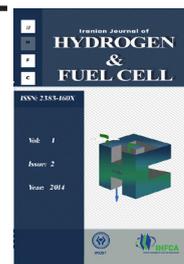


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Reforming integrated with oxidation in a micro-heat exchanger reactor with circular micro-channels

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Abstract

In this work, steam reforming integrated with oxidation of methanol has been considered with numerical simulation. Steam reforming is an endothermic reaction; hence, much heat was needed. To supply this heat, oxidation reaction, which is an exothermic reaction, was used. When the catalyst was deposited inside the rectangular micro-channels, it filled up the edges. Hence, the approximation of cylindrical channels is appropriate for these parallel micro-channels. Effect of this changing in the cross section was considered and the results show that methanol conversion is lower in the circular model. Also, effects of operating conditions were considered. The results show that with increasing inlet temperature, methanol conversion increases, while with increasing feed flow rate, it decreases. The effect of the distance between oxidation and steam reforming micro-channels was considered and the results show that with increasing this parameters, methanol conversion decreases. The distance between the two oxidation micro-channels was considered as geometry parameters as well. The results show that with increasing these parameters, methanol conversion increases.

1. Introduction

Increasing interest in methanol as a fuel for power units can be seen in small size fuel cells, mainly of the proton-exchange-membrane (PEMFC) type. They can be used in many applications as replacement of batteries in portable electronics, in auxiliary power units [1] and transportation. So, in some of the previous works [2, 3], methanol has been used as feed.

The advantages of using methanol for hydrogen production can be summarized as follows [1, 4]: (i) it has high hydrogen to carbon ratio; (ii) it is liquid at ambient conditions, thus overcoming the problems of hydrogen distribution and storage; (iii) it is miscible with water, so both methanol and water can be premixed in fuel cartridges; and (iv) it is biodegradable and free of sulfur. Steam Reforming (SR) is as an effective method for producing

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hydrogen from methanol. SR is highly endothermic and requires large amounts of heat, which is a serious drawback to the cost and practicality of the hydrogen production, especially for on-board applications. Recently, OXidation (OX) was used as the heat source. This reaction is exothermic, and therefore, much heat is significantly released. This heat can be employed in SR section.

On the other hand, in portable applications especially on-board set, availability of a compact and light unit of H₂ supply is important. Therefore, micro-channel reactors are interestingly used in these systems. A higher ratio of surface/volume, lower pressure drop than packed bed micro-reactors and higher heat and mass transfer rates in comparison with other conventional reactors are outstanding characteristics of the micro-reactors. Thus, the above-mentioned methods (SR and OX) in the micro-channel reactor are the main focus of recent investigations. Some of these researches are briefly expressed here.

Tadbir et al. [5, 6] studied methanol reforming in micro-reactors. They investigated autothermal reforming of methanol in a single rectangular micro-channel and multi rows and columns of micro channels. The effects of operating conditions as steam/carbon ratio at the reformer inlet, gas space velocity of both channels, and the reformer catalyst thickness on methanol conversion and hydrogen production were investigated. Also, Stefanidis et al. [7] studied hydrogen production from a multifunctional micro-device consisting of thermally coupled catalytic plate combustion and reforming micro-reactors for methane and methanol reforming in a high and low temperature process, respectively. They found that for hydrogen production for portable devices, methanol has the advantage of producing mainly CO₂, avoiding the need for WGS (Water Gas Shift) reactors. Arzamendi et al. [8] studied the thermal integration of steam reforming of methanol and the combustion of methanol in a catalytic micro-channel reactor. They found that at space velocities as high as 50,000 h⁻¹ and at relatively low temperatures in the 270-290°C range, complete methanol reforming and combustion would be achieved. At these

conditions, selectivity for H₂ reach to above 99%. Ni [9] studied heat and mass transfer in micro-reactor with methane steam reforming and combustion ducts. They found that with increasing the inlet temperature from 1073K to 1173K increases the maximum reaction rates of steam reforming and water-gas shift reactions. Moreover, raising the inlet temperature to 1173K enlarges the temperature drop to about 130K. They also found that increasing the gas velocity and permeability facilitates the gas transport in the porous catalyst layer, which

