A review of recent advances in numerical simulations of microscale fuel processor for hydrogen production

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Abstract

Microscale (<5 W) reformers for hydrogen production have been investigated for over a decade. These devices are intended to provide hydrogen for small fuel cells. Due to the reformer's small size, numerical simulations are critical to understand heat and mass transfer phenomena occurring in the systems and help guide the further improvements. This paper reviews the development of the numerical codes and details the reaction equations used. The majority of the devices utilized methanol as the fuel due to methanol's low reforming temperature and high conversion, although, there are several methane fueled systems. The increased computational power and more complex codes have led to improved accuracy of numerical simulations. Initial models focused on the reformer, while more recently, the simulations began including other unit operations such as vaporizers, inlet manifolds, and combustors. These codes are critical for developing the next generation systems. The systems reviewed included plate reactors, microchannel reactors, and annulus reactors for both wash-coated and packed bed systems.

Keywords: hydrogen production, microchannel, microreformer, methanol reformer, methane reformer, fuel cells

1.0 Introduction

Over the past decade we have witnessed an unprecedented increase in the use and functionality of small personal electronic devices such as smart phones and tablet computers. With each generation, the power demand of these devices has increased. While there has been substantial improvement in batteries over the recent years, batteries still fail to yield the desired energy density for long duration usage. Fuel cells have been proposed to meet the increasing power demands[1]. The primary challenge for a small scale fuel cell is how to safely store hydrogen fuel. To this end many groups have developed microscale fuel processors which can convert a hydrocarbon or ammonia based fuel to a hydrogen rich stream for use in proton exchange membrane (PEM) or solid oxide fuel cells [1-12]. As part of the microscale fuel processor research, various models have been developed as design tools and to better understand the system physics. This paper reviews the microreactor models developed for small scale (<5 W) hydrogen production suitable to power low power personal electronic devices.

1.1 Microreactor General Characteristics

The main factors in considering the microreactor design include: fuel cell choice, fuel choice, fuel processing approach, operating temperature, catalysts, reactor architecture and materials of fabrication. Fuel cell choice determines constraints on gas constituents to the fuel cell. A polymer electrolyte membrane (PEM) fuel cell (FC) operates at low temperatures, typically less than 363 K. The low temperature operation causes the fuel cells to be very sensitive to carbon monoxide poisoning. Therefore fuel processing systems for PEMFC must produce a hydrogen rich gas stream with less than 100 ppm CO, or preferably less than 10 ppm CO[12]. Several higher temperature fuel cells have been proposed for small scale power supplies including phosphoric acid doped polybenzimidazole (PBI), which operates at 388-423 K and solid oxide fuel cells (SOFC), which

typically operate $>973\text{ K}$ [13-15]. PBI FC and SOFC both can tolerate CO at higher concentrations ($>1\%$ and $>10\%$ respectively), making the fuel processing requirements less stringent[13-15]; however, PBI FC and SOFC have some loss in performance compared to PEMFC and the higher temperature operation makes thermal management much harder.

By far the most popular fuel for small scale hydrogen production is methanol. While lacking the high energy density compared to paraffinic hydrocarbons, methanol can be reformed to hydrogen at lower temperatures than paraffinic hydrocarbons; $473\text{-}573\text{ K}$ compared to greater than 775 K [2]. The low temperatures have two advantages, first the lower temperatures make thermal management easier and second the lower temperatures favor higher hydrogen production due to thermodynamic equilibrium. For steam reforming there is an added benefit for methanol compared to other hydrocarbon fuels. Steam reforming requires water. Ideally, water produced by the fuel cell can be recycled for use in the reformer. This works for larger applications, but for these miniature applications, the added balance of plant may become problematic. Therefore it is likely that the water will be carried. Methanol steam reforming requires significantly less water than paraffinic hydrocarbons (1.2:1 steam: carbon compared to 3:1 or more) to mitigate coke formation on the catalysts. If water is included in the energy density, methanol actually has a slightly higher energy density than other hydrocarbons, and is only slightly less than that of methane (Table 1). Other fuels of interest include: ammonia[16], methane[17-19], butane[14], and ethanol[20-22].

Table 1. Fuel and Fuel-Water mix energy density for several common fuels.

For reformers producing less than 5 W equivalent hydrogen there are three main classes of fuel processing used: steam reforming (SR), partial oxidation (POx), and autothermal reforming (ATR). Steam reforming is an endothermic process where the fuel mixed with water is decomposed over a catalyst to produce a hydrogen rich product gas. In partial oxidation, the fuel is mixed with oxygen

and, as the name indicates, is oxidized. The partial oxidation rips apart the molecule producing mostly hydrogen, methane, CO, CO₂, and water. POx can be done with or without a catalyst. ATR is a combination of the two processes where the POx reaction provides heat for the endothermic SR. Table 2 lists some advantages and disadvantages for each of the reforming approaches. More details on the reforming approaches, including catalysts, can be found in review articles by Holladay et al.[2], Song[23], and Bartholomew and Farrauto[24].

Table 2. Comparison of reforming technologies (adapted from[2, 12, 25, 26])

The small nature of low power reactors lends itself to a microchannel or plate architecture; however, small packed bed reactors and membrane reactors have also been examined[12, 27, 28]. Microchannel and plate architectures have high heat and mass transfer rates with the potential to enable high thermal integration and therefore higher efficiencies. Membrane reactors allow for process intensification by integrating multiple unit operations into one reactor. While a packed bed is simplistic in design and fabrication, it must be combined with other approaches, a membrane, microchannels or both, for implementation. Initially, the main material for construction was silicon due to ease of fabrication, or ceramics since they have a low thermal conductivity. However, more designs based on metals are appearing. Table 3 lists advantages and challenges for various classes of materials.

Table 3. Microreactor Material Advantages and Challenges (adapted from [12])

Due to the small nature of these reactors, models (one-dimensional, two-dimensional and three-dimensional) have been developed to aid in understanding the performance and to aid in design. This paper reviews the modeling work that has been reported on this scale of microreformer.

While there has been great interest and many papers involved with modeling microchannel and small reactors, there are relatively few reported results from modeling reactors at the low power (<5 W range).

2.0 One Dimensional Models. One dimensional models are the simplest models to develop and require less computational power. They can be useful to determine trends in performance.

However, many assumptions are required for one dimensional models. For example, they assume that variables such as concentration, velocity, temperature, etc., change predominantly in one defined direction. In most real world situations, this is not the case. There are only two significant papers using a one-dimensional (1-D) model to analyze a microreformer of this scale[16, 29]. In 2006 Kawamura et al.[29] reported the use of 1-D model to aid in their design of a Si-based methanol reformer suitable for powering 1 W class devices when connected to a PEM fuel cell. They correctly identified the thermal management challenge when building a device at such a small scale, and used their 1-D model to optimize the heat and mass flow in their design. They reported a serpentine reactor that was 25 mm long, 17 mm wide, and 1.3 mm thick. The reactor was constructed on silicon and glass substrates using common silicon processing techniques. The reactor was heated by building in a Ta-Si-O-N electrical resistance heater built into the device. The channels were wash coated with a Cu/ZnO/Al₂O₃ catalyst. This catalyst was chosen since it can operate at relatively low temperatures (typically <523 K) with high conversion [29]. The challenge with Cu/ZnO based catalysts is that they are pyrophoric and water sensitive, making the system design challenging for practical applications[13, 30]. A steam to carbon ratio (steam to methanol) ratio of 2 on a molar basis was used. The rate equation used was:

$$r_{SR} = \frac{\eta \rho_{cat} \delta (w + 2h + 2\delta)}{wh} k_0 \exp\left(\frac{-Ea}{RT}\right) (RT)^{0.09} C_{methanol}^{0.26} C_{H_2O}^{0.03} C_{H_2}^{-0.2} \quad (1)$$

Where η is the effectiveness factor of the catalyst, ρ_{cat} is the catalyst's bulk density (1600 kg m⁻³), δ is the thickness of the catalyst layer, w and h are the cross-sectional width and depth of the microchannel catalyst layer, Ea is the activation energy (114.5 kJ mol⁻¹), and k_o is the pre-exponential factor of 1.63*10¹⁰ mol kg⁻¹ s⁻¹ Pa^{-0.09} respectively. This reaction equation was determined at methanol partial pressures in excess of 5 kPa. Knudsen diffusion was assumed to dominate in the catalyst layer and the effective diffusion coefficient of methanol ($D_{e\ meoh}$) was calculated using equation 2:

$$D_{e\ meoh} = 3.067r_e \frac{\epsilon}{\tau} \sqrt{\frac{T}{M_{meoh}}} \quad (2)$$

Where ϵ is the catalyst void volume, τ the tortuosity, r_e the pore radius, M_{meoh} methanol molecular mass, and T is temperature. They used the standard equations for an incompressible fluid for the heat, mass and momentum. The model results were used to design a microreactor which was built and tested. During operation the reactor temperature was fairly well predicted by the model; however, the methanol conversion was not. The authors believe that the discrepancy between actual and predicted performance was due to methanol rate equation. As the methanol reacts, its partial pressure decreases. When greater than 90% conversion is achieved, the methanol partial pressure is 3 kPa or less, which is outside the range of the data used to derive the methanol rate equation. They hypothesize that at the lower partial pressures, the reaction order may be increased making 100% conversion difficult to achieve in their reactor design[29].

