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Effects of Furnace and Inlet Gas Mixture Temperature on Growing Carbon Nanotube in a CVD Reactor

Babak Zahed¹, Tahereh Fanaei Sheikholeslami^{2*}, Amin Behzadmehr³, Hossein Atashi⁴

¹ Ph.D. Student, Mechanical Engineering Department, University of Sistan and Baluchestan, Zahedan, Iran

² Assistant Professor, Electrical and Electronic Department, University of Sistan and Baluchestan, Zahedan, Iran

³ Professor, Mechanical Engineering Department, University of Sistan and Baluchestan, Zahedan, Iran

⁴ Professor, Chemical Engineering Department, University of Sistan and Baluchestan, Zahedan, Iran

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ABSTRACT

Carbon nanotubes (CNTs), nowadays, are one of the important nanomaterials that can be produce with different methods such as chemical vapor deposition (CVD). Growing of CNTs via CVD method can be influenced by several operating parameters that can affect their quality and quantity. In this article, the effects of inlet gas mixture temperature on CNT's local growth rate, total production, and length uniformity are numerically studied in two distinct growth regimes, mass transfer controlled regime and surface reaction controlled regime, separately. Also, the effects of the interaction of inlet gas mixture temperature with furnace temperature on CNT growth are investigated.

Keyword: Chemical vapor deposition; Carbon nanotube; Furnace temperature; Inlet gas mixture temperature, Numerical Analysis.

1. INTRODUCTION

Carbon Nanotube (CNT) has attracted a lot of attention due to its superior mechanical, electrical, and thermal properties [1, 2] during the last decades. There are a wide range of applications for them in many scientific and industrial fields, for example, as electrodes in organic light emitting diodes [3], structural materials [4], and gas detectors [5, 6]; they are also used in Nano-electronic components [7], and so on.

Quality and quantity of produced CNTs are challenging issues for a wide range of industrial applications. Also, as known, CNT growth process can be varied in different CNT synthesis methods; therefore, proper selection of synthesis method is of crucial importance. Nowadays, there are three main methods for producing CNTs: arc discharge [8], laser ablation [9] and chemical vapor deposition (CVD) [10]. Among them, CVD is

(*) Corresponding Author - e-mail: tahere.fanaei@ece.usb.ac.ir

one the most popular methods for growing CNTs that is able to produce high quality CNTs in high quantity. In this method, growing of CNTs depends on various parameters such as inlet gas mixture flow rate, operating pressure, furnace temperature, inlet gas mixture temperature, and so on; therefore, it is essential to select operating conditions properly. Nowadays, numerical methods are used widely to find the effects of operating conditions on the growing of CNTs [11-14]. These methods, also, provide important information of hydrodynamics and transport phenomena throughout the reactor, where visualization of such information in experimental studies is so difficult. In this regard, Grujicic et al. [10, 15] established a model for growing CNT that involves detailed gas phase reactions of methane and the deposition of amorphous carbon. Their model calculated temperature, velocity, and concentration distribution with different operating conditions. Endo et al. [16], also, calculated the CNT production rates in a CVD reactor based on catalytic decomposition of xylene using a CFD model. The model predicted velocity and temperature distributions as well as concentration distributions in the reactor. In particular, total production rates with various inlet xylene concentrations were calculated and measured. As another example, a combined experimental-kinetic model was conducted by Gommès et al. [17] to investigate the effect of operating conditions on the CNT yield in a semicontinuous CVD reactor. They suggested a mathematical model for the reaction rate and used mass spectrometry results for the kinetic study. Besides, the detailed gas phase reactions of C_2H_2 pyrolysis and the surface catalytic reactions as well as the influence of C_4H_4 on the CNT growth were studied by Ma et al. [18].

