition inside the furnace.

It will be understood that the present invention has been described above purely by way of example, and modification of detail can be made within the scope of the invention. Each feature disclosed in the description, and where appropriate the claims and drawings may be provided independently or in any appropriate combination.

CLAIMS

1. A method of detecting an analyte present in a reaction chamber, which method comprises:
 - obtaining a sample containing said analyte from within said reaction chamber;
 - transferring at least a portion of said sample to a detector; and
 - detecting said analyte using said detector;wherein said steps of obtaining and transferring are performed using a device comprising:
 - a tubular member through which said sample is passed from said reaction chamber to said detector, wherein said tubular member comprises a first end which receives said sample within said reaction chamber and a second end which is in communication with a sample inlet of said detector; and
 - a jacket which regulates the temperature of the sample passing through the tubular member, wherein said jacket is disposed about at least a portion of the tubular member.
2. A method according to claim 1, wherein the sample contains a nanomaterial, e.g. selected from fullerenes (e.g. carbon nanotubes or spherical fullerenes, e.g. C₆₀, C₇₀, C₇₆, C₈₄, C₉₀ or C₉₄ spherical fullerenes), layered materials (e.g. graphene), nanowires and nanoclusters.
3. A method according to claim 1 or claim 2, wherein the reaction chamber is a chemical or physical deposition reactor; an industrial drying, baking or roasting oven; or a refrigerator.
4. A method according to any of claims 1 to 3, which comprises obtaining a sample at a plurality of different positions within said reaction chamber.
5. A method according to claim 4, wherein the reaction chamber comprises a tubular chamber and the device is adapted to receive a sample at a plurality of different positions along the length of said chamber.

6. A method according to any of claims 1 to 5, wherein the detector is a mass spectrometer (e.g. a tandem mass spectrometer), a gas chromatograph, or a mass spectrometer-gas chromatograph.
7. A method according to any of claims 1 to 6, wherein the tubular member comprises a material which is substantially chemically inert with respect to the sample under the conditions of use.
8. A method according to any of claims 1 to 7, wherein the tubular member and/or the jacket comprise a ceramic material, e.g. a glass, e.g. a borosilicate or a quartz glass.
9. A method according to any of claims 1 to 8, wherein the temperature of the reaction chamber is from about -100 °C to about 1500 °C, e.g. from about 400 °C to about 1500 °C or from about -100 °C to about 150 °C.
10. A method according to any of claims 1 to 9, wherein the temperature of the sample passing through the tubular member is regulated to a temperature in the range of from about -100 °C to about 500 °C, e.g. from about 100 °C to about 300 °C.
11. A method according to any of claims 1 to 10, wherein the jacket comprises an inlet and an outlet for a fluid, and is adapted for fluid flow therethrough.
12. A method according to any of claims 1 to 11, wherein the device further comprises automated means for controlling movement of the tubular member within the reaction chamber.
13. A device for transferring an analyte from a reaction chamber to a detector, which detector is capable of detecting said analyte, wherein the device comprises:
 - a tubular member having a first end adapted to obtain a sample containing said analyte within said reaction chamber and a second end adapted to communicate with a sample inlet of said detector; and
 - a jacket for regulating the temperature of sample passing through the tubular member, wherein said jacket is disposed about at least a portion of the tubular member.

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14. A device according to claim 13, wherein at least the first end of the device is adapted for insertion into a reaction chamber which is a chemical or physical deposition reactor; an industrial drying, baking or roasting oven; or a refrigerator.

15. A device according to claim 13 or claim 14, wherein the device is adapted to receive a sample at a plurality of different positions within the reaction chamber.

16. A device according to any of claims 13 to 15, wherein the device is adapted to receive a sample at a plurality of different positions along the length of an elongate tubular reaction chamber.

17. A device according to any of claims 13 to 16, wherein the device tapers towards said first end of the tubular member.

18. A device according to any of claims 13 to 17, wherein the device is adapted to connect to the sample inlet of the detector.

19. A device according to any of claims 13 to 18, wherein the device comprises a capillary disposed within said tubular member through which at least a portion of the sample is introduced into said sample inlet of the detector.

20. A device according to any of claims 13 to 19, wherein the device is adapted for connection to the sample inlet of a detector which is a mass spectrometer (*e.g.* a tandem mass spectrometer), a gas chromatograph, or a mass spectrometer-gas chromatograph.