In 2010 Chein et al. [16] reported a one dimensional model for ammonia decomposition using a Ni-Pt/Al₂O₃ catalyst with a packed bed design. (Chiuta et al. (2014) proposed a three dimensional model of a single channel ammonia decomposition reactor, as part of a multi-channel system, but

since the system would likely result in a device larger than 5 W it is not reviewed here [31].) Ammonia was chosen by the authors due to its ease of gas clean up compared to hydrocarbon reforming (i.e. there is no need for carbon monoxide removal, and unreacted ammonia can be adsorbed). They used standard incompressible equations for an incompressible fluid for heat and mass, but the Brinkman-Darcy-Forchheimer theory for momentum. For the thermal conductivity, dynamic viscosity, and molecular diffusivity the Chapman-Enskog theory for multi-component gas mixtures at low density was used[16]. The Carman-Kozeny model was used to determine the permeability. Finally, they defined the catalyst bed's effective thermal conductivity, λ_e , as:

$$\lambda_e = \epsilon\lambda + (1 - \epsilon)\lambda_s \quad (3)$$

Where λ_s is the thermal conductivity of the catalyst, λ is the thermal conductivity of the gas and ϵ is the porosity. The ammonia decomposition reaction can be written as:

There is literature indicating that the decomposition reaction depends solely on ammonia concentration and at low pressure is first order[16]. This is similar to methanol steam reforming and therefore they used a methanol steam reforming equation with Cu/ZnO catalyst for the ammonia decomposition kinetics:

$$rate = C_r(1 - \epsilon)\rho_s A R T \exp\left(\frac{-E}{RT}\right) C_{NH_3} \quad (5)$$

Where C_r is a correction factor accounting for the effectiveness and activity of the catalyst pellet, R is the universal gas constant, A is the pre-exponential factor ($3.639 \times 10^9 \text{ mol g}_{cat}^{-1} \text{ hr}^{-1} \text{ kPa}^{-1}$), E is

the activation energy ($196.2 \text{ kJ mol}^{-1}$), and ρ_s is the catalyst density (catalyst mass/ bed volume).

The numerical simulation was performed using Fluent v6.2 at temperatures of 813-893K and the results compared to data in the literature. They adjusted the correction factor in order to get good correlation between their model and the literature data and found 1.5 to be a good factor.

3.0 Two Dimensional Models. Most of the models found in the literature are two dimensional. Two dimensional models provide more accurate predictions and more complicated designs compared to one dimensional models, while not requiring the high computing power needed for three dimensional simulations. They assume that variables change predominantly in two directions (x and y). This is more realistic compared to one dimensional models. The literature can be divided into methanol and methane microreactor models. We will first review the methanol microreactor and then the methane microreactor models.

One of the earliest two dimensional models was developed by Karim et al. (2005) and used to compare the performance between a packed bed and a wall coated microreactor. They used the model to study the temperature profiles, impact of reactor size on apparent activity and for the wall coated reactor, the effect of catalyst wall-coating thickness and reactor diameter on apparent activity. The study focused on the catalyst bed and ignored microreactor materials of construction and other unit operations. A mixture of 1.1:1 steam to methanol was the fuel and a commercially available Cu/ZnO catalyst from BASF was the catalyst[27]. Since the purpose of the study was to examine the impacts of heat transfer on the methanol conversion, they felt the type of reaction rate law used would not impact the results. Thus they assumed that the reaction rate was first order in methanol, zero order in water and assumed a simplified methanol reforming reaction of:

A $\rightarrow$ 3D

(6)

With a reaction rate equation of:

$$-r_A = k_1 \frac{C_{A_0}(1-X_A)^{T_0}}{(1+\varepsilon X_A)^T} (1 - \phi) \quad (7)$$

Where ϕ is the change in number of moles at complete conversion divided by total number of moles fed to the reactor, k_1 is the rate constant found using the Arrhenius equation with $A = 14.5 \times 10^9 \text{ s}^{-1}$ for the wall coated reactor and $22 \times 10^9 \text{ s}^{-1}$ for the packed bed, and the activation energy being 82 kJ mol^{-1} , and ϕ is the void fraction. Stefan-Maxwell equations were used to calculate the mean binary diffusivity. It was assumed this was weakly dependent on methanol conversion and taken to be a constant in the model. Gas properties were taken as an average over several methanol conversions between 0 and 1[27].

Packed bed reactors with 1 mm to 4 mm i.d. were found to be heat transfer limited with temperature gradients up to 40 K in the bed (Figure 1). At 300 μm i.d. the reactor temperature gradients were eliminated. This diameter for a packed-bed reactor may not be practical[27].

Alternatively, the wall coated reactor model predicted no mass or heat transfer limitations over the range of 0.2 mm to 4.1 mm i.d. (Figure 2). In addition, the modeling indicated that the volumetric efficiency increases with wall coating thickness for the same reactor diameter[27].

Figure 1. Isothermal packed bed performance compared to experimental data at 503 K [27]². W = catalyst weight in kg and F = methanol flow in mol s⁻¹.

Figure 2. Modeling predictions for wall coated reactors at 503 K. Unlike the packed bed reactor, no heat transfer limitations were predicted[27]². W = catalyst weight in kg and F = methanol flow in mol s⁻¹. The numbers in parenthesis represent the catalyst coating thickness.

Fazeli and Behnam[32] built upon Karim et al's work and examined reactor geometry for wall coated microchannel reactors. They used modeling to compare hydrogen production between a straight channel and a zigzag configuration (Figure 3 and Figure 4) constructed of steel. Thermal energy for the reforming reaction was provided by methanol combustion in a channel adjacent to the methanol reforming channel. For a true microreactor multiple channels would be used; however, due to symmetry, only two parallel channels were modeled. The length and dimensions of the straight channel are in Figure 4. The zigzag channel had similar width, and was composed of 21 bends with 22 segments.

Figure 3. Schematic figure of zigzag and straight catalytic wall microchannel reactor configurations. [32] (used with permission).

Figure 4. Dimensions used in microreactor model. TOX is the total oxidation or combustion side[32] [32] (used with permission).

² Reprinted from Catalysis Today, 110, Ayman Karim, Jaime Bravo, David Gorm, Travis Conant, Abhaya Datye, Comparison of wall-coated and packed-bed reactors for steam reforming of methanol, 86-91, Copyright (2005), with permission from Elsevier

In Fazeli and Behnam's work, a Cu/ZnO/Al₂O₃ catalyst was used for the methanol steam reforming, but the combustion catalyst type was not described. The following reactions and rate equations were used for the methanol steam reforming and methanol oxidation reactions.

Methanol oxidation:

$$r_c = \frac{k_c P_{\text{CH}_3\text{OH}}^{0.18} P_{\text{O}_2}^{0.18}}{P_{\text{O}_2}^{0.14}} \quad (9)$$

Where $k_c = A_o \exp(-E_a/RT)$ with E_a equal to 115 kJ mol⁻¹ and A_o being $6.0 \times 10^8 \text{ mol min}^{-1} \text{ g}_{\text{catyst}}^{-1} \text{ kPa}^{-0.22}$ [33].

Three reaction equations were used for methanol reforming as follows:

Methanol steam reforming:

$$r_{SR} = \frac{k_{sr} K (P_{\text{CH}_3\text{OH}} - \frac{P_{\text{H}_2}^3 P_{\text{CO}_2}}{K_{SR} P_{\text{H}_2\text{O}}}) C_{S1} C_{S1a} S_a}{\left(P_{\text{H}_2}^{0.5} + K_{\text{CH}_3\text{OH}(1)} P_{\text{CH}_3\text{OH}} + K_{\text{HCOO}(1)} P_{\text{CO}_2} P_{\text{H}_2} + K_{\text{OH}(1)} P_{\text{H}_2\text{O}} \right) (1 + K_{\text{H}(1a)}^{0.5} P_{\text{H}_2}^{0.5})} \quad (11)$$

Water-gas-shift:

$$r_{WGS} = \frac{k_{WGS} K P_{H_2}^{0.5} (P_{CO} P_{H_2O} - P_{H_2} P_{CO_2} / K_{WGS}) C_{S1}^2 S_a}{\left(P_{H_2}^{0.5} + K_{CH_3OH(1)} P_{CH_3OH} + K_{HCOO(1)} P_{CO_2} P_{H_2} + K_{OH(1)} P_{H_2O} \right)^2} \quad (13)$$

Methanol decomposition (MD):

$$r_{MD} = \frac{k_{MD} K (P_{CH_3OH} - \frac{P_{H_2}^2 P_{CO}}{K_{MD}}) C_{S2} C_{S2a} S_a}{\left(P_{H_2}^{0.5} + K_{CH_3OH(2)} P_{CH_3OH} + K_{OH(2)} P_{H_2O} \right) (1 + K_{H(2a)}^{0.5} P_{H_2}^{0.5})} \quad (15)$$

Unfortunately the equilibrium constants were not provided [32], only a reference to how to calculate them was given[34]. The C_{S1} , C_{S1a} , C_{S2} , C_{S2a} and S_a were not defined nor values given. They used the continuity equations for heat, mass, and momentum. Binary diffusion coefficients were calculated using Chapman-Enskog's equation [32]. The model used momentum, continuity, mass balance, and heat balance equations.

