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ORIGINAL RESEARCH PAPER

Numerical Analysis of Inlet Gas-Mixture Flow Rate Effects on Carbon Nanotube Growth Rate

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Abstract

The growth rate and uniformity of Carbon Nano Tubes (CNTs) based on Chemical Vapor Deposition (CVD) technique is investigated by using a numerical model. In this reactor, inlet gas mixture, including xylene as carbon source and mixture of argon and hydrogen as carrier gas enters into a horizontal CVD reactor at atmospheric pressure. Based on the gas phase and surface reactions, released carbon atoms are grown as CNTs on the iron catalysts at the reactor hot walls. The effect of inlet gas-mixture flow rate, on CNTs growth rate and its uniformity is discussed. In addition the velocity and temperature profile and also species concentrations throughout the reactor are presented.

Keywords: *Chemical Vapor Deposition; Carbon Nanotube; Numerical Analysi*

1. Introduction

Carbon nanotube is a tubular structure, formed by carbon atoms with the diameter of order of nanometer and length of micrometer. It has a wide range of potential applications. Among them, it could be used in nano-electronic components, as electrodes in organic light-emitting diodes and as gas detector. After Iijima's discovery in 1991 [1], carbon nanotubes becomes the most popular nano material for research and industrial research centres because of its unique physical, electrical and thermal and mechanical properties [2-4].

In recent years, the widespread researches have been done to explain the structural theory, production methods and possible applications of CNTs. Some of them lead to industrial applications.

However, one of the important issues in this field is insufficient production and high cost of produced CNTs. The latter pushes the researchers to find more simple production method for these materials with lower cost. Various methods have been used to produce CNTs. Among them, Chemical Vapor Deposition (CVD) becomes the most popular approach, due to its lower cost, simplicity and high mass production. In atmospheric pressure CVD technique, a high temperature is required to decompose the molecules of inlet gases and prepare necessary components to form carbon nanotube. Therefore, CNTs growth rate depends on various parameters such as inlet gas flow rate, hydrocarbon concentration, substrate temperature, catalyst and etc.

Numerical simulation prior to experimental work is useful for finding the appropriate conditions to achieve a desired growth rate and uniformity. In particular, computational fluid dynamics help researchers to well understand and analyze the

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Nomenclature

C_p	Specific heat of the gas mixture ($J.kg^{-1}.K^{-1}$)
$\mathbb{D}^T$	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 $J.mole.K^{-1}$)
$\mathcal{R}_k$	Forward reaction rate of the kth gas phase reaction ($mole.m^{-3}.s^{-1}$)
$\mathcal{R}_{-k}$	Reverse reaction rate of the kth gas phase reaction ($mole.m^{-3}.s^{-1}$)
$\mathcal{R}_l^s$	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 ith/jth species
	Superscripts
c	Due to ordinary diffusion
T	Due to thermal diffusion

reaction mechanisms, growth rate, transport rate, and other important phenomenas. In this regard, Grujicic et al. [5] established a CNT growth model, to explain the details of gas-phase reactions, surface reactions and the included amorphous carbon components in deposited CNTs. Also, Endo et al. [6] proposed a CFD model to predict the deposition rate of nanotubes via catalytic decomposition of xylene in a CVD reactor. Using this model, they calculate the total production rates of CNT with various inlet xylene concentrations. Similar works are done by Kuwana et al. [7], Puretzky et al. [8], Andrew and Chui [9], and Ma et al. [10] to find the appropriate conditions for CNT film deposition rate using different modeling methods.

In this research, an atmosphere pressure CVD reactor for producing CNTs has been numerically modeled. The effects of inlet gas-mixture flow rate on the growth rate and uniformity of CNTs is presented and discussed.

