A NUMERICAL STUDY OF HEAT AND MASS TRANSFER AT CATALYTIC METHANE STEAM REFORMING IN STEADY TWO-DIMENSIONAL FLOW IN MICROCHANNEL.

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ABSTRACT

This research consists of the numerical investigation of the influence of sequence of the surface catalytic reactions on the development of heat and mass transfer at steam methane reforming in a two-dimensional microchannel reactor. The numerical simulation was performed within the framework of two-dimensional stationary Navier-Stokes equations for laminar, compressible, multicomponent gas with variable thermophysical properties of the gas mixture, depending on the temperature and composition of the mixture. The catalytic reactions make transverse moles flux in the gas mixture and reduce the dimensionless coefficients of heat and mass transfer. The expressions for evaluating the magnitude of the local heat and mass transfer coefficients disturbance at catalytic reaction on the wall were obtained under the film theory assumption, they adjusted with the numerical data. The thermophysical properties dependence on the mixture composition and temperature also changes the values of the dimensionless heat and mass transfer coefficients. The effect of variation in the local Sherwood and Nusselt numbers with temperature is greater than the effect of variation with changes in the molar composition of the mixture or the effect of nonzero mole flux from the walls.

INTRODUCTION

Catalytic reactions are widespread in chemical industry and technology. One of the most important catalytic processes is methane steam reforming, it is the cheapest and most efficient way to produce hydrogen, which can be used to power fuel cells. Among the peculiarities of methane steam reforming are the multistage process and the fact that the sum of molar flow onto to the wall and off of the wall is not equal to zero.

Of great interest is the implementation of methane steam reforming on the basis of micro-technology. It will provide a portable device for hydrogen production.

NOMENCLATURE

a	[m^{-1}]	Specific molar flux
Cp	[J/(kgK)]	Specific heat
C	[mol/m^3]	Molar concentration
D_h	[m]	Hydraulic diameter
D	[m^2/s]	Diffusion coefficient
f	[-]	magnification factor
h	[J/kg]	Specific enthalpy
$h0$	[J/kg]	Standard enthalpy of formation
H	[m]	Channel height
k	[mol/m^{2}s]	Mass transport coefficient
M	[kg/mol]	Molar weight
N	[mol/m^{2}s]	Molar flux
P	[kPa]	Pressure
q	[W/m^2]	Heat flux
r	[mol/(m^{2}s)]	Reaction rate
R_{un}	[J/molK]	Gas constant
R	[-]	Flux ratio
s	[mol/(m^{2}s)]	Rate of component appearance (disappearance)
T	[K]	Temperature
U	[m/s]	Longitudinal velocity
V	[m/s]	Transverse velocity
x	[m]	Cartesian axis direction
X	[-]	Mole fraction
y	[m]	Cartesian axis direction
Y	[-]	Mass fraction

Greek characters

α	[W/m^{2}K]	Heat transfer coefficient
θ	[-]	Correction factor
λ	[W/mK]	Thermal conductivity
μ	[kg/ms]	Dynamic viscosity
ρ	[kg/m^3]	Density

Subscripts

0	Wall
t	Total
i	Index
j	Index
loc	local
av	Average
b	Bulk

The high surface to volume ratio of microreactors provides high efficient heat transfer. The small radius of the microchannel results in short times for radial diffusion and thus good mass transfer to catalyst layers on the channel walls.

