

Study on Coupling Model of Methanol Steam Reforming and Simultaneous Hydrogen Combustion in Micro-Channel Reactor

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Abstract : Simplified, “back of the envelope” strategies have been developed for coupled microreactors for hydrogen generation via steam reforming of hydrocarbon fuels and hydrogen/propane combustion. The unconverted hydrogen from fuel cell has been supplied to combustion channel, this way the overall heat cycle has been optimized. The simplified mechanistic model includes developing a code for the reforming section, considering reactor as isothermal PFR then carrying out energy balance over the reactor and finally coupling it with the reaction in the combustion channel. Steam reforming being highly endothermic reaction, requires heat supply to the reactor zone; hence many thermal coupling strategies and different configuration have been looked in the literature. Co-current configuration found to be the best therefore has been used for thermal coupling of endothermic steam reforming reaction with exothermic combustion reaction, in adjacent channels of a parallel plate reactor configuration. This simplified model has been applied to methanol in the reforming channel and hydrogen in the combustion channel.

Keywords: Methanol Reforming, Hydrogen Combustion, Coupling, Modeling, Micro-channel Reactor

I. Introduction

Gradual depletion of the fossil fuels and need to reduce greenhouse gases have generated the interest in using alternative energy resources and also with the exponentially growing requirement of energy worldwide, research on newer and more efficient energy systems has become extremely significant. During the last decade interest in a potential ‘Hydrogen Economy’ has increased and is now discussed in main stream literature [1].

Table.1 shows current battery technologies and energy densities of different hydrocarbons. Even the highly efficient Li polymer batteries may fall short of satisfying the energy requirements and this led to the development of micro fuel cell technology. Hydrocarbon energy sources have a much higher energy density as compared to other normal sources used in batteries. Hence even with very low overall efficiencies we can seek to match or even better the existing battery technology. Micro fuel cells are essentially fuel cell systems on a smaller scale. One of the main concerns with these systems is the storage of hydrogen which is used in the fuel cell. Hydrogen, having very low density, high diffusivity and high flammability [2], is very difficult to store. Hence on-board hydrogen production was proposed to counter this problem and that is where the current research work focuses. Though in its nascent stages of development, these systems show a lot of promise and potential.

Table 1: Some of current practical battery technology and hydrocarbon energy densities [3]

Technology	Energy Density (kWh/kg)	Technology	Energy Density (kWh/kg)	Technology	Energy Density (kWh/kg)
Primary Cell		Secondary Cell		Hydrocarbon	
Alkaline	Methane	Lead acid	0.035	Methane	15.33
Zn-air	Methanol	Ni-Cd	0.035	Methanol	6.3
Li/SOCl ₂	Propane	Li-ion	0.12	Propane	13.972

Steam reforming is highly endothermic reaction and requires effective heat supply to the reaction zone [4]. One of the possible solutions of this problem is heat coupling (integration in one reactor) of the hydrocarbon steam reforming and catalytic combustion of the same hydrocarbon or, more advantageous, of exhaust/anode gas (mainly hydrogen) from the fuel-cell battery. So, endothermic steam reforming reaction has been coupled with the exothermic hydrogen combustion reaction in a microreactor which is basically a small device with number of parallel plates where reforming and combustion reaction takes place in the alternate channel on the wall surface where the catalyst is coated. The unconverted hydrogen is recycled to microreactor in order to optimize the overall heat cycle of the process. This hydrogen has been supplied to fuel cell to produce Hydrogen. The overall cycle of small scale hydrogen production consists of microreactor, followed by Water Gas Shift Reactor (WGS) then Pressure Swing Adsorption (PSA). **Fig.1** shows the diagrammatic representation of the Overall hydrogen fuel cell.