They developed an improved model for the growth of carbon nanotubes in a horizontal tubular reactor and calculated the effects of the operating conditions on the growth of CNT comparing it with the experimental results. In another study, Kim et al. [19] investigated the effect of growing time, flow rate, and direction of the carrier gas on structures and the formation mechanisms of the vertically aligned CNT forests. Also, they employed a CFD model to demonstrate the flow dependent growth of CNT forests. They revealed that the variation of the local pressure is an important

parameter determining the directionality of the CNT growth. However, in spite of the mentioned studies, as far as the authors are concerned, one issue that is not studied in related research in this field is the effects of considering the contribution of furnace temperature to other operating conditions on CNT growth and the effects of their interactions with each other. As known, CNTs' local growth rate is one of the important parameters that can determine the quantity of produced CNTs. Also, the high length uniformity of CNTs across the deposited surface is one of the significant characteristic for the higher quality of produced CNTs. Therefore, in this article, the effect of inlet gas mixture temperature as well as the interaction of inlet gas mixture temperature with furnace temperature effects on growth rate and length uniformity of CNTs is numerically investigated and discussed.

2. PROBLEM DESCRIPTION AND NUMERICAL APPROACH

Horizontal tubular CVD reactor (Figure 1) that was applied for the growing of CNTs had interior diameter and length of 34 mm and 1500 mm, respectively, with 17 mm diameter for inlet and outlet of the reactor. The reactor had two sections including preheater zone (located between 200 to 500 mm from the inlet) and furnace zone (located between 600 to 1250 mm from the inlet). Inlet gas mixture (including xylene (C_8H_{10}) as precursor gas with carrier gas including argon with 10% hydrogen) was entered into the reactor. After two volumetric and four surface reactions, CNTs were deposited on furnace surface, and then by products exited from the outlet.

For modelling the reactor, the researchers consid-

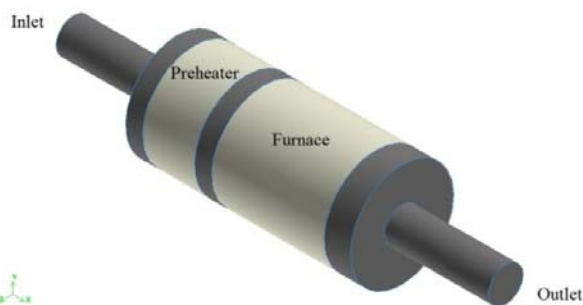


Figure 1: Geometry of the CVD reactor.

ered some governing equations including conservation of mass, momentum, energy, and species transport as follows:

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \vec{V}) \quad (1)$$

Conservation of momentum:

$$\frac{\partial \rho \vec{V}}{\partial t} = -\nabla \cdot (\rho \vec{V} \vec{V}) + \nabla \cdot \tau - \nabla \rho + \rho \vec{g} \quad (2)$$

Where viscous stress tensor is:

$$\tau = \mu \left(\nabla \vec{V} + (\nabla \vec{V})^T \right) + \left(\kappa - \frac{2}{3} \mu \right) (\nabla \cdot \vec{V}) \mathbf{I} \quad (3)$$

Conservation of energy:

$$C_p \frac{\partial \rho T}{\partial t} = -C_p \nabla \cdot (\rho \vec{V} T) + \nabla \cdot (\lambda \nabla T) + \nabla \cdot (RT \sum_{i=1}^N \frac{D_i}{M_i} \nabla (\ln f_i)) + \sum_{i=1}^N \frac{H_i}{m_i} \nabla \cdot \vec{J}_i - \sum_{i=1}^N \sum_{k=1}^N H_i v_{ik} (R_k^g - R_{-k}^g) \quad (4)$$

Conservation of Species:

$$\frac{\partial (\rho \omega_i)}{\partial t} = -\nabla \cdot (\rho \vec{V} \omega_i) + \nabla \cdot \vec{J}_i + m_i \sum_{k=1}^K v_{ik} (R_k^g - R_{-k}^g) \quad (5)$$