By means of computational fluid dynamic simulations transport phenomena can be quantified. However these calculations are very time consuming. For general reactor design the correlations that describe the dependencies of the Nusselt and Sherwood numbers along the channel axial coordinate are preferred. [1]

Results on single-phase heat transfer are contradictory. In the laminar regime, Peng et al. [2], Qu et al. [3] obtained data for Nusselt number well below the values predicted by classical theory. On the contrary, Qu and Mudawar [4] conducted both experimental and numerical investigations and found good agreement of measured temperature distributions with the numerical predictions based on the convectional mass, momentum and energy equations. Gamrat et al [5] performed both two- and three-dimensional numerical analysis of microchannel convection. The results of their numerical simulation confirmed that the continuum model of conventional mass, Navier-Stokes and energy equations of adequate accuracy in representing the microchannel flow and heat transfer characteristics. Jiang-Tao Liu et al [6] investigated the two dimensional low Reynolds number convection of water in microchannel with combination of locally heated wall boundary condition and temperature-dependent viscosity and thermal conductivity of liquid water. Heat transfer performance was evaluated by comparing with constant-property solutions. They noted that the variable-property curves are always higher than their constant-property counterparts.

The Sherwood number correlation can be achieved if the Nusselt correlation is converted using the Chilton-Colburn analogy [7] i.e. substitution of the Sherwood number for the Nusselt number, and of the Schmidt number for the Prandtl number.

The purpose of this paper is to numerically investigate the correlations between the thermal, diffusion and physicochemical processes under the variable thermophysical properties of the compressible, multicomponent gas mixture, depending on the temperature and composition of the mixture and the catalytic reactions when the sum of molar flow onto to the wall and off of the wall is not equal to zero.

MASS AND HEAT TRANSFER AT CATALYTIC REACTIONS

High net mass transfer rates across phase boundaries increase the heat and mass transfer coefficients, if the mass transfer is toward the boundary, and reduce them in the reverse situation. The magnitudes of such changes are dependent on the system geometry, boundary conditions, and they are accompanied by the effects of changes in physical properties.

Heat and mass transfer coefficients are defined as follows:

$$k^*_{x,loc} = \frac{N_i - X_{i0}N_t}{c_t \Delta xi} \tag{1}$$

$$\alpha^*_{x,loc} = \frac{q_w + \sum_i s_{s,i} h_i M_i}{T_w - T_b} \tag{2}$$

The asterisks imply that the distortions of the concentration and temperature profiles resulting from high net mass transfer rates are being included.

The relation between high net transfer coefficients and mass transfer coefficient under infinitesimal rate of mass transfer:

$$k_{x,loc} = \lim_{Nt \to 0} k^*_{x,loc} \tag{3}$$

$$\alpha_{x,loc} = \lim_{\sum_i s_{s,i} h_i M_i \to 0} \alpha^*_{x,loc} \tag{4}$$

The expressions for evaluating the magnitude of the local heat and mass transfer coefficients disturbance at catalytic reaction on the wall under the film theory assumption can be achieved using the technique described in Bird [8] if we replace the constant concentration boundary conditions $X(0)=x_0$ with constant mole flux $X'(0)=a$ at the wall.

$$R_T = \frac{(\sum_j N_{j0} Cp_j)(T_0 - T_b)}{q_0} \tag{5}$$

$$R_m = \frac{(X_{i0} - X_{ib})\sum_j N_{j0}}{ac_t D} \tag{6}$$

The results for heat and mass transfer can be summarized in following equations:

$$\theta_T = \alpha^*/\alpha = \frac{\ln(R_T + 1)}{R_T} \tag{7}$$

$$\theta_m = k^*/k = \frac{\ln(R_m + 1)}{R_m} \tag{8}$$

Equations (7, 8) give the correction factors which the mass and heat transfer coefficients at infinitesimal fluxes must be multiplied to obtain the coefficients at high net mass transfer rates. It should be noted that these relations were derived for laminar flow and constant physical properties.

