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COMBINED EXPERIMENTAL AND SIMULATION (CFD) ANALYSIS ON PERFORMANCE OF A HORIZONTAL TUBE REACTOR USED TO PRODUCE CARBON NANOTUBES

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ABSTRACT

The horizontal tube furnace comes in a variety of configurations and is used in areas such as solid state chemistry and catalysis. We are particularly concerned with its use to produce carbon nanotubes (CNTs) where it is the apparatus of choice. The specific properties of the carbon nanotubes produced have been found to vary significantly with the local conditions inside the horizontal tube furnace. Construction parameters such as tube length and slight variations in operational conditions such as temperature and feed gas flow rate have been found to significantly affect yields and characteristics that affect the quality of the CNTs produced. Measurements have been made in a laboratory tube furnace and a numerical model of the reactor has been developed to provide insight into the internal conditions and to assist in the design process.

INTRODUCTION

The horizontal tube furnace is a long, thin, electrically heated reactor that is widely used for the production of carbon nanotubes (CNTs) in the laboratory, as shown schematically in Figure 1.

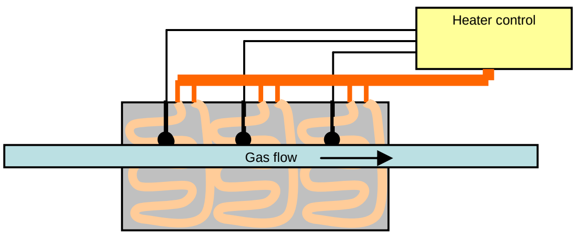

Figure 1 Schematic of tube furnace reactor

Carbon nanotubes can be produced at a wide range of operating conditions, but the properties of the CNT produced generally depend on the local conditions inside the reactor, which in turn depend strongly on the configuration of the reactor (CSIRO, 2009). It is relatively easy to "dial up" the specific operating conditions within a specific laboratory reactor to produce the desired CNT, but it is very difficult to predict how the physical arrangement of the furnace will influence the conditions in the reaction zone where the CNTs are produced. Subtle changes in the reactor configuration, such as altering the length of the exposed inlet or outlet pieces, can produce unexpected changes to the quality of CNT produced in the reaction zone.

CNT with specific properties have been produced in laboratory scale horizontal tube furnaces and there is a desire to increase production to commercial quantities. Scaleup of a process from the laboratory to a commercial scale is well known to be a difficult task that usually requires a very detailed understanding of the important interactions between the various operating variables. Preliminary testing in the laboratory has indicated that the scaleup of the horizontal tube furnace is not a trivial exercise. Even subtle changes to system geometry and furnace temperature have caused significant changes to CNT properties, although this type of reactor is successfully used for large scale production of other materials. For example, Figure 2 shows a schematic of a commercially available tube furnace for production of wafers in the electronics industry (Timedomain CVD, Inc., 2009). It is highly likely that gas flows within this reactor are different to those within the horizontal tube reactor used to produce carbon nanotubes because the carbon nanotubes form on a substrate positioned very close to the base of the tube, whereas the commercial reactor has vertically stacked wafers that are expected to significantly baffle gas flow along the reactor axis.

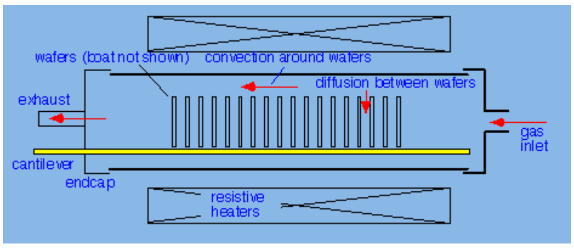

Figure 2 Schematic of commercial tube furnace for processing wafers for use in electronics industry (Timedomain CVD, Inc., 2009).

Computational Fluid Dynamics (CFD) modelling is being used by some research groups to investigate fluid and particle flows inside the horizontal tube furnace and larger laboratory furnaces (TKK-NMG, 2009). CFD predictions of temperature and velocity profiles inside laboratory furnaces are reported to assist in the production of nano particles, but it is unclear exactly what modelling techniques have been used to produce these results, but close inspection of each plot shows a horizontal line at the central axis that may indicate the presence of axial symmetry. This study has developed CFD models to simulate the three dimensional flow of the carrier gas within the horizontal tube furnace.