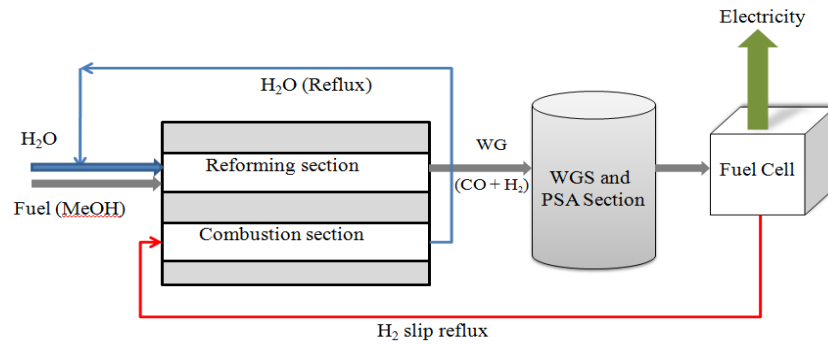


Fig. 1: Schematic of on-board hydrogen production for Fuel Cell

In this article, a simplified mechanistic model – incorporating continuity equation, energy balances, and simulations of ideal PFR reactors – using MATLAB to simulate various parameters like temperature, inlet velocity, conversion and efficiency has been developed.

II. Model Equations And Approach

A. Transport equations

The microreactor has been considered as isothermal PFR. The basic equations equation of PFR has been used. The continuity equation and component balance equations have been solved for isothermal PFR. These equations are nothing but the ordinary differential equations.

$$\frac{d(\rho u)}{dz} = 0$$

$$\rho u \frac{d(y_i)}{dz} = \gamma(-r_{r,c})$$

A mass basis for all the calculations is assumed. Isothermal PFR code accounts for three parameters, velocity of reforming or combustion channel, temperature and conversion. The reactor consists of alternate channel of combustion and reforming. The idea is to couple these channels thermally, i.e. utilize the heat evolved from hydrogen combustion reaction for endothermic reforming reaction of hydrocarbon fuels. Only one reforming and one combustion channel for thermally integrated reactor have been considered in this article.

For a steady-state process, the overall energy balance on the wall dictates that the net heat generated via the exothermic and endothermic reactions is absorbed as sensible heat in the combustion and reforming channels. This is given as

$$y_c^{in} \dot{m}_c \Delta H_c + \dot{m}_c (C_{p,c}^{out} T_c^{out} - C_{p,c}^{in} T_c^{in}) + \dot{m}_r (C_{p,r}^{out} T_r^{out} - C_{p,r}^{in} T_r^{in}) + y_r^{in} \dot{m}_r \Delta H_r = 0$$

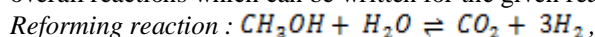
We have assumed reactor as isothermal, thus T_c^{out} & T_r^{out} are same and denoted as T . The inlet temperature is considered as 300K.

The complete reactor system is defined by five parameters temperature of reactor (T), velocity (u) and conversion (X) of reforming and combustion fuel. Solving isothermal PFR gives the range of velocities for which reforming fuel conversion is 1 considering complete combustion. The global energy balance of the system gives the range of combustion velocity for the reforming reaction and its isothermal breakthrough limit. i.e. complete conversion. Efficiency is defined for better understanding of the performance of the microreactor system. Efficiency of the microreactor is defined in 2 ways. The idea of generating hydrogen above “H₂-neutral operation”, i.e. amount of hydrogen produced must exceed the amount of hydrogen combusted in the microreactor is used to define the efficiency. Hence, efficiency 1 and 2 are defined as

$$\eta_1 = \frac{n_r - n_c}{n_r} \text{ and } \eta_2 = \frac{Q_{H_2}(n_r - n_c)}{Q_f n_f}$$

B. Kinetic Rate Expression: Methanol Reforming

Catalytic production of hydrogen by steam reforming of methanol is an attractive option for use in decentralized production of clean electrical energy from fuel cells. Methanol is considered as “storable” form of hydrogen. Methanol fuelled solid polymer fuel cell systems are promising candidates for small scale application, hence methanol steam reforming has been considered for modelling. Methanol and steam in the presence of a Cu/ZnO/Al₂O₃ catalyst at temperatures greater than 160⁰C react to form a hydrogen-rich gas [5]. The three overall reactions which can be written for the given reactants and products are