NUMERICAL SIMULATION METHOD

The 2D gas flow and transfer processes in a slot 2D microchannel at chemical transformations activated on channel walls were simulated numerically in the framework of Navier-Stokes equations of a laminar flow of multicomponent compressible gas:

$$\frac{\partial(\rho U)}{\partial x} + \frac{\partial(\rho V)}{\partial y} = 0 \tag{9}$$

$$\frac{\partial(\rho U^2)}{\partial x} + \frac{\partial(\rho UV)}{\partial y} + \frac{dP}{dx} = \frac{\partial}{\partial x}\left(\mu\left(2\frac{\partial U}{\partial x} - \frac{2}{3}\left(\frac{\partial U}{\partial x} + \frac{\partial V}{\partial y}\right)\right)\right)$$
$$+ \frac{\partial}{\partial y}\left(\mu\left(\frac{\partial U}{\partial y} + \frac{\partial V}{\partial x}\right)\right) \tag{10}$$

$$\frac{\partial(\rho UV)}{\partial x} + \frac{\partial(\rho V^2)}{\partial y} + \frac{dP}{dy} = \frac{\partial}{\partial y}\left(\mu\left(2\frac{\partial V}{\partial y} - \frac{2}{3}\left(\frac{\partial U}{\partial x} + \frac{\partial V}{\partial y}\right)\right)\right)$$
$$+ \frac{\partial}{\partial x}\left(\mu\left(\frac{\partial U}{\partial y} + \frac{\partial V}{\partial x}\right)\right) \tag{11}$$

$$\frac{\partial(\rho Uh)}{\partial x}+\frac{\partial(\rho Vh)}{\partial y}=\frac{\partial}{\partial x}\left(\sum h_i \rho D_{im}\frac{\partial Y_i}{\partial x}\right)+\frac{\partial}{\partial y}\left(\sum h_i \rho D_{im}\frac{\partial Y_i}{\partial y}\right)+$$

$$+\frac{\partial}{\partial x}\left(\lambda\frac{\partial T}{\partial x}\right)+\frac{\partial}{\partial y}\left(\lambda\frac{\partial T}{\partial y}\right)+U\frac{\partial P}{\partial x}+V\frac{\partial P}{\partial y}+\mu\left(\frac{\partial U}{\partial y}+\frac{\partial V}{\partial x}\right)^2 \qquad (12)$$

$$\frac{\partial(\rho UY_i)}{\partial x}+\frac{\partial(\rho VY_i)}{\partial y}=\frac{\partial}{\partial x}\left(\rho D_{im}\frac{\partial Y_i}{\partial x}\right)+\frac{\partial}{\partial y}\left(\rho D_{im}\frac{\partial Y_i}{\partial y}\right) \qquad (13)$$

$$P=\frac{\rho R_{un}T}{M} \qquad\qquad M=\frac{1}{\sum Y_i/M_i} \qquad (14,15)$$

Viscosity μ and heat conductivity λ of the gas mixture depend on component temperature and concentration; they are calculated by the following equations [9−10]:

$$\mu=\sum_{i=1}^{n}\frac{\mu_i X_i}{\sum_{k=1}^{n}G_{ik}X_k} \qquad (16)$$

$$\lambda=\sum_{i=1}^{n}\frac{\lambda_i X_i}{\sum_{k=1}^{n}A_{ik}X_k} \qquad (17)$$

$$G_{ik}=\frac{1}{2\sqrt{2}}\frac{\left(1+(\mu_i/\mu_k)^{1/2}(M_k/M_i)^{1/4}\right)^2}{(1+M_i/M_k)^{1/2}} \qquad (18)$$

$$A_{ik}=\frac{1}{2\sqrt{2}}\frac{\left(1+(\lambda_i/\lambda_k)^{1/2}(M_i/M_k)^{1/4}\right)^2}{(1+M_i/M_k)^{1/2}} \qquad (19)$$

Values of viscosity and heat conductivity of every mixture component were set by polynomial functions of temperature of the 5th degree, plotted on the basis of references of [11]. For numerical simulations with constant properties the viscosity and heat conductivity were defined according equations (16,17) and initial values of temperature and mole concentrations. Diffusion coefficient and enthalpy of the mixture were determined as:

$$D=\frac{9.99\cdot10^{-5}T^{1.75}}{P} \qquad (20)$$

$$h=\sum_{i}^{N}Y_i h_i \qquad\qquad h_i=h_{i,0}+\int_{298}^{T}Cp_i dT \qquad (21,22)$$

The capacity at a constant pressure was determined as a polynomial function of temperature.

