Synthesis of carbon nanotube aerogel by chemical vapour deposition - A CFD Study

Amit Kaushal[1,2]*, Rajath Alexander[1,2], P.T. Rao[1], Jyoti Prakash[1], Kinshuk Dasgupta[1,2]

[1]Glass and Advanced Materials Division
Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India
[2]Homi Bhabha National Institute, Anushaktinagar, Mumbai-400094, India

ABSTRACT

Carbon nanotubes (CNTs) and various carbon nanostructures (0D, 1D, 2D and 3D) are gaining importance in material research due to their unique properties owing to nano dimensions. Chemical vapour deposition (CVD) process is found to be one of the economic ways to produce these structures in large quantities and thus capable of fulfilling the future demand. Providing a wide range of operating window suitable to produce property specific customised material is the special attraction of the CVD process. Despite various advantages, lower conversion of the precursor and catalyst remain the greatest challenge associated with this process. Predicting the flow pattern and temperature profile inside a CVD reactor are important steps to enhance process efficiency. In this work computational fluid dynamics (CFD) analysis is carried out to analyse flow dynamics inside a CVD reactor. The deviation from plug flow behaviour due to recirculation of incoming gas is found to be correlated with diameter and thus properties of the synthesized CNTs. Catalyst agglomeration, the prime contributor of large diameter CNTs, can be prevented by selecting suitable flow and temperature conditions inside the reactor. Knowledge of location of decomposition of all the precursors is the key to control the size of CNTs as different precursors decompose at different temperatures. Recirculation tendency has also been investigated and compared at various carrier flow for argon and hydrogen as carrier gases. Narrow distribution of diameter is observed using hydrogen as a carrier and correlated with no recirculation inside the heating zone while use of argon provides wider diameter distribution due to decomposition of thiophene and its recirculation in heating zone.

Keywords: Carbon Nanotube, Chemical Vapour Deposition, Computational Fluid Dynamics

Introduction

Carbon nanotube (CNT) finds application in the field of nano-electronics, nano-medicine, nano-sensors, high strength and low-density composites, energy storage solutions, stealth technology and others due to very high thermal & electrical conductivities, high tensile strength, high modulus of elasticity, low density, high specific surface area, chemical stability, and high aspect ratio. Some of the novel applications include high strength composites, EMI shielding, supercapacitor, battery electrodes, green catalysis, efficient drug delivery and biosensors, energy storage and energy conversion devices, transparent conducting films, field emission display, highly porous membrane, thermal interface, electrical interconnect, etc. [1,2] It is also highly demanded for used in materials of sustainable future and green technologies. CNTs can be synthesized by various methods. However, being continuous process and low-cost operation, chemical vapour deposition (CVD) has many advantages over other methods like laser ablation, arc discharge and is capable to produce CNTs in large quantity [2-4]. In the present CVD process, carbon precursor is allowed to decompose in presence of a catalyst in a tubular reactor in continuous mode to produce CNTs of various shape and size. There are flexibilities with respect to selection of catalyst (transition metal single or bimetallic) and carbon precursor (liquid or gaseous hydrocarbon feed), reactor operating conditions along with addition of growth promoter and reaction controlling agent like oxygen containing compound, which lead to evolution of various useful carbon nano structures like single-walled carbon nanotube (SWCNT), multi-walled carbon nanotube (MWCNT), CNT aerogel, CNT fibre, carbon nano dots and doped CNT. In this way, CVD process provides an ability to produce customised carbon nano materials of desired properties for the given purpose with greater control. Nano-electronics, sensor development and other applications require production of CNTs with enhanced control as electronic properties are very sensitive to CNT diameter and internal structures. CFD study is required to correlate the diameter of CNT produced in a CVD reactor with various operating conditions. Various CFD work reported in literature were focused on predicting growth rate of CNT and ferrocene decomposition in the temperature range of 800-1000K [5-7], which is not suitable for synthesis of CNT aerogel. Recirculation of carrier gas at the inlet and the outlet of heating zone plays important role in deciding the product quality for synthesis of CNT aerogel and it has been predicted by various researchers [8-10]. However, the location and degree of recirculation have not been quantified and reported in a scientific manner so far for the synthesis of CNTs. Hou *et. al.* [10] have shown that recirculation at the outlet helps in stable sock formation which is required for direct spinning of CNT aerogel to produce fibre. This recirculation decreases with increase in the flow rate and spinning ability vanishes above a flow rate of 3200 standard cubic centimetre per minute (SCCM). The reduction in specific strength of CNT fibre due to recirculation has been shown by Oh *et al.* [8]. They found the effect of recirculation