Ordinary diffusion flux (J_i) obtained from Stefan-Maxwell equations and reaction rate constant determines from the modified Arrhenius equation:

$$K_k = A_k T^{n_k} e^{-\frac{E_k}{RT}} \quad (6)$$

Where A denotes the Arrhenius pre-exponential factor

$((m^3 \cdot mol^{-1})^{a-1} \cdot s^{-1})$, a is the order of reaction), n is the exponent for temperature dependence of A, E represents the activation energy ($J \cdot mol^{-1}$), R indicates the universal gas constant, $8.314 (J \cdot mol^{-1} \cdot K^{-1})$ and T refers to the absolute temperature (K). Considered volumetric and surface reactions for the model are shown in Tables 1 and 2, respectively. The rate constants for volumetric reactions and surface reactions were obtained from the works of Benson et al. [20] and Endo et al. [16], respectively.

These sets of equations were solved by using finite volume method. Non-uniform structured and quadrilateral grids that are finer at the near walls regions (where the gradient of the parameters are important) were selected for discretization of the computational domain. QUICK method was used to discretize the convective terms, while the central difference scheme was adopted for the discretization of diffusion terms. SIMPLE algorithm was used for the pressure-velocity coupling. Several different grid distributions had been tested to ensure that the results were grid independent. Moreover, the accuracy of the results of the CFD model was validated with Endo et al.'s [16] numerical work; a good concordance was observed between the results of these two studies [13].

3. RESULTS AND DISCUSSION

To study the effects of inlet gas mixture temperature on the growing of CNTs, local growth rate of CNTs must be calculated. In a CVD reactor, it obtains from

Table 2: Considered volumetric reactions.

Reaction	Volumetric Reactions	A	E	n
1	$C_8H_{10} + H_2 \rightarrow C_7H_8 + CH_4$	9.2×10^9	220000	0
2	$C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4$	4×10^9	224000	0

Table 2: Considered surface reactions.

Reaction	Surface Reactions	A	E	n
3	$C_8H_{10} \rightarrow 8C + 5H_2$	0.00034	0	0
4	$C_7H_8 \rightarrow 7C + 4H_2$	0.00034	0	0
5	$C_6H_6 \rightarrow 6C + 3H_2$	0.00034	0	0
6	$CH_4 \rightarrow C + 2H_2$	0.008	0	0

[21]:

$$GR = \frac{K_s h_G C_T Y}{K_s + h_G N} \quad (7)$$

Where:

$$Y \equiv \frac{C_G}{C_T} = \frac{P_G}{P_{Total}} \quad (8)$$

$$P_{Total} = \sum p_{Gi} \quad (9)$$

Where C_T and C_G are the concentration of all molecules in the gas phase and the concentration of reactant species in the main gas flow, respectively; N is the number of atoms incorporated per unit volume in the deposition layer; Y is mole fraction of the incorporating species in gas phase; P_G and P_{Total} represented partial pressure of the incorporating species and total pressure in the system, respectively; h_G is mass transfer coefficient; and K_s is surface reaction rate which was calculated from modified Arrhenius equation.

As studied in previous paper [14], furnace temperature has a major effect on CNT growth; based on that, two distinct growth regime (mass transfer controlled (MTC) regime and surface reaction controlled (RC) regime) were specified. Moreover, it was also studied that working growth regime influenced the effects of other operating conditions on CNT growth [14].

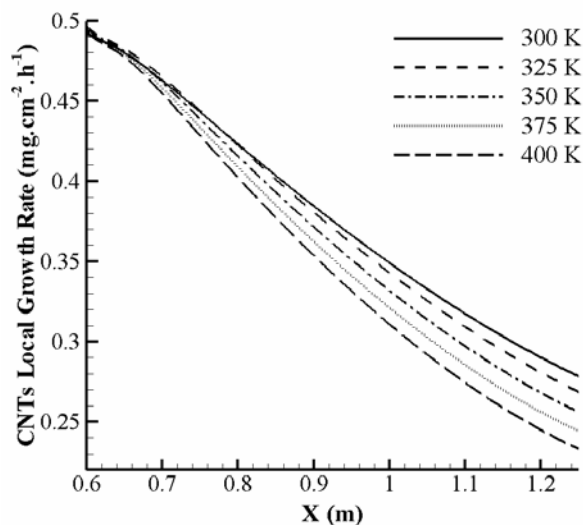


Figure 2: CNTs local growth rate in furnace zone with different inlet gas mixture temperature in surface reaction controlled regime.