The system of Navier-Stokes equations was written in the stream function-vorticity formulation, and it was solved by the finite-difference method according to implicit three-layer difference scheme. The differential scheme was approximated with the so-called cross scheme. To solve the system of algebraic equations, derived by substitution of derivatives by their difference approximations, we have used the Seidel iteration method. A uniform rectangular mesh was used. At mach numbers below 0.005 the hydrodynamic pressure drop in the channel was not taken into account to reduce the time of calculations. The shock velocity profile was set at the channel inlet together with zero transverse velocity and constants over the channel cross-section: mixture temperature and mass concentrations of initial reaction components, such as methane

and steam. Calculations were carried out in assumption of mirror symmetry of a stationary flow relative to the middle plane of the flow, where only a half of the channel was considered. The no-slip conditions were set on the channel walls for the velocity components. The following boundary conditions were used on the wall within the reaction zone:

$$-\rho D_i\frac{\partial Y_i}{\partial y}=s_{s,i}M_i, \qquad (23)$$

$$-\lambda\frac{\partial T}{\partial y}=\sum_i s_{s,i}h_i M_i+q_w \qquad (24)$$

In front of the reaction zone in the channel there was a region without reactions and heating for stabilization of the mixture velocity profile.

Methane steam reforming is a complex process, consisting not only of some reactions on a catalyst, but also including reagent and product exchange between the gas phase and reaction zone. The following mechanism of methane steam reforming is suggested in [12], where the main reactions are

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 \qquad (25)$$

$$CH_4 + 2H_2O \Leftrightarrow CO_2 + 4H_2 \qquad (26)$$

$$CO_2 + H_2 \Leftrightarrow CO + H_2O \qquad (27)$$

It was shown for these reactions that their rates are determined by partial pressures and rates of component absorption on the active sites of a catalyst. The derived expressions for the reaction rates depend on partial pressures of the components and temperatures as [12]:

$$r_1=\frac{k_1\left(\frac{P_{CH_4}P_{H_2O}^{0.5}}{P_{H_2}^{1.25}}\right)\left(1-\frac{P_{CO}P_{H_2}^3}{K_{P1}P_{CH_4}P_{H_2O}}\right)}{\left(1+K_{CO}P_{CO}+K_{H_2}P_{H_2}^{0.5}+K_{H_2O}\left(P_{H_2O}/P_{H_2}\right)\right)^2} \qquad (28)$$

$$r_2=\frac{k_2\left(\frac{P_{CH_4}P_{H_2O}}{P_{H_2}^{1.75}}\right)\left(1-\frac{P_{CO_2}P_{H_2}^4}{K_{P2}P_{CH_4}P_{H_2O}^2}\right)}{\left(1+K_{CO}P_{CO}+K_{H_2}P_{H_2}^{0.5}+K_{H_2O}\left(P_{H_2O}/P_{H_2}\right)\right)^2} \qquad (29)$$

$$r_3=\frac{k_3\left(\frac{P_{CO}P_{H_2O}^{0.5}}{P_{H_2}^{0.5}}\right)\left(1-\frac{P_{CO_2}P_{H_2}}{K_{P3}P_{CO}P_{H2O}}\right)}{\left(1+K_{CO}P_{CO}+K_{H_2}P_{H_2}^{0.5}+K_{H_2O}\left(P_{H_2O}/P_{H_2}\right)\right)^2} \qquad (30)$$

The expressions for reaction rates (28-30) were used in this work for investigations of heat and mass transfer at catalytic methane steam reforming. The only one reaction (28) with constant reaction rate was considered to describe influence non zero molar flow from the mall on heat and mass transfer coefficients. The value of constant reaction rate was defined as product of 0.003 mol/(m^2 s) by magnification factor **f**.

