

Investigation of CNT Growth Regimes in a Tubular CVD Reactor Considering Growth Temperature

B. Zahed¹, T. Fanaei Sheikholeslami^{2,*}, A. Behzadmehr³, H. Atashi⁴

¹PhD Student, Mechanical Engineering Department, University of Sistan and Baluchestan, Zahedan, Iran

bzahed@gmail.com

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

tahere.fanaei@ece.usb.ac.ir

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

amin.behzadmehr@eng.usb.ac.ir

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

h.ateshy@hamoon.usb.ac.ir

Abstract

In Carbon nanotube (CNT) growth process via Chemical vapor deposition (CVD) method, there are two distinct regimes based on growth temperatures, so called mass transfer controlled and surface reaction controlled regimes, which represent different type of behaviour in growth. Operating in each regime has different characteristic that can influence on other operating condition effects on CNTs growth. Thus study of these regimes is important for better understanding of CNTs growth; also it helps to control of other operating conditions effect on growing CNTs. In this paper these two regimes is established and then relevant processes in reactor is studied in details. Results show that CNTs total production in mass transfer controlled regime has higher order and less sensitivity to the growth temperature compared to surface reaction controlled regime. Also produced CNTs in mass transfer controlled regime has less length uniformity compared to surface reaction controlled regime.

Keywords: carbon nanotube; chemical vapor deposition; growth regimes; growth temperature

Introduction

Carbon nanotube (CNT) has become one of the most famous and applicable nanomaterial due to their superior properties and wide range of applications. Chemical Vapor Deposition (CVD) is a common method for preparing CNTs due to its ability to produce highly ordered CNT material with large yields. Despite a huge progress in CNT research over the years, producing CNTs of well-defined properties in large quantities with a cost effective technique is a challenge. The root of this problem is the lack of proper understanding of the CNT growth mechanism. CNTs synthesis via CVD method involves many parameters such as precursors, operating pressure [1], inlet gas mixture flow rate and growth temperature [2,3] that the latter can affect on CNTs growing behavior significantly. Bases on the growth temperature there are two different types of growth regimes [4] that influence on other parameter effects

on CNTs growing. Thus understanding of processes occurring in these two regimes can be helpful to control the quality and quantity of produced CNTs. Therefore in this article a CFD model established for analysis of CVD method and then effects of growth temperature on growth behaviour of produced CNTs via CVD method is studied and discussed in details.

Materials and method

Modelled CVD hot wall reactor (fig. 1) used for CNTs fabrication in this study is a horizontal tubular reactor. Inlet gas mixture enters from inlet, heated up in preheater, and then enters into furnace zone. After surface and gas phase reactions, through the catalytic decomposition of xylene, carbon atoms released and CNTs grow on furnace wall and then gas mixture exits from the outlet.

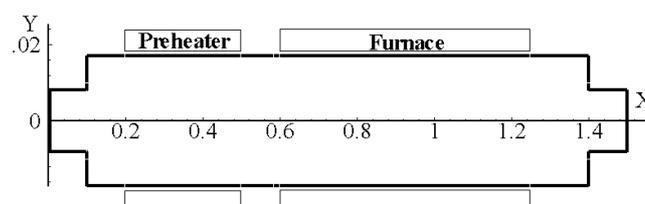


Fig. 1. Geometry of CVD Reactor

Applied CFD model solved conservation of mass, momentum, energy and species (equation (1) - (4)) with the aid of the ideal gas law:

Conservation of Mass:

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

Conservation of Momentum:

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

That for Newtonian fluids such as existent gases in CVD reactors, viscous stress tensor is as follows:

