3-D Model of a Radial Flow Sub-Watt Methanol Fuel Processor

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Abstract:

A 3-D model is presented for a novel sub-watt packed bed reactor. The reactor uses an annular inlet flow combined with a radial flow packed bed reactor. The baseline reactor is compared to a reactor with multiple outlets and a reactor with 3 internal fins. Increasing the outlets from 1 to 4 may have improved flow distribution, but did not increase the performance. However, inserting fins allowed >99% methanol conversion with approximately 30K decrease in temperature with same inlet flow.

Keywords: microreactor, hydrogen production, methanol reforming, modeling

1. Introduction

Driven by Mohr's law and exceptional ingenuity of modern engineers and scientists, electronic devices continue to shrink in mass and volume while increasing in capabilities. Despite great improvements in the efficiency of the device electronics, the power and

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energy demand for these devices has also increased. While Mohr's law applies to semi-conductor devices, similar improvements in batteries have not been realized. Miniature proton exchange membrane fuel cells (PEMFC) have been proposed to fill this gap, but these fuel cells typically utilize gaseous hydrogen which is difficult to store⁽¹⁻¹²⁾. However, the advances in semi-conductor processing can be applied to the development of chemical processing systems resulting in miniature fuel processors which can produce hydrogen from chemicals⁽¹⁻¹³⁾.

Methanol is an ideal fuel for such miniature devices since it: (i) has a high gravimetric density of hydrogen (12.5 wt%), (ii) is a liquid at ambient temperatures, (iii) is miscible in water enabling premixing of the fuel required for steam reforming, (iv) is biodegradable, (v) is sulfur and other contaminant free, (vi) reforms at low temperatures (typically 200-350°C) making thermal integration much easier than paraffinic hydrocarbons such as butane, propane, or methane which reform at temperatures greater than 600°C, (vii) the low temperature reforming favors water-gas-shift and, consequently, produces a low CO content stream which can be utilized directly by Polybenzimidazole fuel cells^(14,15), or can be readily cleaned-up via the selective oxidation⁽¹⁶⁻¹⁸⁾ or methanation^(10,11,19) to levels suitable for PEMFC and (viii) the low steam to carbon (S:C) ratio required for methanol reforming (1.2:1) compared to the >3:1 typically required for paraffinic hydrocarbons to minimize coke formation^(19,20). The major disadvantage of methanol is its relatively high toxicity, which can be handled by engineering solutions to minimize exposure.

2. Reactor Design

Numerous miniature fuel processors have been proposed, designed, and built for this application. The most common designs are variations of a coated wall plate reactor with zig-zag's internal fluid flow, coated wall Swiss-roll reactors, and packed bed reactors⁽²¹⁻²⁸⁾. For this work a radial flow packed bed fuel processor first proposed by Holladay et al. is considered^(15,19,29-31). This fuel processor was scaled to produce less than 1W hydrogen equivalent from a compact source and was composed of a radial flow methanol steam reforming reactor in intimate contact with a catalytic combustor (Figure 1). The direct contact of the endothermic methanol steam reforming reactor with the exothermic combustor focused the thermal energy where it was most needed with the intention of maximizing efficiency. Unlike many of the other proposed designs, this design included an internal vaporizer coupled with the methanol reformer, catalytic combustor and a unique design which enables some heat recuperation via preheating the inlet streams. The methanol- water mix was vaporized and preheated by entering the reactor through a central tube in an annulus configuration, thus capturing waste heat further improving efficiency. On the combustor side, the fuel air mixture was also fed through a central tube in annulus configuration which would pre-heat the incoming fuel/air mix also, with the intention of improving efficiency^(15,19,30,31). The design had a single exit point and no internal mixing other than that which occurred in the packed bed (i.e. no internal baffles or fins). In this paper we use a 3-D model to explore two proposed design changes with the intention of improving the reactor performance. The first is to increase the single outlet to four exit points with the intention of equalizing flow throughout the reactor. The second is the inclusion of several baffles or fins to control the flow to better utilize the reactor bed the flow. The inclusion of fins in reactors is well known to improve performance ⁽³²⁻³⁴⁾.