EXPERIMENTAL STUDIES

Horizontal tube furnaces are generally expected to have a well defined internal temperature profile along the central axis and Figure 3 shows the temperature profile inside commercial units used for solid state chemistry (Timedomain CVD, Inc., 2009).

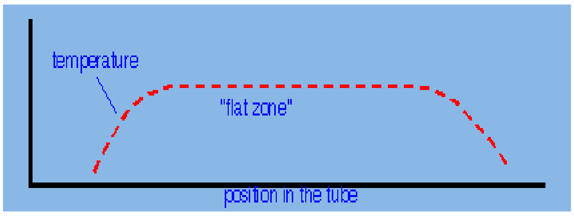

Figure 3 Temperature profile in commercial tube furnace (Timedomain CVD, Inc., 2009).

A principle activity in the experimental studies was the measurement of temperature profiles inside the horizontal tube reactor. A metal sheathed thermocouple was moved along the central axis and temperature readings were made at a number of locations and the temperature profile is shown in Figure 4. The general form of this profile is an acceptable match with the expected profile from a commercial tube furnace because the "flat zone" was present throughout most of the reactor.

However, as a result of this study we suggest that the temperature profile measured inside the horizontal tube reactor using a metal sheathed thermocouple does not actually indicate the true gas temperature inside the reactor, which is expected to be a critical parameter in the control of a process to manufacture CNTs.

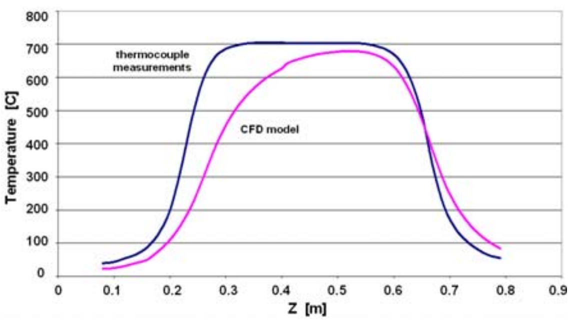

Figure 4 Temperature measured using bare thermocouple on reactor centre line compared with CFD prediction. (Helium carrier gas flow of 1L/min and all heater temperatures 705°C.)

The influence of radiative heat transfer from the furnace wall to the metal sheathed thermocouple has not been taken into account and it is suggested that the temperature reported by the thermocouple is strongly affected by heat absorbed through the metal sheath. To investigate this further a short radiation shield of thin silver foil was attached to the tip of the metal sheathed thermocouple. Figure 5 shows differences in temperature profiles measured by inserting both the shielded and bare tipped thermocouples into the exit of the reactor at 1 L/min Helium flow with the furnace set at 705°C. The temperature indicated by the thermocouple with the shielded tip is initially lower than that indicated by the thermocouple with the bare tip but rises as the thermocouple penetrates deeper into the reactor, which is attributed to the metal sheath behind the shielded tip heating up due to radiative heat transfer. We therefore expect that the actual gas temperature in the reactor is significantly lower than that measured by the bare tipped metal sheathed thermocouple but have not been able to directly measure the temperature profile when the furnace is operating because a suction thermocouple apparatus is not available (Z'Graggen et al, 2007).

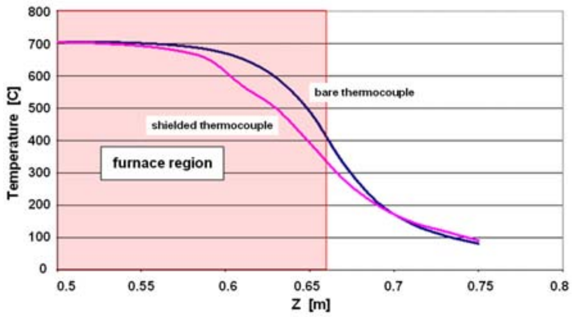

Figure 5 Temperature measurements in exit end of reactor. (Helium carrier gas flow of 1L/min and all heater temperatures 705°C.)

