SYNTHESIS OF CARBON NANOTUBES USING CVD REACTOR: NUMERICAL SIMULATIONS OF HEAT AND MASS TRANSFER

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Introduction

Arrays of aligned carbon nanotubes, where nanotubes are oriented in parallel to each other and perpendicular to growth surface, are of great interest for many potential applications. Because of the excellent electron emission properties of carbon nanotubes, some researchers [1] proposed to utilize aligned carbon nanotubes for flat panel displays and highly efficient media for high harmonic generation. Several groups have [1-3] developed differing production methods for producing aligned multi-walled nanotubes (MWNTs) using chemical vapor deposition (CVD).

At the Center for Applied Energy Research at the University of Kentucky, a method for producing bulk quantities of high-purity aligned MWNTs through the catalytic decomposition of a ferrocene-xylene mixture at temperatures around 700 °C has been developed [2]. Carbon deposits are formed on both the walls of the quartz furnace tube and quartz substrate that was placed within the furnace to act as additional sites for nanotube growth.

The growth rate of nanotubes depends on temperature, flow rate, and total pressure of feed gas and geometry of reactor. Computational fluid dynamics (CFD) can be used to study on effects of these parameters on the production rate of nanotubes [4-8].

In the present study, a series of numerical simulations on heat and mass transfer processes in the CVD reactor have been performed using CFD2000. Based on these numerical results, effects of reactor geometry and its orientation on the temperature and velocity fields are discussed and a new type of flow-injection geometry that can enhance the contact time between the feed gas and the reactor wall (growth surface) was identified.

Model

Figure 1 shows a schematic of the CVD reactor developed at the University of Kentucky. Based on the symmetrical design of the reactor, only half of the reactor needs to be taken into account for simulation. Feed gas is Ar/H_2 mixture at room temperature, 300 K. The uniformity of the 700 °C temperature on the furnace wall and substrate was confirmed experimentally. Chemical reactions at both the reactor wall and the substrate surface are not included in our calculation.

The numerical model is based on the unsteady, compressible fluid flow with variable fluid properties. Temperature dependent thermal conductivity, viscosity and specific heat were used. The density of gas mixture was calculated assuming that each gas follows the ideal gas law. A set of unsteady equations was numerically solved until a steady solution was obtained. Five different reactor geometry and injection conditions that were simulated in this study are shown in Table 1.

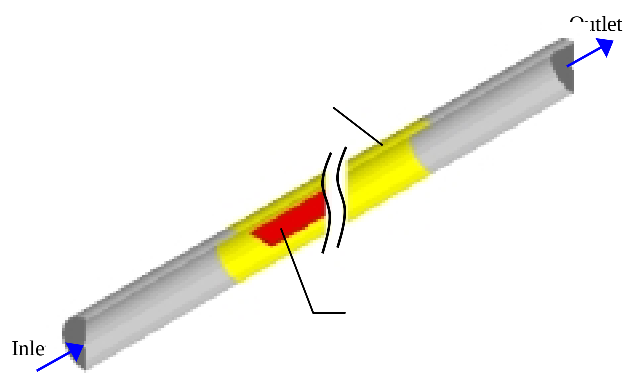

Figure 1. Geometrical configuration of CVD reactor.

Table 1. Conditions of simulations performed in this study.

Case No.	Geometry	Orientation
Case I	Center injection with substrate (Figure 1)	Horizontal
Case II	Center injection without substrate	Horizontal
Case III	Center injection without substrate	Vertical (injection at top)
Case IV	Center injection without substrate	Vertical (injection at bottom)
Case V	Side injection without substrate	Horizontal

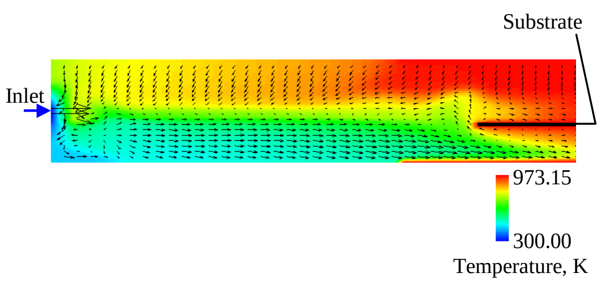

Figure 2. Temperature and velocity profiles near the inlet (Case I).