in a 70 mm diameter quartz tube reactor operating at 1200°C but no recirculation is observed in alumina tube reactor of the same dimension. Lee *et.al* [9] found the recirculation at 3200 SCCM flow rate in 50 mm diameter alumina tube reactor at 1250°C and observed increase in specific strength with reduction in recirculating behaviour. The impact of recirculating flow has also not been evaluated in great detail. In this work we used COMSOL Multiphysics 5.5 for flow and temperature analysis inside the reactor to predict the recirculation at various operating conditions. Flow and temperature profiles have been generated in order to get the idea of thermal decomposition timeline. These plots have been used as a strategy input for controlling CNT diameter by providing a sulphur coating on catalyst particles before start of catalyst agglomeration. Grashoff number and Rayleigh number have been plotted along the length of the reactor in order to provide a qualitative analysis of recirculation. The properties of CNTs synthesized in different conditions have been compared to find out the effect of recirculation on diameter. Recirculation has also been compared at different carrier flow conditions. A mixture of argon and hydrogen has been used as a carrier flow in order to get advantage of lower recirculation in presence of hydrogen due to lower molecular mass while maintain a reducing environment for better yield.

Materials & Methods

CNT synthesis process:

CNTs in this work has been synthesized by floating catalyst chemical vapor deposition (FC-CVD) process in a horizontal tubular reactor (40mm ID, Alumina) shown in Fig.1. Ethanol, ferrocene and thiophene have been used as precursors for carbon, catalyst and sulfur promoter, respectively. Liquid feed (1 weight percent ferrocene and 0.5 weight percentage thiophene mixed in 80ml ethanol) is pumped to the preheater zone maintained at 200°C and is allowed to be carried in the main furnace with a carrier flow (mixture of argon and hydrogen) of 1-3 lpm. Reaction took place in the main furnace maintained at 1250°C temperature where CNT aerogel was produced through catalytic cracking of carbon precursor in presence of catalyst. CNT produced in the form of spinnable sock along with other gaseous product was continuously drawn in a harvest box. Gaseous product was diluted through supply of excess inert gas (argon) in the harvest box in order to prevent any fire related hazard.

CNT synthesized was characterised by Raman spectroscopy, scanning electron microscope and thermogravimetric analysis. Raman spectra of the synthesized SWCNT was obtained using a WITec alpha 300R polarized Raman instrument with a laser wavelength of 514 nm and a 50X objective lens. RBM peak position (characteristics feature of SWCNT) has been used to calculate the diameter as per Eq. (1).

$$\omega_{RBM} = \frac{233}{d} + 10 \quad (1)$$

Structural analysis of the synthesized material was carried using field emission scanning electron microscope (Model-SIGMA, Carl Zeiss, Germany) at 5 kV accelerating voltage using In-lens Detector. Thermal analysis of the synthesized sample was carried out using Thermal Gravimetric Analyzer (TGA) (Setaram TGA 1600, France). The mass change and its corresponding temperature range were used for the quantification of CNT, amorphous carbon and catalyst present in the sample.

CFD study

To understand the flow condition in the FC-CVD reactor, we used computational fluid dynamics modelling to solve the continuity, momentum and energy equation in the reactor. Numerical simulation was carried out using COMSOL Multiphysics (COMSOL, Inc.). The continuity, momentum and energy equations are shown in Eqs. (2-5)

$$\nabla.\rho\boldsymbol{u} = 0 \quad (2)$$

$$\rho(\boldsymbol{u}\nabla)\boldsymbol{u} = \nabla.[-p\boldsymbol{I} + \mu(\nabla\boldsymbol{u} + (\nabla\boldsymbol{u})^{T})] + \boldsymbol{F_g} \quad (3)$$

$$\rho C_p(\boldsymbol{u}.\nabla)T = \nabla.(k\nabla T) + W_p \quad (4)$$

$$\boldsymbol{n.q} = \varepsilon\sigma(T^4 - T_s^4) \quad (5)$$

ρ[g/cm^3] is the density of the gas, $\boldsymbol{u}$ [m/s] is the velocity field of the gas, p[kg/(m·s^2)] is the fluid pressure, μ[kg/(m·s)] is the viscosity of the gas, C_p[J/(K·kg)] is the thermal capacity of the gas, k[W/(m·K)] is the thermal conductivity of the gas, T [K] is the gas temperature, $\boldsymbol{F_g}$[kg/(m^{2}s^2)] is the body force due to gravity. W_p [kg/(m^{2}s^2)] is the pressure work induced by density variation. $\boldsymbol{q}$ [W/m^2] is the net radiative heat flux through a heated surface. ε[m^2] is emissivity of surface, T_s is temperature of the heated surface and σ[J/s/m^2/K^4] = 5.67x10^{-8} is Stefan-Boltzmann constant.