in turn enhances the reaction rates of steam reforming and water-gas shift reactions in the downstream. Zhai et al. [10] studied the modeling and simulation of a micro-reactor design for SRM reaction with endothermic reaction in detail. They considered the effect of some parameters such as: thermal conductivity of catalyst wall, and the ratio of fuel gas to reforming gas. Wang et al. [11] studied methane steam reforming with combustion reactions in micro-channel reactor. They considered the effect of inlet parameters and transport characters. They found that methane conversion was greatly influenced by inlet velocity in the catalytic combustion channel. Also, temperature distributions of the centerline and walls in both channels were T-shaped distribution due to the strong exothermic catalytic combustion reaction. In all above publications [5-12], micro-channels with square cross section were used with parallel arrangement and catalyst was deposited on the wall.

On the other hands, Poulidakos et al. [13] studied the effects of micro-reactor wall heat conduction. They found that when the catalyst was deposited inside the micro-channels, it filled up the edges (Figure 1). Hence, the approximation of a cylindrical micro-channel is appropriate. So, it seems that when rectangular micro-channel was deposited with catalyst, the cross section of micro-channel was changed from rectangular to circular shape.

On the other hand, modeling is one method for considering in details and was used for reforming system [14-16]. Computational fluid dynamics (abbreviated as CFD) is particularly dedicated to the

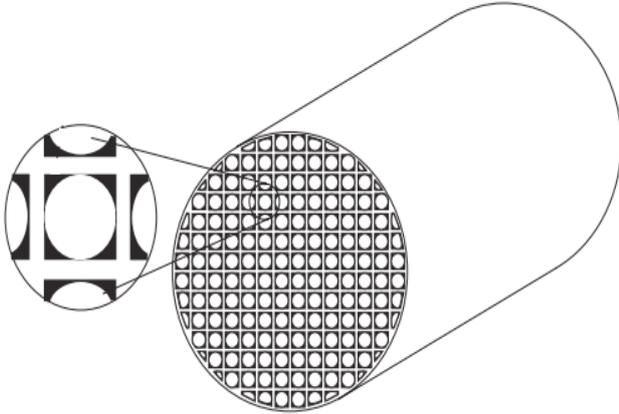


Figure 1. Catalyst deposited fills up the edge, square cross section of micro-channel was changed to circular [13].

reformer, fluids that are in motion, and how the fluid flow behavior influences processes that may include heat transfer and possibly chemical reactions in combusting flows. There are many advantages in considering CFD method [17]. Accordingly, CFD is significantly used in industrial applications and academia research.

In this work, SR of methanol integrated with the OX reaction of methanol was investigated in a micro-channel reactor with circular cross section for considering real model. In this structure, parallel micro-channels were used while in one of the rows OX reaction occurred, while in the next row, SR reaction was done. Two sections were separated by a solid section. Effects of operating conditions as inlet temperature, feed flow rate, inlet composition as steam to carbon (S/C) ratio and geometry parameters such as the distance between two rows and two columns and the flow direction were considered.

2. CFD model

2.1. Geometry of micro-reactor

A micro-channel heat exchanger reactor with circular cross section was studied in the present model (Figure 2). A series of circular micro-channels were placed

in a rectangular cubic solid section. In one row, OX reaction of methanol occurred, while in the next row, SR reaction of methanol was done. Inlet diameter of micro-channel is 0.7mm and the length is 10mm. Because of comparing results of our model with Tadbir's work [6], this scale was selected for the geometry. The catalyst deposited on circular micro-channel walls. On the other hand, because of the symmetry of the shape, only dashed section in Figure 2 was simulated.

