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COMPUTATIONAL FLUID DYNAMICS SIMULATION OF CARBON NANOTUBE SYNTHESIS IN A CARBON VAPOUR DEPOSITION SYSTEM USING FE-CO/ CACO3 AS CATALYST

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Abstract: This paper presents the 3-dimensional (3D) computational fluid dynamics (CFD) simulation study of carbon nanotube (CNT) synthesis and deposition in a chemical vapour deposition (CVD) using Fe-Co/ CaCO3 as catalyst. It aims to provide better understanding of the CVD synthesis system regarding the carbon tube deposition process and the fluid dynamic behaviour inside the reactor. The simulated model adopted temperature dependent variable scheme to predict velocity, temperature, mass fraction of reactants and products and surface deposition profiles. Simulation results were compared with the experimental data for CNT deposition in a CVD reactor. The results of this study showed that, there is a good agreement between experimental data and simulation results, thereby confirming the reliability of this simulation work. The developments in this work build the ground work in order to explain how flow characteristics affect carbon nanotube deposition, which invariably will be crucial for the design, optimization and scale-up of a CVD reactor.

Keywords: Computational Fluid Dynamics, Carbon Vapour Deposition, Carbon Nanotube, Velocity, Temperature, Deposition

1. INTRODUCTION

Carbon nanotube (CNT) has experienced growing interest among researchers recently, owing to its excellent properties in which it is found to be stronger than steel, harder than diamond, conducts electricity better than copper and its thermal conductivity is higher than diamond (Kumal and Andi, 2010). CNT has the basic structure of a hollow cylindrical tube of graphite carbon that is capped by fullerene hemispheres, the diameter is nanometer sized and microscopic size in length (Koziol *et al.*, 2010). Nanotubes can be single wall carbon nanotubes (SWCNTs) or multiwall carbon nanotube (MWCNTs). MWCNT are made of two or more concentric shells and in reality, contains different lattice orientation (described with vectors and angles) with defect concentration (Koziol *et. al.*, 2010). Meyyappan et. al., (2003) reported MWCNT as a pile of graphene sheets rolled- up into concentric cylinders and the walls of each layer (the graphite basal planes) are parallel to the central axis ($\theta = 0$).

Various techniques have been used in the production of CNTs; the first attempt for CNT production involved the use of high temperature preparation methods which includes arc discharge method or laser ablation techniques. However, due to advances in technologies, CNTs are being synthesized using other various methods like Chemical Vapour Deposition (CVD). Some advantages of the CVD technique include controllability of the orientation, alignment, diameter, length, density and purity of CNTs. These advantages make CVD technique, a preferred method all the other techniques in the synthesis of CNTs. In addition, the CVD technique is observed to be cheap in term of cost and simple to operate, thereby, making its experimental data to be reproducible numerically (Raji and Sobhan, 2013).

In a CVD reactor, there is a need to determine some properties such as gas velocity and pressure at multiple points. In order to achieve this without the need for extreme and obstructive instrumentation, fluid dynamics can be employed to determine the flow behaviour and deposition in a CVD reactor. The process in minor cases requires solving simple partial differential equations with basic boundary conditions. However, in more complex cases, making necessary assumptions becomes inevitable in order to solve the equations used to describe the processes occurring in a CVD system. Moreover, when confronted with a very complex equation, solving the equation analytically becomes impossible analytically as they are rather solved numerically using a method known as computational fluid dynamics (CFD) (Daugherty, 2016). CFD majorly involves approximation of partial equations as simple linear relations with the area of interest splitted into finite grids often known as mesh. The finer the mesh, the smaller and closer the element becomes, and this led it to converge approximately to the actual solution. This method is best conducted using software due to its computer intense nature. (Timothy, 2016). According to Kuwana and Saito (2015), Computational simulations of a CVD reactor can be of tremendous help in optimizing reaction conditions and maximizing the yield of CNTs. Kuwana and Saito (2015 observed that, diameter of the catalyst particle determines the outer diameter of the nanotube. Therefore, CFD is potentially useful in the predicting catalyst particle formation which is a very important factor in optimizing CNTs production via a CVD reactor. This research is aimed at investigating and understanding the fluid dynamics of Carbon Nanotube synthesis by (Fe-Co) Catalyst on Calcium Carbonate (CaCO3) support in a Carbon Vapour Deposition System using ANSYS Fluent CFD package. Comparison of the CFD analysis with the experimental data and evaluation of the ability of the model to predict correctly the CNTs deposition in a CVD system were carried out.