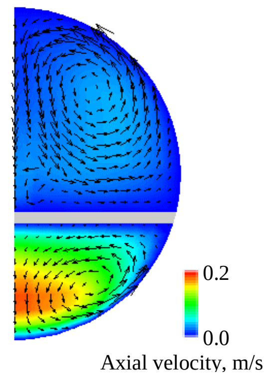

Figure 3. A cross-sectional view of velocity field (Case I). Axial velocity is color-coded.

Results and Discussion

Figure 2 shows velocity and temperature profiles near the inlet for the original design shown in Figure 1. This configuration is shown in Case I in Table 1. It can be seen that a downward flow near the inlet is generated and the temperature of the feed gas near the substrate is somewhat lower than the furnace temperature. This downward flow created two separate axial flow patterns, forward flow in the bottom half of the tube and backward flow in the upper half of the tube.

Figure 3 shows radial profiles of velocity and temperature (the axial velocity distributions are color-coded and shown in the figure). Two anti-clockwise circulations can be seen, separated by the substrate, at both the upper section and the lower section. Both circulations were generated by gravity effect associated with the density difference created by a non-uniform temperature distribution in the feed gas. Because of the existence of a substrate, both circulations are separated and there is no momentum exchange between them. Because of the current reactor design configuration, the upper section volume is more than twice as large as lower section causing the upper section axial flow to be less than one-half of the lower section axial flow. This non-uniform flow pattern may cause the growth of amorphous carbon (an unwanted impurity to the carbon nanotube growth process) on the substrate surface.

To assess the effect of substrate on the non-uniform flow pattern, a series of CFD flow calculations were performed for three different cases (as shown in Table 1) without the substrate. All of Cases II, III and IV have the same basic reactor design configuration as Case I, but they have no substrate. Case II has a horizontal orientation, Case III has a vertical orientation with the feed gas injection at its top and Case IV has a vertical orientation with the feed gas injection at its bottom.

Figure 4 shows the radial velocity and temperature profiles for Case II (the axial velocity profiles are color-coded and shown in the figure). There is only one circulation in the radial direction and the axial velocity profiles are more uniform than Case I (Figure 3). A vertically oriented CVD design has the advantage of obtaining a continuous production of carbon nanotubes. We calculated flow

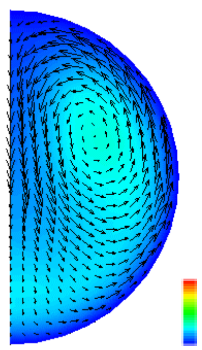

Figure 4. A cross-sectional view of velocity field (Case II). Axial velocity is color-coded.

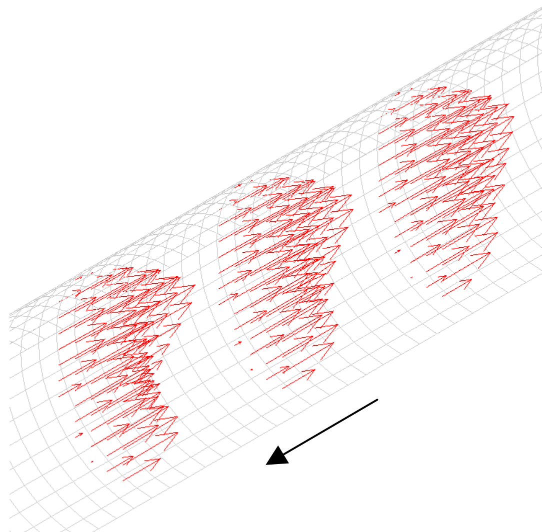

Figure 5. Velocity field in the CVD reactor (Case IV).