A 3-D, steady-state, non-isothermal laminar flow model was used for study. The low-Mach-number formulation has been used to account for density variations. Radiative heat transfer in the reactor has been incorporated using 'Hemicube' model available

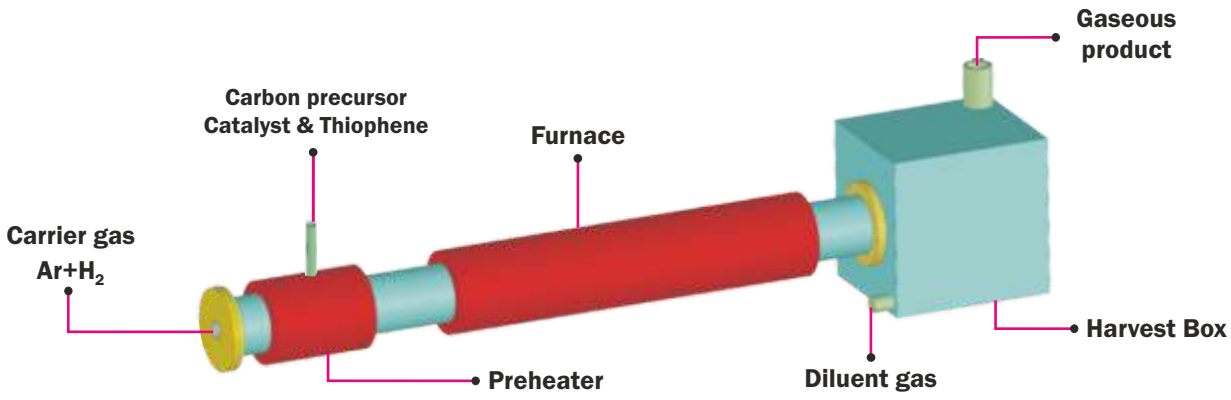

Fig.1: Schematic of floating catalyst chemical vapour deposition system for CNT aerogel synthesis