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

These equations are coupled with energy equation:

$$\begin{aligned} C_p \frac{\partial \rho T}{\partial t} = & -C_p \nabla \cdot (\rho \vec{v} T) + \nabla \cdot (\lambda \nabla T) + \\ & \nabla \cdot (RT \sum_{i=1}^N \frac{D_i}{m_i} \nabla (\ln f_i)) + \sum_{i=1}^N \frac{H_i}{m_i} \nabla \cdot \vec{J}_i - \\ & \sum_{i=1}^N \sum_{k=1}^K H_i v_{ik} (\mathcal{R}_k^g - \mathcal{R}_{-k}^g) \end{aligned} \quad (4)$$

and Species transport equation:

$$\begin{aligned} \frac{\partial (\rho \omega_i)}{\partial t} = & -\nabla \cdot (\rho \vec{v} \omega_i) - \nabla \cdot \vec{J}_i + \\ & + m_i \sum_{k=1}^K v_{ik} (\mathcal{R}_k^g - \mathcal{R}_{-k}^g) \end{aligned} \quad (5)$$

Ordinary diffusion flux \vec{J}_i obtained using Stefan-Maxwell equations and reaction rate constant determines from the modified Arrhenius equation:

$$k_{ik} = A_k T^{n_k} \exp \left(\frac{-E_k}{RT} \right) \quad (6)$$

Where A denotes the Arrhenius pre-exponential factor ($(\text{m}^3 \cdot \text{mol}^{-1})^{a-1} \cdot \text{s}^{-1}$, a is the order of reaction), n is the exponent for temperature dependence of A, E presents the activation energy ($\text{J} \cdot \text{mol}^{-1}$), R indicates the universal gas constant, $8.314 \text{ (J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$ and T refers to the absolute temperature (K).

Two volumetric reactions and four surface reactions are considered to modelling CNTs growing in the reactor (see [1]).

The set of equations was solved using the finite volume method with segregated grid and results are validated with numerical work of Endo et al. [4]. Maximum of error is obtained below 5% and good concordance between the results is seen.

Results and Discussion

The local growth rate (LGR) of CNTs in a CVD process is given by [5]:

$$LGR = \frac{K_s h_G C_G}{K_s + h_G N} \quad (7)$$

Where C_G is concentrations of reactant species in the main gas flow, K_s is chemical surface reaction rate (calculated by using modified Arrhenius equation), h_G is mass transfer coefficient and N is the number of atoms incorporated per unit volume in the deposition layer.

Where h_G calculating based on the following equations:

$$h_G = \frac{D_G}{\delta_S} \quad (8)$$

where D_G is the diffusion coefficient of the reacting species across the boundary layer in the gas phase and δ_S is gas phase boundary layer thickness:

$$\delta_S(x) = \left(\frac{\mu x}{\rho U} \right)^{1/2} \quad (9)$$

In this equation U is the bulk gas velocity, μ and ρ are the gas mixture viscosity and density respectively and x is distance from the reactor inlet from start of surface.

Local growth rate along the furnace for four different growth temperatures is represented in fig. 2. For better studying of growth temperature effects on CNTs production, CNT local growth rate is integrated along the furnace (fig. 3).

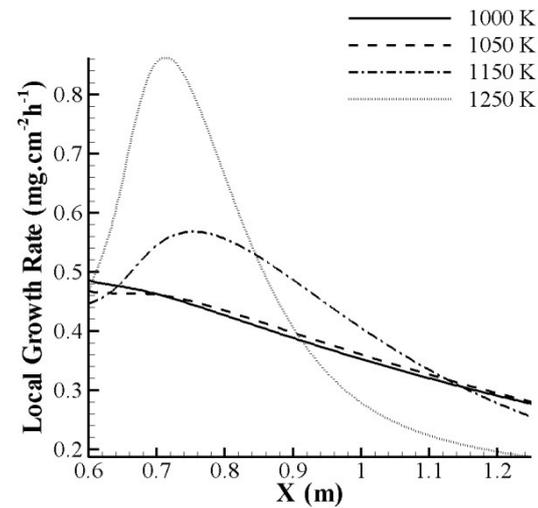


Fig. 2. Local growth rate along the furnace with four different growth temperatures

As seen in fig. 3, total production of CNTs in higher growth temperatures has less sensitivity to the temperature and in the lower range process is very sensitive to the temperature.