2.2. Governing equations

In this model, it is assumed that the flow is laminar and in steady state, gravitation force is neglected, and the inlet flow is an ideal gas. The governing equations for these systems in the gas phase consist of continuity, momentum, energy transport and species mass balance equations which are: Continuity equation:

$$\rho_{mix} \nabla \cdot (\vec{v}) = 0 \quad (1)$$

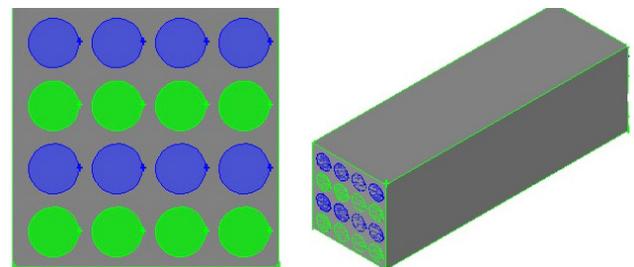


Figure 2. Micro-channel reactor with circular cross section, in blue channel SR reaction and in green channel OX reaction were occurred.

Momentum transport equation:

$$\rho_{mix} \vec{v} \cdot \nabla \vec{v} = -\nabla P + \mu_{mix} (\nabla^2 \vec{v}) \quad (2)$$

Energy transport equation:

$$\rho_{mix} c_{pmix} \nabla \cdot (\vec{v}T) = k_{mix} \nabla^2 T + \Delta H_R \quad (3)$$

Species mass balance equation:

$$\rho_{mix} \nabla \cdot (\vec{v}y_i) = -\nabla \cdot \vec{J}_i + R_i \quad (4)$$

In Equations (1-4), ρ_{gmix} , μ_{gmix} , c_{pmix} and k_{gmix} , respectively are density, viscosity, specific heat capacity and the thermal conductivity of the gaseous mixture, and the thermal conductivity of the gaseous mixture, and are defined in section 2.4. Also, Q_r is heat of reaction for SR or OX reactions and their values are listed in Table 1. R_i is the rate of SR or OX reactions and has non-zero value only on reaction walls.

Table 1. Heat of two reactions, OX and SR.

Reaction	ΔH	Reference
Steam Reforming	ΔH_{298} (kJmol ⁻¹) = 49.5	[18]
Oxidation	ΔH_{298} (kJmol ⁻¹) = -676.0	[20]

In the solid section between the two SR and OX channels, only energy transport equation is solved. The energy equation for this section was written as:

$$\nabla^2 T = 0 \quad (5)$$

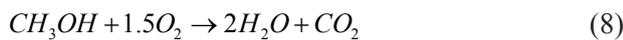
2.3. Kinetic models

The methanol steam reforming reaction is given as Equation (6). The rate expressions reported by Jiang et al. [19] was used for the steam reforming of methanol as Equation (7).



$$r_{SR} = 5.3 \times 10^{12} \exp(-105/RT) P_{Methanol}^{0.26} P_{H_2O}^{0.03} \quad (7)$$

where r_{SR} and P are the rate and pressure, respectively. On the other hand, the methanol oxidation reaction is given as Equation (8). The rate of reaction adopted according to Reitz et al. [20] was used for oxidation as Equation (9).



$$r_{OX} = 2.761 \times 10^5 \exp(-13.1/RT) C_{Methanol}^{1.3} \quad (9)$$

And r_{OX} and C are the rate and concentration, respectively.

2.4. Physical properties

Five chemical species: methanol, water, oxygen, hydrogen and carbon dioxide, are used as ideal gases. The density of the gaseous mixture, ρ_{gmix} , is defined as incompressible ideal gas law and can be expressed as follows:

$$\rho_{gmix} = \frac{P}{RT \sum_i \frac{y_i}{Mw_i}} \quad (10)$$

where R is the universal gas constant, y_i the mass fraction of species i , Mw_i the molecular weight of species i and p the operating pressure.

The specific heat capacity of the mixture was computed as a mass fraction average of the heat capacities of pure species:

$$c_{pmix} = \sum_i y_i c_{p,i} \quad (11)$$

The thermal conductivity of the gaseous mixture, k_{gmix} , was calculated in the same manner as μ_{gmix} from Wilke's mixture rule. The viscosity of the gaseous mixture, μ_{gmix} , can be calculated as follows:

$$\mu_{gmix} = \sum_i \frac{x_i \mu_i}{\sum_j x_j \phi_{ij}} \quad (12)$$

$$\phi_{ij} = \frac{\left[1 + \left(\frac{\mu_i}{\mu_j} \right)^{1/2} \left(\frac{Mw_j}{Mw_i} \right)^{1/4} \right]^2}{\left[8 \left(1 + \frac{Mw_i}{Mw_j} \right) \right]^{1/2}} \quad (13)$$

x_i is the mole fraction of species i .