MODEL DESCRIPTION

A single phase CFD model that uses the k-epsilson turbulence model has been developed of this horizontal tube furnace, as shown in Figure 6. The inlet and outlet section could lose heat to the ambient environment with a heat transfer coefficient of 15 W/m^2K. The inlet and outlet cuffs were set up in the model as isothermal wall boundary conditions to correspond with thermal insulating material present in the physical tube furnace and all external walls were no slip. It is assumed that the heater sections of the reactor walls achieve the furnace set point instantly. Heat loss from the tube furnace due to thermal radiation was considered to be small because of the view factor associated with the geometry and a radiation model was not incorporated in the CFD model.

The model was developed in ANSYS-CFX version 11 and was run in steady state and transient modes. Several geometries were drawn in Design Modeler and each unstructured computational mesh has around 100000 nodes. The presence of the axial thermocouple was not included in any geometry, but the rectangular prism stage was included in the reaction zone when necessary

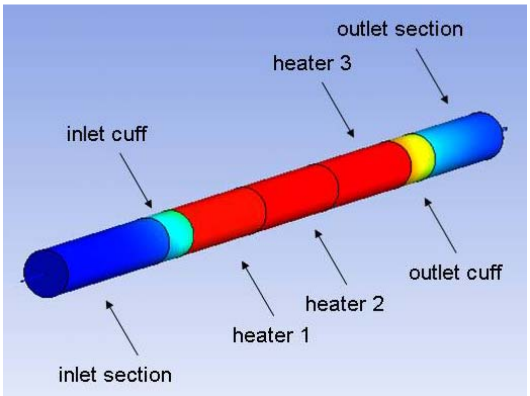

Figure 6 Schematic of CFD model of tube furnace

The temperature profile at the central axis predicted by the CFD model has been compared with the temperature profile measured with a bare thermocouple at the central axis of the empty reactor, as shown in Figure 4. Although there are some differences between these profiles, the test work undertaken in the laboratory to investigate the effect of a radiation shield at the tip of the thermocouple has confirmed that the measured temperature profile does not accurately indicate the gas temperature. The temperature profile predicted by the CFD model is now believed to provide a useful estimation of the gas temperature in the horizontal tube furnace.

RESULTS

A swirling gas flow inside the horizontal tube furnace was predicted by the CFD model and has provided useful insight into fluid flow through the reaction zone within the heated section of the horizontal tube reactor. Figure 7 shows streamlines indicating the path taken by fluid flow entering the cool inlet region, being raised to operating temperature in the heated section, passing through the reaction zone, then cooling down and leaving the reactor. CNT production occurs on the upper face of a rectangular prism shaped stage located close to the centre of heated reactor. This stage rests on the internal surface of the circular tube, resulting in a small elliptical opening available for flow beneath the stage. This stage is included in the CFD model and the stream lines shown in Figure 7 indicate that gas passes over the top of the stage where CNT would form in the actual reactor and also beneath the stage.

Before this CFD modelling was carried out the flow pattern of carrier gas inside the reactor is widely assumed to closely approximate plug-flow because the flow can be characterised by a low Reynolds number at ambient conditions, which is associated with the laminar flow regime. The CFD model has been used to investigate the internal flow pattern at ambient conditions and the conventionally accepted flow pattern has been predicted, as shown in Figure 8. It is interesting to note the presence of an inlet jet extending into the reactor, resulting in some back-mixing that is often overlooked in the conventionally accepted flow pattern.

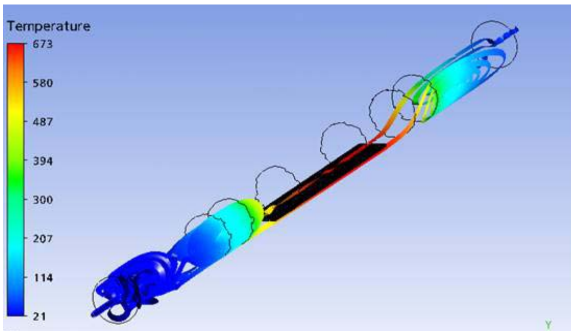

Figure 7 Flow streamlines in reactor predicted using CFD model. (Helium carrier gas flow of 1L/min and all heater temperatures 705°C.)