21. A device according to any of claims 13 to 20, wherein the tubular member and/or the jacket comprise a ceramic material, *e.g.* a glass, *e.g.* a borosilicate glass or a quartz glass.

22. A device according to any of claims 13 to 21, wherein the jacket surrounds substantially all of the external surface area of the tubular member.

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23. A device according to any of claims 13 to 22, wherein the jacket comprises an inlet and an outlet for a fluid, and is adapted for fluid flow therethrough.

24. A device according to claim 23, wherein the fluid inlet and outlet are positioned towards the second end of the tubular member.

25. A device according to claim 23 or claim 24, wherein the jacket is disposed about at least a portion of the tubular member such that a channel is formed between an inner surface of the jacket and an outer surface of the tubular member, through which passage a fluid can be passed.

26. A device according to any of claims 13 to 25, wherein the jacket and/or the tubular member comprise a radiation resistant coating.

27. A device according to any of claims 13 to 26, wherein the device further comprises automated means for controlling movement of the tubular member within the reaction chamber.

28. An apparatus for detecting an analyte present in a reaction chamber, wherein the apparatus comprises a detector capable of detecting said analyte and a device for transferring said analyte from said reaction chamber to said detector, wherein the device is a device according to any of claims 13 to 27.

29. An apparatus according to claim 28, wherein the detector is a mass spectrometer (*e.g.* a tandem mass spectrometer), a gas chromatograph, or a mass spectrometer-gas chromatograph.

30. An apparatus according to claim 28 or claim 29, further comprising a reaction chamber.

31. An apparatus according to claim 30, wherein the reaction chamber is a chemical or physical deposition reactor; an industrial drying, baking or roasting oven; or a refrigerator.

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32. Use of a device of any of claims 13 to 27, or an apparatus of any of claims 28 to 31, in the detection of an analyte present in a reaction chamber.
33. The use of claim 32, in the detection of a nanomaterial in a reaction chamber.
34. Use of a device of any of claims 13 to 27, or an apparatus of any of claims 28 to 31, for monitoring a chemical reaction *in situ*.
35. The use of claim 34, for monitoring the production of a nanomaterial *in situ*.

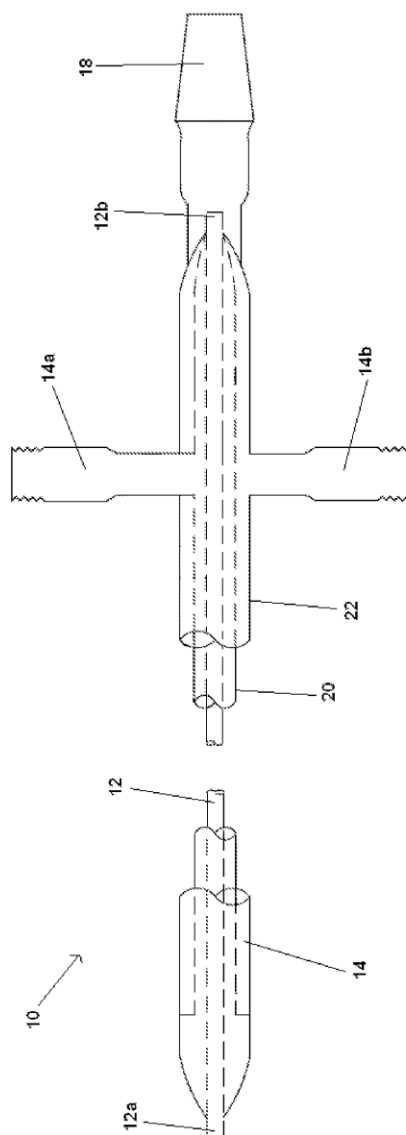
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Fig. 1

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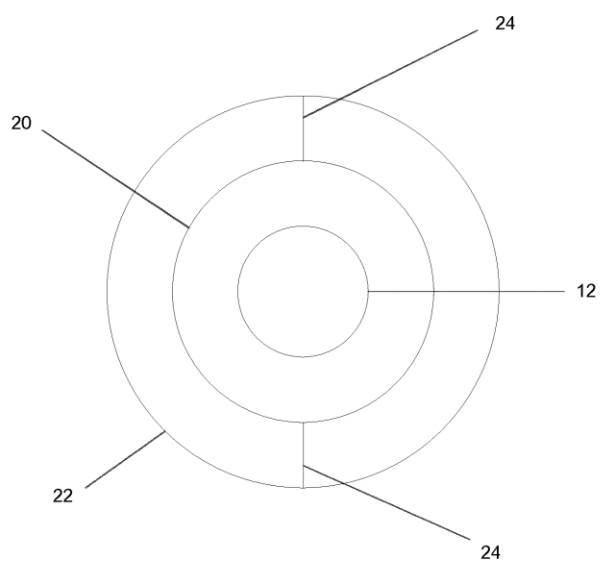