The model results indicated that the zigzag design promoted heat and mass transfer. These improvements increased the hydrogen production rate while lowering the carbon monoxide selectivity. Interestingly, the outlet temperature was lower and the temperature drop between the inlet and outlet was greater for the zigzag design than the straight design.

Figure 5. Zigzag configuration has a higher (a) hydrogen production (mole fraction) and a lower CO selectivity (b) than the straight configuration [32] (used with permission).

Chein et al.[35] studied the impact of heat supply mechanisms and materials on tubular reactor performance. The analysis was done on a cylinder reactor of 1mm diameter, 10mm in length,

packed with CuO/ZnO/Al₂O₃ catalyst. The reactor wall was assumed to be infinitely thin at a constant wall temperature. They looked at four different materials chromium alloy, silica, copper, and stainless steel (AISI4340). Ideal gas was assumed with gas flow that is weakly compressible, axisymmetric, steady state and laminar. They used Brinkman-Darcy-Forcheimer model for fluid flow through porous media. For the reformer wall they assumed only conduction heat flow, but conduction plus convection in the reactor. For the reactions, they used the reaction equations [10], [12], and [14]. The reaction rate equations for the reforming reaction [10] and decomposition reaction [14] were respectively:

$$r_R = (1 - \varepsilon)\rho_s k_R C_{CH_3OH} \quad (16)$$

$$r_D = (1 - \varepsilon)\rho_s k_D \quad (17)$$

Where ρ_s is the catalyst density, k_R and k_D were rate constants calculated as:

$$k_R = C_R [A_1 + B_1 \ln \varphi] \exp\left(-\frac{E_R}{RT}\right) \quad (18)$$

$$k_D = C_D A_2 \exp\left(-\frac{E_D}{RT}\right) \quad (19)$$

Where A_1 , A_2 , and B_1 were $1.15 \cdot 10^6 \text{ m}^3 \text{ s}^{-1} \text{ kg}^{-1}$, $7.09 \cdot 10^7 \text{ mol s}^{-1} \text{ kg}^{-1}$, $9.41 \cdot 10^5$ respectively, C_R and C_D were correction factors to account for catalyst activity and effectiveness chosen as 5.5[35]. The water-gas-shift reaction rate equation used was:

$$r_{WGS} = C_{WGS} k_{WGS} (P_{CO} P_{H_2O} - P_{CO_2} P_{H_2}) / K_{eq} \quad (20)$$

With

$$K_{WGS} = 1.78 \times 10^{22} (1 - 0.154\delta + 0.008\delta^2) T^{-\alpha} \exp\left(-\frac{E_{WGS}}{RT}\right) \quad (21)$$

$$K_{eq} = \exp\left(\frac{4577.8}{T} - 4.33\right) \quad (22)$$

Where P was the species partial pressure, α was -8 as determined by experiments, and δ was the molar ratio of water to CO. The activation energy E_{WGS} was 70 kJ mol⁻¹. They verified their model by comparing their computational results with literature values and found they were in acceptable agreement[35].

Three heat supply mechanisms were examined in the study: constant heat flux, internal heat generation, and constant temperature all at the reformer outer wall[35]. For the first two mechanisms it was found that axial heat flux played had an impact on heat transfer and therefore the methanol reforming performance. They developed an axial conduction parameter, dependent on the gas inlet rate ($\rho_{ave} Q_{in}$), wall conductivity, λ_c , wall cross sectional area, A_c , reformer length, L_b , and gas mixture specific heat, $c_{p,ave}$:

$$\Lambda = \frac{\lambda_c A_c}{\rho_{ave} Q_{in} c_{p,ave} L_b} \quad (23)$$

As the axial conduction parameter increased, the actual heat transferred to the methanol reforming reaction decreased. The decrease in heat transfer negatively impacted the reaction temperature and therefore the reactor performance. By examining the equation, it can be determined that

several ways to mitigate this effect would be to 1) choose materials with low thermal conductivity, and/or 2) construct the device with thin walls[35]. Their analysis revealed that choosing a metal with a low thermal conductivity improved reformer performance since there was an excess heat flux supply due to the wall's temperature distribution. This effect was determined to be more significant, i.e. reformer performance was greater, than an infinitely thin walled reformer. Finally, their analysis revealed that the impact of axial conduction decreased with rising temperature since at the higher temperatures the temperature distribution at the wall was negligible. They recommended that for lower temperature reformers, the materials of construction should have a low thermal conductivity and be thin. As operational temperatures increase, these considerations were less important[35].

In addition to studying the axial heat effects, Chein et al. did a numerical simulation of a miniature annulus methanol reformer[36]. They examined a tubular annular reactor where hot gas is in the outer shell with the inner tube being a packed bed reformer. They used the model to compare reactor performance with incline and fishbone shaped fins (Figure 6), and a baseline without any baffles. The distance between the fins was varied by modeling a system with baffles at a distance of $L/5$ and a second system with baffles spaced at $L/9$ (Figure 6)[36].

Figure 6. Annular reformer with hot gas in the outer tube and packed bed reformer with incline and fishbone-shaped baffle plates inside the reformer from reference [36] Reprinted with permission from Energy and Fuels reference 35. Copyright (2012) American Chemical Society.

Chen et al. modeled a stainless steel reactor using a $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ as the catalyst. They used the same reaction rate detailed in equations (16) through (22). The ideal gas law was assumed, with gas flow that was weakly compressible, axisymmetric, steady state and laminar. The Brinkman-Darcy-Forcheimer model for fluid flow through porous media and Chapman-Enskog theory for

multicomponent gas mixtures at low pressure for the thermal conductivity, dynamic viscosity and molecular diffusivity was assumed. The model was validated by comparing it to experimental results of an annular reactor, without baffles, reported by Suh et al.[37]. The major findings included[36]:

- The baffles increased the flow disturbances increasing the mass transfer between the catalyst particle and reactant flow improving conversion.
- The baffles increased the heat transfer raising the temperature closer to the hot gas temperature.
- The pressure dropped through the catalyst bed, but not significantly.
- There was not a significant difference between the L/5 and L/9 baffle placements.
- They indicated that the performance improvements of including the baffles in the annular reactor could be done by using a plate type reactor system. The plate type system would be easier to build than the annular reactor with baffles.

In 2013 Chein et al.[38] published a third paper on an annulus methanol reformer. In this paper, they added a methanol air catalytic combustor for methanol-air. They examined the impact of the combustor being in the shell side of the annulus or the inner tube (Figure 7).

Figure 7. Physical domain of the annulus design methanol reformer with methanol air combustor proposed by Chen et al. [38]³. $Q_{in,R}$ is reformer inlet volumetric flow rate ($m^3 s^{-1}$), T_{in} is inlet temperature (K), R_b is reformer radius (m), R_c is combustor radius (m), t_c is combustion wall

³ Reprinted from Applied Energy, 102, Reiyu Chein, Yen-Cho Chen, J.N. Chung, Numerical study of methanol-steam reforming and methanol-air catalytic combustion in annulus reactors for hydrogen production, 1022-1034, Copyright (2013), with permission from Elsevier

thickness (m), t_r is reformer wall thickness (m), L is the inlet and outlet length (m), and L_b is the reformer length (m).