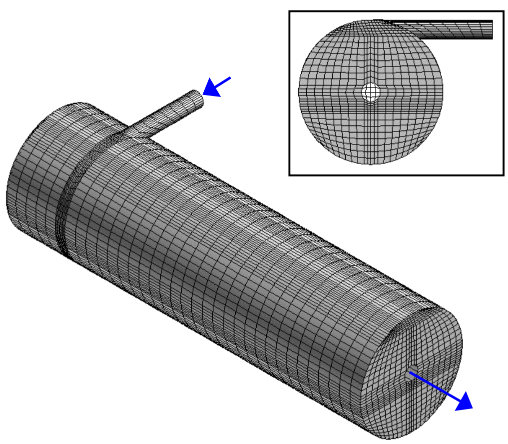

Figure 6. Geometry of side-wall injection (Case V). Body fitted coordinates are also shown.

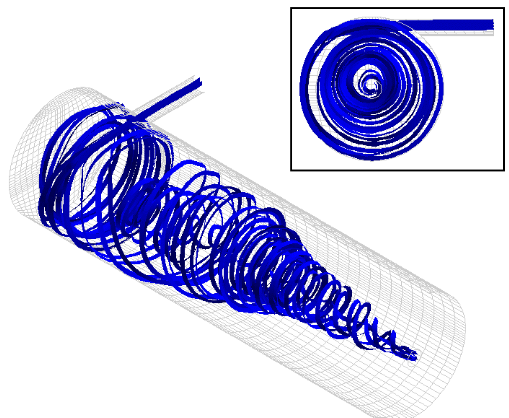

Figure 7. Typical streamlines.

profiles created by Cases III and IV. No steady-state solution was obtained for Case III due to the instability of flow. Figure 5 shows velocity profiles at three different axial locations indicating no circulation (the direction of gravitational force is also shown in the figure). The circulation in the radial direction enhances the contact time of the feed gas and the reactor wall helping an increase of the yield of carbon nanotubes.

To optimize the carbon nanotube yield in the current straight tube CVD reactor configuration, we came up with an idea to inject the feed gas from an off-centered side wall location (Case V). Figure 6 shows a schematic of Case V and body fitted grids and coordinates. We performed CFD calculations for Case V without the gravity term. Figure 7 - a typical result of flow profiles, demonstrates a stronger circulation than any of other four cases. An advantage of Case V design is its simple design that requires no substrates and the reactor wall itself can be used as a substrate for carbon nanotube to grow. Figure 8 is radial profiles of the feed gas velocity showing much stronger and more uniform circulation than any of other cases.

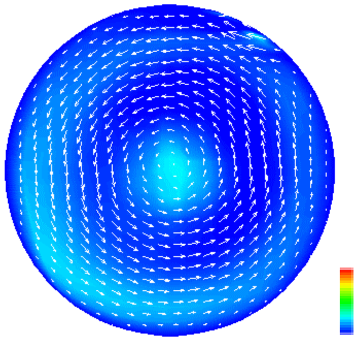

Figure 8. Cross-sectional view of velocity field (Case V). Colors show axial velocity.

Conclusions

We performed a series of CFD calculations to simulate heat and mass transfer processes that take place during the carbon nanotube growth in a CVD reactor. Substrates in our current CVD design were found to create non-uniform flow velocity of feed gas that may cause unwanted growth of amorphous carbon. A straight tube flow reactor without substrates has one single circulation across the cross section of the tube. Horizontal orientation of the tube can create a circulation along the radial direction, while vertical orientation of the tube creates either unstable feed gas flow or no circulation at all. To improve the current CVD design, we proposed to attach a feed gas injection port at an off-centered sidewall location. This new injection method, called spin injection, has a definite advantage of increased contact time of the feed gas and the reactor wall. The longer the contact time is, the higher the carbon nanotube yield might be.

Acknowledgements

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