Figure 1. Schematic of baseline reactor design

The fuel processor was constructed of stainless steel as previously described ^(15,19,30,31). The outer wall thickness was approximately 0.25mm. The inlet and outlet tubes OD and ID of 0.46mm and 0.25mm respectively. The fuel processor's diameter was 6.35mm OD, and approximately 5.8mm ID. The entire fuel processor had a length of approximately 10mm which included the combustor, methanol steam reforming reactor, and end-caps. The steam reformer and combustor sections were each 4.4mm in length. The plungers had a diameter of 5mm and there was approximately 2.5mm of catalyst bed between the plunger and shim separating the methanol steam reformer reactor and the catalytic combustor. The fluid enters the middle tube, where it is vaporized and preheated. It exits the tube into the catalyst bed where it moves radially to get to the edge of the reactor and go around the plunger. For the reformer section, the gases then flow through the packed bed reactor and exit. On the combustor side, there is no additional catalyst between the plunger and outlet tube, so the gases flow through the empty section and then exit the reactor. A thermocouple was inserted into the exit tube of the combustion section to monitor and control the reactor temperature. Since the reactor is not isothermal, it is difficult to identify a single condition for comparison purposes especially for conversion. Therefore, all temperatures in the figures for conversion reported are from the combustion side as

measured by this thermocouple and are referenced as Tcr. Kao-wool, approximately 25mm thick was used as the insulation. The fuel processor operation was described previously. The methanol steam reformer used a Pd/ZnO catalyst. Details on the Pd/ZnO methanol reforming catalyst used was described previously⁽⁷⁾. The combustion catalyst was 10 wt% Pd on γ -alumina prepared by incipient wetness technique.

3. Model development

COMSOL 4.2 was used to develop a 3-D model the fuel processor. A line of symmetry through the length of the reactor was used to decrease computational time. Continuity, momentum balance, mass conservation and energy conservation equations were used to model the fuel processor. The methanol water mixture entered the system as a liquid and was vaporized in the inlet tube. For the momentum balance, the fluids in the packed bed reactors were assumed to follow Darcy's law in the packed bed reactor.

$$U = -\frac{\kappa}{\mu} \nabla P \quad [1]$$

Where μ is the fluid viscosity (Pa*s), P is the pressure (Pa), κ is the permeability (m²) and U is the flow rate (m s⁻¹).

The Reynolds number (equation 2) for the flow in the inlet and exit tubes was between approximately 6 to 1 for the methanol reformer portion and 600 and 32 for the combustor portion. Since this is laminar flow in a tube, equation 3, was used in the inlet and exit tubes⁽³⁵⁾.

$$Re = \frac{\rho U d_h}{\mu} \quad [2]$$

Where ρ is the fluid density (kg m^{-3}), and d_h is the hydraulic diameter with $d_h = 4 \cdot \text{area} / \text{perimeter}$ (m) which for a tube is twice the radius ($2r$).

$$U = -\frac{r^2}{8} \frac{\nabla P}{\mu} \quad [3]$$

We used COMSOL's transport of concentrated species equations for the conservation of mass:

$$\nabla \left(-\rho D_{i,L}^m \nabla w_i - \rho w_i D_{i,L}^m \frac{\nabla M_n}{M_n} \right) + \rho (U \cdot \nabla) w_i = R_i \quad [4]$$

Where $D_{i,L}^m$ is the diffusivity ($\text{m}^2 \text{s}^{-1}$) which included the dispersion effects, w_i is the mass fraction of component i , and R_i is the change in mass of component i from reactions.

$$M_n = \left(\sum_i \frac{w_i}{M_i} \right)^{-1} \quad [5]$$

We used the Stefan-Maxwell diffusivity

$$D_i^m = \frac{1-w_i}{\sum_{k \neq i} \frac{x_k}{D_{ik}}} \quad [6]$$

The Stefan-Maxwell equations were used to estimate the mean effective binary diffusivity and the dispersion effects were accounted for by using $D_{i,L}^m = D_i^m \left(0.7 + 0.5 \frac{d_p \mu}{\rho D_i^m} \right)$ with units of $\text{m}^2 \text{s}^{-1}$ (36). In these equations x_k is the mole fraction of component k , D_{ik} ($\text{m}^2 \text{s}^{-1}$) is the mutual diffusivity of components i and k , D_i^m is the Stefan-Maxwell diffusivity ($\text{m}^2 \text{s}^{-1}$) and $D_{i,L}^m$ is the effective diffusivity taking into account dispersion due to the packed bed.