The Modified Chapman-Enskog formula was used to compute the diffusion coefficient using kinetic theory:

$$D_{ij} = 0.0188 \frac{\left[T^3 \left(\frac{1}{Mw_i} + \frac{1}{Mw_j} \right) \right]^{1/2}}{P_{abs} \sigma_{ij}^2 \Omega_D} \quad (14)$$

p_{abs} is the absolute pressure and Ω_D is the diffusion collision integral, which is a measure of the interaction of the molecules in the system. Ω_D is a function of the quantity T_D^* as:

$$T_D^* = \frac{T}{\left(\frac{\varepsilon}{k_B}\right)_j} \tag{15}$$

k_B is the Boltzmann constant, which is defined as the gas constant, R , divided by the Avagadro's number. $(\varepsilon/k_B)_{ij}$ for the mixture is the geometric average:

$$\left(\frac{\varepsilon}{k_B}\right)_{ij} = \sqrt{\left(\frac{\varepsilon}{k_B}\right)_i \left(\frac{\varepsilon}{k_B}\right)_j} \tag{16}$$

Lennard-Jones parameters, σ_i and $(\varepsilon/k_B)_i$ for each species can be found in textbooks such as [21].

2.5. Boundary conditions and numerical method

Reactions were done on circular micro-channel walls; other walls have no slip conditions. In the Inlet flow, temperature and composition and flow rate of feed is specified. Only the symmetry section shown in Figure 3 was simulated. The boundary conditions are listed in Table 2. Governing equations (1-5) are solved by the finite volume method over control volume in three dimensions. First-order upwind discretization scheme was used for governing equations except of for pressure. The simple algorithm was employed to solve the convection-diffusion equations. The used grid is shown in Figure 3.

Table 2. Types of boundary conditions used in this model.

Boundary	Condition
Inlet	Velocity, mass flow rate and Temperature are specified. $v = \text{specific}$ $T = \text{specific}$ $m_i = \text{specific}$
Walls	No slip condition Symmetry $v = 0$ $\frac{\partial T}{\partial r} = 0$
Circular micro-channel wall	No slip condition Surface reaction $v = 0$

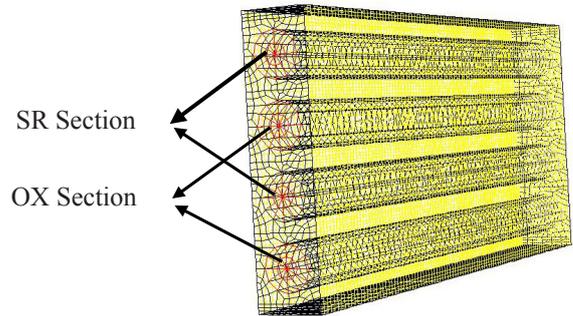


Figure 3. The grid was used in this model with the location of SR and OX sections.

3. Results and discussion

3.1. Model validation

In the first step, the model was validated. For validation, Tadbir's work [6] was used. In their work, rectangular micro-channel was studied. The cross section is $0.7 * 0.7 \text{ mm}^2$ and the length is 10 mm. Inlet conditions of their work are listed in Table 3. The comparison between the results of our model and experimental data is shown in Figure 4. Inlet temperature of SR and OX sections are 423 and 473K, respectively. The used catalyst weight is 0.052 kgm^{-2} . The composition of SR section changed with S/C ratio. With neglecting the first point, there is good agreement between our simulation results and Tadbir's work [6]. Average error is 4.5%, excluding the first point. So, the model is acceptable.

Table 3. Operating and boundary conditions of Tadbir's work [6] for validation of the model.