Fig. 2

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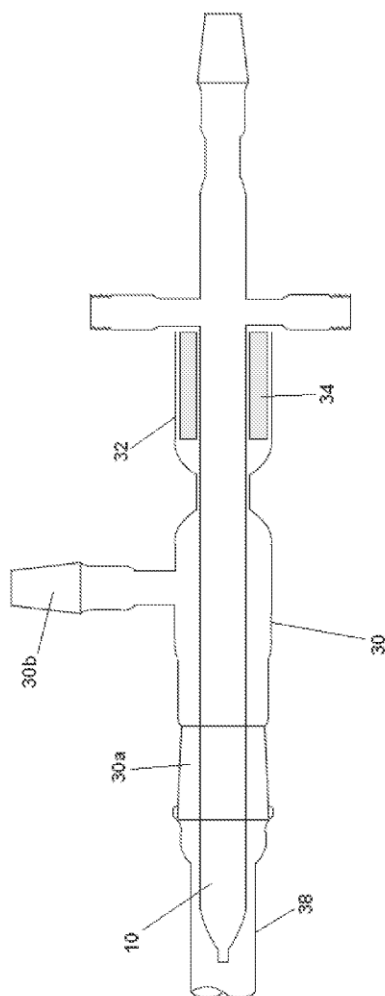


Fig. 3

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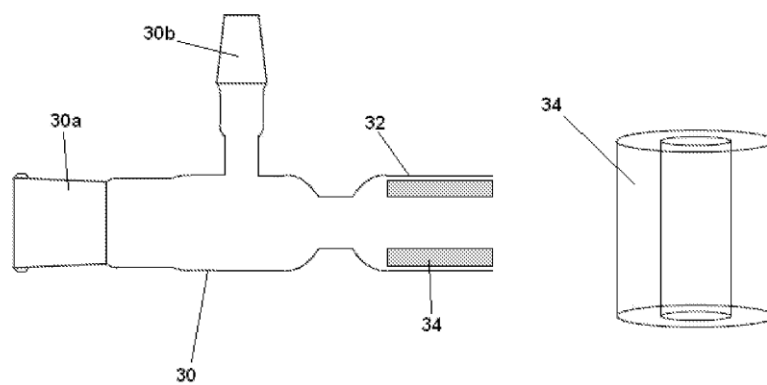


Fig. 4

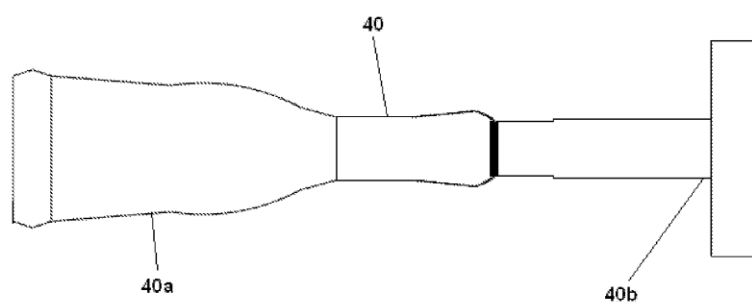


Fig. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2012/052071

A. CLASSIFICATION OF SUBJECT MATTER INV. G01N30/04 G01N33/00 G01N35/10 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) G01N B01L B01J H01J Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 20 2005 021407 U1 (ANTON PAAR GMBH [AT]) 13 December 2007 (2007-12-13) the whole document -----	1-35
X	US 6 245 298 B1 (BREMER RALF [DE] ET AL) 12 June 2001 (2001-06-12) abstract figures column 2, line 36 - column 3, line 51 -----	13
X	US 2006/097152 A1 (CURRIER NEAL W [US] ET AL) 11 May 2006 (2006-05-11) abstract figures 1,2 paragraph [0028] - paragraph [0037] ----- -/-	13
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 30 January 2013		Date of mailing of the international search report 07/02/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Ruchaud, Nicolas

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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	JP 2008 081772 A (FUJIFILM CORP) 10 April 2008 (2008-04-10) abstract figure 3 paragraph [0078] -----	1-35
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