2. MODELLING EQUATIONS

2.1 Mathematical Modelling

In Chemical Vapour Deposition systems, chemically reacting laminar flows occurs and it is important to accurately model temperature- dependent hydrodynamics, heat and mass

transfer as well as chemical reactions including wall surface reaction (ANSYS, 16.0). ANSYS Fluent solves conservation equations for mass and momentum. However, an additional conservation equation for energy is solved for flows involving heat transfer or compressibility. Species conservation equation is as well solved for flows involving species mixing or reactions. Thus, these equations are all enabled for ANSYS Fluent to solve in order to simulate the CNT deposition in a CVD reactor.

2.1.1 Mass Conservation equation

The equation for conservation of mass, or continuity equation, can be written as

$$\frac{\partial p}{\partial t} + \nabla.(\rho\,\vec{v}) = S_m \qquad (1)$$

Equation (1) is the general form of the mass conservation equation and is valid for incompressible as well as compressible flows. The source S_m is the mass added to the continuous phase from the dispersed second phase.

2.1.2 Momentum Conservation Equation

The conservation equation for momentum is described by Equation (2) below

$$\frac{\partial p}{\partial t}(\rho\vec{v}) + \nabla.(\rho\vec{v}\,\vec{v}) = -\nabla p + \nabla.(\bar{\bar{\tau}}) + \rho\bar{g} + \bar{F} \qquad (2)$$

where

p is the static pressure. ρ, $\bar{g}$ and $\bar{F}$ are the gravitational body force and external body forces.

$\bar{\bar{\tau}}$ is the stress tensor and it is defined as;

$$\bar{\bar{\tau}} = \mu\left[(\nabla\vec{v} + \nabla\vec{v}^{T}) - \frac{2}{3}\nabla.\vec{v}I\right] \qquad (3)$$

Where μ is the molecular viscosity

I is the unit tensor

And the second term on the right hand side is the effective volume dilation.

2.1.3 Energy Equation

The energy equation is expressed as

$$\frac{\partial}{\partial t}(\rho E) + \nabla.\left(\vec{v}(\rho E + p)\right) = \nabla.\left(k_{eff}\nabla T\right) + S_h \qquad (4)$$

Where, ρ is the density

k_{eff} is effective thermal conductivity.

S_h is the heat source term.

The properties ρ and k_{eff} are shared by the phases. The source term, S_h contains contributions from radiation, as well as any other volumetric heat sources.

2.1.4 Species Transport Equation

The conservation equation for chemical species takes the general form in equation 5;

$$\frac{\partial}{\partial t}(\rho Y_i) + \nabla.(\rho\vec{v}\,Y_i) = -\nabla.J_i + R_i + S_i \qquad (5)$$

Where R_i is the net production rate of species i by chemical reaction.

S_i is the rate of creation and addition from the dispersed phase plus any user defined sources (ANSYS FLUENT, 16.0).

3. MATERIALS AND METHOD

3.1 Model Description

The CVD reactor geometry consist of a quartz tube with 52 mm internal diameter and 62 mm external diameter, 4 mm wall thickness and 1010 mm length, placed in a furnace that has heating capacity up to about 1200 o C. Gas cylinders for the carbon source (acetylene) and the carrier gas (Argon) were connected to the inlet of the reactor where flow meters were available for control of gas flows. A detailed sketch of the CVD system is shown in Figure 1.

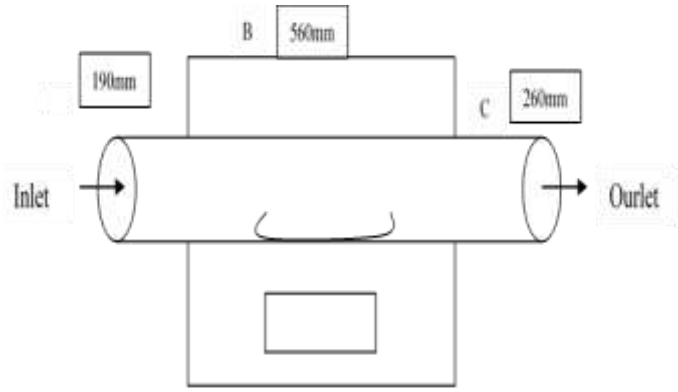
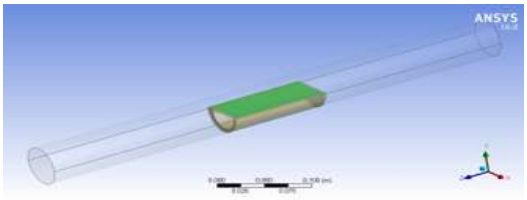