The model development presented was the same as they used in their previous studies[35, 36, 38], with the addition of a packed bed combustor. The physics for the combustor were the same as used for the reformer, and the methanol combustion reaction rate equation was:

$$r_c = k_c \exp\left(-E_c/RT\right) C_{CH_3OH}^{1.4} \quad (24)$$

Where k_c and E_c are the reaction constant ($3.153 \times 10^6 \text{ m}^{1.2} \text{ mol}^{-0.4} \text{ s}^{-1}$) and the combustion reaction activation energy (18.1 kJ mol^{-1}) [38]. The combustion catalyst is Pt/ Al_2O_3 . The combustor and reformer were set up in a co-flow configuration. Again the reformer model was validated by comparing the methanol conversion to the literature. Using the model, they were able to show that the methanol-air combustor can be lit off at room temperature without an external heating source. This was significant since it simplifies the design of the entire system. Similar to their other studies, they found that high temperatures resulted in higher CO production due to an increase in the reverse WGS reaction. They also studied the impact of insulation. As was mentioned previously, heat loss to the environment is significant issue for micro-scale reactors. The heat transfer coefficient was varied from 0 to $50 \text{ W m}^{-2} \text{ K}^{-1}$ and found that as heat loss increased the methanol conversion decreased with limited methanol conversion occurring when the heat transfer coefficient was $50 \text{ W m}^{-2} \text{ K}^{-1}$. Finally, the shell side combustor configuration yielded better performance compared to when the combustor was located in the inner tube of the annulus. The simulations showed a larger bulk gas temperature drop occurred in the combustor entrance for the tube combustor configuration compared to the shell side configuration. This implies that methanol-water vaporization was more effective and efficient (i.e. less heat loss to the environment) for shell-

combustor configuration compared to the tube-combustor configuration[38]. All of the simulations were done in the co-flow configuration. It would have been interesting to see a counter-flow configuration to see if there would be any significant changes.

In addition to the methanol reformers, several methane microscale reformers have been modeled. In 2008, Stefanidis and Vlachos[18] developed a model of a parallel plate microscale reactor where propane combustion and methane steam reforming occur on opposite sides of the wall. They used a Pt combustion catalyst and Rh steam reformer catalyst. In their prior work they determined that a co-current flow distribution would minimize hot spots and give better overlap of reaction zones, so this configuration was used[18]. The reactor length was 5 cm, with a wall thickness (d_w) of 750 μm , CR gap (d_1) was 300 μm , SR gap (d_2) was 200 μm . The propane air equivalence ratio was 0.85. For the methane reformer the steam to carbon ratio used was only 2. This seems rather low, as typically S:C for methane reforming is 3-4 (usually closer to 4), in order to ensure conversion and prevent coking[2]. They should have used a higher S:C ratio and this may impact their findings.

For the heat and mass transfer, they used standard continuity equations, gas-phase and solid phase energy balance, and the gas and surface species mass balance. CHEMKIN was used to determine the thermophysical and transport properties for the model. The solving strategy was as follows. The continuity equation was solved using a backward Euler scheme, and the rest were solved with central difference. The partial differential equations were solved with a DASK solver. Global rate equations for propane combustion, methane reforming and WGS were used. Kaisare et al.'s[39] propane combustion on Pt was used to represent the combustor. They used a rather complex set of equations to represent the methane SR on Rh and WGS and the reader is referred to the paper for details. The major findings in this work include[18]:

- Methane can be reformed on a highly active catalyst such as Rh in a microscale reformer with millisecond contact times.
- The reaction rates can be increased by increasing the catalyst loading and decreasing mass transfer limitations.
- Operation at lower S:C increases the power output at lower reaction temperatures. This point is well known in the literature, but was not typically pursued in practice since the lower S:C decreases the catalyst life.
- Using microchannel architecture decreases transport limitations making the SR to be essentially reaction controlled. Interestingly, the combustion process was determined to be both reaction and transport controlled even with the small gap. Therefore, they recommend a low combustion channel gap size of 0.6 mm or less for complete fuel conversion in the combustor and reformer channels.

In a companion article Stefanidis et al.[19] continued the examination of steam methane reforming in their microchannel system by looking at operating regions, operating strategies, and materials of construction. They used the same equations and approach reported[18]. From their analysis, they recommended the following operating strategies for methane reforming:

- First, derive an approximate ratio of reforming to combustible stream that is close to the breakthrough limit. This can be done using an energy balance and an outlet temperature. From their simulations, they recommended 1300 K for methane.
- Adjust the flow rates to the desired power output
- The maximum power output is limited by temperature and therefore materials. Similarly, the minimum operating conditions were dictated by heat losses to the environment that would cause combustion extension.

- In addition to adjusting the flow rates, the desired power output can be achieved by adding multiple reactors.
- For system design, the dimensions must be picked to minimize transfer limitations, achieve an acceptable pressure drop and avoid plugging.
- The construction materials will depend on the overall system optimization. In particular the most important was the thermal conductivity. They found that a highly conductive material was good for eliminating hot spots, while conversion increased with a decrease in conductivity. Thus, they recommended “medium” thermal conductivity materials as a suitable compromise.

While the two dimensional models are far superior to one dimensional models, they still have some limitations. They are able to show changes in the x and y direction for many situations. They must assume that changes in the z direction are not significant. This works well for modeling of cylindrical designs. Two dimensional models require less computational power than three dimensional designs, which can be an advantage. However, most small scale reformers are plate type systems which means that the physical phenomena changes in the z-direction are significant. Therefore, to achieve greater accuracy in predicting and understanding reactor performance, three dimensional models are needed.

3.0 Three Dimensional Models

With an increase in computing power, 3-D reactor modeling became more prevalent. One of the first 3-D models was proposed by Alfadhel and Kothare published in 2005[28]. They modeled a silicon based membrane water-gas-shift reactor using Navier-Stokes equation. They solved the equations analytically using Fourier Transforms. The modeled reactor was a rectangular

microchannel (Figure 8). Three sides of the channel are made of silicon with the top of the channel being made of palladium, which hydrogen can permeate, but other gases cannot. The channel width ($2L_x$) was 1000 μm , depth (L_z) was 500 μm , and length (L_y) was 1cm making the hydraulic diameter the same order of magnitude as L_z . This resulted in a low Reynolds number, but high Knudsen number. They simplified the Navier-Stokes equation in a rectangular duct at steady state with assumed constant viscosity and density shown in equations 25 and 26.

For flow in the Y direction:

$$\frac{1}{\mu} \frac{dP}{dY} = \frac{d^2 v_y}{dX^2} + \frac{d^2 v_y}{dY^2} + \frac{d^2 v_y}{dZ^2} \quad (25)$$

since there was no flow in the x direction. Note that in this case P is the dynamic pressure which was assumed to only be a function of flow direction (y).

Figure 8. Microchannel cross section. This drawing shows the dimensions, location of coordinate axes and direction of flow[28]⁴.

The boundary conditions were slip conditions along the walls, symmetry along the x-axis and the dynamic pressure at the inlet being the set. For the Z velocity component, the Navier-Stokes equation

$$\frac{1}{\mu} \frac{dP}{dZ} = \frac{d^2 v_z}{dX^2} + \frac{d^2 v_z}{dY^2} + \frac{d^2 v_z}{dZ^2} \quad (26)$$

⁴ Reprinted from Chemical Engineering Science 60, Khaled AliAlfadhel, Mayuresh V. Kothare, Microfluidic modeling and simulation of flowing membrane microreactors, 2911-2926, Copyright (2005), with permission from Elsevier.

However, since the dynamic pressure was only a function of Y, eqn 26 simplified to:

$$\frac{d^2 v_y}{dX^2} + \frac{d^2 v_y}{dY^2} + \frac{d^2 v_y}{dZ^2} = 0 \quad (27)$$

The boundary conditions for [27] were slip only occurs on surfaces where the velocity had a tangential component and symmetry on the x-axis. The last boundary condition takes into account permeation of the hydrogen through the permeable membrane with the assumption that the velocity of the gases through the membrane was only a function of temperature due to an Arrhenius type of diffusivity[28]. They then did a dimensionless analysis to simplify the equations and solve them analytically using Fourier transforms.

The dimensionless velocity ($\theta_y(x,y,z)$) in the Y direction was found to be:

$$\theta_y(x, y, z) = I(x, z) - \left[\frac{1}{\eta_z} + \frac{2}{\eta_z} \sum_{n=1}^{\infty} \frac{(-1)^n \cos(\lambda_n z) \cosh \lambda_n x / \cosh \lambda_n \eta_x}{1 + \zeta \lambda_n \tanh \lambda_n \eta_x} \right] \times \int_0^y \theta_p(y) dy \quad (28)$$

Where $I(x,y)$ was the dimensionless inlet velocity, η was dimensionless length, λ was the mean free path, and ζ was the dimensionless slip length. And the dimensionless pressure (τ) was

$$\tau = \tau_0 + y \nabla^2 I(x, z). \quad (29)$$

Finally, the dimensionless inlet velocity was determined to be:

$$I(x, z) = \left(\frac{d\tau}{dy} \right)_{\infty} \left[\frac{z^2 - (z + \zeta)\eta_z}{2} + 2 \sum_{m=1}^{\infty} \frac{[(\zeta \lambda_m)^2 + 1][\cos(\varepsilon_m) - \cos(\eta_z \lambda_m + \varepsilon_m)] \sin(z \lambda_m + \varepsilon_m) \cosh(\lambda_m x)}{\lambda_m^3 (2\zeta + \eta_z [\zeta \lambda_m^2 + 1])[1 + \zeta \lambda_m \tanh(\eta_x \lambda_m)] \cosh(\eta_x \lambda_m)} \right]. \quad (30)$$

They validated their result against reported findings in the literature. The major findings of this paper were the analytical solution for the complex 3-D model for gas permeation through a membrane in microchannels. In addition, they compared their pressure drop equations found in the literature and were able to show that their correlation was superior in that it was not limited to a no slip condition (Knudsen number less than 0.001) and eliminated the need for use of correlated values[28].