2. Problem Description

Geometry of the reactor is shown in Figure 1. It is a tubular hot wall horizontal reactor that works in atmosphere pressure, with 34 mm diameter, 1.5 m length. The inlet and outlet diameter is 17 mm. Reactor walls is made of quartz. Inlet gas mixture, including xylene with 3750 ppm concentration as process gas and argon with 10% hydrogen as carrier gas enter the reactor at 300K. Gas mixture heated up to 513K through the preheater and then enters into the furnace zone for which the gas mixture heated up to 975K.Preheater zone is considered from 20 to 50 cm from the inlet section and furnace zone from 60 to 125cm from the inlet. Except for the preheater and furnace walls that are isothermal (513K and 975K respectively), other walls considered to be adiabatic. Reactions that is used in this model, is shown in table 1. There are two gas phase reactions and four surface reactions apply for this model. All reactions are irreversible. Also kinetic rate coefficients determined with no catalyst deactivation assumption.

The considered process is described as follow:

Gas mixture enters the horizontal reactor that works at atmosphere pressure. Layer of iron catalyst particles covers the reactor hot walls. Inlet gas mixture, including xylene (C_8H_{10}) as process gas and carrier gas (argon with 10% hydrogen) continuously feed the reactor.

Table 1
Gas phase and Surface Reactions

Gas Phase Reactions	Pre-Exponential Factor	Activation Energy	Temp Exp-onent
$C_8H_{10}+H_2 \rightarrow C_7H_8+CH_4$	2.512e8	1.674e8	0
$C_7H_8+H_2 \rightarrow C_6H_6+CH_4$	1.259e11	2.224e8	0
Surface Reactions			
$C_8H_{10} \rightarrow 8C+5H_2$	0.00034	0	0
$C_7H_8 \rightarrow 7C+4H_2$	0.00034	0	0
$C_6H_6 \rightarrow 6C+3H_2$	0.00034	0	0
$CH_4 \rightarrow C+2H_2$	0.008	0	0

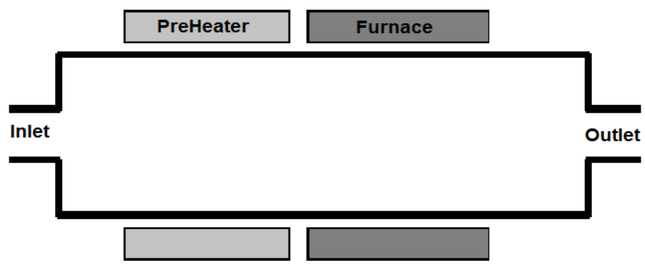

Fig. 1. Schematic of CVD Reactor

In this process, two gas phase reactions and four surface reactions are considered. Carbon nanotubes grow at the sites of the iron catalyst.

For modeling the process some assumptions can be used to reduce computational complexity for solving the governing equations. These are:

- Gas mixture has continuum behavior.
- Ideal gas behavior.
- Laminar flow regime
- Viscous dissipation is neglected
- Steady state condition

3. Mathematical modeling

Considering the mentioned assumptions and two dimensional axisymmetric model of the reactor, the governing equations are as follow:

Continuity Equation:

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

Navier-Stokes Equation:

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

For Newtonian fluids viscous stress tensor is as follows:

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

Energy Equation:

$$C_p \frac{\partial \rho T}{\partial t} = -C_p \nabla.\left(\rho \vec{V} T\right) + \nabla.(\lambda \nabla T) + \nabla.\left(RT \sum_{i=1}^{N} \frac{\mathbb{D}_i^T}{m_i} \nabla(\ln f_i)\right) + \sum_{i=1}^{N} \frac{H_i}{m_i} \nabla.\vec{j}_i - \sum_{i=1}^{N} \sum_{k=1}^{K} H_i \nu_{ik}\left(\mathcal{R}_k^g - \mathcal{R}_{-k}^g\right) \quad (4)$$

and Species Transport Equation:

$$\frac{\partial(\rho \omega_i)}{\partial t} = -\nabla.\left(\rho \vec{V} \omega_i\right) - \nabla.\vec{j}_i + m_i \sum_{k=1}^{K} \nu_{ik}\left(\mathcal{R}_k^g - \mathcal{R}_{-k}^g\right) \quad (5)$$

These equations solve subject to the following boundary conditions:

- Reactor walls are impermeable and no slip condition is considered for the velocity at walls.
- Constant temperature at the heated walls and zero heat flux at the adiabatic walls.
- At the non-reactant walls, mass flux vector for each species must be zero.
- Due to surface reactions, net mass production rate $\mathcal{P}_i$ for ith gas specie at the surface of furnace is:

$$\mathcal{P}_i = m_i \sum_{l=1}^{L} \sigma_{il} \mathcal{R}_l^s \quad (6)$$

Thus the normal velocity on the surface of furnace can be express by:

$$\vec{n}.\vec{V} = \frac{1}{\rho} \sum_{i=1}^{N} m_i \sum_{l=1}^{L} \sigma_{il} \mathcal{R}_l^s \quad (7)$$

- Total net mass flux of ith specie, normal to the surface of furnace must be equal to P_i. Thus:

$$\vec{n}.\left(\rho \omega_i \vec{V} + \vec{j}_i^c + \vec{j}_i^T\right) = m_i \sum_{i=1}^{L} \sigma_{il} \mathcal{R}_l^s \quad (8)$$

4. Numerical analysis and validation

The governing equations are discretized using finite volume approach. SIMPLE algorithm is adopted for the pressure-velocity coupling.

Physical properties (viscosity, thermal conductivity and specific heat capacity) for each species are assumed to be thermal dependent [11]. These properties for the gas mixture obtain using the mixing law.

Convergence criterion for energy equation is 10^{-10} and for other equations (continuity, momentum and species transport) is 10^{-6}.

Non-uniform structured grid that is refined at the near walls where the gradient of the parameters are important is selected. Several different grid distributions have been selected to ensure the results are grid independence. The selected grid number is 10998. In addition to show the accuracy of the results, comparisons are made between the numerical results and experimental results of Endo et al. [6] for two different xylene concentrations. It is shown in figure 2. As seen good concordance between the results is obtained (Maximum of error 5%).

Thus the numerical procedure is reliable and can well predict the process throughout the reactor.

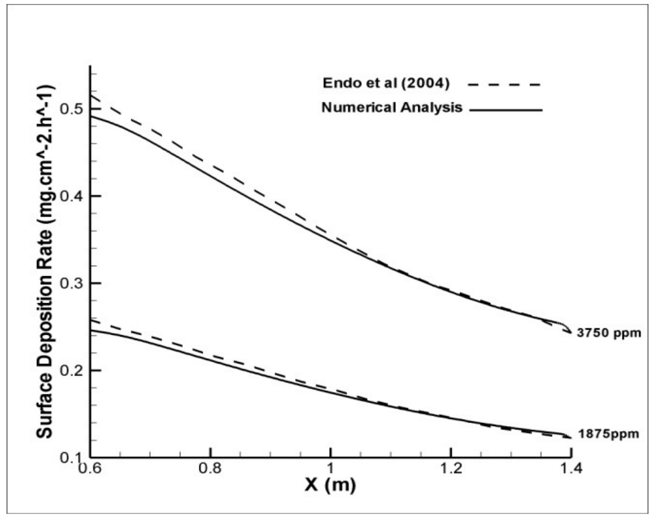

Fig. 2. Validation with Endo et al. work [6]

5. Results and discussion

The thermo-fluid behaviors of the inlet gas mixture throughout the reactor are investigated. Its effects on the deposition rate and contour of velocity, temperature and material concentration will be presented and discussed. Figure 3 shows the effect of different inlet gas mixture flow rate (230, 460, 1145,3440 sccm) on the growth rate and uniformity of CNT along the furnace zone. As seen with increasing the inlet gas mixture flow rate, CNTs growth rate and its uniformity improve.

It is partially because of more available carbon source near the walls that is covered with layer of iron catalyst particles. This is clearly shown by velocity contours in figure 4. As it is seen velocity at the near wall region increases with the gas mixture flow rate. There are two non-uniformities on the velocity profile. The first one occurs near the entrance because of sudden enlargement at the inlet. The second one appears at the starting the furnace region for which a chain of chemical reactions takes place.