Figure 1: Schematic representation of CVD reactor

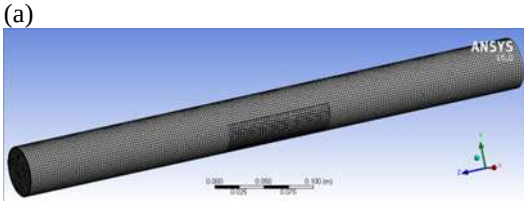
Sections A and C are the inlet and outlet respectively. The inlet section is heated at 10 º C/ min and the outlet is cooled at atmospheric temperature of 25ºC. Section B is the furnace zone, where the reaction responsible for the synthesis and deposition of CNT actually took place and has a dimension 560 mm.

3.2 Geometry and Mesh Creation

The geometry was created using the design modeller of ANSYS Fluent and solid works. The dimension of CVD reactor used are given in Figure 1 and numerical solution domain of this geometry corresponds to a dimension of 0.885 m, 1.82 m and 0.646 m in radial, axial and tangential direction respectively. The boat was developed in such a way that solid/fluid can be enabled in order to allow the use of source terms to place the catalyst inside the boat. As shown in Figure 2, the whole geometry was simplified in such a way that sections A and C were cut off, since the CNT deposition reaction occurs mostly at section B.



(a)



(b)

Figure 2: (a) CVD Reactor geometry with platform coloured green (b) Meshed geometry

Meshing was done using ANSYS Fluent meshing option with Multi zone method enabled. This is due to their possibility to be identified by regular connectivity which gives quadrilateral element in 2D and hexahedral in 3D. Fluent was selected as the solver preference with smoothing option changed to high and fine relevance centre selected. A full quadrilateral mesh (best quality mesh) was enforced and inflation was inserted on the body to ensure a denser mesh at the wall and boat area. Total thickness was enabled and growth rate was set to 1.2.

3.3 Grid Independence Test

Grid independence test was carried out for 5 different mesh densities between 40,000 and 600,000 cells. Simulations were carried out at the same boundary condition with water as fluid flowing through the meshed geometry. Grid independence study was said to be established as the simulation converged and solution obtained showed little or no significant difference at the same location of the solution field. In order to improve the mesh and allow ANSYS Fluent allocate more cell to area deemed necessary, grid adaptation option was activated. The numerical solution was then after adapter based on pressure gradient so as to resolve flow details. The numerical results analysed and mesh density of 232,885 cells was finally chosen for all other simulation used in this work.

3.4 Simulation

In this work, steady and time-dependent hydrodynamics, heat and mass transfer, and chemical reactions (including wall surface reactions at the boat) were carried out with respect to the following assumptions:

- Reactor walls are impermeable and no slip condition is considered for the velocity at walls.
- Constant temperature at the wall of the furnace.
- Laminar flow regime
- Ideal gas behaviour
- Gas has a continuum behaviour
- Viscous dissipation is neglected

Three stages were developed to describe the CVD process for the synthesis and deposition of CNT. Firstly, a single-phase numerical simulation of argon used as carrier gas to purge the system was carried out. Then after convergence was established, ethylene gas as the precursor gas was introduced to the already single-phase argon simulation and a non-reacting solution to establish the flow carried out. Thirdly, building upon non-reacting solution, volumetric and mass deposition source options were activated in order to ensure reacting flow solution established. In this stage, multi-species thermo-fluid flow activated and acetylene species consumption at the boat template surface assumed.

In all simulation considered, piece-wise linear approximations for temperature-dependent viscosity and thermal conductivity were incorporated to account for buoyancy and flow shear effects in the physical system (Rogers and Mayhew 1994). The convergence criteria used in this work is net mass imbalance which is assumed to be a small fraction (for example, 0.5% or less) of the total flux through the system. In a situation where a significant imbalance occurs, residual tolerances obtained were reduced by at least an order of magnitude and continue iterating until this criterion is met.

3.4.1 Boundary conditions

Mixture velocity of acetylene and argon was used at the inlet with the mass fraction of acetylene at the inlet. The outlet consists of the mass fraction of unreacted acetylene and hydrogen. A reacting pressure of 10000 Pa was used. Table 2.2 and 2.3 below shows the summary of boundary conditions used at the inlet and outlet.