	SR section	OX section
Inlet temperature (K)	423	473
Inlet Composition	To be changed	1% Methanol 99% O ₂

3.2. Effect of shape of cross section

In this section, the rectangular and circular cross

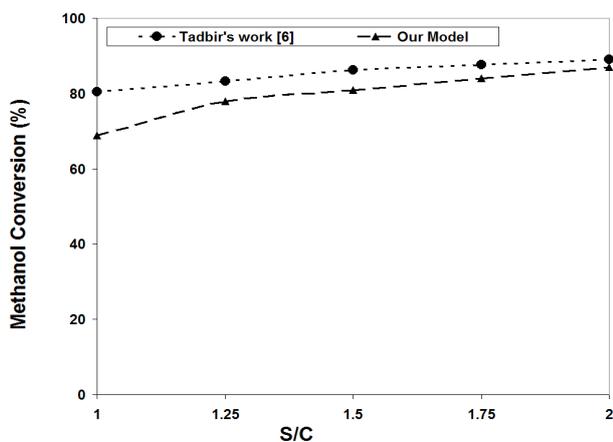


Figure 4. Comparison of simulation results with Tadbir's work [6].

sections were studied. Rectangular micro-channel with square cross section is usually used. But, when catalyst deposited on wall, in practice, square cross section changed to circular shape. So, in this section these models were studied. The edge of the square and the diameter of the circle are both 0.7mm. Also, the length of both models is 10mm. Inlet conditions are listed in Table 3. Figure 5 shows methanol conversion versus S/C ratio for both models. It can be seen that methanol conversion in circular model is less compared to that in the rectangular one. When cross section is circular, the reactor has smaller volume, so residence time of reactant is less, and less reaction is done; and hence, less methanol conversion.

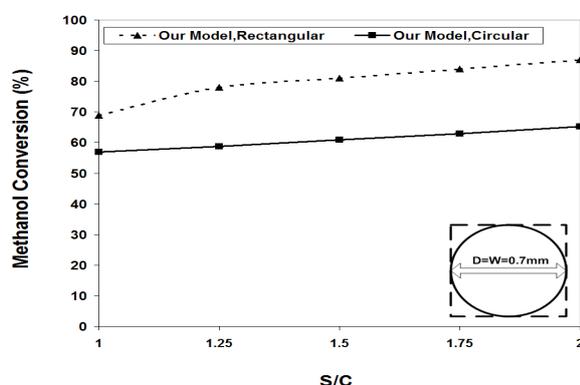


Figure 5. Effect of shape of cross section on methanol conversion.

Also, Figure 6 (A-B) shows variation of temperature

in OX and SR channels. These results show that the temperature in the rectangular model is higher than that in the circular model.

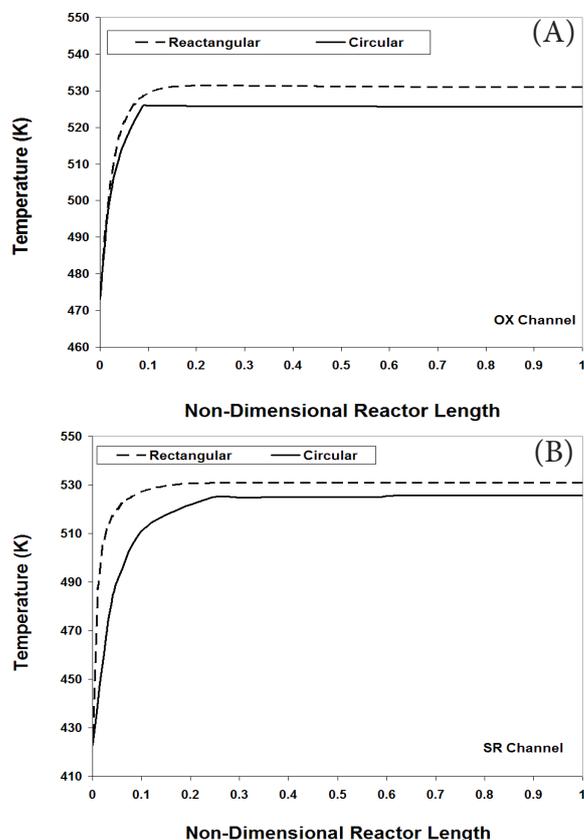


Figure 6. Effect of shape of cross section on temperature, (A) OX channel, (B) SR channel.

