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# Hydrogen production by methanol steam reforming in a disc microreactor with tree-shaped flow architectures

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## ABSTRACT

A disc microreactor with constructal tree-shaped flow architecture is introduced for methanol steam reforming. For this design, a three-dimensional model is developed and analyzed numerically to predict the resulting hydrogen production. The methanol conversion ratio, yield of hydrogen production in the product of the tree-shaped microreactor, are all evaluated and compared with the corresponding microreactor using a parallel flow pattern. In addition, the effect of branching level, steam to methanol ratio (SMR), and inlet velocity on the reaction performance of the microreactor with a constructal tree-shaped network are also investigated and discussed. The results indicate that the methanol conversion in the disc tree-shaped microreactor is more than 10% better than that of a parallel microreactor. Furthermore, the yield of hydrogen at the outlet of the disc tree-shaped microreator is greater than the parallel flow configuration. The CO concentration in the products of the disc tree-shaped microreactor is higher than that of parallel microreactor. In addition, the disc tree-shaped microreactor with a larger branch level behaves enhanced performance on the methanol conversion and hydrogen production.

## 1. Introduction

Hydrogen is typically generated in a fuel processor from available hydrocarbons by means of the reforming reaction [1–4]. One method of great interest is methanol steam reforming (MSR) over catalysts [5–11]. Methanol is one of the best choices for hydrogen production, since it has a high H:C ratio (4:1), equal to that of methane. And it exists as a liquid at atmospheric pressure and normal environmental temperatures, unlike methane or liquefied petroleum gas. Furthermore, methanol can be converted to hydrogen at lower temperatures (150–350 °C) rather than most other fuels (>500 °C), which leads to a low level of CO formation [12]. Therefore, methanol steam reforming is regarded as an attractive method for hydrogen production.

In recent years, small micro-fabricated reactors have been shown to provide excellent mass and heat transfer properties, controllable short residence times, and uniform flow patterns, which implies that the micro reactors have considerable potential in chemical production processes, which relies on an increased speed of reaction time, increasing selectivity, and safe operation in explosive regimes [13,14]. In particular, a number of methanol steam micro-reformers with various structures such as micro-pin-fin arrays [15], serpentine channels [16,17], and parallel channels [18,19] have been designed and investigated to supply hydrogen. Recent researches show that the geometric and operating conditions have significant influence on the hydrogen production performance of the micro-methanol steam reformer. For instance, compared with MSR in straight microchannel, the zigzag geometry shows more $H_2$ selectivity and less CO selectivity. Also microreactor with zigzag microchannels has more methanol conversion and low temperature than straight one [20]. In addition, a microreactor with eight non-parallel channels [21] is proposed to improve the performance of SMR. The optimal inclination angles of the channels and catalyst thickness are obtained based on the simulating results. Jang et al. [22] build a three-dimensional model of the micro-methanol steam reformer, the effects of wall temperature, channel geometry, inlet and outlet manifold configuration, and flow rate on the performance of chemical reaction were predicted by the model. The effects of the catalyst thickness on the wall surface of the microreactor plays an important role in its performance. Since increasing catalyst thickness can compensate the lower reactants concentration along the reforming channel, increases in catalyst thickness lead to a reaction enhancement, which enhances the methanol conversion and hydrogen yield [23].

However, until recently, the most commonly used microchannel structures in a microreactor continue to rely on single channel or parallel channels. As the microchannel structure has significant

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**Nomenclature**

| | |
|---|---|
| $A,B$ | pre-exponential term in the arrhenius expression |
| $c_i$ | molar concentration of of species $i$, mol/m$^3$ |
| $C_D,C_R$ | modification factors of decomposition and reforming reaction |
| $C_{p,i}$ | specific heat capacity of species $i$, j/(kg k) |
| $C_{p,mix}$ | specific heat capacity of the gas mixture, j/(kg k) |
| $d_0$ | branch hydraulic diameters of the 0th level, m |
| $d_k$ | branch hydraulic diameters of the $k$th level, m |
| $E_D,E_R,E_W$ | activation energy in arrhenius expression for decomposition, reforming and rWGS reaction, j/mol |
| $F$ | mole fraction |
| $h$ | depth of channels, m |
| $h_i$ | enthalpy of species $i$, j/mol |
| $H$ | height of microreactor, m |
| $\Delta H$ | enthalpy of reaction, j/mol |
| $\vec{J}_i$ | diffusion flux of species $i$, kg/(m k) |
| $k_i$ | thermal conductivity of species $i$, w/(m k) |
| $k_{mix}$ | thermal conductivity of the gas mixture, w/(m k) |
| $k_D,k_R,k_W$ | rate constant for decomposition, reforming and rWGS reaction |
| $L_k$ | branch length of the $k$th level, m |
| $L_x$ | length of the parallel microreactor at $x$-direction, m |
| $L_y$ | length of the parallel microreactor at $y$-direction, m |
| $m$ | branching levels |
| $M$ | molecular weight, kg/mol |
| $n$ | number of parallel channels |
| $n_{CH_3OH}$ | mole number of $CH_3OH$ |
| $N$ | branching number |
| $P$ | pressure, pa |
| $r_i$ | molar rate of creation/destruction of species $i$, mol/(s m$^2$) |
| $r_D,r_R,r_W$ | chemical reaction rate of decomposition, reforming and rWGS reaction, mol/(s m$^2$) |
| $R$ | radius of disc-shaped microreactor, m |
| $R_u$ | universal gas constant, J/(kg mol) |
| $T$ | temperature, K |
| $\vec{V}$ | velocity, m/s |
| $w$ | channel width of the parallel channel, m |
| $w_{cat}$ | catalyst density, kg/m$^2$ |
| $w_k$ | channel width of the $k$th level, m |
| $Y_i$ | mass fraction of species $i$ |