TABLE 1: Inlet and outlet mass fractions

	Inlet mass fraction C_2H_2	Outlet mass fraction Unreacted C_2H_2	Hydrogen	Yield (%)
CASE A	0.3007	0.0304	0.0263	62
CASE B	0.3526	0.0358	0.0308	72

TABLE 2: Velocities at the inlet

	Time (seconds)	C_2H_2 (m/s)	Argon (m/s)
CASE A	2700	0.0011765	0.0018039
CASE B	2700	0.0014902	0.0018039

4. RESULTS AND DISCUSSION

4.1 Validation of the Numerical Simulation Results

In validating the simulation results, the results of this work were compared with experimental data obtained from Mohammed (2015). He optimized the process of bimetallic (Fe/Co) catalyst on CaCO3 support for possible application in Carbon nanotubes synthesis by Catalytic vapour deposition method. As shown in Figure 3, where percentage deposition of CNT is plotted against feed rate in order to compare experimental data with numerical simulations at steady and unsteady states. It can be seen that the simulation results indicated a very good agreement with the experimental data.

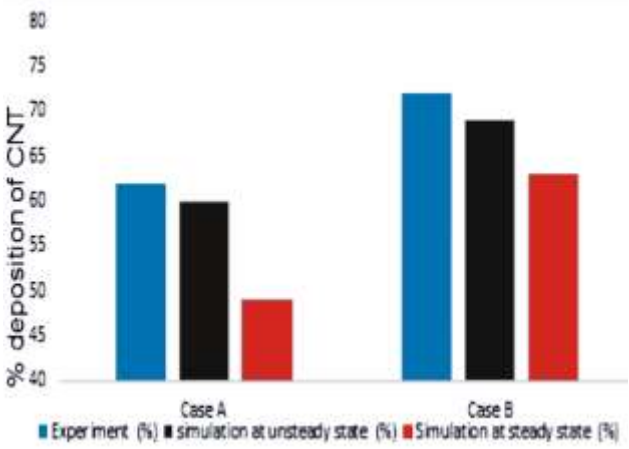


Figure 3: Comparison between Simulation Results and Experimental Data at Different Feed Flow Rates.

For example, percentage deposition of CNT in Case A for experimental data, numerical simulation results at steady and unsteady states was found to be 62, 49 and 60% respectively.

It can be observed that simulation result at steady state have the least deposition of 49%, followed by simulation result at unsteady state of 60% on comparison with the experimental deposition of 62%. Therefore, numerical simulation at unsteady state is more reliable and gives better percentage deposition of CNT when compared with the experimental data. This clearly revealed .numerical simulation of CNT deposition at unsteady state demonstrates buoyancy and flow shear effects dominant in the CNT process of a CVD reactor. The same pattern was observed in Case B, when comparing the experimental data with the simulation results at steady and

unsteady state. The results obtained in this work is in agreement with the work of Durosimi (2018), Vahedein and Schrlau (2005). They all observed that 3D modelling and temperature dependent properties in an unsteady state provide a more accurate representation of the CNT deposition in a CVD system.