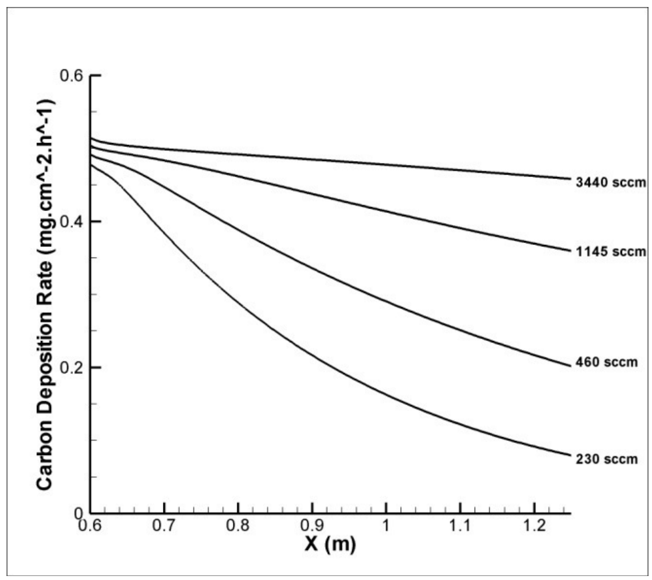

Fig. 3. Local CNT growth rate in furnace zone with various inlet flow rates

The uniformity on the velocity profile improves with increasing the inlet flow rate. This could be more clearly presented by the flow stream line. Figure 5 shows the effect of inlet gas mixture on the uniformity of the flow stream line throughout the reactor with increasing the inlet gas flow rate. The uniformity of the streamline could result more uniform CNTs growth.