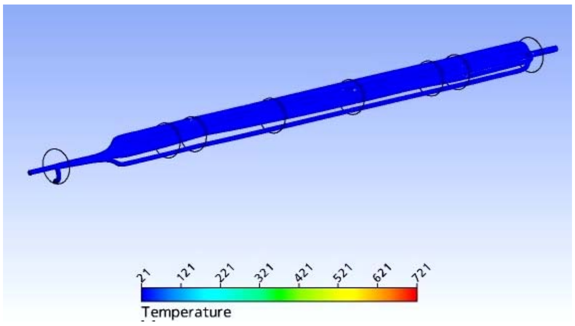

Figure 8 Flow streamlines in reactor at ambient temperature predicted using CFD model. (Helium carrier gas flow of 1L/min.)

This CFD model was run as a transient simulation to illustrate the development of complex swirling flow patterns inside the inlet section and outlet section of the operating tube furnace. The transient model assumed that heaters would reach their operating temperature instantly, which is an unrealistic expectation in a real furnace. A swirling flow pattern at the entrance to the heated reactor appears to develop a short period of time after the ambient gas is introduced into the operating furnace, as shown in Figure 9. A swirling flow pattern near the exit of the heated reactor appears to develop some time later when the exit gas temperature has increased to around 500°C, as shown in Figure 10.

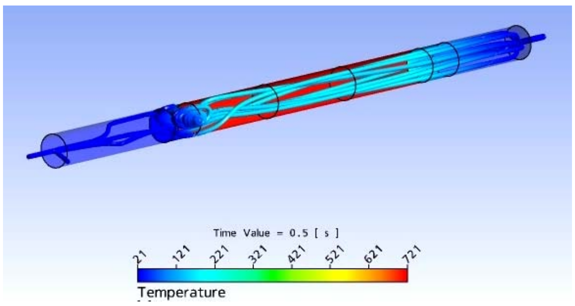

Figure 9 Swirling flow near the reactor inlet is predicted to develop around 0.5 seconds after all heaters reach operating temperature. (Helium carrier gas flow of 1L/min and all heater temperatures 705°C.)

The CFD simulation predicts that swirling flow patterns exist near the reactor inlet and outlet which seriously affect the gas residence time in the operating horizontal tube furnace. As noted earlier, the specific properties of the carbon nanotubes produced have been found to vary significantly with the local conditions inside the horizontal tube furnace. It is well known that the reacting gas in CNT manufacture undergoes a complex series of thermal decomposition reactions inside the heated reactor. The CFD model has provided useful insight into the reactor design process because provides important insight into the gas residence time within the reactor

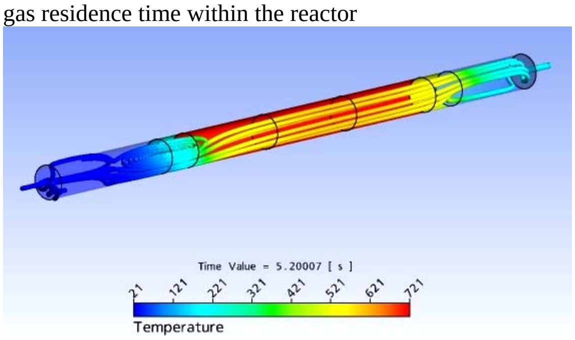

Figure 10 Swirling flow near the reactor outlet is predicted to develop around 5.2 seconds after all heaters reach operating temperature. (Helium carrier gas flow of 1L/min and all heater temperatures 705°C.)

Assessment of alternative designs

The CFD model has been used to investigate the different internal flow patterns in a number of different horizontal tube furnace configurations. As noted earlier, the properties of the CNT produced in the reaction zone are greatly influenced by the physical arrangement of the horizontal tube furnace. Several different arrangements and diameters of reactor and types of conveying gas have been investigated, but only limited results will be presented here.