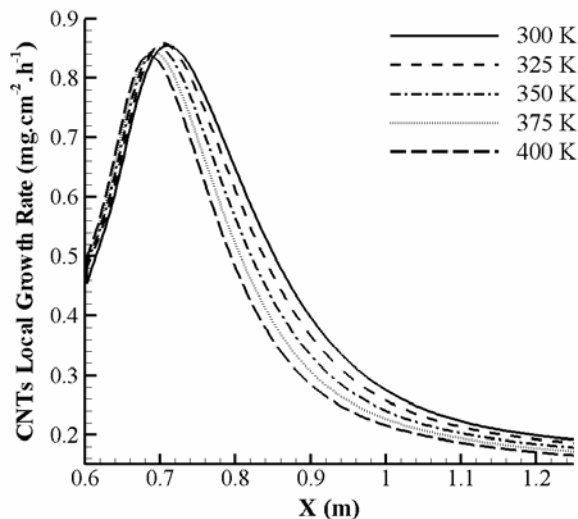


Figure 3: CNTs local growth rate in furnace zone with different inlet gas mixture temperature in mass transfer controlled regime.

Thus, in this paper, effects of inlet gas mixture temperature on CNTs' local growth rate have been studied in these two regimes, separately, the results of which are reported in Figures 2 and 3. In the current study, boundary conditions for inlet gas flow rate and pre-heater temperature were 685 sccm and 513 K, respectively. Moreover, concentration of xylene as precursor gas in inlet gas mixture was 3750 ppm, and temperatures of furnace for mass transfer controlled regime and surface reaction controlled regime were selected

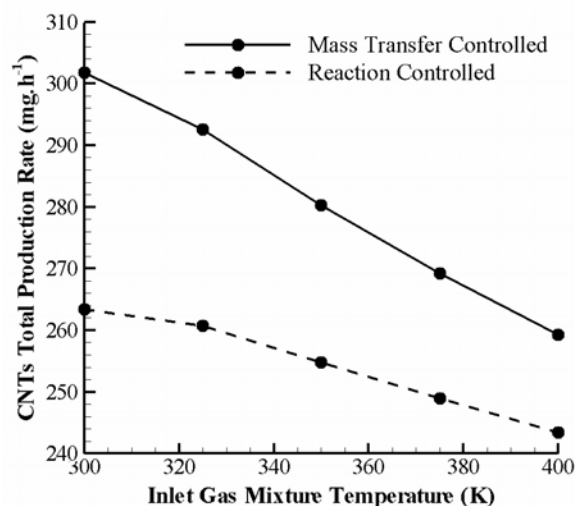


Figure 4: CNTs total production versus inlet gas mixture temperature in mass transfer controlled and surface reaction controlled regimes.

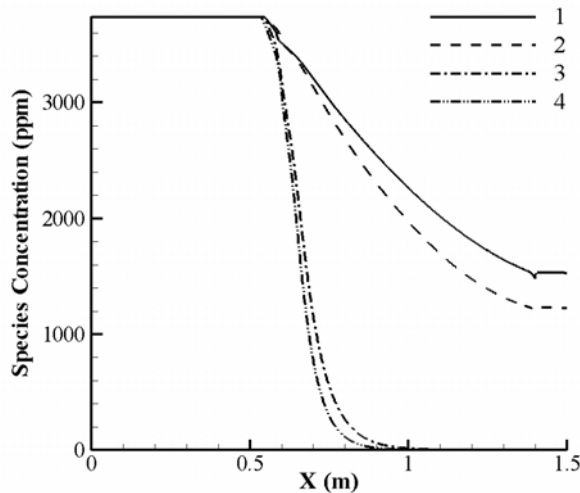


Figure 5: Concentration of C_8H_{10} near the surface of the reactor.