The methanol reforming reaction was simplified to:

We used the reaction rate equation developed by Cao et al.⁽⁷⁾:

$$-r_{meoh} = 2.9047 * 10^{10} e^{\frac{-E_a}{RT}} P_{meoh}^{0.715} P_{H_2O}^{0.088} \quad [8]$$

Where $-r_{meoh}$ is the reaction rate of methanol in $\text{mmol kg cat}^{-1} \text{s}^{-1}$, and P_{meoh} and P_{H_2O} are the partial pressures of methanol and water in kPa, respectively and E_a is the activation energy $94,800 \text{ J mol}^{-1} \text{K}^{-1}$. Standard energy conservation equations were used in the model:

$$\rho C_p V \cdot \nabla T = \nabla \cdot (\lambda \nabla T) + Q \quad [9]$$

Where C_p is the heat capacity, λ is the thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$), and Q is heat (W m^{-3}) into or out of the model. This is from the endothermic methanol reforming reaction or the exothermic combustion reaction plus losses to the environment. For the heat input from the combustor, a thermal heat source was used in place of the combustion reaction. In the model, this heat source was located in the combustor catalyst section. The heat losses due to the endothermic methanol reforming reaction were calculated as the heat of reaction, found in Table 1, times the moles methanol reacted.

As mentioned previously, the methanol-water mix entered the reactor as a liquid and was vaporized. Vaporization can be difficult to simulate. So for only the methanol water mixture inlet tube on the methanol reformer portion of the fuel processor, the C_p and density were estimated as follows. C_p was estimated by taking into account the heat of vaporization.

Recognizing that $C_p = dH/dT$, we used ChemCad® to determine the ΔH of the mixture over a temperature range from room temperature 293K – 475K (Figure 2). Using these numbers

we were able to calculate an average C_p over the vaporization range (346K-359K) calculated to be $122.1 \text{ J g}^{-1} \text{ K}^{-1}$. The data was entered into a table format into the COMSOL model and used the interpolation function. Similar, for the density, ChemCad® software was utilized to determine the vapor and liquid mole fraction over the same range (Figure 3). This approximated the density during vaporization. The methanol-water mixture liquid phase density was 898 kg m^{-3} and the ideal gas law was employed to calculate the density in the vapor phase. It was assumed that the vaporization would occur quickly so two phase flow could be neglected. In the methanol reactor portion and exit tubes where the reactants and products are gases, the ideal gas law was used for the density. The heat capacity of a gas mixture of methanol, water, H_2 and CO_2 at 50% methanol conversion and 575K was used as the C_p (Table 1). For the combustion sections, the density and C_p of air as found in Table 1 was used.

Figure 2. Enthalpy change of the water-methanol mixture (1.2:1 molar). This was used to calculate a C_p over the vaporization range to simulate vaporization in the reformer.

Figure 3. Density change of the water-methanol mixture (1.2:1 molar).

For the bed thermal conductivity an effective thermal conductivity was found using, Yagi and Kunii's⁽³⁷⁾ formulas as proposed by Karim et al⁽³⁸⁾:

$$\frac{\lambda_{eff}}{\lambda_{gas}} = \frac{\lambda_{eff}^0}{\lambda_{gas}} + (\alpha\beta)(PrRe) \quad [10]$$

Where λ_{eff}^0 is the effective conductivity with a stagnant gas ($Re=0$); λ_{gas} is the gas thermal conductivity, α is the mass velocity in the direction of heat transfer/mass velocity based on area of the empty tube in the direction of fluid flow, and β is the effective length between the centers of two particles/mean particle diameter. It was reported⁽³⁸⁾ that $\alpha\beta = 0.05$ for a diameter of the reactor/particle diameter ratio of ~ 29 similar to this reactor. Yagi and Kunii⁽³⁷⁾ gave equation [13] for calculating $\frac{\lambda_{eff}^0}{\lambda_{gas}}$:

$$\frac{\lambda_{eff}^o}{\lambda_{gas}} = \beta \left(\frac{1-\phi}{\lambda_{gas}/\lambda_p + \psi} \right) \quad [11]$$

Where, for spherical particles $\beta = 1$; ϕ is the void fraction which was 0.4 and ψ was the effective thickness of fluid film adjacent to contact surface between two solid articles/mean particle diameter. From the literature 0.04 was a good number for round particles in a packed bed for methanol steam reforming⁽³⁸⁾. The thermal conductivity of the catalyst particles (λ_p) was $1.3 \text{ W m}^{-1} \text{ K}^{-1}$ ⁽³⁹⁾. Other parameters used in the model are in Table 1.