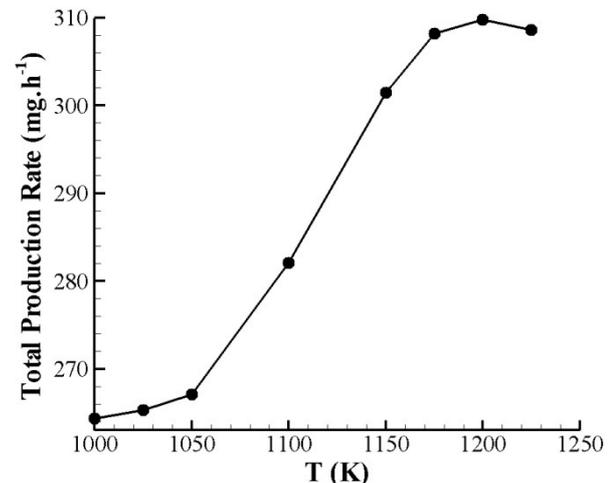


Fig. 3. CNTs total production rate versus growth temperature

Also, with calculating CNTs length uniformity by:

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

results showed produced CNTs in higher growth temperature have less length uniformity compared to lower growth temperature (fig. 4). Moreover as seen in fig. 4, increasing of temperature leads to enhancement and decreasing of length uniformity in lower temperatures and higher temperatures, respectively.

These two types of growth behaviour based on growth temperature represent two distinct regimes so called mass transfer controlled regime (1100K – 1250K) and surface reaction controlled regime (1000K – 1100K) [5].

One of the importance of understanding these two regimes is that in surface reaction controlled regime, surface reactions dominate on the process and mass transport of species through boundary layer is not important compared to mass transfer controlled regime so there is less restriction about equipment configuration and substrate location in the reactor but it has lower growth rate due to perform in lower temperature compared to mass transfer controlled regime. Also these two regimes can influence on effects of other operating conditions on CNTs growth. Thus to better control of CNTs growing, it is important to survey processes in these two regimes distinctively.

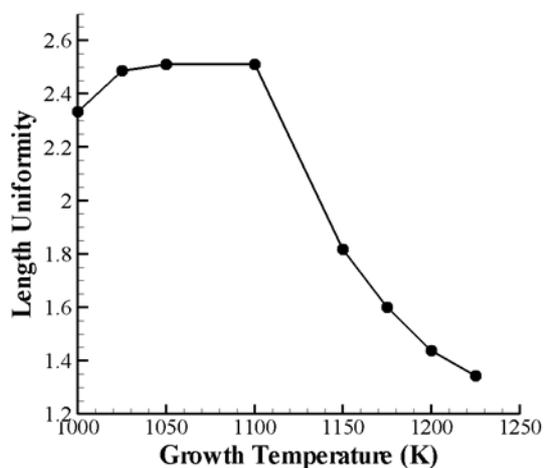


Fig. 4. CNTs length uniformity versus growth temperature

In mass transfer controlled regime (1150 K and 1250K) as seen in fig. 3, local growth rate graph has a peak in studying growth temperature between distance 70 to 80 centimetres from the inlet. Isothermal contour that is exhibited in fig. 5c and 5d (in mass transfer controlled regime), can explain this issue. As observed in fig. 5c and 5d, between 70 to 80 centimetres from inlet, the temperature reaches to fully developed conditions and maximum temperature throughout the reactor start in this distance.

Therefore kinetic rates of gas phase reactions are enhanced in mass transfer controlled regime (1150 K and 1250 K). These reactions represented thermal

decomposition of main carbon source of the CNTs growth process.

This enhancement in the kinetic rates of gas phase reactions leads to more consumption of xylene and increasing of thermal decomposition of xylene leads to more amount of by-products as other carbon sources in the region of 0.7-0.8 centimetres from the inlet. This causes decreasing of production of CNTs released carbon atoms released from xylene due to decreasing concentration of it in 0.7-0.8 centimetres region (Figs. 6c and 6d). But also increasing of production of CNTs from released carbon atoms from by-products happened due to enhancement of concentration of these species in this region due to mentioned reasons.