- (1): with 300 K inlet gas mixture temperature in RC regime
 (2): with 400 K inlet gas mixture temperature in RC regime
 (3): with 300 K inlet gas mixture temperature in MTC regime
 (4): with 400 K inlet gas mixture temperature in MTC regime

1250 K and 975 K, respectively.

To better investigate the effects of inlet gas mixture temperature, the researchers integrated CNTs' local growth rate along the surface of furnace. The results are presented in Figure 4. As observed, for both of the regimes, increasing of the inlet gas mixture temperature leads to the decrease of CNTs' total production.

As seen in Figures 5 and 6, with increasing inlet gas mixture temperature from 300 K to 400 K, concentration of C_8H_{10} and C_7H_8 (main carbon sources) decreased in both surface reaction controlled and mass transfer controlled regimes. This happens due to the enhancement of thermal decomposition of these two species to their by-products (C_6H_6 and CH_4) (see Table 1). And, because C_8H_{10} and C_7H_8 had more influence on the amount of carbon deposition (according to Table 2) compared with other carbon sources (because concentrations of C_8H_{10} and C_7H_8 were much more than C_6H_6 and CH_4 throughout the reactor, and C_8H_{10} and C_7H_8 released more carbon atoms compared with C_6H_6 and CH_4). Therefore, this decrease in the concentration of these species led to the decrease of main carbon sources throughout the reactor. And, according to equation (7), reduction of CNTs' production happens as a result of this. As seen in Figure 4,

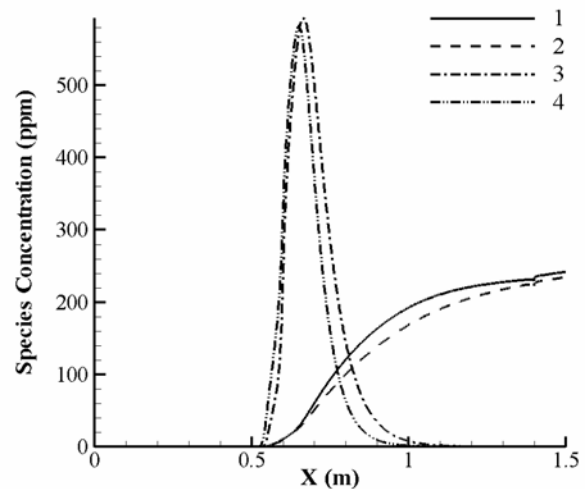


Figure 6: Concentration of C_7H_8 near the surface of the reactor.

- (1): with 300 K inlet gas mixture temperature in RC regime
 (2): with 400 K inlet gas mixture temperature in RC regime
 (3): with 300 K inlet gas mixture temperature in MTC regime
 (4): with 400 K inlet gas mixture temperature in MTC regime

the order of CNTs' total production in mass transfer controlled regime is higher than that of the surface reaction controlled regime. This is because mass transfer controlled regime works at higher growth temperature (in this case, it was considered 1250 K) compared with surface reaction controlled regime (in this case, it was considered 975 K). Therefore, this has led to a higher kinetic rate of reactions and, as a result, to higher CNTs' production.