Figures 7 and 8 show the mole fraction of components and contour of the methanol conversion along the reactor length for both models. Figure 7 shows that mole fractions of produced hydrogen in rectangular and circular models reached 53% and 40%, respectively. Also, from Figure 8 can be seen that methanol conversion is less in the circular model than in rectangular one. When the cross section is circular, the volume of the reactor is less, so residence time of the reactant is less and less reaction is done; and hence, less methanol conversion occurs.

3.3. Effect of inlet conditions in circular micro-channel

In this section, inlet temperature and inlet feed

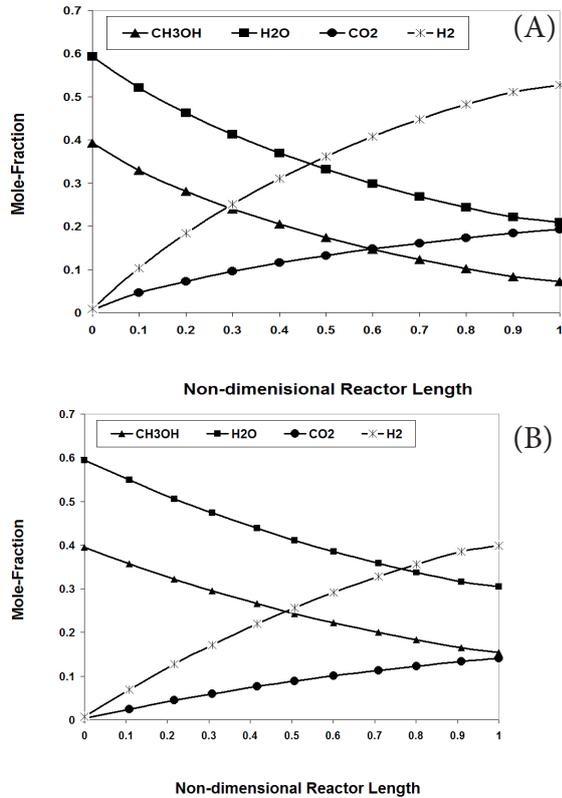


Figure 7. Mole fraction of components along the reactor length for: (A) Rectangular, and (B) Circular model.

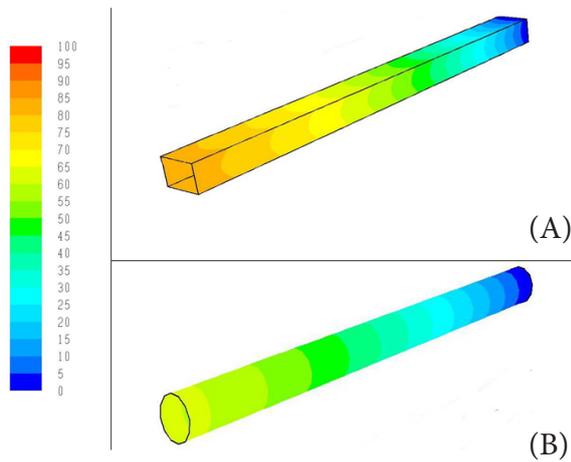


Figure 8. Contours of Methanol Conversion in (A) Rectangular and (B) Circular model.

flow rate as inlet conditions were considered in circular micro-channel. Figure 9 shows variations of methanol conversion with different inlet temperatures of SR section. In this section, S/C ratio and GHSV are 1.5 and 6900h⁻¹, respectively. It can be seen that with

increasing inlet temperature, methanol conversion increases. With increasing the temperature, more reaction is done, so methanol conversion increases. Also, Figure 10 shows variations of methanol conversion with different GHSV. GHSV is defined as Gas Hours Space Velocity and is the ratio of feed flow rate (of SR section) to weight of used catalyst. In this section, S/C ratio and inlet temperature of SR section are 1.5 and 423K, respectively. It can be seen that with increasing GHSV, methanol conversion decreases. With increasing GHSV, feed flow rate increases, so reactants leave the reactor faster and spend less time for the reaction; therefore, conversion decreases. However, the rate of decreasing conversion in this section is more than its rate of increase with temperature.