The CFD model has provided insight into the internal conditions with alternative conveying gases used in the production of CNT. Internal flow patterns in the region close to the reaction zone have been shown to vary considerably depending on the thermal properties of the carrier gas. There can be significant differences in the heating up of the gas at the reactor inlet and the cooling down of the gas at the reactor exit, which can directly affect the pathway of carrier gas through the reaction zone.

It is particularly interesting to visualise the flow streamline as it passes through the reaction zone because it can give an indication of the temperature and thermal history of the gas. Figure 11 shows this flow streamline for helium carrier gas and Figure 13 shows this flow streamline for argon carrier gas. It is interesting to see that gas swirling at the inlet and outlet of the heated reactor is significantly more intense when argon carrier gas is used, resulting in a much narrower reaction zone.

The CFD model can predict the temperature profile along the flow streamlines that pass through the reaction zone to provide useful insight into the thermal history of the gas. Figure 12 shows the temperature profile along the flow streamline for helium carrier gas identified in Figure 11. Figure 14 shows the temperature profile along the flow streamline for argon carrier gas identified in Figure 13.

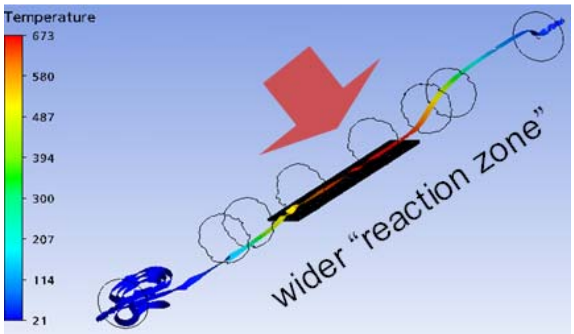

Figure 11 Flow streamlines through a point in the reaction zone predicted using CFD model. (Helium carrier gas flow of 1L/min and all heater temperatures 705°C.)

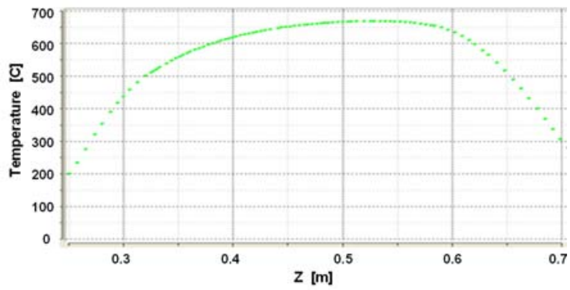

Figure 12 Temperature profile along the flow streamlines through a point in the reaction zone predicted using CFD model. (Helium carrier gas flow of 1L/min and all heater temperatures 705°C.)

A relatively steep temperature profile is predicted when argon gas is used as a carrier, resulting in a very short region where the high temperature is achieved that is likely to have significant effect on the production of CNT's. It is well known that argon is widely used as an alternative carrier gas to helium in the manufacture of CNTs because it is a significantly cheaper gas to use but has significantly different thermal properties. In practice, argon gas is usually supplemented with a very small percentage of hydrogen to improve its thermal properties of the carrier gas. The CFD model could be used to specify the carrier gas blend of argon and hydrogen that produce a temperature profile similar that of a system where helium is used as the carrier gas.

The effect of slight changes in system geometry on the internal conditions can also be investigated using the CFD model. Varying the position of the tube within the furnace, or adding additional insulation can greatly influence the internal flow patterns in the region close to the reaction zone. For example, Figure 15 shows the effect of insulating the outlet section and shortening the inlet section.