Methane steam reforming was simulated in a channel with gap H = 0.6 mm for the uniform mesh with 41 nodes across the channel. The length of reaction zone in these calculations was L= 12 mm. The inlet temperature of mixture was 1133 K. The gas mixture velocity at the inlet was U = 0.67 m/s. The initial ratio of steam and methane mass fractions equals to Y_{H2O}/Y_{CH4} = 7/3. The pressure in a microchannel is 1 bar.

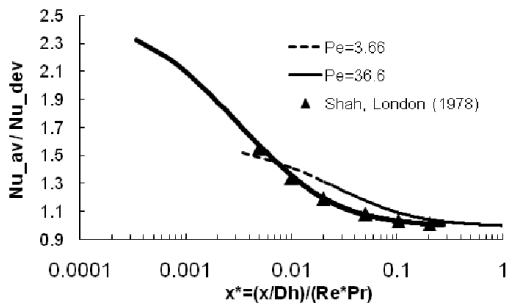**Figure 1**   The ratio of laminar developing to developed Nu

Figure 2   The distribution of methane mole fraction over the length and width of the channel

Validation of Numerical Model

The thermal entry region heat transfer problem which takes into account both transverse non-uniformity in the velocity field and axial conduction was solved numerically. To validate the solution the comparison with literature and reference data was carried out. Data from [13,14] were used for validation. In agreement with Figure 1, for the Peclet numbers higher than 10, the Nusselt number at the thermal entry region doesn't differ from one published in [13]. For the case with Peclet number lower than 10 the effect of the diffusion and longitudinal heat conductivity becomes significant in entrance region. Nusselt numbers achieved at the last case agrees with data from [14].

HEAT AND MASS TRANSSFER AT CONSTANT REACTION RATE WITH NONZERO MOLE FLUX FROM THE WALLS

The distribution of methane mole fraction over the length and width of the channel is shown in Figure 2. It is obvious that external diffusion resistance in a microchannel is low and a change in mixture component concentration over the channel cross-section is insignificant.

Figure 3 shows the values of Sh* and Sh in the case when all the thermophysical properties are constant. One can see that the of Sh* lies below the value of Sherwood number in case of an infinitesimal reaction rate, and well-described by Eq.(8)

As shown in Figure 4 with the increasing of the reaction rate in the case of variable properties of the mixture enhances the mass transfer coefficients. High net reaction rate values of Sherwood number exceed the Sherwood number for the case with an infinitely small rate of mass transfer on the walls. The increasing of Sherwood number in case non-isothermal reaction conditions at a constant rate on the channel wall, is a consequence of the transport coefficients dependence on temperature and composition of the gas mixture (Figure 5).
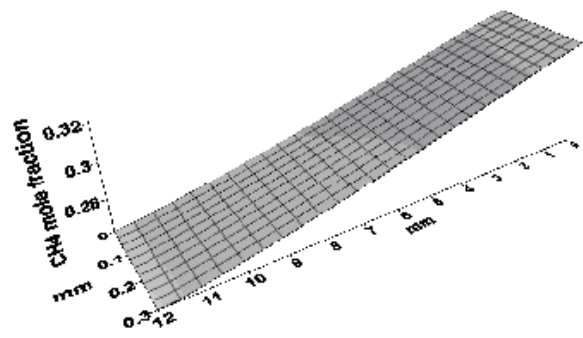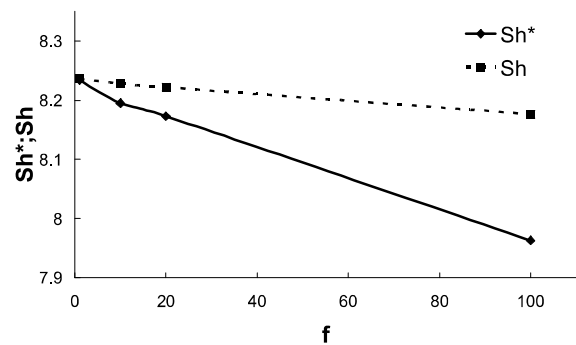