Water-gas shift reaction : $CO + H_2O \rightleftharpoons CO_2 + H_2$

Decomposition reaction : $CH_3OH \rightleftharpoons CO + 2H_2$

Final forms of the rate expressions for the overall reactions involved in the process of steam reforming of methanol can be expressed as :

$$r_R = \frac{k_R K_{CH_3O'}^* (p_{CH_3OH}/p_{H_2}^{0.5}) (1 - p_{H_2}^3 p_{CO_2} / K_R p_{CH_3OH} p_{H_2O}) C_{S1}^T C_{S1a}^T}{(1 + K_{H(1a)}^{0.5} p_{H_2}^{0.5}) ((1 + K_{CH_3O'}^* (p_{CH_3OH}/p_{H_2}^{0.5}) + K_{HCOO'}^* p_{CO_2} p_{H_2}^{0.5} + K_{OH'}^* (p_{H_2O}/p_{H_2}^{0.5}))}$$

$$r_W = \frac{k_W K_{OH'}^* (p_{CO} p_{H_2O} / p_{H_2}^{0.5}) (1 - p_{H_2} p_{CO_2} / K_W p_{CO} p_{H_2O}) (C_{S1}^T)^2}{((1 + K_{CH_3O'}^* (p_{CH_3OH}/p_{H_2}^{0.5}) + K_{HCOO'}^* p_{CO_2} p_{H_2}^{0.5} + K_{OH'}^* (p_{H_2O}/p_{H_2}^{0.5}))^2}$$

$$r_D = \frac{k_D K_{CH_3O'}^* (p_{CH_3OH}/p_{H_2}^{0.5}) (1 - p_{H_2}^3 p_{CO} / K_D p_{CH_3OH} p_{H_2O}) C_{S2}^T C_{S2a}^T}{(1 + K_{H(2a)}^{0.5} p_{H_2}^{0.5}) ((1 + K_{CH_3O'}^* (p_{CH_3OH}/p_{H_2}^{0.5}) + K_{HCOO'}^* p_{CO_2} p_{H_2}^{0.5} + K_{OH'}^* (p_{H_2O}/p_{H_2}^{0.5}))}$$

Where,

$$k_R = k_R^\infty \exp\left(\frac{-E_{a,R}}{RT}\right)$$

$$k_D = k_D^\infty \exp\left(\frac{-E_{a,D}}{RT}\right)$$

$$k_W = k_W^{\infty,*} \exp\left(\frac{-E_{a,W}}{RT}\right)$$

$$K_{CH_3O',CH_3O''}^* = \exp\left(\frac{\Delta S_{CH_3O',CH_3O''}^*}{R} - \frac{\Delta H_{CH_3O',CH_3O''}^*}{RT}\right)$$

$$K_{HCOO',HCOO''}^* = \exp\left(\frac{\Delta S_{HCOO',HCOO''}^*}{R} - \frac{\Delta H_{HCOO',HCOO''}^*}{RT}\right)$$

$$K_{OH',OH''}^* = \exp\left(\frac{\Delta S_{OH',OH''}^*}{R} - \frac{\Delta H_{OH',OH''}^*}{RT}\right)$$

$$K_{CO_2',CO_2''} = \exp\left(\frac{\Delta S_{CO_2',CO_2''}}{R} - \frac{\Delta H_{CO_2',CO_2''}}{RT}\right)$$

$$K_{H(1,2a)} = \exp\left(\frac{\Delta S_{H(1,2a)}}{R} - \frac{\Delta H_{H(1,2a)}}{RT}\right)$$

$$K_{OH',OH''}^* = \frac{K_{OH',OH''}}{K_{H(1,2a)}}$$

$$K_{CH_3O',CH_3O''}^* = \frac{K_{CH_3O',CH_3O''}}{K_{H(1,2a)}}$$

Where, the rate-determining step chosen for both the methanol steam reforming reaction and the decomposition reaction was the dehydrogenation of adsorbed methoxy. The rates of each component are calculated by following rate expression

$$r_{CO_2} = (r_R + r_W) S_A, (mol.s^{-1})$$

$$r_{CO} = (r_D - r_W) S_A, (mol.s^{-1}.kg^{-1})$$

The parameters used in the above equations are given in **Table.2**

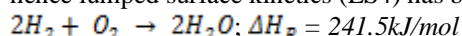
Table 2 : Parameters for comprehensive kinetic model of methanol steam reforming. [5]