In 2009, a group out of Hufan University and National Chiao Tung University published two papers on numerical studies on plate type microreformers[40, 41]. In the first paper (ref 34), they examined a multi-channel parallel plate reactor with diagonal inlets and outlets with the focus on the impact of the aspect ratio on methanol conversion, hydrogen and carbon monoxide generation rate. The stainless steel reactor had 10 channels, each channel with a depth of 0.5 mm and configuration shown in Figure 9. It was presumed that the channel surfaces were coated with a 30 μm thick Cu/ZnO/Al₂O₃ catalyst. For the model, it was assumed the methanol water mixture entered the reactor as a gas, was an incompressible fluid, behaves as an ideal gas, and the reactions only occur within the catalyst layer[40].

Figure 9. Top view of microchannel plate reactor modeled by Chen et al.[34]⁵. The dimesions are in mm and the channel depth is 0.5 mm.

⁵ Reprinted from International Journal of Heat and Mass Transfer 55, Reiyu Chein, Yen-Cho Chen, J.N. Chung, Axial heat conduction and heat supply effects on methanol-steam reforming performance in micro-scale reformers, 3029-3042, Copyright (2012), with permission from Elsevier.

They used standard continuity and momentum equations from the Fluent software programs. For the source term (S_i), they used flow through a porous media to simulate the catalyst layer.

$$S_i = -\frac{\gamma u_i}{k_p} - \frac{\beta u_i}{2} |u_i| \quad (31)$$

Where k_p was the permeability, β is the inertial loss coefficient which exists only in the catalyst layer and was zero in the flow channel. The energy balance equation was

$$\rho C_p u_j \frac{dT}{dx_i} = k_{eff} \frac{d^2 T}{dx_i^2} + S_t \quad (32)$$

Where S_t was the heat source term from the reactions and k_{eff} was the effective thermal conductivity which was the volume average of the fluid conductivity and the solid conductivity essentially the same as eqn [3]. The reaction pathway assumed methanol decomposing to carbon monoxide followed by a water gas shift reaction. The rate equations were:

$$r_{sr} = k_1 C_{CH_3OH}^{0.6} C_{H_2O}^{0.4} \exp \left(-\frac{E_a^1}{RT} \right) \quad (33)$$

$$r_{rWGS} = k_2 C_{CO_2} C_{H_2} \exp \left(-\frac{E_a^2}{RT} \right) - k_{-2} C_{CO} C_{H_2O} \exp \left(-\frac{E_a^2}{RT} \right) \quad (34)$$

Where E_a^1 was 76 kJ mol⁻¹ and E_a^2 was 108 kJ mol⁻¹. The pre-exponential factors were 8.8*10⁸, 6.5*10⁹, and 4.0*10⁷ for k_1 , k_2 and k_{-2} respectively[42]. They examined the impact of temperature, flow rate, S:C, and channel dimensions. Unsurprisingly, they found that conversion and CO production increases with temperature when at a given feed rate and S:C. At a constant temperature and feed rate, the CO production decreased with increasing S:C ratio. The more

interesting results were that, with this design, there are non-uniform reaction rates in each microchannel which impacts the reactor performance. The concentration non-uniformities were heavily dependent on temperature, S:C, and feed rate, an example of which is shown in Figure 10[40]. While they do not discuss this, the non-uniformities are likely caused by uneven flow distribution to the channels due to the inlet and outlet design. Ensuring even flow distribution in multi-channel designs is difficult, especially in designs with catalyst coating walls since, it is difficult to ensure even wall coating of the catalyst.

Figure 10. Methanol conversion at three different temperatures. Notice the differences in methanol conversion between the channels illustrating the non-uniform reaction rates [40].⁶

The same group published a second paper in 2009[41] which varied the height and width ratio as well as Reynolds numbers to understand their impacts on methanol conversion and gas transport. They used essentially the same equations, but a different geometry, Figure 11, compared to the paper just discussed. The simulation results predicted that lower H/W ratio resulted in better overall performance (Figure 12). This was ascribed to the improved surface area to volume ratio. A smaller micro channel size would make the temperature distribution more even, thereby increasing the methanol conversion. And finally, methanol conversion would decrease with increased Reynolds number[41].

Figure 11. Schematic diagram used by Hseuh et al.[41]⁷. H is the microchannel height (m), W is the microchannel width (m), L is the microchannel length (m), T_w is the wall temperature ($^{\circ}\text{C}$), x, y, and z are coordinates, h_1 is the open channel height (m), and h_2 is the catalyst thickness (m).

⁶ Reprinted with permission from Energy & Fuels, 23, Falin Chen, Min-Hsing Chang, Chih-Yi Kuo, et al . Analysis of a Plate-Type Microreformer for Methanol Steam Reforming Reaction, 5092-5098. Copyright (2009) American Chemical Society.

Figure 12. Effect of microchannel aspect ratio ($\gamma=H/W$) and wall temperature on methanol conversion (η) and CO concentration at channel outlet[41]⁷.

Finally, in 2010, this group published a third study on plate type micro reactors[43]. This study examined the performance of a serpentine flow field (Figure 13). Again, they used essentially the same equations as their previous studies[40, 41, 43]. Similar to their previous studies, a higher wall temperature increases the reaction rate and therefore the methanol conversion, increasing the S:C increases the conversion, as does lowering the Reynolds number. They examined the impact of heating the reactor from the bottom or the top and found that heating from the top improved performance. This was not surprising since the catalyst was on the top plate, so it would be directly heated. It would have been interesting to see if heating from the bottom would be superior if the catalyst was on the bottom. The most interesting point finding was that axial conduction through the wall had a non-trivial effect on the local temperature distribution (Figure 14)and must therefore be included in the model[43].

Figure 13. Schematic of Hseuh et al. 2010 serpentine microreactor design[43]⁸. T_w is the wall temperature ($^{\circ}\text{C}$), H is the channel height (m), W_x is the solids width in the channel (m), x_w is the open portion of the channel (m), δ_1 is the catalyst thickness (m), δ_2 is the open channel height (m), and x , y , and z are coordinates (m).

⁷ Reprinted from Journal of Power Sources 187, Ching-Yi Hsueh, Hsin-Sen Chu, Wei-Mon Yan, Numerical study on micro-reformer performance and local transport phenomena of the plate methanol steam micro-reformer, 535-543, Copyright (2009), with permission from Elsevier.

⁸ Reprinted with permission from Applied Energy, **87**, Ching-Yi Hsueh, Hsin-Sen Chu, Wei-Mon Yan, Chiun-Hsun Chen. Transport phenomena and performance of a plate methanol steam micro-reformer with serpentine flow field design, 3137-3147. Copyright (2010), with permission from Elsevier .

Figure 14 Local temperature distribution (θ) and methanol conversion predicted results with and without wall conduction. This shows that wall conduction must be considered[43]⁸. T_w is the wall temperature ($^{\circ}\text{C}$), T_o is the inlet temperature ($^{\circ}\text{C}$), Re is the Reynolds number, S/C is the steam to carbon ration, X is the dimensionless distance from the flow channel inlet to outlet, $M_{\text{CH}_3\text{OH}}$ is the mole fraction of methanol.

Apparently the first 3-D model of a plate type microreactor integrated with a combustor was presented in 2009 by Arzamendi et al[44]. The reformer plate converted methanol water mixture to hydrogen with the heat provided by a combustor plate, in physical contact, which oxidized methanol. They considered a 4-channel system and a reformer plate of 20 channels. For both systems half the number of channels was for fuel processing the other for combustion. Each channel was 20 mm long, 0.35 mm, 0.7 mm, or 1.4 mm of side. The 4-channel reactor was in co-flow configuration. However, the 20-channel reactor was in co-flow, counter flow, and cross-flow configurations. They used Ansys CFX package for their simulations with Navier-Stokes as the governing equations. They used the Chapman-Enskog kinetic theory to estimate the diffusion coefficient ($7.8 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$). For the methanol decomposition to hydrogen and carbon monoxide they used:

$$r_{SR} = 5.3 * 10^{12} \exp\left(\frac{-105 \text{ kJ/mol}}{RT}\right) P_{\text{CH}_3\text{OH}}^{0.26} P_{\text{H}_2\text{O}}^{0.03} \quad (35)$$

With the rate in mmol methanol $\text{kg}^{-1} \text{ s}^{-1}$ and the pressure in kPa[44, 45]. The WGS reaction rate equation was[44, 46]:

$$r_{CO} = 2.96 * 10^5 \exp\left(-\frac{47,400 \text{ J/mol}}{RT}\right) \left(P_{CO} P_{\text{H}_2\text{O}} - \frac{P_{\text{CO}_2} P_{\text{H}_2}}{K_e}\right) \quad (36)$$

With the rate in mol gcat⁻¹ hr⁻¹, pressures in atmospheres, and K_e given being:

$$K_e = \exp\left(\frac{4577.8}{T} - 4.33\right) \quad (37)$$

The methanol combustion reaction was the same as equation (9).