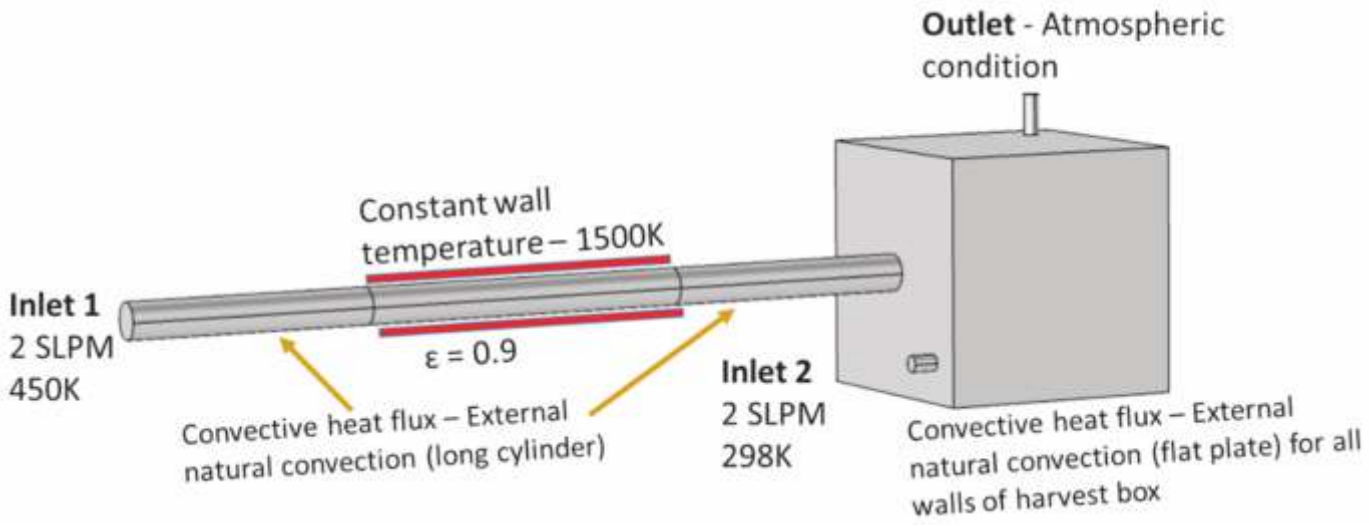

Fig.2: Computational domain along with boundary conditions

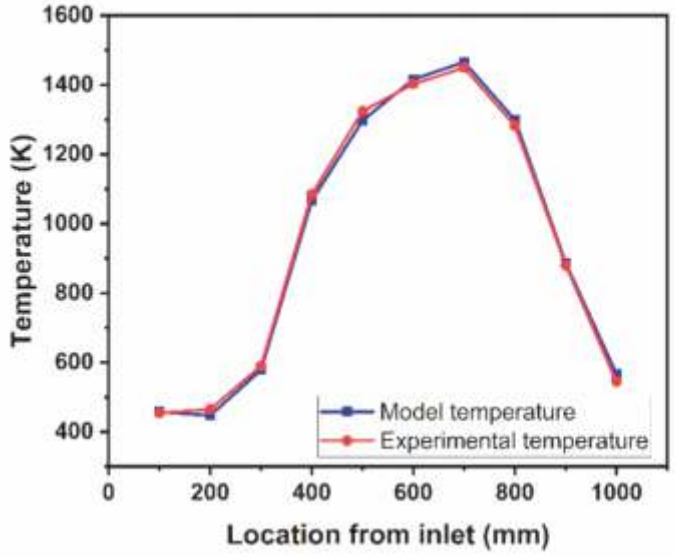

Fig.3: Comparison of experimentally measured temperature profile with model predicted temperature profile

in COMSOL Multiphysics. Boundary conditions along with computational domain over which conservation equations were solved are shown in Fig.2. Discretization was carried out using physics controlled meshing option available in COMSOL Multiphysics where 116633 domain elements, 11286 boundary elements, and 816 edge elements were used for entire domain. To verify the simulation model, the numerical results were compared with the temperature distribution inside the reactor heated at experimental condition with argon flow and without precursor flow using external thermocouple and readout box (shown in Fig.3)

Results and discussion

CNT aerogel is self-agglomerated long CNT produced at higher temperatures (>1200°C) in CVD furnace as compared to powder CNT which consist of mainly short length CNTs. CNT fibre can easily be produced by direct spinning of CNT aerogel on continuous basis in FC-CVD furnace. Properties of fibre produced are highly dependent on length of constituent CNT which is very sensitive to amount and size of the catalyst used. Catalyst particle grows in size with increase in temperature along the axial direction due to agglomeration. It is found that larger size of catalyst yields MWCNT while smaller size catalyst yields SWCNT. In addition to this, a critical amount of catalyst is also required to produce SWCNT/MWCNT. It is very difficult to maintain smaller size of catalyst above this critical mass requirement but can be possible by providing a sulphur coating as soon as catalyst starts nucleating [11]. Ferrocene (catalyst precursor) decomposition and nucleation of iron particle start at about 550°C temperature, while thiophene (sulphur precursor) decomposition starts at 850°C [12]. Hence, local flow and temperature conditions inside the reactor are very critical to prevent agglomeration and thus controlling the diameter of CNT, which is predicted using CFD simulations. Fluid flow streamlines along with temperature surface are generated and shown in Fig.4 (a, b and c). It is observed that a recirculation cell is formed just before the high temperature zone of the reactor and extends inside the reactor (indicated in the left box in Fig. 4 c).