Rate constant or equilibrium constant	ΔS_i (J mol ⁻¹ K ⁻¹) or k_i^∞ (m ² s ⁻¹ mol ⁻¹)	ΔH_i (kJ/mol)
k_R (m ² s ⁻¹ mol ⁻¹)	7.4exp(14)	102.8
$K_{CH_3O'}^*$ (bar ^{-0.5})	-41.8	-20.0
$K_{OH'}^*$ (bar ^{-0.5})	-44.5	-20.0
$K_{H(1a)}$ (bar ^{-0.5})	-100.8	-50.0

K_{HCOO}^* (bar ^{-0.5})	179.2	100.0
k_D (m ² s ⁻¹ mol ⁻¹)	3.8exp(20)	170.0
$K_{\text{CH}_3\text{O}}^*$ (bar ^{-0.5})	-30.0	-20.0
K_{OH}^* (bar ^{-0.5})	30	-20.0
$K_{\text{H}(2a)}$ (bar ^{-0.5})	-46.2	-50.0
K_W^* (m ² s ⁻¹ mol ⁻¹)	5.9exp(13)	87.6

B. Kinetic Rate Expression: Hydrogen Combustion

The hydrogen air mixture used for the simulations in this work lies in 0.3% to 15% H₂/air ratio and hence lumped surface kinetics (LS4) has been used [6]. For the following reaction



And the kinetic rate expression is given as : $r_{LS4} = 1.28E03(\sqrt{T_5} \cdot C_{\text{H}_2}^2)$, (mole/cm²sec)

III. Results And Discussions

Simplified model with methanol reforming and hydrogen combustion has been simulated in MATLAB. Operative diagrams which includes **temperature as a function of reforming velocity and** feed ratio for complete conversion of reforming fuel were obtained. **Fig. 2(Left)** shows the velocity of methanol at different temperature for the complete methanol conversion. The methanol reforming channel velocity is varied from 0.2m/s to 1.19m/s for the temperature range of 800K to 1500K and the corresponding hydrogen velocity can be calculated from global energy balance. Whereas **Fig. 2(Right)** shows the range of temperature as a function of the feed ratio. The hydrogen velocity for same temperature range is 0.25m/s to 1.147m/s, however it has been assumed that the complete conversion occurs in the reforming channel. It has shown that the maximum hydrogen velocity 1.147m/s has been reached at a temperature of 1500K at the methanol velocity of 1.19m/s. This hydrogen velocity is well below the breakthrough velocity which implies that the assumption of complete combustion still holds good. The material stability limit of 1500K is reached here at hydrogen combustion velocity of 1.19m/s. The methanol breakthrough point is 1.147m/s at the limiting temperature of 1500K.

Reforming velocity has been kept constant with varying combustion velocity. The breakthrough reforming velocity at 1500K was kept fixed as this velocity gives the maximum hydrogen velocity at which reforming conversion is 100% and the reactor temperature at 1500K. The **Fig. 3** shows the efficiency 1 and 2 curves of methanol for different feed ratio (Reforming fuel velocity to Hydrogen velocity). Efficiency 1 gives an