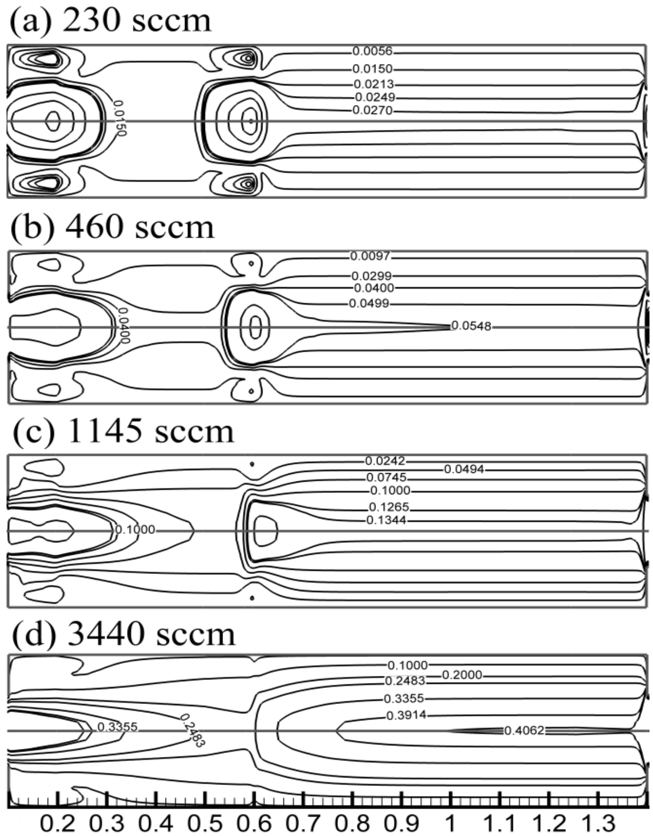

Fig. 4. Velocity contours (m/s) in reactor for different flow rates

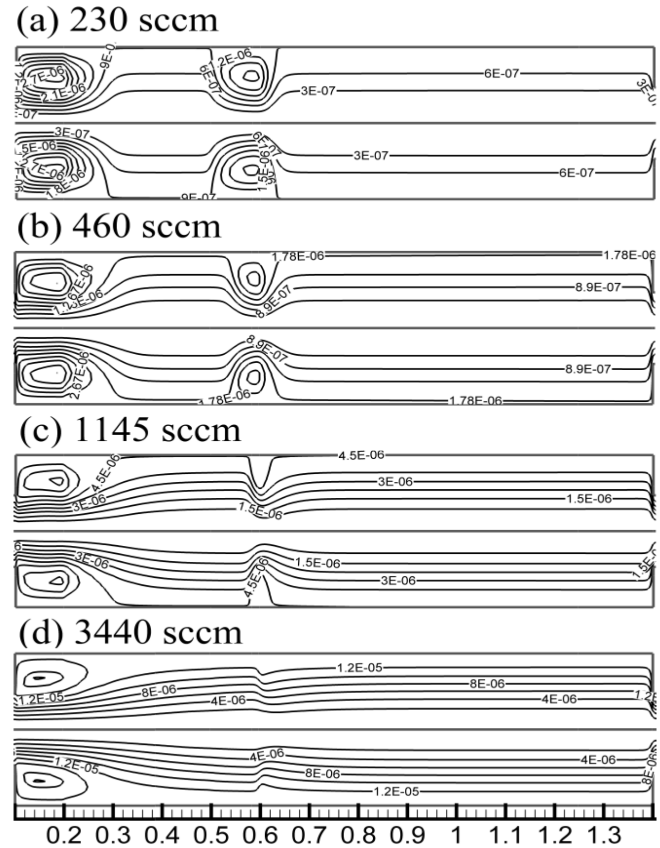

Fig. 5. Stream lines (kg/s) in reactor for various flow rates

Hydrocarbon concentration throughout the furnace zone is a significant parameter on the CNTs growth rate. It is shown in figure 6. As seen increasing the inlet gas mixture causes higher hydrocarbon concentration further downstream at the furnace zone. The latter could well uniformly saturate the iron catalyst particles entire the region. In spite of positive effect of higher inlet gas mixture flow rate on the CNT growth and its uniformity there is a negative aspect on the hydrocarbon concentration.

As seen in figure 6, hydrocarbon concentration increases at the outlet with increasing the inlet flow rate. This shows that with increasing the inlet flow rate, there is more non-used hydrocarbon at the outlet. The latter augments the process cost and in some case may cause an environmental pollution.

To see the concentration of other reaction products throughout the reactor figure 7 is presented for different inlet gas mixture flow rate. In general the gas phase reaction through the reactor partially increases along the furnace length.

At the lower gas mixture inlet, C_7H_8 production as result of gas phase reaction increases. However, at the same time it consumes because of surface reaction of C_7H_8. The latter causes to see the concentration of C_7H_8 decreases from the certain distance of inlet of furnace zone in the case of lower inlet gas mixture (see figure 7a and 7b). Increasing the inlet gas flow rate produces significant amount of C_7H_8 throughout the reactor. In other word the rate of C_7H_8 production as a result of gas phase reaction is more important than the rate of C_7H_8 consumption because of surface reaction. This figure clearly shows that the effect of C_6H_6 and CH_4 in CNTs production is less important than the contribution of C_7H_8.

Figure 8 shows the contour of temperature for different inlet gas mixture flow rate throughout the reactor. It is well known that the gas phase and gas surface reaction depend (through the Arrhenius equation) on the reactor temperature. As seen for a given furnace temperature with increasing the inlet gas mixture flow rate, higher temperature appears further downstream from the heating zone and consequently it is limited the reactions zone.