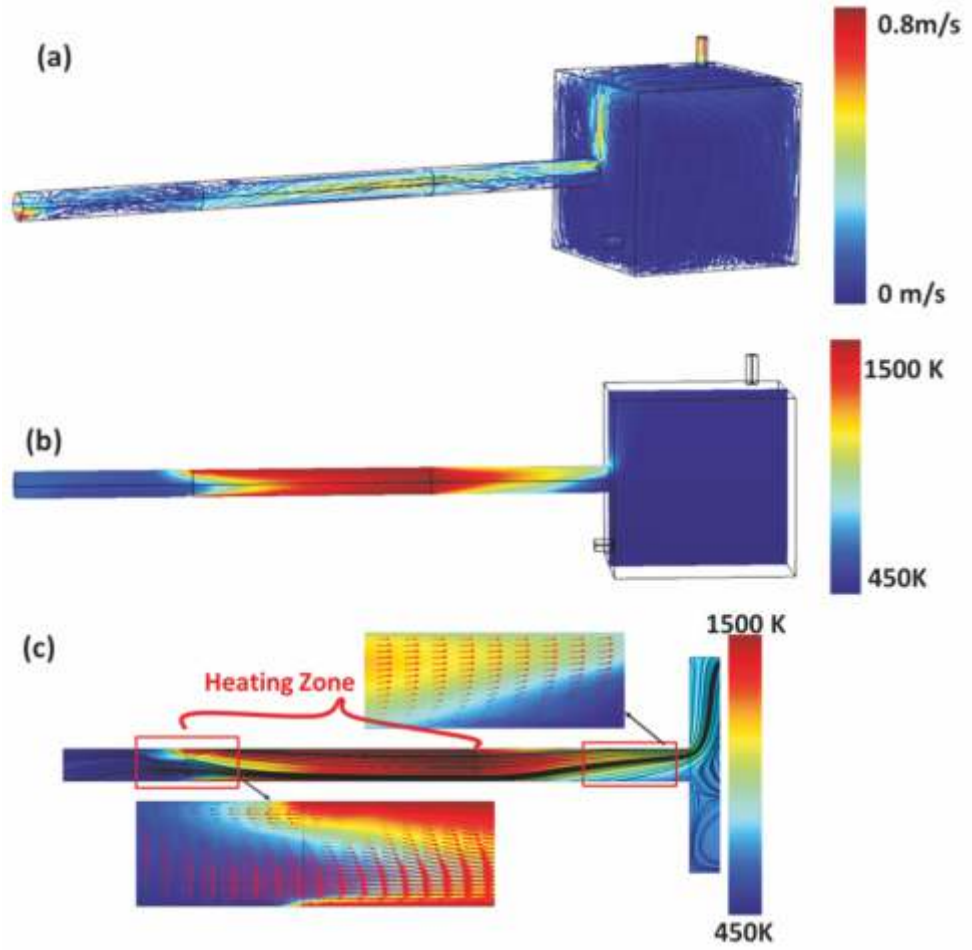

Fig.4: (a) Streamlines with velocity magnitude represented by colour code (b) temperature profile in central 2D plane and (c) flow field represented by streamlines overly on the temperature contour showing recirculation at the inlet and the outlet of heating zone in case of pure argon flow

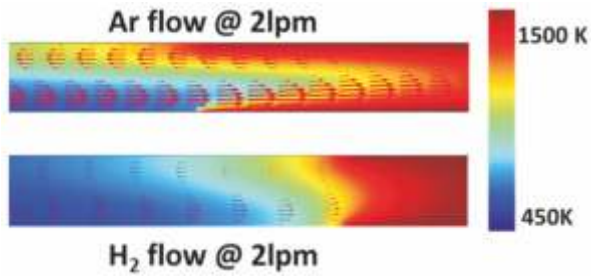

Fig.5: Velocity vectors overly on the temperature contour for argon and hydrogen used as carrier showing recirculation penetrating deeper inside the heating zone in case of argon

Effect of carrier gas on recirculation and CNT aerogel

CNT starts growing once the feed mixture reaches yellow and red colour region, corresponding to start and end of thermal decomposition of thiophene (Fig.4 and 5). In high temperature zone, catalyst particle starts nucleating and CNT grows. If recirculation penetrate the heating zone, some of nucleated catalyst particles come out of high temperature zone and growth of CNT terminates as reaction mixture goes to the lower temperature region. In this way recirculation in heating zone causes the formation of short length CNT which ultimately reduces the product uniformity and thus property of CNT aerogel. Length and position of this recirculation can be controlled by adjusting flow rate and composition of feed. Fig.5 shows recirculation cell extended deep inside the reactor when only argon is used as carrier gas while it is formed outside the heating zone if only hydrogen is used as carrier gas. Recirculation outside heating zone does not contain nucleated catalyst particle and there is no chance of CNT growth in recirculating stream. Higher fraction of feed is converted into short length CNT if recirculation cell extended deep inside the reactor. Thus, pure hydrogen as a carrier produces CNT aerogel with more uniform length and diameter as CNT grows only in high temperature zone. While a mixture of short and large length CNT can be found and the uniformity of product reduces significantly as CNT grows in two different regions (recirculation stream and high temperature zone) when pure argon is used as carrier gas. The diameter of CNT is also found to be affected by carrier gas flow and the location of recirculation. Diameter distribution of CNT aerogel produced