They assumed a wall coated Cu/ZnO catalyst for the methanol decomposition and WGS reactions, and found that high gas hourly space velocities (GHSV) of 50,000 hr⁻¹ could be achieved on the methanol reforming side (Figure 15)[44]. The 20-channel arrangement allowed for examination of larger systems and predicting the impacts of different flow configurations. The results showed the channel width can be scaled from 0.35 mm to 1.4 mm with only some loss in conversion occurring at the highest GHSV for the largest (1.4 mm) channel width. The co-flow configuration had the smallest variation in temperature of approximately 4 K, while the counter flow had the highest difference in temperature of 17 K. The counter flow also had the coolest inlet and hottest outlet. The cross flow configuration had the widest relatively hot zone compared to the three designs. There was no significant difference in performance, so the cross-flow was recommended since it would allow for the easiest manifolding[44]. A weakness of this model was that no experimental validation was performed[44].

Figure 15. Methanol conversion (circles) and mean channel temperatures at the outlet (triangles) as a function of the GHSV in the 4 channel arrangement[44]⁹. The 1.40 mm, 0.70 mm and 0.35 mm refer to the channel size. SRM is the steam reforming of methanol to distinguish from combustion reactions.

⁹ Reprinted with permission from Catalysis Today, 143, G. Arzamendi, P.M. Diéguez, M. Montes, M.A. Centeno, J.A. Odriozola, L.M. Gandía. Integration of methanol steam reforming and combustion in a microchannel reactor for H₂ production: A CFD simulation study, 25-31. Copyright (2009), with permission from Elsevier

Figure 16. Temperature distribution in the co flow, counter flow and cross flow configurations $d=0.7\text{mm}$, reforming $28,224\text{ hr}^{-1}$, and combustion at $75,263\text{ hr}^{-1}$ [44]⁹.

Tadbir and Akbari[1] performed a very similar analysis as Hseuh et al[41, 43]. They looked at an array of microchannels in a cluster for methanol reforming directly heated by combustion (Figure 17). For their model, they used two channels, a steam reforming channel on top of a combustion channel (Figure 17). The channels were 0.7 mm on a side and 1 cm long. The plate between the combustion and reforming channels was 0.3 mm thick. They assumed a catalyst coating of $\text{Cu/ZnO/Al}_2\text{O}_3$ (0.052 kg m^{-2}) on walls for both the combustor and reformer. The proposed construction material was not reported. The methanol water mixture flow rate and steam to carbon ratio were varied to find the best combination for the proposed reactor. On the combustion side, methanol was oxidized. Co-flow configuration was assumed[1].

Figure 17. An array of microchannels forming a complete reactor and the reactor specifications for the baseline case[1].

Due to the low Knudsen number for their case, the flow regime was continuum and therefore the Navier-Stokes equations as well as no-slip conditions were used[1]. For the source terms in the Navier-Stokes equations, they used a three step mechanism proposed by Peppley et al. [47]

The rate equations and constants are listed in reference [47]. They used the SIMPLE algorithm to solve the coupled velocity and pressure fields. A computer code was developed in the FORTRAN language to generate the meshing and solving the governing equations.

The baseline simulations (SR inlet temperature of 423 K with a 1:1 S:C feed and oxidation channel temperature of 473 K with 1% methanol in the feed) illustrated that the reaction rates started low as the reactants heated up on entering the channels. The maximum was in the middle of the channel length with the rates decreasing as the reactants are consumed. The methanol decomposition reaction had a higher rate than the WGS reaction. This was not surprising since in the baseline only 40% of the methanol was reacted. By increasing the methanol in the combustion channels to 2% they were able to raise the temperature to 477 K and increased the S:C to 2. With these changes methanol conversion >90% was achieved. The S:C was kept low in order to decrease the amount of water in the exit. Finally, by increasing the length of the reactor from 10 mm to 20 mm and operating under the baseline conditions the conversion was increased from 40% to almost 80%. The outcome from all these simulations was recommendations for reactor operations being- 20 mm in length, 1.5% methanol in combustor inlet, S:C 1.5, catalyst thickness of 0.13 kg m⁻² (twice the baseline), and a gas hourly space velocity of 4000 hr⁻¹. Under these conditions, the projected conversion, % CO in the output and efficiency were >97%, 0.56% CO and 55% respectively. The reactor output was 0.039 W for this block[1].

In 2010 a group from the National Cheng-Kung University in Taiwan reported a 3-D model on a reactor system using a microchannel architecture. The reactor was built of stainless steel with 20 microchannels each 33 mm long, 0.5 mm wide and 0.6 mm deep. The catalyst layer, Cu/ZnO/Al₂O₃ was 0.03 mm thick on the bottom of the channel[48].

Figure 18. Microchannel plate reactor by Jang et al.[48]¹⁰.

The model used standard continuity and momentum equations. The dynamic viscosity was based upon the Chapman-Enskog theory for multi-component gas mixtures at low density described by Bird et al. [49]. The energy equation was also detailed in Bird et al. [49] as

$$\nabla(\varepsilon\rho v h_o) = -\nabla q + \varepsilon\tau\nabla v \quad (42)$$

Where h_o is the total enthalpy and q accounts for thermal conduction and energy transport equations as developed in Bird et al[49]. Fick's diffusion caused by concentration gradients and also thermal diffusion was assumed. Stefan-Maxwell equations for multi-component systems were used. The following multi-step methanol reforming reaction with methanol decomposing to carbon dioxide and hydrogen and then the reverse water gas shift reaction causing some of the carbon dioxide to react with hydrogen to form water and carbon monoxide was used:

¹⁰ Reprinted with permission from Chem Eng Sci, 65, Jiin-Yuh Jang, Yu-Xian Huang, Chin-Hsiang Cheng. The effects of geometric and operating conditions on the hydrogen production performance of a micro-methanol steam reformer, 5495-5506. Copyright (2010), with permission from Elsevier

The reaction rate equations for this mechanism were proposed by Coltrin et al.[50]

$$r_1 = A_1 T^\eta \left(\frac{p}{p_{atm}} \right)^m \exp \left(-\frac{E_{a1}}{RT} \right) C_{CH_3OH}^{\alpha_{1a}} C_{H_2O}^{\alpha_{1b}} \quad (45)$$

$$r_2 = A_2 T^\eta \left(\frac{p}{p_{atm}} \right)^m \exp \left(-\frac{E_{a2}}{RT} \right) C_{CO_2}^{\alpha_{2a}} C_{H_2}^{\alpha_{2b}} \quad (46)$$

Where m , A_1, A_2 , n , E_{a1} , E_{a2} , α_{1a} , α_{1b} , α_{2a} , α_{2b} are found in Chemkin as reported in references[48]. The inlet flow rate was varied from 0.1 ml min^{-1} to 1 ml min^{-1} of a methanol water mixture (1:1.1 S:C). Vaporization was assumed to happen at the inlet and the inlet temperature was held constant at 393 K[48]. Ideal insulation, except for the top surface which was electrically heated, was used. The top surface temperature was assumed to be uniform and ranged from 473 to 533 K. They used a CFD-ACE+ commercial simulation package for the modeling. The package uses a finite volume method with SIMPLEC algorithm. To better understand the impact of the inlet and outlet manifolds, they used five different configurations: right inlet/left outlet, right inlet/right outlet, right inlet/central outlet, central inlet/central outlet, central inlet/two outlets (Figure 19).

Figure 19. Inlet and outlet configurations considered by Jang et al. [48]¹⁰.

They compared their simulation results using the right inlet/left outlet configuration with experimental data provided by Seo et al.[51] and found good agreement giving confidence in the model. The right inlet/right outlet had the lowest methanol conversion and CO concentration with the central inlet/two outlets having the best conversion over the range of flow rates.

Figure 20. Methanol conversion and mole fraction of CO with different configurations and over a range of flow rates. The Central inlet/two outlets had the best performance[48]¹⁰.