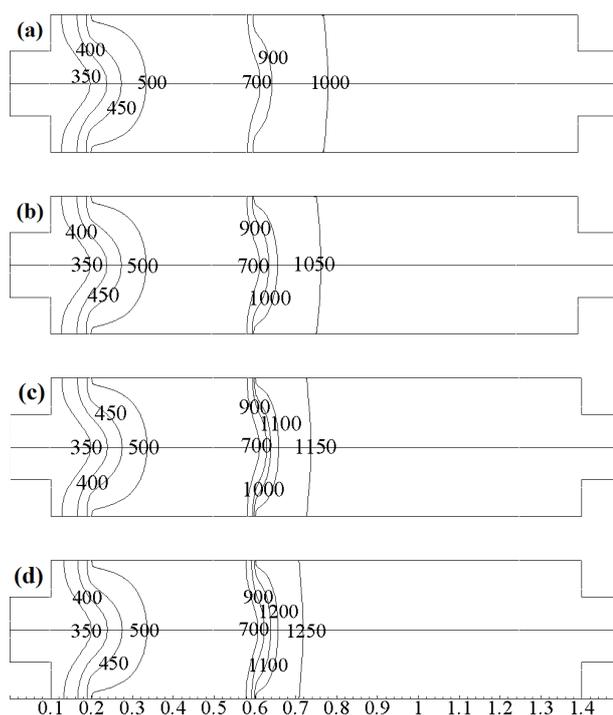


Fig. 5. Temperature distribution in the reactor with different furnace temperatures:
(a) 1000 K, (b) 1050 K, (c) 1150 K and (d) 1250 K.

The result of these reactions leads to a peak in the local CNTs growth rate in mass transfer controlled regime (fig. 2) and strong decrease of the CNT growth rate in downstream. These peak is not strong in surface reaction controlled regime (Figs. 5a and 5b) because this regime operates in lower temperature compared to mass transfer controlled regime and decomposition of xylene (fig. 6a and 6b) has not enough rate to happen in entrance of furnace region strongly and also temperature fully development delayed so decomposition of xylene happened gradually with fewer rates compared to mass transfer controlled regime.

Otherwise As seen in fig. 2, local growth rate begins in reaction controlled regime (1000K and 1050K) with higher amount at the entrance of the furnace zone but decreased along the surface.

This is due to existence of higher amount of main carbon source gas (xylene) at the entrance of furnace but along the reactor, depletion of main carbon source gas occurs in

downstream of the reactor (see Figs. 6a and 6b). Although other hydrocarbons (by-products) were produce along the furnace zone and amount of them increased because of xylene decomposition but due to xylene has more influence compared to other hydrocarbons for producing CNTs, so sum up of these effects lead to decreasing of produced CNTs in downstream. As reacting gases are consumed, their concentrations decrease with distance along the surface. Since the growth rate is proportional to the partial pressure of the reacting species, the growth rate will decrease going to downstream.