Table 1. Model Parameters

Parameter	Value	Ref.
Insulation		
Density	128 kg m^{-3}	(40)
Heat capacity	$835 \text{ W m}^{-1} \text{ K}^{-1}$	(40)
Methanol reformer		
Heat of Reaction	$201.2 \text{ kJ mol}^{-1}$	(20)
Heat Capacity	$0.0794 \text{ W m}^{-1} \text{ K}^{-1}$	(41)
Viscosity (at 50% methanol conversion at 575K)	$196.7\text{e-}7 \text{ *Pa*s}$	(41)
Permeability (packed bed)	$4.76\text{e-}11 \text{ m}^2$	
Porosity	0.72	
Catalyst thermal conductivity	$1.3 \text{ W m}^{-1} \text{ K}^{-1}$	(39)
Combustor		

Catalyst thermal conductivity	$1.3 \text{ W m}^{-1} \text{ K}^{-1}$	(39)
Volume fraction	0.6	
Air		
Thermal conductivity	$(-2.664\text{e-}8*T^2+9.149\text{e-}5*T+1.415\text{e-}3) \text{ W m}^{-1} \text{ K}^{-1}$	Data from (41)
Density	$(-2.954\text{e-}9*T^3+7.523\text{e-}6*T^2-6.827\text{e-}3*T+2.6) \text{ kg m}^{-3}$	Data from (41)
Heat capacity	$(-3.8172\text{e-}7*T^3+8.3379\text{e-}4*T^2-0.36177*T+1050) \text{ W m}^{-1} \text{ K}^{-1}$	Data from (41)
Viscosity	$(7.076\text{e-}11*T^2+6.046\text{e-}8*T-8.945\text{e-}6) \text{ Pa*s}$	Data from (41)
Steel		
Thermal conductivity	$19.8 \text{ W m}^{-1} \text{ K}^{-1}$	(41)
Heat capacity	$557 \text{ W m}^{-1} \text{ K}^{-1}$	(41)
Density	7900 kg m^{-3}	(41)

The boundary conditions were as follows. The incoming liquids and gases were at room temperature (298K). The methanol water mixture was at 1.2:1 steam to carbon ratio and had a flow rate as indicated in the text. Exit was at convective flux for heat and mass. For the insulation convective flux the heat transfer coefficient of $12 \text{ W m}^{-2} \text{ K}^{-1}$ which was estimated using the procedure described by Raithby and Hollands⁽⁴⁰⁾ for small horizontal cylinders. The exit pressure was 1 atmosphere.

4. Results

The baseline model was exercised at a methanol water mix feed rates of 0.15 ml hr⁻¹ and 0.2 ml hr⁻¹. On the combustion side, the inlet air flow was held constant at 25 sccm while the thermal energy input was adjusted until the desired temperatures were reached. It was assumed that increasing the methanol for the combustor did not significantly increase the gas flow. The methanol conversion model results were compared to experimental data from Holladay et al. in reference ⁽³⁰⁾. The model predicts a large temperature gradient in the reactor, which was consistent with the microreactor design intentions ^(15,19,30,31). In fact, the design theory was to have the hottest portion of the system be in the middle where the thermal energy is needed for the reaction, and then to have the system cool from the middle to the outer edges in order to make thermal insulation easier. The design accomplishes that goal as can be seen in an example temperature profile shown in Figure 4. The reactor had a temperature differential of approximately 75-100K with the middle of the combustor projected to be around ~655K and the temperature at the exit of the steam reformer reactor bed at the exit tube being projected to be approximately 550 - 575K during the hottest conditions. As discussed previously, for the experiments as reported in reference ⁽³⁰⁾, a thermocouple was inserted through the combustor exit tube and connected to the plunger on the combustor side. This thermocouple position was outside the hottest point in the combustor and measured ~618K when the reactor achieved 100% conversion. The approximate position of the thermocouple was located in the model and the temperature at this point was designated as T_{cr} which would correspond to the thermocouple temperature in the experimental data. The conversion data are presented using this temperature (T_{cr}). Figure 5 shows the reaction rate in kg m⁻³ s⁻¹ which clearly shows the majority of the reaction occurs at the reactor inlet where it is hottest and the rest

of the bed serves to achieve the high conversion desired. Finally, as shown in Figure 6, there is fairly good agreement between the predicted methanol conversion results and the limited available experimental data. This gave us confidence that simulation can then be used to explore variations in the methanol reformer design.