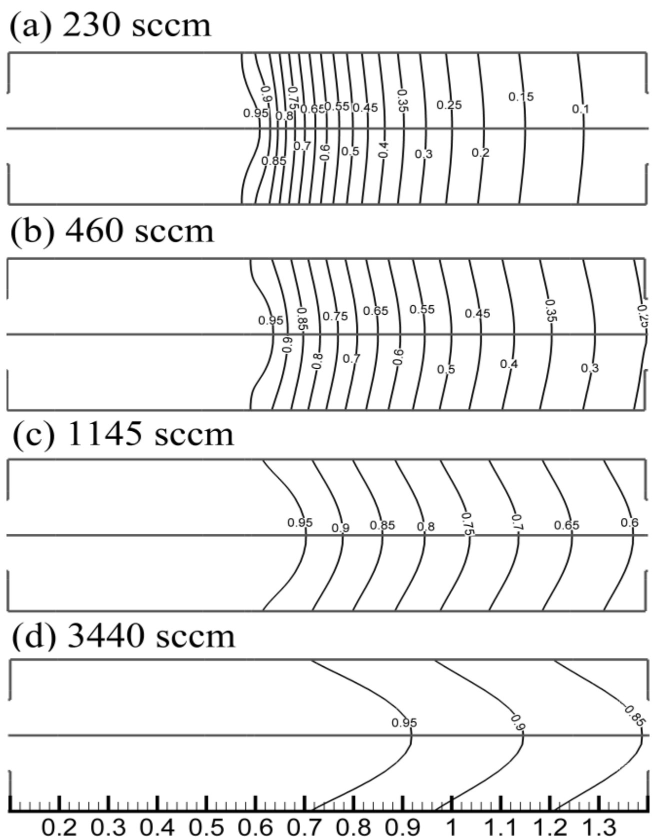

Fig. 6. Non dimensional inlet hydrocarbon (xylene) concentration in various flow rate

This causes decreasing on C_8H_{10} consumption (more available C_8H_{10}) and then decreasing of C_7H_8, C_6H_6 and CH_4 (based on the reaction in table 1). More C_8H_{10} intensifies the CNTs growth rate.

6. Conclusion

The effects of inlet gas-mixture flow rate on the growth rate and uniformity of CNTs are investigated numerically. Increasing the inlet gas flow rate augments the rate of CNTs growth and improves its uniformity. It is shown that more uniform streamline could be seen at the furnace zone with increasing the inlet gas flow rate. While the latter decreases the flow temperature at the entrance of heating zone. It is caused to have more available C_8H_{10} which has significant positive effect on both growth rate and uniformity of CNTs. It is seen that the effect of C6H6 and CH_4 in CNTs production is less important than the contribution of C_7H_8.

An atmosphere pressure CVD reactor for producing CNTs has been numerically modelled. The effects of inlet gas-mixture flow rate on the growth rate and uniformity of CNTs is presented and discussed.

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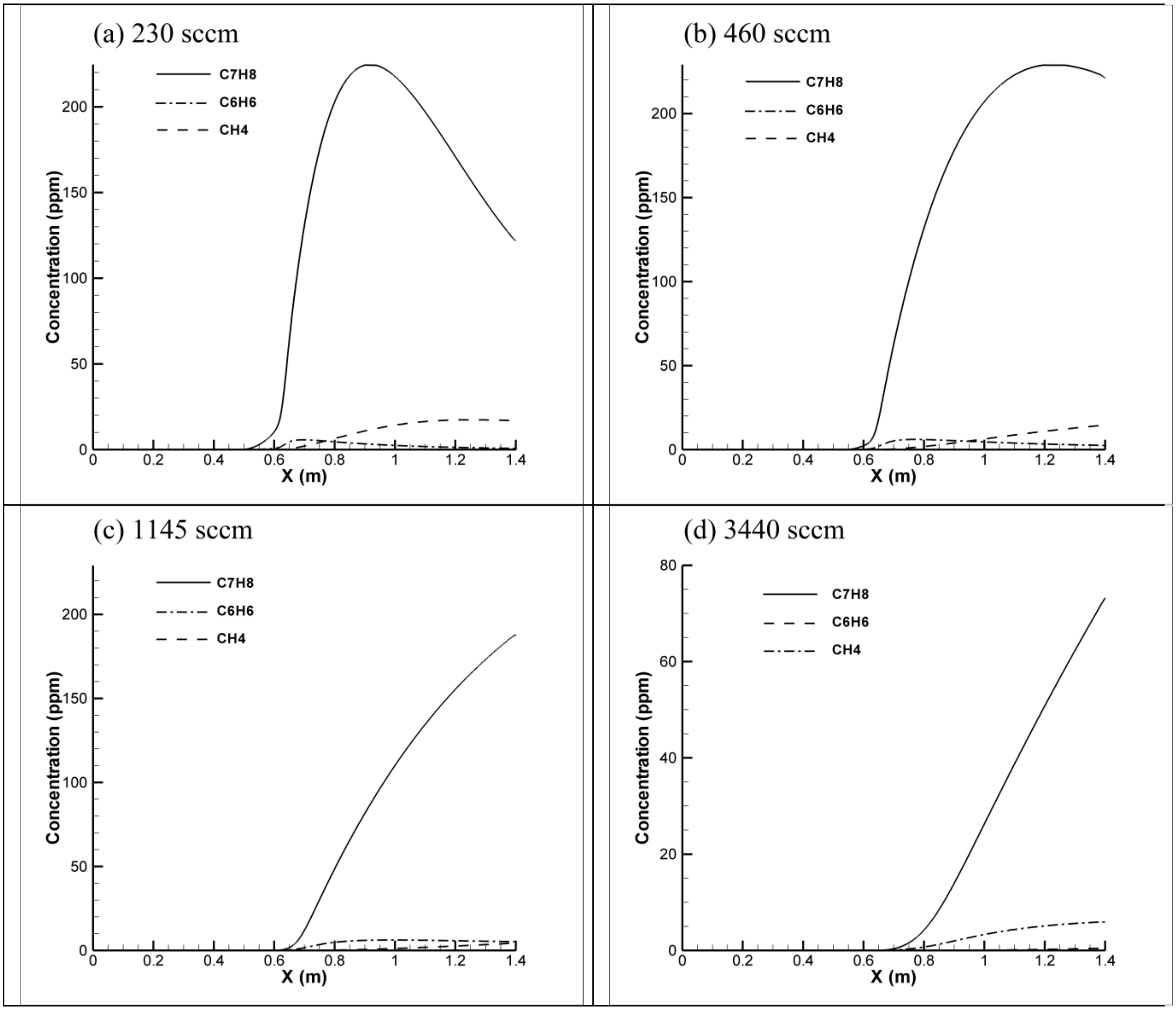