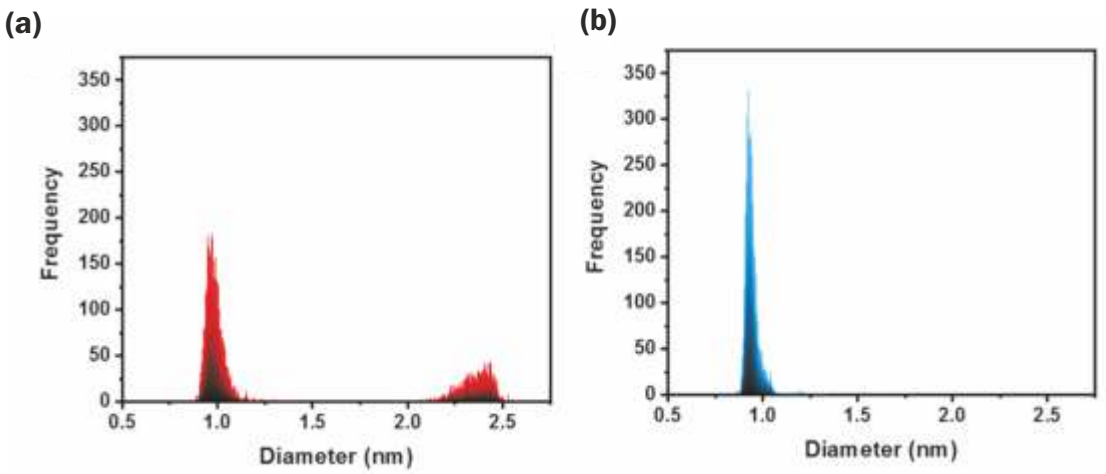

Fig.6: Diameter distribution in the CNT aerogel sample using (a) argon and (b) hydrogen as a carrier gas (calculated using RBM peak position observed in Raman spectrum)

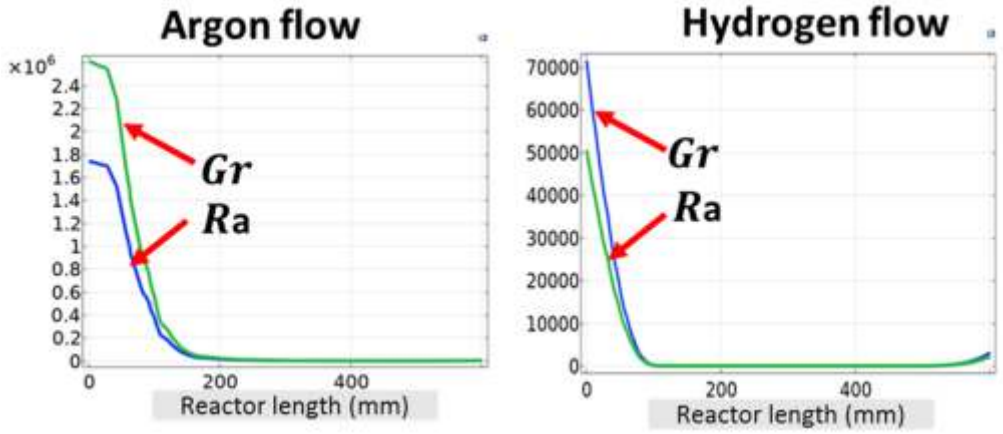

Fig.7: Grashoff and Rayleigh numbers plotted along the reactor length (starting from 100 mm before the heating zone)

using hydrogen and argon as a carrier gas is shown in Fig. 6. RBM peak position in Raman spectra of these two samples were used to calculate diameter according to formulae given in Eq. (1).

Effect of flow rate on recirculation and CNT aerogel

Grashoff number (*Gr*) and Rayleigh number (*Ra*) are defined as given by Eq. 6 and 7,respectively. The plot of these numbers for argon and hydrogen flow along the length of reactor (starting from 100 mm before heating zone) are shown in Fig.7. Higher values of *Gr* and *Ra* indicate the significance of buoyancy effect which causes recirculation. In this way the location of recirculation can be predicted by these numbers. Higher values of *Gr* and *Ra* (>10^4) are found only in first 100 mm which reduce to a very low value indicating no recirculation in heating zone in case of hydrogen. But in case of argon these values are much higher as compared to hydrogen and also extended beyond 100 mm, meaning there exists a recirculation current penetrating deeper into the heating zone.

$$Gr = \frac{g*\beta\,\Delta T*D^3}{\upsilon^2} \quad (6)$$

$$Ra = Gr * Pr \quad (7)$$

β is expansion coefficient, D is the diameter of reactor and υ is kinematic viscosity of carrier gas.

The strength and location of recirculation at 2 lpm flow rate has been shown in Fig.8 for argon flow and hydrogen flow while at various flow rate of argon in Fig.9. It is found that recirculation reduces and shift in position with increase in flow velocity of carrier gas. Higher flow velocity have been achieved by using hydrogen as a carrier gas in place of argon (Fig.8) and increasing the total flow rate of argon gas (Fig.9). The retreat of recirculation at high flow velocity is attributed to increase in Peclet number (a dimensionless number defined as ratio of advective transport to diffusive transport of heat or momentum). Lower amount of short length CNT is produced at higher carrier flow rate as the recirculation zone is outside the thermal cracking zone of thiophene but the carbon conversion also decreases due to reduction in residence time. Fig.10(a) shows that RBM peak position changes with increase in argon flow rate and smaller diameter CNT is synthesized at higher flow rate. Fig.10 (b1 & b2) shows SEM images of CNT aerogel synthesized using hydrogen and argon flow, respectively. Hence, an optimum flow condition for feed (composition and flow rate) is required to be worked out for synthesis of high purity and uniform diameter CNT aerogel for continuous spinning of CNT fibre.