Figure 3   The dependence of the Sherwood numbers on the catalytic reaction rate under constant properties conditions. Re = 40.
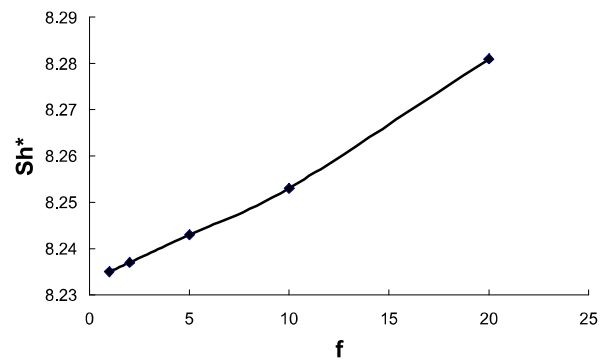

Figure 4   The dependence of the Sherwood numbers on the catalytic reaction rate under variable thermophysical properties of the gas mixture, depending on the temperature and composition of the mixture. Re = 40
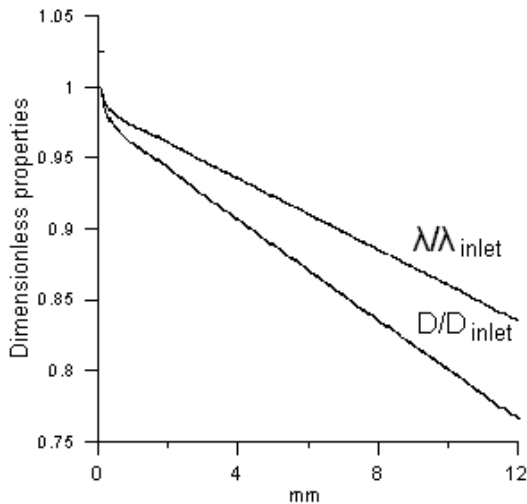
Figure 5 Variation of the heat conductivity and diffusion coefficient at the wall along the channel. Re= 40
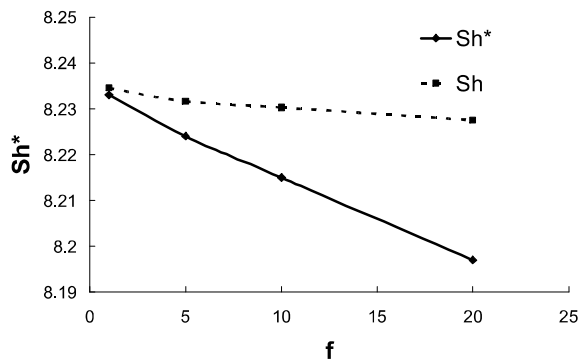

Figure 6 The dependence of the Sherwood numbers on the catalytic reaction rate under isothermal conditions and variable thermophysical properties. Re = 40

So when strongly endothermic or exothermic reactions occur the effect of variation in the local Sherwood and Nusselt numbers with temperature is greater than the effect of variation with changes in the molar composition of the mixture or the effect of nonzero mole flux from the walls.

Reactions take place in close to isothermal conditions when quantity of heat supplied to the wall is equal to quantity of heat consuming by endothermic reaction. The values of Sherwood numbers in the case when the reaction proceeds under isothermal conditions are presented in Figure. 6. The values of Sherwood numbers are lower than the values in the case of an infinitesimal rate of mass transfer on the walls, but greater than the values obtained in the case of constant thermophysical properties of the mixture.