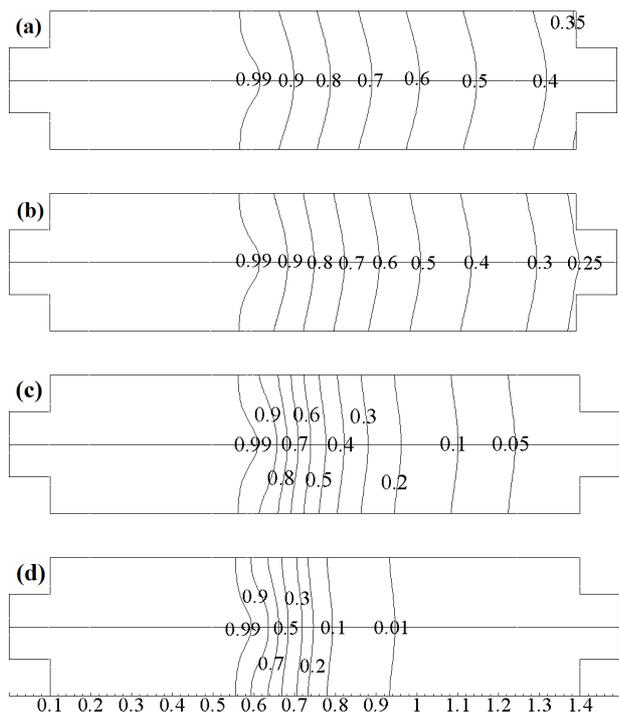


Fig. 6. Non dimensional xylene concentration (xylene consumption) throughout the reactor with various furnace temperatures: (a) 1000 K, (b) 1050 K, (c) 1150 K and (d) 1250 K.

With attention to fig. 6 and observed the percentage of consuming xylene as main carbon source gas, it is clarified that with increasing of growth temperature, consumption of source gas in entrance of furnace is increased. As seen in Figs. 6c and 6d (that growth temperature is in mass transfer controlled regime) representing xylene as the source gas is consumed completely at about the middle of the furnace zone (reaction surface). Thus depletion of main carbon sources, and in particular xylene in downstream due to fast consuming of the species in upstream is one of two major reasons for intense reduction of the local growth rate in mass transfer controlled regime.

Another important reason is related to the nature of behaviour in mass transfer controlled regime described before. As mentioned, the growth rate (equation (7)) is determined by the smaller of K_s or h_G , so in mass transfer controlled regime, growth rate determined by h_G . According to equation (8), h_G related to boundary layer thickness inversely. Since δ_s

increases along the surface (equation (9)), then effective mass transfer coefficient (h_G) decreased along the surface. Therefore because of the dependency of kinetic rate of reactions to boundary layer thickness and also due to the increasing of this thickness along the surface, in mass transfer controlled regime growth rate has reduced along the surface to downstream.

While the growth rate decrease due to the increasing of boundary layer thickness is only important in the mass transfer regime, but this decrease due to reactant depletion occurs in both the mass transfer and surface reaction controlled regimes. To sum up these two issues (increasing boundary layer thickness and depletion) leads intense reduction of local growth rate (fig. 2) after the peaks of graphs in 70-80 cm region in mass transfer controlled regime.

Another interesting issue that represented in fig. 2, is the convergence of the graphs in downstream of the reactor. This happens since gas mixture flow is fully developed in this region and boundary layer thickness has no change after that so the effect of boundary layer thickness on CNTs production in this regime is omitted proportionally. Therefore source gas depletion is the only reason left to reduction of the CNTs local growth rate in this area.

By studying the total production rate of CNTs in mass transfer controlled regime (see fig. 3), it is obvious that mass transfer controlled regime has less sensitivity to the growth temperature. This occurs because in this regime h_G dominates in the process (as mentioned) and h_G has no growth temperature sensitivity (equation (8)). Otherwise in surface reaction controlled regime, the total production rate has a strong dependency to growth temperature due to the Arrhenius dependency of kinetic rates of reactions to temperature (equation (6)) and due to in surface reaction controlled regime, K_s dominates in the process, so growth temperature affects on total production strongly.

Also as seen in mass transfer controlled regime, CNTs total production has higher order compared to surface controlled regime. This is due to reactions in mass transfer controlled regime works on higher temperatures and so higher kinetic rate for reactions.

The reason of the slight decrease of CNTs total production in mass transfer controlled regime (see fig. 6) with increasing temperature is that D_G (the diffusion coefficient of the reacting species across the boundary layer in the gas phase) decreased with increasing of temperature and thus more movement of atoms. Then decreasing of D_G leads to reduction of h_G and so reduction of growth rate according to equation (8) and (7), respectively.