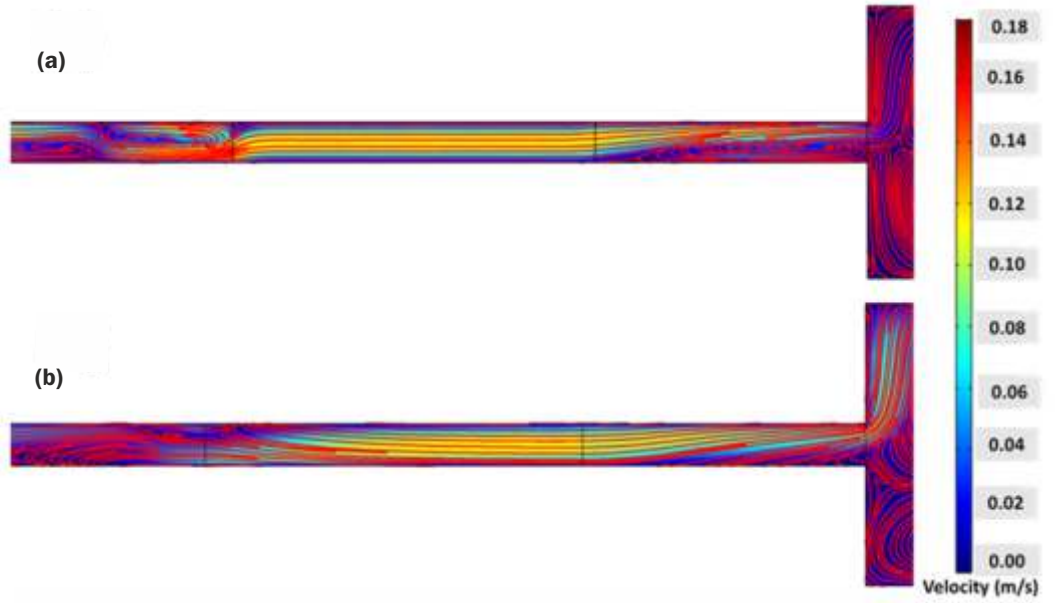

Fig.8: Flow field represented by streamlines overly on the velocity contour (colour map) showing recirculation at inlet and outlet of heating zone for (a) hydrogen and (b) argon flow

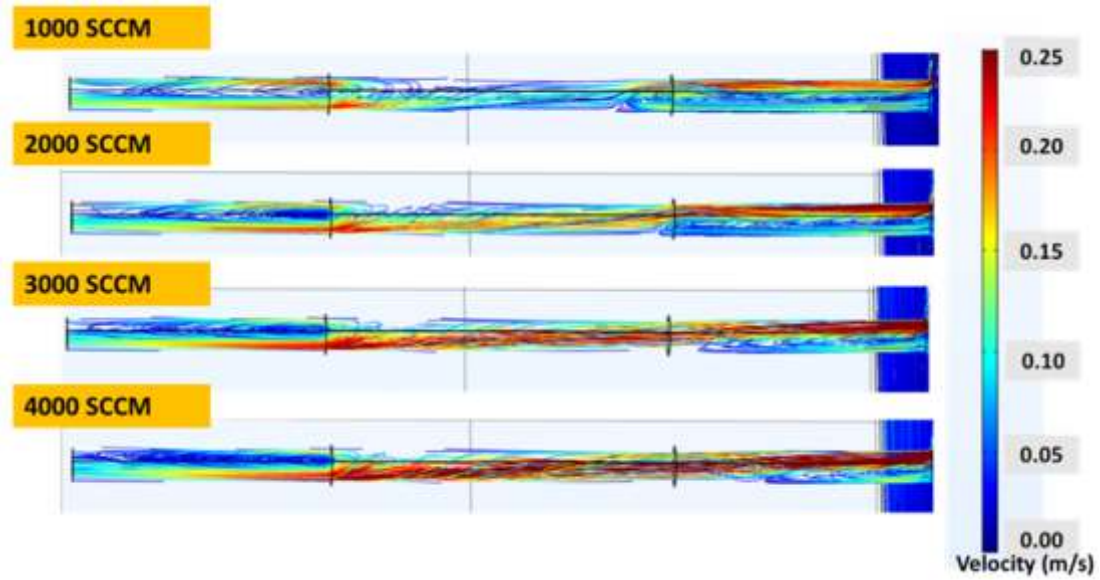

Fig.9: Streamline (colour representing the magnitude of flow velocity) showing the effect of argon flow rate on recirculation at inlet and outlet of heating zone

Conclusion

- CFD analysis has been used to demonstrate the effect of flow and temperature conditions inside the reactor on the diameter distribution of CNTs in aerogel produced by FC-CVD process.
- The quality and properties of CNT aerogel synthesized in this process are affected by the location of recirculation in the flow field which is highly correlated with the selection of carrier gas and its flow rate.
- The recirculation penetrating deep inside the heating zone (in case of argon used as a carrier) provides a second zone of CNT growth where relatively lower size of CNT is produced.
- Recirculation decreases with increase in Peclet number due to reduction in diffusion transport as compared to advective transport of heat and momentum.