HEAT AND MASS TRANSSFER AT METHANE STEAM REFORMING

The steam reforming of methane is a strongly endothermic reaction. Therefore, it requires a heat supply to the reacting mixture. One can see from equations (28-30) that the catalytic reaction rate greatly depends on temperature of the reacting mixture of gases and the species concentrations. There are non-uniform along the channel the molar and heat fluxes onto the walls of the microchannel at the steam reforming of methane with or without supply of heat. The higher the temperature of the mixture in the reaction zone, the more intensive the steam reforming of methane and the greater the cooling of the mixture of the reacting gases. Also the reaction rates (28, 29) decreases along the channel in consequence of the decreasing methane concentration. So the regimes may occur when the value of the total heat flux from the wall changes sign. The reaction rates of the methane steam reforming are presented in Figure 7. Nevertheless, the values of the coefficients of heat and mass transfer in microchannel with steam reforming of methane close to the values of Nusselt and Sherwood numbers for the case with constant fluxes at the wall.

Figure 8 presents the dimensionless coefficients of mass transfer in the case of the methane steam reforming. One can see that for different regimes (different density of a heat flux) in the case of low Reynolds numbers, the local mass transfer coefficient decreasing shows a minimum at the entrance region, due to the influence of longitudinal diffusion. The more the diffusion equalizes the concentrations of the components in the flow, the lower the value of the mass transfer coefficient. The lowest value approaches the Sherwood number with a constant concentration boundary condition on the wall. Downstream, the value of the local Sherwood number returned to a value close to one in case of constant components flux at the wall.
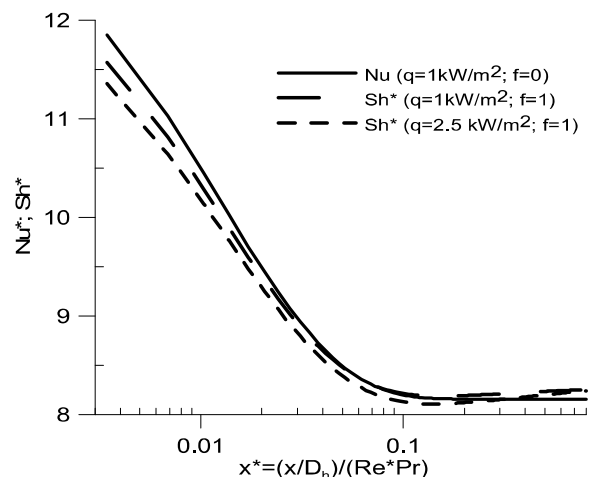

Figure 8 Variation the Sherwood number at catalytic methane steam reforming along the channel Re=4.

CONCLUSION

The peculiarities of the flow of the reacting mixture in a microchannel are large gradients of temperature and concentration along the channel, while across the channel diffusion processes equalize the concentration field and temperature. Methane steam reforming is a highly endothermic process that requires a supply of heat, so regimes may occur when the value of the total heat flux from the wall changes sign, due to the decreasing of the reaction rate at the wall in the process of methane conversion. In this case, the use of Nusselt numbers in the range near the sign change of the heat flux is incorrect. Numerical study showed that at low Peclet numbers (less than 10), effect of the diffusion and longitudinal heat conductivity become significant in entrance region. Far from the entrance region and points where heat flux changes the sign, the dimensionless coefficients of heat and mass transfer at the steam reforming of methane take on values close to the well known values for the case of heat transfer in a slot channel with constant heat flux boundary conditions even there are non-uniform along the channel the molar and heat fluxes onto the walls. The catalytic reactions make transverse moles flux in the gas mixture and reduce the dimensionless coefficients of heat and mass transfer. The thermophysical properties dependence on the mixture composition and temperature also changes the values of the dimensionless heat and mass transfer coefficients. The effect of variation in the local Sherwood and Nusselt numbers with temperature is greater than the effect of variation with changes in the molar composition of the mixture or the effect of nonzero mole flux from the walls. In the case of small Reynolds numbers, the dimensionless mass transfer coefficient decreasing shows a minimum at the entrance region, due to the influence of longitudinal diffusion. Downstream, the value of the local Sherwood number returned to a value close to one in case of constant components flux at the wall.

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