Another important issue is variation of length uniformity of CNTs with different inlet gas mixture temperatures. A criterion for calculating length uniformity is defined as:

$$LU = \frac{GR_{max}}{GR_{max} - GR_{min}} \quad (10)$$

Thus, as seen in Figure 7, in mass transfer controlled regime, inlet gas mixture temperature had less effect on the CNTs' length uniformity compared with surface reaction controlled regime. As explained before, this is because CNTs' growth rate in reaction controlled regime has higher sensitivity to temperature compared with mass transfer controlled regime. Also, as seen in Figure 7, mass transfer controlled regime had a lower order of length uniformity compared with

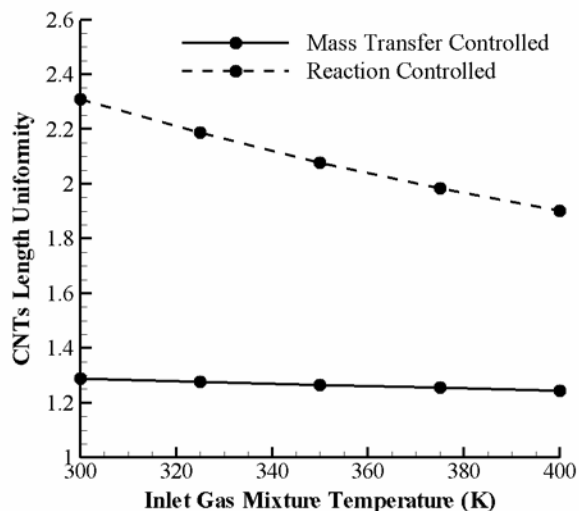


Figure 7: CNTs length uniformity with various inlet gas mixture temperature in mass transfer controlled and surface reaction controlled regimes.

reaction controlled regime because of the nature of reactions' behavior in these regimes that was discussed before [14].

Otherwise, inlet gas mixture temperature would influence the effect of furnace temperature on CNT growth. As known, reaction surface controlled regime is distinguished from mass transfer controlled regime by its different characteristics. In surface reaction controlled regime, deposition layer of CNTs has higher length uniformity compared with mass transfer controlled regime. Also, in mass transfer controlled regime, CNT growth has less sensitivity to furnace temperature compared with surface reaction controlled regime [14]. Growing of CNTs in mass transfer controlled regime (higher furnace temperatures) leads to strong film thickness non-uniformity and this can make major restrictions on the configuration of the equipment and the placement of the reaction surfaces. By contrast, when the growing of CNTs occurs in surface reaction controlled regime (lower furnace temperatures), the process is very sensitive to the furnace temperature. However, the mass transfer through the boundary layer is not so important, which leads to fewer restrictions on the gas flow and reaction surface placement. This is a desired characteristic for CNTs' production in industrial scale. However, because this regime works at lower temperatures, produced CNTs

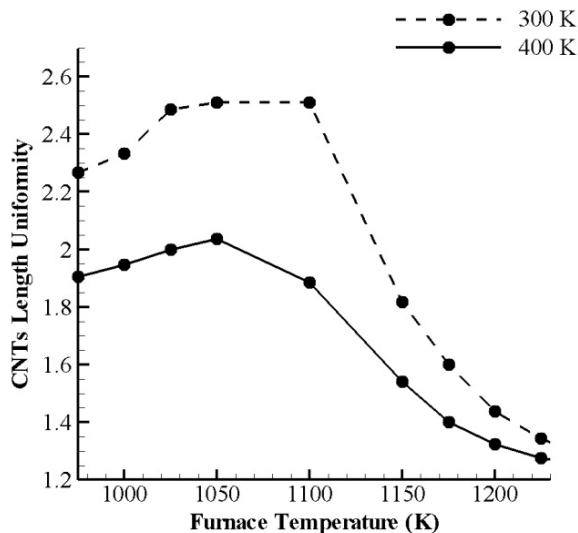


Figure 8: CNTs length uniformity versus furnace temperature with various inlet gas mixture temperatures.

may have more structure defect compared with CNTs produced using mass transfer controlled regime [21]. Therefore, as clarified, these two regimes have significant influence on quantity and quality of produced CNTs.

As seen, in Figure 8, for 300 K as inlet gas mixture temperature, changing in CNTs' length uniformity behavior started after 1150 K as furnace temperature; however, by increasing inlet gas mixture temperature to 400 K, this behavior change happens before 1150 K.