As seen in fig. 4, in surface reaction controlled regime (lower temperatures) with increasing growth temperature, CNTs length uniformity is enhanced. This is due to that increasing of temperature leads to reduction of depletion problem (the major reason of decreasing of growth rate in downstream in this regime) and reduction of amount of non-using main carbon source gases (fig. 6). This leads to increasing of growth rate at downstream of the reactor and so enhancement of CNTs length uniformity along the reaction surface (furnace). But in temperatures higher than 1100 K, length uniformity reduced strongly. This is due to that the reactions, happen in the mass transfer

controlled regime and in this regime boundary layer thickness has important effects on growth rate. Therefore due to this reason, mass transfer controlled regime naturally has higher non-uniformity compared to surface reaction controlled regime. But the reason of increasing this non-uniformity with increasing growth temperature is the source gas in start of furnace consumed exceedingly and therefore higher temperature in entrance makes higher consumption of species in upstream then deficiency of carbon source in downstream leads to reduction of growth rate in that region and this makes strong non-uniformity. Thus with increasing reaction temperature it gets worst. In surface reaction controlled regime unused main carbon source gas exist in end of the reactor but in this regime main source gas completely consumed before the end of reactor so increasing of temperature has negative effects on length uniformity in this regime compared to surface reaction controlled regime.

In CNTs fabrication, results of local growth rate (fig. 2) and CNTs total production versus inverse growth temperature (fig. 3) can be used for selecting the best configuration of substrates. For example, if CNTs is needed to grow in high temperature e.g. 1250 K (for fewer defects in their structure or some desired properties), fig. 3 can clarified that desired temperature is in mass transfer controlled regime so due to mass transport through the boundary layer is important in this regime, substrates should be place edge to edge for reaching same gas mixture flow to reaction surface (in surface controlled regime substrates can place without this restriction, see [4]). Also with according to fig. 2, can be clarified that with placing the substrates in distance between 0.7-0.8 meters from the inlet, the CNTs growth rate can reach to maximum of available amount. This proved again the importance of studying CNTs production by CVD process, with considering of these two distinct regimes that neglected in previous works in this regard. Therefore from the results of this study about CNTs local growth rate and total production can be used for optimization of CNTs production. Also with an investigation of the relation between amount of CNTs growth rate and quality, defect of CNTs structure, production of amorphous carbon by experimental studies may reach to a way to control of CNTs properties probably.

Conclusion

In this work effects of growth temperatures on CNTs growth behaviour is studied and therefore established two different regimes with distinct behaviours for CNTs growth rate based on different growth temperatures (mass transfer controlled regime and surface reaction controlled regime).

The results showed that increasing of growth temperature leads to enhancement of CNTs total production in surface reaction controlled regime (very sensitive to temperature) while slight decreasing of CNTs total production in mass transfer controlled regime (almost insensitive to temperature).

Also increasing of growth temperature leads to slight increase in CNTs length uniformity in surface reaction controlled regime while leads to strong decrease of length uniformity in mass transfer controlled regime.

In addition, was clarified that order of CNTs total production in mass transfer controlled regime is higher than surface reaction controlled regime due to works in higher temperatures. Also order of CNTs length uniformity in mass transfer controlled regime is lower compared to surface reaction controlled regime due to nature of processes of these regimes.

The results of this research can help for better scientific understanding of processes in CNTs fabrication by CVD and can be used for optimization of CNTs production for obtain higher yield of CNTs with effective costs.

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List of Symbols

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
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 ith 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 kth gas phase reaction ($mole.m^{-3}.s^{-1}$)
R_{-k}	Reverse reaction rate of the kth gas phase reaction ($mole.m^{-3}.s^{-1}$)
R_l^s	Reaction rate for the lth 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 ith gaseous species in the kth gas phase reaction
ρ	Density ($kg.m^{-3}$)
σ_{il}	Stoichiometric coefficient for the ith gaseous species in the lth 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

Superscripts

c Due to ordinary diffusion

T Due to thermal diffusion

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