Figure 4. Reformer system projected temperature isotherm (temperature in K) contours with 0.2 ml hr^{-1} methanol water mix flow and a $>99.5\%$ methanol conversion. The steam reformer is the upper reactor and the combustor is in the lower section.

Figure 5. Baseline methanol steam reformer system projected reaction rate in kg methanol converted $\text{m}^{-3} \text{s}^{-1}$ at >99.5% methanol conversion.

Figure 6. Predicted methanol conversion (solid line) compared to experimental results at 0.15 ml hr^{-1} and 0.2 ml hr^{-1} methanol-water mixture flow rates. Temperature corresponds to the thermocouple temperature in the experiments and the temperature at approximate location of the thermocouple in the model (T_{cr}).

The baseline reactor worked well; however, it was believed that the performance could be improved. The baseline model showed that there was poor utilization of the reactor bed since the gases would preferentially flow towards the exit leaving large portions of the bed stagnant as illustrated by the velocity contour plot shown in Figure 7. These conditions would be caused by the tendency of the gas to flow through the path of least resistance.

Therefore, with only one exit and nothing blocking the gas's path, the gases will preferentially flow to the side of the reactor with the exit and large portions of the catalyst bed will be by-passed. Two simple design variations were proposed and explored to address these issues. The first was to increase the number of exits. It was hypothesized that with exits equidistant from each other, the flow distribution should become more uniform and more of the catalyst bed would be accessed. The second permutation was the inclusion of fins. The fins would force the gases to take a longer pathway to the exit. More details on how these permutations were implemented and the study results are presented next.

Figure 7. Predicted velocity profiles (velocity in m s^{-1}) at inlet fluid flow for 0.2 ml hr^{-1} methanol water mixture feed and $>99.5\%$ methanol conversion. A) shows the cross-section and B) shows the outside. The methanol reformer is the top reactor and the combustor is the bottom reactor. The maximum velocity of the methanol section was $\sim 3.1 \text{ m s}^{-1}$, but a finer scale was used in order to see the velocity profile in the reactor sections more clearly.

4.2 Multiple Outlets.

The first modification was to increase the number of reformer outlets from 1 to 4. It was believed that by increasing the number of outlets the flow distribution would be improved through the catalyst bed which would increase the amount of catalyst utilized resulting in improved reactor performance. As shown in velocity contour plot in Figure 8, the fluid flow uniformity was somewhat improved. Increasing the number of exits may have improved the flow distribution, but the reactor performance did not increase as shown in Figure 9. It is believed that the improve flow distribution minimized gas channeling, but did not change the residence time. While some additional catalyst may have been accessed, the amount was not increased enough to improve performance. In addition, the portion of the reactor where the flow was increased was located in the sector of the methanol reformer that had the lowest temperature and reaction rate (see Figures 4 and 5). Therefore, it is necessary to improve the gas flow in the areas where the reaction rate is higher in order to improve performance.

Figure 8. Predicted velocity profiles (velocity in m s^{-1}) for the reactor design with 4 outlets at inlet fluid flow for 0.2 ml hr^{-1} methanol water mixture feed and $>99.5\%$ methanol conversion. A) shows the cross-section and B) shows the outside. The methanol reformer is the top reactor and the combustor is the bottom reactor. The maximum velocity of the methanol section was $\sim 3.1 \text{ m}^{-1}$, but a finer scale was used in order to see the velocity profile in the reactor sections more clearly.

Figure 9. Predicted baseline methanol conversion and predicted methanol conversion with multiple outlets. No significant improvement was predicted in the numerical simulation. Temperature corresponds to the thermocouple temperature in the experiments and the temperature at approximate location of the thermocouple in the model (Tcr).