Corresponding author*

Amit Kaushal (akaushal@barc.gov.in)

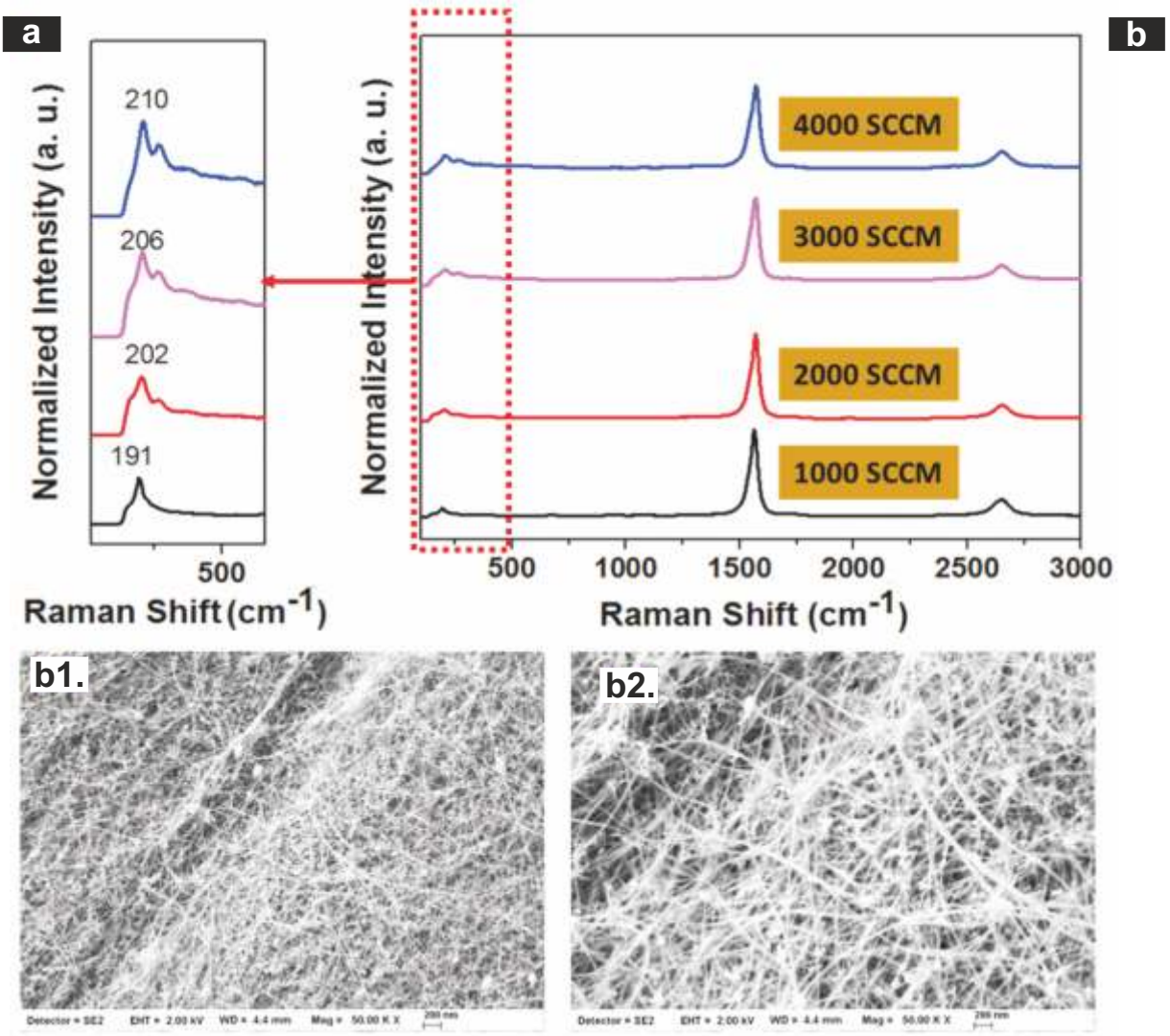

Fig.10: (a) Raman spectrum of CNT aerogel at different argon flow rate and (b) SEM images of CNT aerogel for hydrogen (b1) and argon (b2) used as a carrier flow

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