Fig. 7. Different gas concentrations for (a) 230 sccm flow rates (b) 460 sccm flow rates (c) 1145 sccm flow rates (d) 3430 sccm flow rates

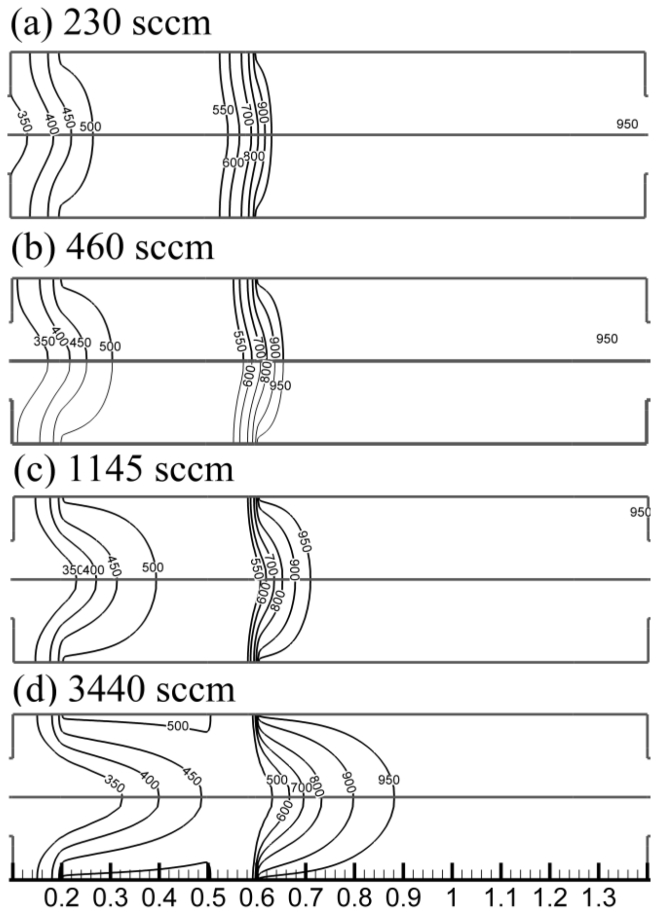

Fig. 8. Temperature Contour (K) throughout the reactor for different gas mixture flow rates