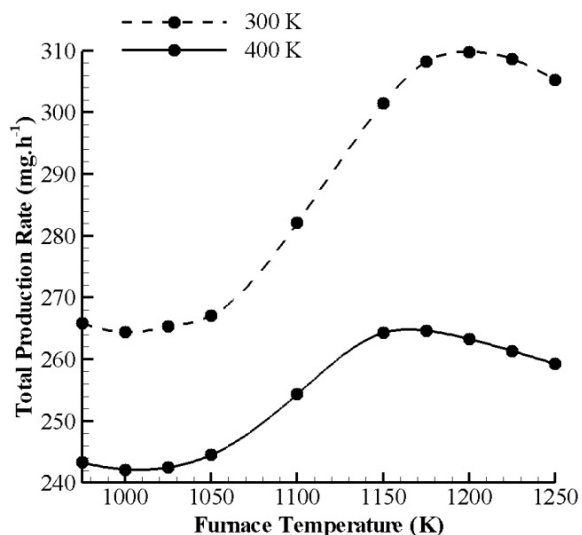


Figure 9: CNTs total production rate versus furnace temperature with various inlet gas mixture temperatures.

This means that increasing the inlet gas mixture temperature leads to extending mass transfer controlled regime to lower temperatures. This result is evident in Figure 9. As can be seen, mass transfer controlled regime that has less sensitivity to furnace temperature happens in lower temperature for 400 K as inlet gas mixture temperature compared with lower inlet gas mixture temperature.

4. CONCLUSIONS

Results of the study showed that increasing inlet gas mixture temperature led to reduction of CNTs' total production in both of the regimes (mass transfer controlled and surface reaction controlled regimes). This is due to the decomposition of main carbon source and decrease of their concentrations throughout the reactor. Also, increasing inlet gas mixture temperature led to degradation of CNTs' length uniformity in surface reaction controlled regime; however, in mass transfer controlled regime, it had not significant effect on length uniformity of CNTs. This is due to the different natures of processes that happen in these two regimes. Also, increasing the inlet gas mixture temperature led to extending mass transfer controlled regime to lower temperatures.

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Nomenclature

C_p	Specific heat of the gas mixture ($J.kg^{-1}.K^{-1}$)
D^T	Multicomponent thermal diffusion coefficient ($kg.m^{-1}.s^{-1}$)
f	Species mole fraction
\vec{g}	Gravity vector ($m.s^{-2}$)
H	Molar enthalpy ($J.mole^{-1}$)
I	Unity tensor
\vec{J}	Diffusive mass flux vector ($kg.m^{-2}.s^{-1}$)
m_i	Mole mass of the i th species ($kg.mole^{-1}$)
\vec{n}	Unity vector normal to the inflow/outflow opening or wall
P	Pressure (pa)
R	Universal gas constant ($= 8.314 J.mole.K^{-1}$)
R_K	Forward reaction rate of the k th gas phase reaction ($mole.m^{-3}.s^{-1}$)
R_{-K}	Reverse reaction rate of the k th gas phase reaction ($mole.m^{-3}.s^{-1}$)
R_l^s	Reaction rate for the l th surface reaction ($mole.m^{-2}.s^{-1}$)
t	Time (s)
T	Temperature (K)
\vec{V}	Velocity vector ($m.s^{-1}$)

Greek Symbols

κ	Volume viscosity ($kg.m^{-1}.s^{-1}$)
λ	Thermal conductivity of the gas mixture ($W.m^{-1}.K^{-1}$)
μ	Dynamic viscosity of the gas mixture ($kg.m^{-1}.K^{-1}$)
ν_{ik}	Stoichiometric coefficient for the i th gaseous species in the k th gas phase reaction
ρ	Density ($kg.m^{-3}$)
σ_{il}	Stoichiometric coefficient for the i th gaseous species in the l th surface reaction
τ	Viscous stress tensor ($N.m^{-2}$)
ω	Species mass fraction

Subscripts

i, j	With respect to the i th/ j th species
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Superscripts

\dagger	Transpose of vector
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