The velocity distributions in the channels showed that there was uneven flow distribution between the channels. Based upon the model simulations they recommend that a central inlet/two outlet configuration be used[48].

Figure 21. Flow velocity in the channels[48]¹⁰.

Zeng et al. (2012) [52] used simulations to investigate the impact of manifold shape on methanol microchannel plate reactor performance. Specifically they examined a right-angle manifold (MPRM) and an oblique angle manifold (MPOM). Each plate contained 50 microchannels (35 mm long, 0.27 mm width, and 1 mm in depth). The channels were made by micro-milling a 2 mm thick copper plate. Cu/Zn/Al/Zr catalyst was wash-coated in the microchannels. The same reactions as eqns [37]-[39] were used, but different reaction rate equations were assigned as follows:

Figure 22. Microchannel plates with two different manifold structures[52]¹¹.

$$r_{SR} = 1.152 \times 10^{17} \exp\left(\frac{-149,700}{RT}\right) P_{CH_3OH}^{1.002} P_{H_2O}^{0.9105} \left[1 - \frac{P_{H_2O}^3 P_{CO_2}}{K_{p,SR} P_{CH_3OH} P_{H_2O}}\right] \quad (47)$$

¹¹ Reprinted with permission from Renewable Energy, 39, Dehuai Zeng, Minqiang Pan, Yong Tang. Qualitative investigation on effects of manifold shape on methanol steam reforming for hydrogen production, 313-322. Copyright (2012), with permission from Elsevier

$$r_{DE} = 4.58 \times 10^{14} \exp\left(\frac{-181,700}{RT}\right) P_{CH_3OH}^{-0.01496} \left[1 - \frac{P_{H_2O}^2 P_{CO}}{K_{p,DE} P_{CH_3OH}}\right] \quad (48)$$

$$r_{CO} = 2.96 \times 10^5 \exp\left(\frac{-47,400}{RT}\right) \left[P_{CO} P_{H_2O} - \frac{P_{CO_2} P_{H_2}}{K_e}\right] \quad (49)$$

Where $K_e = \exp(4577.8/T-4.33)$ [46], and $K_{p,SR}$ and $K_{p,DE}$ are given by Dong et al [53]. The methanol water mixture feed (1.3 S:C) was assumed to be in the gas phase. Navier-Stokes equation with non-slip boundary conditions, laminar flow, gravity impact was negligible, and an outlet pressure of zero were used. The simulations were run with Fluent software. Of particular interest was that they defined an estimating parameter $\sigma_u\%$ where the smaller the number the more uniform the distribution. $\sigma_u\%$ is defined as:

$$\sigma_u\% = \sqrt{\frac{1}{N} \sum_{i=1}^N \left(\frac{U_c(i)}{U_m} - 1\right)^2} \times 100 (i = 1, 2, \dots, N) \quad (50)$$

Where $U_c(i)$ was the velocity in the center of each microchannel and U_m was the microchannel velocity mean value defined as:

$$U_m = \frac{1}{N} \sum_{i=1}^N U_c(i) \quad (i = 1, 2, \dots, N) \quad (51)$$

The simulations compared the velocity distribution with and without reaction occurring for both manifold designs. The mixture flow rate was 0.5 to 12 ml hr⁻¹ and heating temperature of 673-723K[52].

When no reaction was used, the temperature did not seem to impact the flow distribution. Under low inlet velocities the distribution seemed symmetrical. However, as inlet velocity increased, the flow became asymmetrical with larger velocities found to be in the channels further away from the inlet. Finally, the MPRM had a lower $\sigma_u\%$ than the MPORM indicating that it had a more uniform distribution[52].

When reaction was included the flow distribution changed from a “U” shape when no reaction was flowing to a “wave” shape (Figure 23). Figure 24a shows the $\sigma_u\%$ plotted against the inlet velocity which clearly indicates that the right angle manifold has better flow distribution compared to the oblique. This resulted in improved methanol conversion (Figure 24b). Thus they recommend the right angle manifold[52].

Figure 23. Velocity Distribution (a) without reaction and (b) with reaction. MPOM is oblique manifold and MPRM is the right angle manifold[52]¹¹.

Figure 24. (a) Comparison of velocity degree of uniformity and (b) methanol conversion in the MPOM and MPRM with reaction[52]¹¹.

The next 3-D microscale methanol reformer reviewed here is a microreformer with a micro-pin-fin array (Figure 25) designed and modeled by Mei et al.[7] and Qian et al. [54]. The objective of this work was to increase the surface area to volume ratio using the micro-pin-fin design thus “enhancing the compactness” of the reactor[7]. They used the semi-solid micro thixo-forming

process. In this process the desired material, aluminum alloy A356 in this case, was hot stamped to form the micro-pins. The thixo-forming process is capable of making the desired 3-D microstructures required and was developed to be able to do large volume, low cost manufacturing[7]. Both the experimental and modeled results indicated that the micro-pin design reactor performed better than a flat plate microchannel reactor under the same operating conditions. However, the authors indicated that the 87.5% methanol conversion and CO amount of <1% was acceptable for fuel cell applications. This may not be true for some types of PEM fuel cells which require extremely high purity hydrogen (CO lower than 10 ppm) and the unreacted methanol may substantially decrease the fuel cell performance. In a subsequent paper, the same group used their model to improve the velocity distribution in their reactor by modifying the manifold [54]. An equivalent electrical resistance network model validated via simulation was used. The results showed that by increasing the y-direction coordinate of the flow manifold inlet tube, improved velocity distribution could be obtained[54].

Figure 25. Micro-pin-fin methanol reformer design. a) is the 2-D diagram, b) fabricated catalyst support, and c) completed microreactor[7]¹².

Finally, Yao et al. proposed an interesting disc microreactor with tree-shaped flow architectures[55]. Their objective was to improve the flow distribution in the microreactor compared to single or parallel channel designs. The design consisted of three branches connected to one central flow point (Figure 26. Schematic of disc reactor with tree shaped network (a) compared to microreactor with parallel flow pattern (b) [55]¹³.Figure). The radius of the disc was 15 mm and the microchannels had a depth of 2 mm. Four different scenarios of channel width were examined

¹² Reprinted with permission from Journal of Power Sources, 205, Deqing Mei, Miao Qian, Binhong Liu, Biao Jin, Zhehe Yao, Zichen Chen. A micro-reactor with micro-pin-fin arrays for hydrogen production via methanol steam reforming, 367-376. Copyright (2012), with permission from Elsevier

to identify the optimal width. In the model, the total channel volume was the same. They compared the performance of their disc reactor with that of a more conventional parallel channel reactor with the same reactor volume. The reactors were assumed to be made out of silicon with CuO/ZnO catalyst on an Al₂O₃ support. For the reaction equations and kinetics they used equations (38)-(40) and with kinetics described by Peppley et al and Amphlett et al [47, 56].

Figure 26. Schematic of disc reactor with tree shaped network (a) compared to microreactor with parallel flow pattern (b)¹³ [55].

The governing equations for the microreactors were the Continuity equation, Momentum and Energy conservation, and chemical species conservation with Maxwell-Stefan for diffusion and mixing. These equations were solved using a finite volume approach and the SIMPLE algorithm for the pressure velocity coupling. The model was validated against a wall-coated tubular microreactor reported in the literature[55].

The model results predicted that the bifurcation effect of the tree-shaped branches caused the reactant gas mixture to come in better contact with the catalyst layer compared to the parallel channel design. This resulted in improved conversion and increased hydrogen production.

Figure 27. Hydrogen mole fraction distribution at T=503 K, V_{in}=0.3 m s⁻¹, and steam to carbon ratio of 1.3 for the (a) tree shaped network and (b) parallel flow channel¹³[55].

Figure 28. Methanol conversion of the tree shaped (Constructal) and parallel channel reactors¹³[55].

¹³ Reprinted with permission from International Journal of Heat and Mass Transfer, 64, Feng Yao, Yongping Chen, G.P. Peterson. Hydrogen production by methanol steam reforming in a disc microreactor with tree-shaped flow architectures, 418-425. Copyright (2013), with permission from Elsevier

The major findings of the model were the methanol conversion was 10% higher in the tree-shaped network compared to the parallel channel and the branching increases the surface to volume ratio resulting in an improved conversion for the same reactor volume[55]. This paper proposed a novel design. It would be interesting to see the results of a manufactured device.