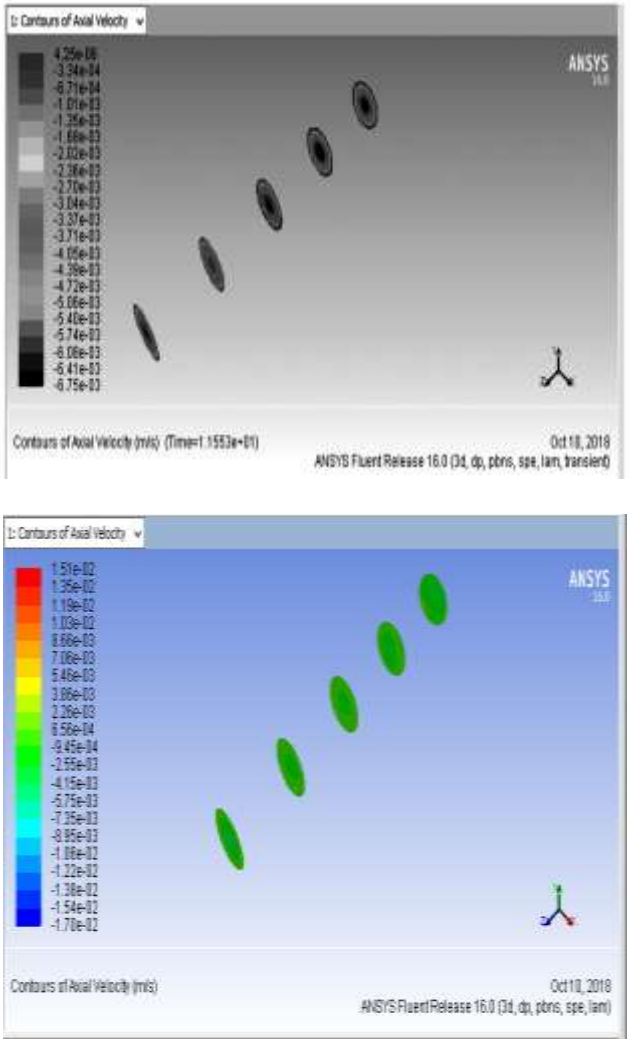


Figure 4: Comparison of axial velocity profiles for unsteady and Steady State Simulations

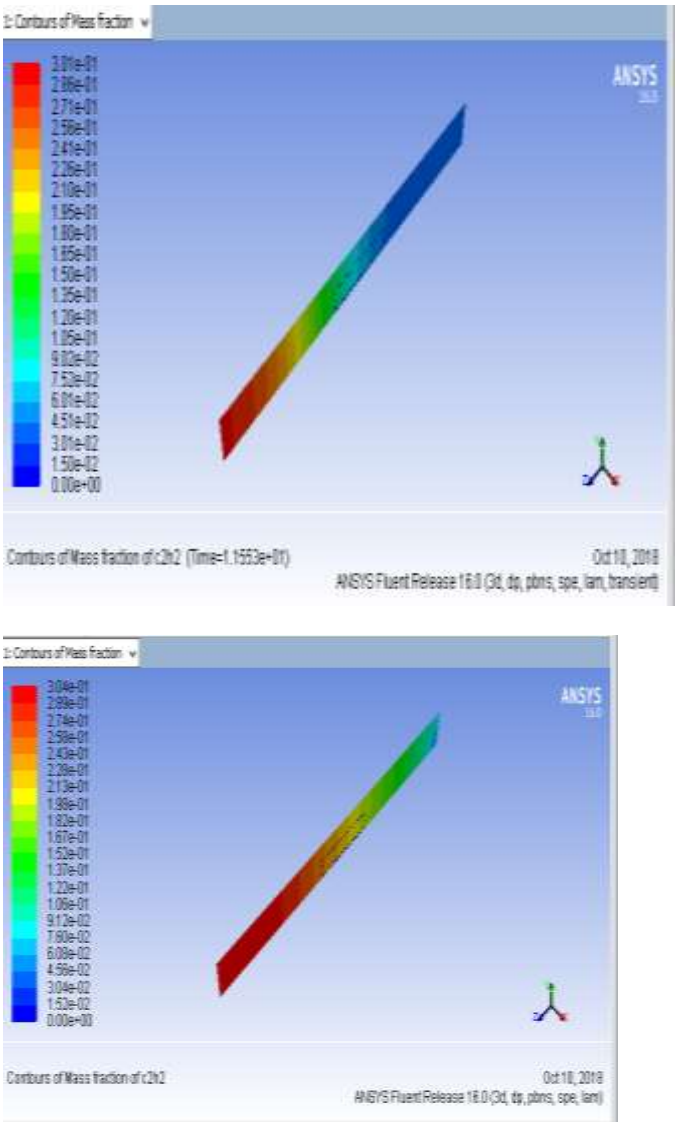


Figure 5: Comparison of Mass Fraction of Acetylene Profiles for unsteady and Steady State Simulations