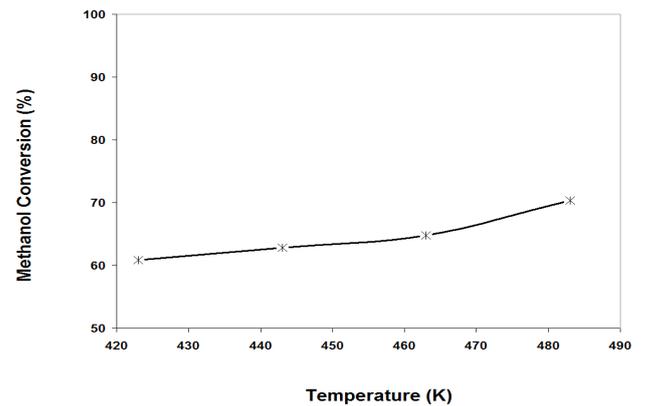


Figure 9. Effect of inlet temperature on methanol conversion in SR channel, S/C=1.5, GHSV=6900 h⁻¹.

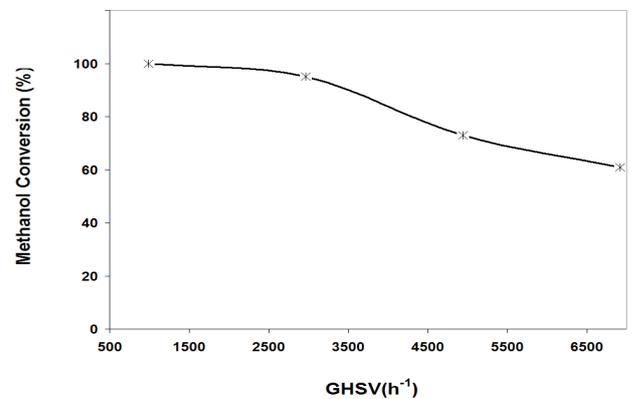


Figure 10. Effect of GHSV on methanol conversion in SR channel, S/C=1.5 and TSR=423K.

3.4. Effect of geometry parameters in circular micro-channel

In this section, two parameters were considered. The first parameter, t_1 , (see Figure 11) is the distance between OX and SR channels in each column. The second parameter is the ratio of t_1/t_2 , where t_2 is the distance between two OX channels or two SR channels in each row.

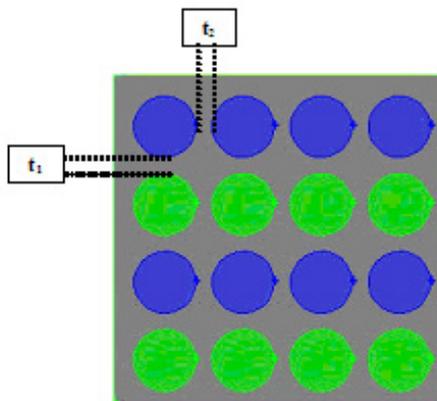


Figure 11. The locations of two geometries parameters, t_1 and t_2 . t_1 is the distance between OX and SR channels in each column and t_2 is the distance between two OX channels or two SR channels in each row.

Figure 12 shows variations of methanol conversion with t_1 . It can be seen that with increasing t_1 , methanol conversion decreases, although, at first, this trend is slow. With increasing t_1 , the distance between OX and SR channel increases and SR section receives less heat, so temperature is lower and consequently, methanol conversion is lower. Also, Figure 13 shows the effect of the parameter t_1/t_2 . In this section, t_1 was kept constant and with changing t_2 , this effect was evaluated. It can be seen that increasing t_1/t_2 ratio, that is decreasing t_2 , methanol conversion increases first and then becomes almost constant. With these results, it seems that smaller t_1 and larger t_2 are better choices to achieving higher performance.