4.0 Conclusion.

Considerable progress has been made on the development of microscale low power fuel processors for hydrogen production. These systems utilize many of the manufacturing technologies developed for microelectronics. In these miniature systems, it is extremely difficult to be able to determine the heat and mass transfer characteristics (i.e. flow distribution, temperature distribution, etc.) internal to the reactors and other unit operations. Numerical simulations are critical to understand what is occurring internal to the reformers and be able to improve the designs to achieve the desired performance. Numerous simulation models have been developed ranging from one to three dimensions. As computational power has increased and cost has decreased, the models have increased in complexity and accuracy. The new three dimensional models are very powerful and allow faster, less expensive, and more accurate design. The primary fuel used has been methanol due to its lower reforming temperature. However, several interesting designs have been reviewed which use methane. Initial simulations were simple and focused on wash coated plates and packed bed designs. The recent simulations increased in complexity and included multiple unit operations beyond just the reactor to include vaporization and heat recovery. The majority of designs analyzed were flat plate or annulus designs with the micropin and disc designs as variations from the conventional parallel channels. The numerical simulation tools have proven to be extremely useful in evaluating new designs, understanding the manifold impact on flow distribution, projecting thermal distribution and efficiency.

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Table Captions

Table 1. Fuel and fuel-water mix energy density for several common fuels.

Table 2. Comparison of reforming technologies (adapted from [2,12,25,26])

Table 3. Microreactor material advantages and challenges (adapted from [12])

Figure Captions

Figure 1. Isothermal packed bed performance compared to experimental data at 503K[27]². W = catalyst weight in kg and F = methanol flow in mol s⁻¹.

Figure 2. Modeling predictions for wall coated reactors at 503K. Unlike the packed bed reactor, no heat transfer limitations were predicted[27]². W = catalyst weight in kg and F = methanol flow in mol s⁻¹. The numbers in parenthesis represent the catalyst coating thickness.

Figure 3. Schematic figure of zigzag and straight catalytic wall microchannel reactor configurations. [32] (used with permission).

Figure 4. Dimensions used in microreactor model. TOX is the total oxidation or combustion side[32] (used with permission).

Figure 5. Zigzag configuration has a higher (a) hydrogen production (mole fraction) and a lower CO selectivity (b) than the straight configuration. From [32] used with permission.

Figure 6. Annular reformer with hot gas in the outer tube and packed bed reformer with incline and fishbone-shaped baffle plates inside the reformer from reference Reprinted with permission from Energy and Fuels reference 35. Copyright (2012) American Chemical Society.

Figure 7. Physical domain of the annulus design methanol reformer with methanol air combustor proposed by Chen et al. [38]³. $Q_{in,R}$ is reformer inlet volumetric flow rate (m³ s⁻¹), T_{in} is inlet temperature (K), R_b is reformer radius (m), R_c is combustor radius (m), t_c is combustion wall thickness (m), t_r is reformer wall thickness (m), L is the inlet and outlet length (m), and L_b is the reformer length (m).

Figure 8. Microchannel cross section. This drawing shows the dimensions, location of coordinate axes and direction of flow[28]⁴.

Figure 9. Top view of microchannel plate reactor modeled by Chen et al. [34]⁵. The dimensions are in mm and the channel depth is 0.5mm.

Figure 10. Methanol conversion at three different temperatures. Notice the differences in methanol conversion between the channels illustrating the non-uniform reaction rates[40]⁶.

Figure 11. Schematic diagram used by Hseuh et al.[41]⁷. H is the microchannel height (m), W is the microchannel width (m), L is the microchannel length (m), T_w is the wall temperature ($^{\circ}\text{C}$), x , y , and z are coordinates, h_1 is the open channel height (m), and h_2 is the catalyst thickness (m).

Figure 12. Effect of microchannel aspect ratio ($\gamma=H/W$) and wall temperature on methanol conversion (η) and CO concentration at channel outlet[41]⁷.

Figure 13. Schematic of Hseuh et al. 2010 serpentine microreactor design[43]⁸. T_w is the wall temperature ($^{\circ}\text{C}$), H is the channel height (m), W_x is the solids width in the channel (m), x_w is the open portion of the channel (m), δ_1 is the catalyst thickness (m), δ_2 is the open channel height (m), and x , y , and z are coordinates (m).

Figure 14 Local temperature distribution (θ) and methanol conversion predicted results with and without wall conduction. This shows that wall conduction must be considered[43]⁸. T_w is the wall temperature ($^{\circ}\text{C}$), T_o is the inlet temperature ($^{\circ}\text{C}$), Re is the Reynolds number, S/C is the steam to carbon ration, X is the dimensionless distance from the flow channel inlet to outlet, $M_{\text{CH}_3\text{OH}}$ is the mole fraction of methanol.

Figure 15. Methanol conversion (circles) and mean channel temperatures at the outlet (triangles) as a function of GHSV in the 4 channel arrangement[44]⁹. The 1.40 mm, 0.70 mm and 0.35 mm refer to the channel size. SRM is the steam reforming of methanol to distinguish from combustion reactions.

Figure 16. Temperature distribution in the co flow, counter flow and cross flow configurations $d=0.7\text{mm}$, reforming $28,224\text{ hr}^{-1}$, and combustion at $75,263\text{ hr}^{-1}$ [44]⁹.

Figure 17. An array of microchannels forming a complete reactor and the reactor specifications for the baseline case[1] (used with permission).

Figure 18. Microchannel plate reactor by Jang et al.[48]¹⁰.

Figure 19. Inlet and outlet configurations considered by Jang et al. [48]¹⁰.

Figure 20. Methanol conversion and mole fraction of CO with different configurations and over a range of flow rates. The Central inlet/two outlets had the best performance[48]¹⁰.

Figure 21. Flow velocity in the channels[48]¹⁰.

Figure 22. Microchannel plates with two different manifold structures[52]¹¹.

Figure 23. Velocity distribution (a) without reaction and (b) with reaction. MPOM is oblique manifold and MPRM is the right angle manifold[52]¹¹.

Figure 24. (a) Comparison of velocity degree of uniformity and (b) methanol conversion in the MPOM and MPRM with reaction[52]¹¹.

Figure 25. Micro-pin-fin methanol reformer design. a) is the 2-D diagram, b) fabricated catalyst support, and c) completed microreactor[7]¹².

Figure 26. Schematic of disc reactor with tree shaped network (a) compared to microreactor with parallel flow pattern (b) [55]¹³.

Figure 27. Hydrogen mole fraction distribution at $T=503\text{K}$, $V_{\text{in}}=0.3\text{ m s}^{-1}$, and steam to carbon ratio of 1.3 for the (a) tree shaped network and (b) parallel flow channel[55]¹³.

Figure 28. Methanol conversion of the tree shaped (Constructal) and parallel channel reactors[55]¹³.

Table(s)

Fuel	Fuel Energy Density (kW-hr kg ⁻¹)	Fuel-Water Energy Density (kW-hr kg ⁻¹)*
Methane	13.9	3.8
Propane	12.7	3.2
Iso-octane	12.3	3.05
Methanol	5.6	3.7
*Fuel-water mix represents the stoichiometric requirement for steam reforming, defined as a molar S/C of 3.0 for paraffinic hydrocarbons and 1.2 for methanol. Fuel-water energy density is based upon the lower heating value of the hydrogen produced from reforming the mixture with 100% conversion to CO ₂ and H ₂ . (i.e. CH ₄ + 2H ₂ O → CO ₂ + 4H ₂).		

Table(s)

Technology	Advantages	Disadvantages
Steam Reforming	Most extensive industrial experience Oxygen not required Lowest processing temperature Best H ₂ /CO ratio for H ₂ production	Highly endothermic
Autothermal reforming	Lower process temperature than POX Low fuel slip	Limited commercial experience Requires air or oxygen
Partial oxidation	Decreased desulfurization requirement No catalyst required (although sometimes used) Low fuel slip	Low H ₂ /CO ratio Requires air or oxygen Very high processing temperatures Soot formation / handling adds process Complexity

Table(s)

Material	Advantages	Challenges
Metal	Conventional fabrication techniques Durable Low to modest costs No clean room required	Poor compatibility with ceramics and glass
Silicon and silicon type of materials	Well characterized silicon fabrication techniques High precision manufacturing Low cost, high volume manufacturing	Fragile material Requires a clean room
Low Temperature Co-Fired Ceramics	Flexible fabrication Refractory and durable materials Low cost No clean room required	Non-standard fabrication Sealing
Polymers	Low cost Flexible Fabrication	Chemical compatibility Thermal stability Sealing

Figure(s)

Figure(s)

a Zigzag catalytic wall coated two passes micro channel reactor

b Straight catalytic wall coated two passes micro channel reactor

Figure(s)

Figure(s)

Figure(s)

$$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightleftharpoons \text{mixture}$$

Hot gas
 $F_{g,in}, T_{g,in}$

(b)

$$\text{H}_3\text{OH} + \text{H}_2\text{O}$$

mixture

Hot gas
 $F_{g,in}, T_{g,in}$

Figure(s)

Figure(s)

Figure(s)

Figure(s)

(a)

Figure(s)

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Right-angle manifolds

Oblique- angle manifolds

Figure(s)

Figure(s)

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Figure(s)

(a)

(b)

(c)

Figure(s)

Figure(s)

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