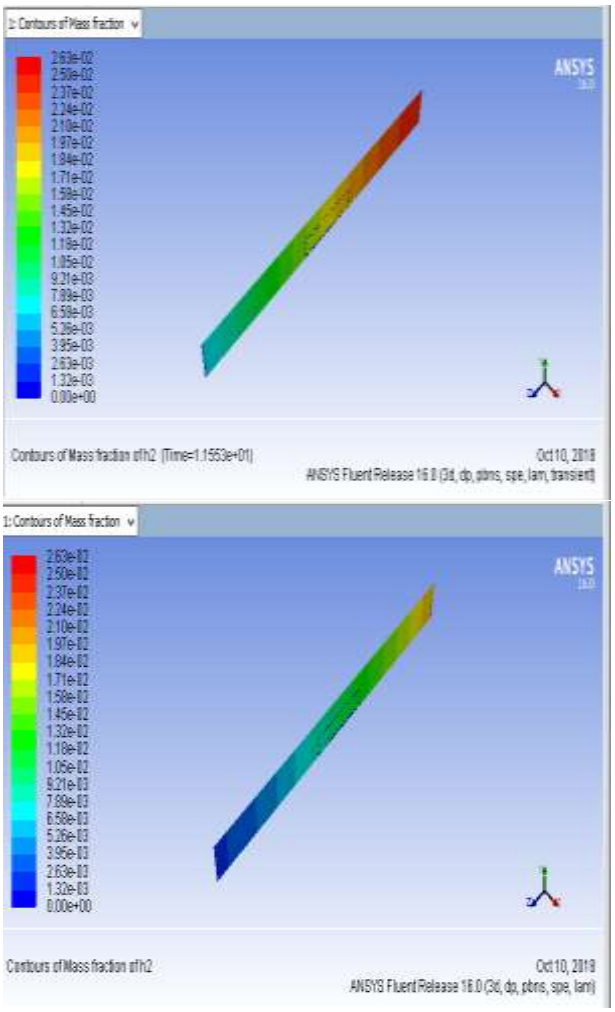


Figure 6: Comparison of Mass Fraction of Hydrogen Profiles for unsteady and Steady State Simulations

Figures 4 -6 showed the comparison between velocity and mass fraction profile of unsteady and steady state simulations. It was observed that better flow features are clearly revealed in unsteady simulations than steady simulations. This implies that, numerical simulation of CNT deposition in a CVD reactor in unsteady conditions were able to resolved better feed compositions which are temperature dependent variables.

CONCLUSION

By using a ANSYS Fluent software, three-dimensional (3D) computational fluid dynamics (CFD) simulation of carbon nanotube (CNT) synthesis and deposition in a chemical vapour deposition (CVD) using Fe-Co/ CaCO3 as catalyst was carried out. Numerical simulation at unsteady state gives an accurate result than that of steady state in term of percentage deposition of CNT in CVD on comparison with experimental data. The velocity profiles obtained in this work explain how unsteady state model equations capture better the flow features of CNT deposition in a CVD reactor.

REFERENCES

ANSYS Fluent, (2016). ANSYS Fluent 16.0.Tutorial manual

Durosinmi S. O. (2018). "Numerical analysis of controlling parameters on carbon nanotube synthesis in a chemical vapour deposition reactor system". Master of Engineering thesis, FUT., Minna..

Kuwana K., and Saito K. (2005). "Modeling CVD synthesis of carbon nanotubes: Nanoparticle formation from ferrocene", Carbon, 43 (10), 2088-2095. doi:10.1016/j.carbon.2005.03.016.

Kumar M. and Ando Y. (2010). "Chemical vapor deposition of carbon nanotubes: a review ongrowth mechanism and mass production". Journal of nanoscience and nanotechnology, 10 (16), 3739-3758.

Koizol K, Boskovic B. O., Yahya N. (2010). "Synthesis of carbon nanostructures by CVD Method in Carbon and oxide nanostructures Advanced structured materials", 5, 23-49. doi:10.1007/8611_2010_12.

Meyyappan M., Delziet L., Cassell A., Hash D. (2003). "Carbon nanotube growth by PECVD: a review". Plasma science and Technology 12 (2), 205. doi:10.1088/0963-0252/12/2/312/meta.

Mohammed I. A. (2015), "Formulation of bi- metallic (Fe-Co) catalyst on CaCO3 support for carbon nanotube synthesis", Master Engineering thesis, FUT, Minna.

Raji K. and Sobhan C. B. (2013). "Simulation and modelling of carbon nanotube synthesis: current trends and investigations". Nanotechnology reviews, 2 (1), 73-105. doi:10.1515/ntrev-2012-0038.

Rogers G. F. C, and Yon R. Mayhew. (1994). "Thermodynamic and transport properties of fluids": S. I. Units. 5th Edition edition. Oxford: Wiley-Blackwell.

Daugherty T. J. (2016). "Computational fluid dynamics modelling and experimental investigation of a chemical vapor deposition Synthesis of ZnO Nanostructures". An unpublished master's thesis from the department of mechanical engineering Youngstown state university Ohio.

Vahedein Y. S. and Schrlau M. G. (2015). "Numerical model of template-based chemical vapor deposition processes to manufacture carbon nanotubes for biological devices," July, V001T03A005. doi:10.1115/ICNMM2015-48520.