4.3 Fined design

The final design permutation was to add a series of three fins to the baseline model to force the gases to flow through more of the reactor effectively increasing the amount of time the gases would need to be in the reactor as well as increasing the catalyst amount actively participating in the reaction and improve mixing. The hypothesis was that a design which uses fins or baffles would better be able to distribute the flow. The fins were 10 μ m thick with a diameter of 5.4mm and spaced evenly apart in the bed. Using the reactor geometry and ignoring tortuosity caused by the packed bed, a minimum distance for the gases to travel from exiting the plunger to the exit tube can be estimated. The minimum distance in the baseline reactor was approximately 6.5mm, whereas by adding the fins the minimum length increased >95% to approximately 12.8mm. Figure 10 shows the velocity contour plot which indicates better flow distribution until the section closest to the outlet. Another useful plot is a streamline velocity plot, which visualizes the path a particle would take as carried in the fluid and shows the highest probability of flow and the flow at the highest magnitude for the fluids. A streamline plot of all three reactors is shown in Figure 11 which reveals that there is improved catalyst bed utilization in the finned reactor compared to the other designs. In addition, it was anticipated that the fins would also increase or change the temperature distribution. However, by comparing Figure 4 and 12, it can be seen that no significant changes in the temperature distribution were observed.

Figure 10. Predicted velocity profiles (velocity in m s^{-1}) for the finned reactor design at inlet fluid flow for 0.2 ml hr^{-1} methanol water mixture feed and $>99.5\%$ methanol conversion. A) shows the cross-section view and B) shows the outside view. The methanol reformer is the top reactor and the combustor is the bottom reactor. The maximum velocity of the methanol section was $\sim 3 \text{ m s}^{-1}$, but a finer scale was used in order to see the velocity profile in the reactor sections more clearly.

Figure 11. Velocity streamlines (velocity in m s^{-1}) in the methanol reformer section only of the A) baseline reactor, B) multi-exit reactor design and C) finned reactor design. Inlet flow was 0.2 ml hr^{-1} and $>99.5\%$ methanol conversion. The maximum flow was $\sim 3.1 \text{ m s}^{-1}$.

Figure 12. Predicted temperature distribution (temperature in K) in finned reformer at 0.2 ml hr^{-1} inlet rate and $>99.5\%$ methanol conversion. The top portion is the steam reformer reactor and the bottom section is the combustor.

As shown in Figure 13 the reactor with added fins improved the reactor performance as evidenced by the fact that >99.5% methanol conversion was attained at 29K lower temperature ($\sim 589\text{K}$) compared to the original design which required $\sim 618\text{K}$ to achieve the same methanol. The improved performance was attributed two primary reasons. First, the finned reactor design had a longer residence time forced by the longer distance the gases traveled from entrance to exit compared to the baseline reactor. This increased the amount of catalyst participating in the reaction and gave more time for the reactions to occur. It is believed that this is the primary reason for the improved performance. The second reason for improved performance was the finned design increased the mixing of the gases improving mass transfer. The achievement of >99% conversion at lower temperatures and the increased residence time suggested that higher feed rates at the same reactor temperature could be achieved with a 2x increase expected. Using the finned steam reformer reactor model, we tested this expectation and predicted that at $\sim 618\text{K}$ the inlet flow could be increased 2.7x from 0.2ml hr^{-1} (baseline reactor inlet flow at this temperature) to 0.54ml hr^{-1} while still achieving >99.5% conversion. This would increase the potential hydrogen power from $\sim 640\text{mW}_t$ to $\sim 1720\text{mW}_t$. This improved production was more than the expected 2x increase could be explained by improved mixing mentioned previously and perhaps some improved heat transfer. The mass fraction of methanol in the reactor can also be helpful in understanding the reactor performance. Figures 14 and 15 show the mass fraction of the baseline and the finned reactor system at 0.2 ml hr^{-1} and 0.54 ml hr^{-1} at methanol conversion >99.5%. Figure 14 has the full range (0.6 to $\sim 0\text{ wt}\%$) while Figure 15 has a more refined scale of 0.05 to $\sim 0\text{wt}\%$ which enables tracking of the

methanol with better precision. In the baseline reactor, the majority of the methanol is reacted as it enters the reactor with the portion of the packed bed after the plunger reacting the remaining methanol. Whereas in the finned reactor, the concentration remains higher over half-way through the reactor which indicates the catalyst bed is better utilized and illustrates the improved reactor performance.

Figure 13. Predicted methanol conversion for 0.2 ml hr⁻¹ methanol water mix inlet flow for the original reactor design (blue line) and the finned reactor (dotted red line). Temperature corresponds to the thermocouple temperature in the experiments and the temperature at approximate location of the thermocouple in the model (T_{cr}).