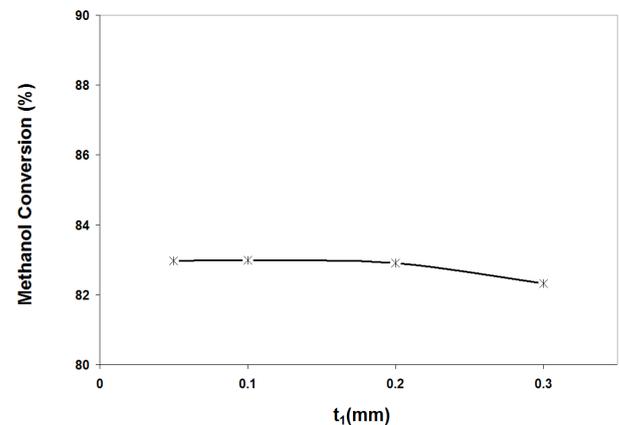


Figure 12. Effect of t_1 on methanol conversion in SR channel.

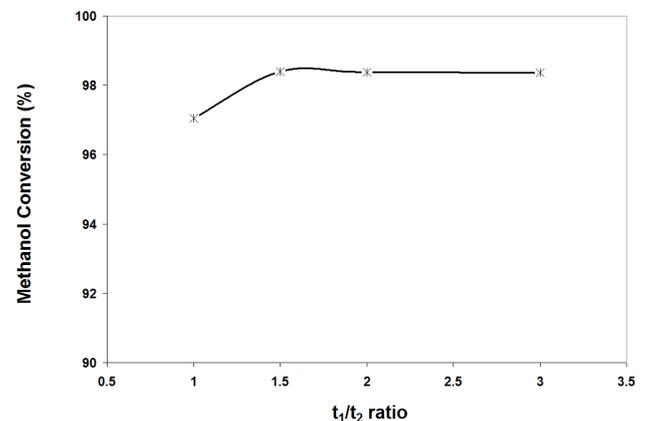


Figure 13. Effect of t_1/t_2 on methanol conversion in SR channel.

4. Conclusion

Steam reforming integrated with oxidation (OX) in parallel circular micro-channels reactor was studied in present work. In one row of circular micro-channels, oxidation took place, while steam reforming occurred in the next row. When catalyst was deposited on the edge of the rectangular micro-channel, its cross section changed to circular. Effect of this changing cross section was studied and results show that methanol conversion is lower in a circular micro-channel than in rectangular micro-channel reactor. Then, effects of operating conditions including inlet temperature, feed flow rate, inlet composition (as steam to carbon ratio (S/C)) and geometry

parameters such as distance between two rows and two columns were considered. Results show that with increasing inlet temperature and S/C ratio, methanol conversion increases; however, it decreases with increasing feed flow rate. On the other hand, with increasing t_1 (distance between OX and SR channel), methanol conversion decreases. Also, with increasing t_1/t_2 ratio (t_2 is the distance between two OX channels or two SR channels), methanol conversion increases at first and then becomes almost constant.

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Nomenclature

C_i	molar concentration, molm ⁻³
c_p	specific heat at constant pressure, J kg ⁻¹ K ⁻¹
D	mass diffusion coefficient, m ² s ⁻¹
k	thermal conductivity coefficient, W m ⁻¹ K ⁻¹
ΔH	enthalpy of reaction, kJ kmol ⁻¹
M_w	molar mass, kg kmol ⁻¹
P	Pressure, Pa
P_i	Partial pressure, Pa
R	universal gas constant, 8.315 J mol ⁻¹ K ⁻¹
r_i	rate of reaction i
T	temperature, K
\bar{v}	Velocity vector, m s ⁻¹
x_i	mole fraction of species i
y_i	mass fraction of species i

Greek symbols

η_{conv}	conversion
μ	viscosity, kg m ⁻¹ s ⁻¹
ρ	density, kg m ⁻³

Subscripts

gmix	gas mixture
OX	oxidation
SR	steam reforming
R	reaction

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