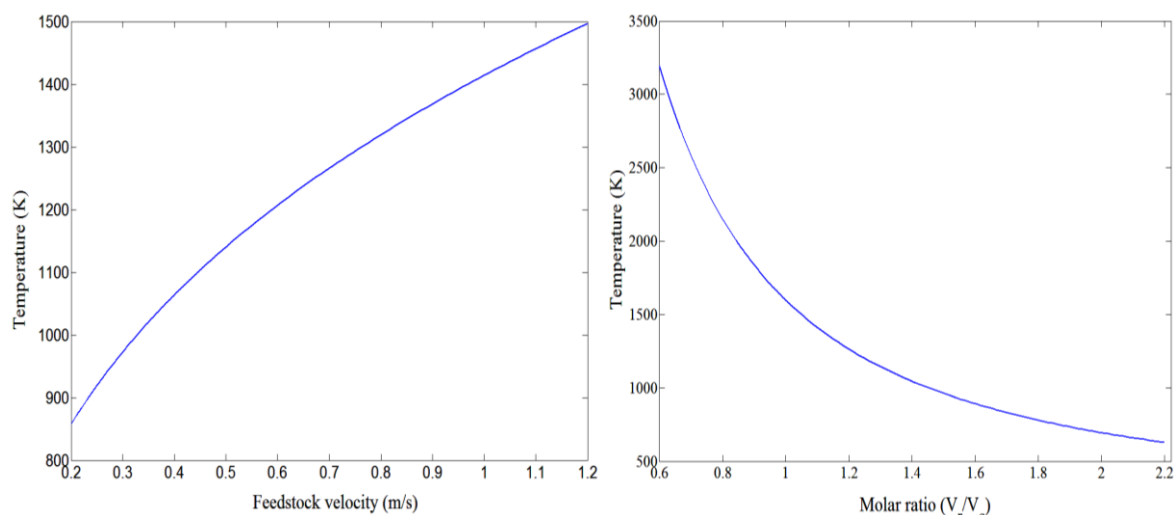


Figure 2 : Results of the simplified model for Methanol reforming coupled with hydrogen combustion (Left) Temperature Vs Methanol Velocity, (Right) Temperature Vs Feed Ratio

Actual picture of the hydrogen economy, as we are directly comparing the total moles of hydrogen available for the next step for fuel cells to the number of moles generated in microreactor. The vertical line indicated in the **Fig. 3** is the point where reforming fuel conversion falls below 100%. In other words, it is the maximum efficiency achievable given the constraint of complete conversion in both the channels. On the other hand, it also predicts the Efficiency 2 of methanol for different feed ratio by using simplified model. The

vertical line indicated in the Fig. 3 is the maximum efficiency achievable given the constraint of complete conversion in both the channels. For both the efficiencies, here for the entire range of shown in figure the hydrogen conversion in the combustion channel is 100%. The results of the efficiency curve have been tabulated in Table. 3.

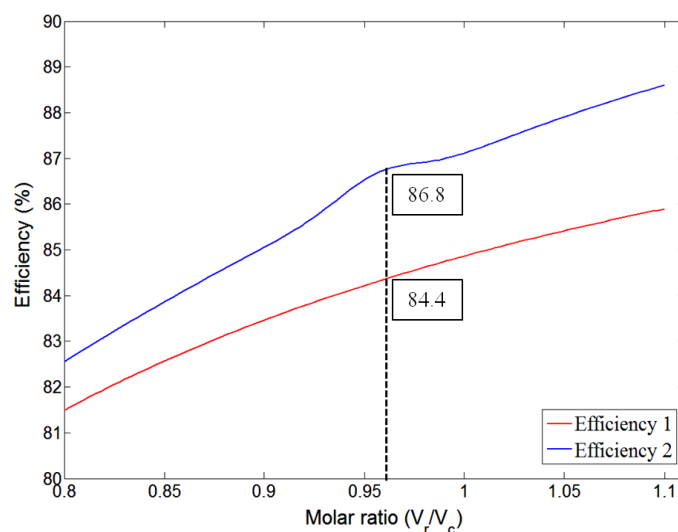


Figure 3: Efficiency curves as a function of molar ratio for Methanol reforming coupled with hydrogen combustion

IV. Conclusions

PFR reactor model with energy balances was studied in a decoupled approach by which detailed observations were made on reforming and combustion independently. This approach basically paves a path, a particular set of calculations or a set procedure of calculations that any researcher can perform, quite easily, and get a very good idea about the system and how it would perform with more rigorous model environment [7]. Also a feasible operating region, which can be used for further studies of the same system, can be obtained by this simplified model approach. On a more general and practical cornerstone, cumbersome simulations can be replaced with simpler analyses such as this and it can be observed that how close the real system behaves to what is computationally predicted.

Table 3 : Results of the efficiency 1 and 2 curves for methanol - hydrogen system

Mixture (reforming – combustion)	Efficiency 1 (%)	Efficiency 2 (%)	Feed ratio (V_r/V_c)
Methanol – Hydrogen	84.4	86.8	0.9664

However, it became very much sound that methanol reforming in microreactors coupled with combustion of hydrogen can have efficiency (both 1 and 2) > 80%. Efficiency 2 is considered as more proficient as it accounts the calorific value of the fuels and products. From this work, efficiency of methanol reforming was found to be 86.8% with a feed molar ratio of 0.9664. The very same model can be used for other hydrocarbon feedstock (methane, ethane, ethanol, propane etc.) reforming along with coupled hydrogen combustion and a comparison can be performed to predict better fuel. And an overall model can also be studied taking WGS and PSA into consideration.

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