Figure 14. Methanol mass fraction (wt% methanol) in (A) the baseline reactor, 0.2 ml hr^{-1} inlet feed and $>99.5\%$ methanol conversion, (B) finned reactor, 0.2 ml hr^{-1} inlet feed, and $>99.5\%$ methanol conversion, and (C) finned reactor, 0.54 ml hr^{-1} inlet feed, and $>99.5\%$ methanol conversion.

Figure 15. Methanol mass fraction (wt% methanol) in the reactors with finer scale. (A) the baseline reactor, 0.2 ml hr^{-1} inlet feed and $>99.5\%$ methanol conversion, (B) finned reactor, 0.2 ml hr^{-1} inlet feed, and $>99.5\%$ methanol conversion, and (C) finned reactor, 0.54 ml hr^{-1} inlet feed, and $>99.5\%$ methanol conversion.

This design could possibly be implemented by creating metal inserts with the fins going from the outer wall towards the middle for the 1st and 3rd fins. The middle fin could have a hole close to the inlet tube diameter and slid into place after the first fin and associated catalyst layer is inserted. This would necessarily need to be a tight fit in order to prevent gases from flowing to the next layer through a gap between the middle fin and tube. It could be assembled by adding a catalyst felt followed by the plunger as is currently done. Next the insert with the 1st fin would be positioned. The catalyst powder would be added. Next the middle fin would be inserted followed by a catalyst layer. Subsequently, the 3rd fin would be put in place. Finally, the rest of the catalyst powder would be added. It may be a challenge to ensure that the catalyst beds between fins is completely filled with catalyst to prevent bypass.

There are a couple of alternative designs that could also be considered. The first would be rather than using a loose powder, the catalysts could be coated onto the reactor walls and the fins with an open channel or the catalyst could be coated onto a porous metal felt. Both of these options would decrease the manufacturing complexity. Wall coating for methanol reformers in microreactors has been demonstrated with CuZnO catalysts and there are several models of such reactors reported in the literature ⁽⁴²⁻⁴⁴⁾. Similarly, PdZnO coated porous felts for methanol reforming has also been reported ^(11,31). Although the advanced finned reactor design requires more complicated assembly compared to the baseline system, the finned reactor's improved performance makes this an attractive option.

An examination of the concentration profile in Figure 15 revealed that the majority of the reaction occurred in the first half of the methanol reformer with most at the entry point while very little occurred in the last section prior to the exit. Since the entry point was the location with the highest reactant concentration, the highest temperature (see Figure 12 and 15), and the reaction is not zero order⁷ this seemed reasonable. The low temperatures near the exit indicate that the reactor might be heat transfer limited. This suggested that the reactor performance and catalyst utilization could be improved by improving the heat transfer in the system. There are several ways this could be achieved such as, 1) increasing the thickness of the metal walls, 2) connecting the fins to the plunger directly, 3) increasing the reactor diameter and decreasing the length, or 4) by changing the combustor exhaust flow such that it wraps around the reformer. Proposed improvements 1 and 2 would likely result in only a minimal increase in heat transfer since the reactor bed is already full of catalyst and the distances are relatively short. In addition, building this into the small device may be difficult. Increasing the reactor diameter (improvement 3) could have a significant effect while being simple to implement. For example, if the diameter was increased by 41% the length could be decreased by 50% while keeping the same reactor volume. This design would increase the percentage of the reactor at high temperatures which would also improve the reactor rates and better utilize the catalyst. Benefits could include operating the reactor at a lower temperature for improved efficiencies or increasing the hydrogen productivity by increasing the inlet flow rates while operating at the same temperatures. The number of fins may need to be decreased from three to two since the shortened reactor length may make inclusion of all three fins difficult. The final design suggestion to improve heat transfer could be included in the finned reactor design

or combined with improvement 3. In the current designs, the combustor exhaust gases are vented with relatively little heat recovery. However, by wrapping the exhaust gas around the methanol reformer portion as shown in Figure 16 the thermal energy in the exhaust gas could be better utilized. This design would heat the methanol reformer walls thereby increasing the temperature of the reactor, particularly near the exit. In addition, it would be an insulating layer decreasing heat loss. The design is more complicated and may create a manifold challenge, but the potential improved performance may be worth the increased complexity.