*Greek*

| | |
|---|---|
| $\Delta$ | diameter dimension |
| $\alpha_k$ | branching angle of the $k$th level, degree |
| $\eta$ | conversion rate |
| $\mu$ | viscosity, kg/(m s) |
| $\rho$ | density, kg/m$^3$ |

*Subcripts*

| | |
|---|---|
| *cat* | catalyst |
| *D* | decomposition |
| *i* | species index (1-$CH_3OH$, 2-$H_2O$,3-$H_2$, 4-CO, 5-$CO_2$) |
| *in* | inlet |
| *k* | branching level |
| *mix* | mixture |
| *out* | outlet |
| *R* | reforming |
| *W* | reverse water gas shift |

influence on the flow distribution and the heat transfer enhancement, which results in an improvement in the efficiency of reforming process, it is desirable to develop a microreactor configuration with optimized conversion and flow performance.

The principal of the constructal theory is formulated by Bejan as the law of the generation of flow configuration [24,25]. Recently, the constructal theory has been successfully applied in optimization of heat sinks [26–29], design of fuel cells [30,31] and chemical reactors [32–34].

Here, we would like to introduce the constructal theory into the design of a disc methanol steam microreactor in the context of optimization of flow reaction configuration. As a point-circle flow configuration, the disc architecture with tree-shaped network was already recognized as useful designs for the flow distribution uniformity and the heat transfer enhancement [36]. In the configuration, the inlet of the microreactor is set at the center of the disc. The outlet ports are positioned equidistantly along the rim, which is quite convenient for the collection of the reaction products. The disc tree-shaped microchannel network can be fabricated in a single layer, which is feasible in the manufacture and actual utilization. For highly-branched tree-shaped flow architecture, large surface-to-volume ratio leads to a short radial diffusion time and therefore the narrow residence time distributions can be obtained [35], which finally contributes to good heat and mass transfer properties and hence the process intensification of steam reforming for hydrogen production. In the context, a disc microreactor with constructal tree-shaped networks is developed and the flow reaction in such a microreactor is three-dimensionally modeled and numerically analyzed. The effect of branching levels, steam to methanol ratio (SMR) and inlet velocity on the methanol conversion ratio, the yield of hydrogen in the product of the microreactor with constructal tree-shaped network are evaluated and compared with those in the microreactor with parallel flow pattern.

## 2. Flow configuration

As suggested by Wechastol et al. [37], the flow structure with three branches is the best way to connect the flow to one central point. Fig. 1 shows a typical constructal structure of disc tree-shaped network flow configuration with 5 branching levels. As shown in Fig. 1, the central region of the tree-shaped network has three ducts, and every channel is divided into two branches at the next level i.e. the branching number $N = 2$.

The optimal length ratio of the tree-shaped nets, which is the same as diameter branching ratio via minimizing the flow resistance, is derived under fixed volume and area for Y-shaped single branch [37–39]. Thus, the length of microchannels $L_k$ can be determined according to the space constrains in the current model. To achieve the flow uniformity, the branching angle $\alpha_k$ is adjusted to make sure that the branching points at each level distribute evenly on the same circle.

The ratio of hydraulic diameter branching for the tree-shaped nets should be:

$$d_{k+1}/d_k = N^{-1/\Delta} \tag{1}$$

where $d_k$ and $d_{k+1}$ are the branch hydraulic diameters before and after bifurcation, respectively. Here, the diameter dimension $\Delta = 3$ is chosen based on the Murray's law [39], which is the optimum value that makes the transportation cost minimum. It follows that