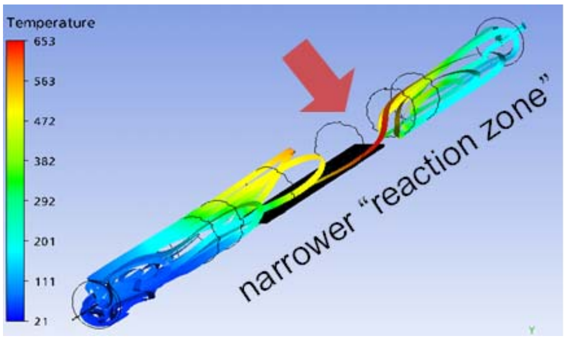

Figure 13 Flow streamlines through a point in the reaction zone predicted using CFD model. (Argon carrier gas flow of 1L/min and all heater temperatures 705°C.)

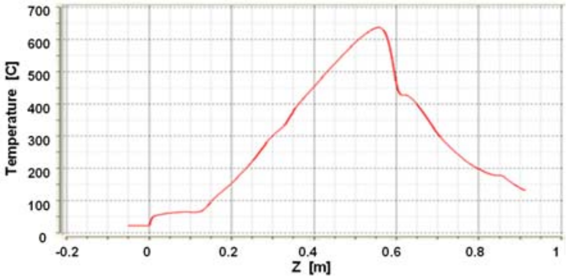

Figure 14 Temperature profile along the flow streamlines through a point in the reaction zone predicted using CFD model. (Argon carrier gas flow of 1L/min and all heater temperatures 705°C.)

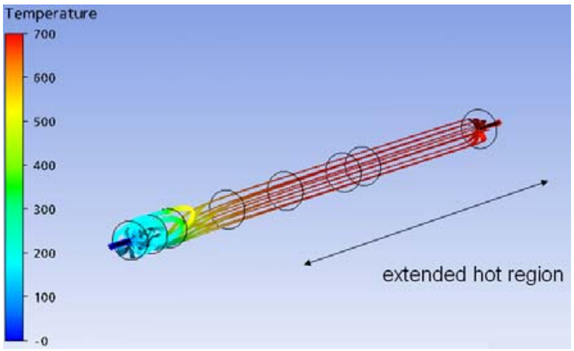

Figure 15 Flow streamlines in reactor with shortened inlet section and insulated outlet section predicted using CFD model. (Helium carrier gas flow of 1L/min and all heater temperatures 705°C.)

CONCLUSION

Direct measurements of gas temperature in a laboratory tube furnace are difficult to obtain because the metal sheathed thermocouple can be considerably influenced by radiative heat transfer. It is possible to measure the gas temperature if the thermocouple is fitted with a radiation shield, but it is difficult to traverse the length of the reactor because the radiation shield needs to protect the whole thermocouple.

A CFD model of the reactor can be used to provide insight into the internal conditions of laboratory horizontal tube furnaces and to assist in the design process.

The model has been validated reasonably well using temperature measurements along the reactor axis and has provided new insights into the internal flow patterns that have challenged conventional assumptions.

Gas flow through the horizontal tube furnace is relatively complex with distinct zones of internal recirculation adjacent to air-cooled walls at the inlet and outlet of the heated region.

A number of different observations in the laboratory reactor have been explained using the CFD model, such as the reason why the surface temperatures of the inlet and outlet sections are low, which allows oils condense on the inside of the tube during certain operating conditions.

ACKNOWLEDGEMENTS

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REFERENCES

ANSYS INC, A., (2007), *ANSYS-CFX Version 11.0 Documentation*. Pittsburgh, Pennsylvania, United States of America.

CSIRO, (2009), “Exploring applications for carbon nanotubes” website, accessed 30/6/2009, http://www.csiro.au/science/CarbonNanotubes.html

TIMEDOMAIN CVD, Inc., (2009), “Tube reactor overview” website, accessed 30/6/2009, http://timedomaincvd.com/CVD_Fundamentals/reactors/tube_reactor.html

TKK-NMG (2009), “Carbon nanotube synthesis” website, accessed 30/6/2009, http://www.fyslab.hut.fi/nanomat/Aerosol%20Modelling%20No%20Details.htm

Z’GRAGGEN, A., FRIESS, H. and STEINFELD, A.(2007), “Gas temperature measurement in thermal radiating environments using a suction thermocouple apparatus”, Meas. Sci. Technol., **18,** 3329–3334, doi:10.1088/0957-0233/18/11/010