Figure 13 Fuel processor with the combustor exhaust flowing around the methanol reformer.

While significant improvements in the methanol reformer design have been explored using numerical simulation, there are still development opportunities for the system. The next steps would include building and testing the proposed reactor, optimization of the finned reactor design in terms of number of fins and operating conditions. In addition, the combustion side needs to be addressed. Currently, the combustor requires a blower to provide the air. A new design that would siphon air into the combustor would be of interest. Finally, this design approach has been shown to be effective for micro-scale reactors. Obviously the design can be scaled-up for larger systems. The model can be used to predict what the limits for scaling up the device may be.

5. Conclusions

A model for a methanol fuel process was developed for an annular system. The model was validated against data we previously published and then used to propose improvements to the reactor design. The predicted internal gas flow path in the original design showed significant portion of the catalyst bed was being underutilized. Two design changes were proposed to improve the bed utilization. The first design change was to increase the number of outlet tubes from one to four. This had minimum impact on the predicted performance. The second design change was to insert several fins into the reactor. This substantially improved the predicted performance. The model predicted a 29K lowering of the reactor temperature to achieve >99.5% methanol conversion at an inlet flow of 0.2 ml hr⁻¹. In addition, at the original reactor temperature of $T_{cr} \sim 618\text{K}$ an increase in inlet flow of 2.7x was predicted. This would increase the reactor power from $\sim 640\text{mW}_t$ to

$\sim 1720 \text{ mW}_t$. A manufacturing method was proposed for the new design. The reactor does have some thermal transport limitations. Several design modifications were proposed to minimize the limitations with the most likely to succeed being increasing the diameter and decreasing the thickness and/or wrapping the combustor exhaust around the steam reformer to heat and insulate the reformer section.

6. Nomenclature

C_p : heat capacity ($\text{J g}^{-1} \text{ K}^{-1}$)

d : diameter (m)

d_h : hydraulic diameter (m)

D : diffusivity ($\text{m}^2 \text{ s}^{-1}$)

D_{ik} : mutual diffusivity of components i and k ($\text{m}^2 \text{ s}^{-1}$)

D_t^m : Stefan-Maxwell diffusivity ($\text{m}^2 \text{ s}^{-1}$)

$D_{i,L}^m$: diffusivity taking into account dispersion effects ($\text{m}^2 \text{ s}^{-1}$)

DOE: Department of Energy

E_a : activation energy ($94,800 \text{ J mol}^{-1} \text{ K}^{-1}$)

H : Enthalpy (J g^{-1})

i : component

ID: inner diameter

k : component

M : mass (kg)

OD: outer diameter

P: Pressure (Pa)

p: particle

PEMFC: Proton exchange membrane fuel cell

PNNL: Pacific Northwest National Laboratory

Pr: Prandtl = momentum diffusivity / thermal diffusivity = $\mu C_p \lambda^{-1}$

Q: heat $W m^{-3}$

R: change in mass

r: radius (m)

r_{meth} : methanol reaction rate ($\text{mmol kg}_{\text{cat}}^{-1} \text{s}^{-1}$)

Re: Reynolds number = convective momentum transport / viscous momentum transport = $\rho U D_h \mu^{-1}$

S:C: steam to carbon ratio

T: Temperature (K)

T_{cr} = Temperature (K) at the approximate location of the thermocouple in the experimental data.

U = velocity

W = Watt

w_i or w_k : mass fraction

x_k : mole fraction

Greek

α : mass velocity in the direction of heat transfer/mass velocity based on area of the empty tube in the direction of fluid flow

β : effective length between the centers of two particles/mean particle diameter

λ : thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)

λ_{eff} : effective thermal conductivity of the bed for both gas and solids ($\text{W m}^{-1} \text{K}^{-1}$)

λ_{eff}^0 : effective conductivity with a stagnant gas ($\text{Re}=0$) ($\text{W m}^{-1} \text{K}^{-1}$)

λ_{gas} : gas thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)

λ_{p} : thermal conductivity of the solid particle ($\text{W m}^{-1} \text{K}^{-1}$)

ϕ : void fraction

κ : permeability (m^2)

μ : viscosity ($\text{Pa}\cdot\text{s}$)

ρ : density (kg m^{-3})

ψ : effective thickness of fluid film adjacent to contact surface between two solid particles/mean particle diameter

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