OPTIMAL DESIGN OF PROPANE REFORMING SYSTEMS

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Abstract— Combined micro-fuel processor and proton exchange membrane fuel cell system is a high energy density device for power generation. In this study, the ready-made propane is used as a fuel to reform it to generate hydrogen. The device can be expected as portable power in the future. According to feed selection (propane, air and steam), different reaction pathways maybe take place in the propane reformer, which are steam reforming and partial oxidation reaction. In this work, the kinetics of reaction pathways were investigated. The objective function, optimization variables and process constrains were defined in order to meet target for portable power used. Finally, the SR reaction pathway for propane reforming was decided due to above assessment.

Index Terms— Propane Reforming, Optimization, Design, Reaction Pathway.

I. INTRODUCTION

Hydrogen has shown the potential to become an energy carrier due to high efficiency and zero carbon emission for fuel cells used. Because of the difficulty associated with hydrogen storage, a reformer is often employed to convert hydrocarbons to hydrogen-rich synthesis gas ('syngas'). Most researchers paid much attention on fossil fuel, e.g., methane, methanol. But still have some potential problems have to overcome. In this work, ready-made propane is used as a fuel. However, few paper discuss about the design and optimization problem in micro-channel.

This study presents a systematic approach design a micro-channel propane reforming systems. First, the model of micro-channel reformer was built and verified with literature. Then, objective function was built to perform the optimization. Finally, the two reaction pathways, SR and POX, for hydrogen generation were investaged based on proposed optimization procedure. And the best reaction pathway for portable power can be found.

II. PROCESS DESCRIPTION AND MODELING

In this study, different reaction pathways of propane reforming systems were investaged for hydrogen production. This system included two parts: 1. Propane reforming units for producing syn-gas(CO and H_2) e.g., steam reforming(SR), and partial oxidation(POX), 2. Gas cleaning units for eliminating or converting CO, e.g., water gas shift reaction (WGS), preferential oxidation (PrOX). Schematic illustration of propane fuel processor systems was shown in Fig. 1. Propane and water(or Air) was preheated via a preheater and sent to the reformer. After propane reforming, there is still 10~20 mol % of methane in the reactor outlet. Then, the reformer effluent syn-gas was flowed into an auto-thermal reformer for continuously converting methane to hydrogen. Finally, the resduel CO in syn-gas was removed by using consective WGS and PrOX reactors in order to meet hydrogen specification for proton exchanger membrane fuel cell used.

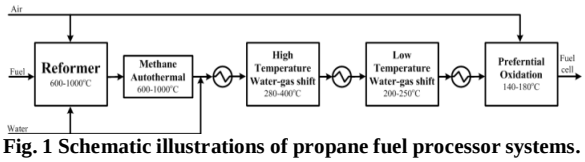


Fig. 1 Schematic illustrations of propane fuel processor systems.

Modeling

The micro-channel reactors were used in each reactor. The detail structure of micro-channel propane reformers was shown in Fig.2. The model for each micro-channel was shown below:

Flow channel

Equation of continuity:

$$\frac{\partial \rho_{g,bulk}}{\partial t}+\frac{\partial\left(\rho_{g,bulk}V_z\right)}{\partial z}=0 \quad (1)$$

Mass balance:

$$\varepsilon_g\frac{\partial\left(\rho_{g,bulk}x_{g,i}\right)}{\partial t}=-\frac{1}{A_{reactor}}\frac{\partial\left(M_g x_{g,i}\right)}{\partial z}+k_{g,i}\rho_{g,bulk}a_{wc,g}\left(x_{int,i}-x_{g,i}\right) \quad (2)$$

Energy balance:

$$\varepsilon_g\frac{\partial\left(\rho_{g,bulk}C_{p,bulk}T_g\right)}{\partial t}=-\frac{1}{A_{reactor}}\frac{\partial\left(M_g C_{p,bulk}T_g\right)}{\partial z}-h_{sg}a_{wc,g}\left(T_g-T_{wc}\right) \quad (3)$$

Catalyst layer

Mass balance:

$$\varepsilon_{wc}\frac{\partial\left(\rho_{g,cat}x_{g,i}\right)}{\partial t}=-k_{s,i}\rho_{g,cat}a_{wc,g}\left(x_{s,i}-x_{int,i}\right)+Mw_i S_{c,i} \quad (4)$$

Boundary conditions:

$$x_{g,i}\left(z=0,t\right)=x_{int,i}\left(z=0,t\right)=x_{s,i}\left(z=0,t\right)$$

$$k_{g,i}\rho_{g,bulk}a_{wc,g}\left(x_{int,i}-x_{g,i}\right)=k_{s,i}\rho_{g,cat}a_{wc,g}\left(x_{s,i}-x_{int,i}\right)$$

Energy balance:

$$\varepsilon_{wc}\rho_w C_{pw}\frac{\partial\left(T_{wc}\right)}{\partial t}=\varepsilon_{wc}k_{c,w}\frac{\partial^2\left(T_{wc}\right)}{\partial z^2}+h_{sg}a_{wc,g}\left(T_g-T_{wc}\right)+S_e+h_{sl}a_{ex}\left(T_{wc}-T_c\right) \quad (5)$$

Boundary conditions:

$$T_g\left(z=0,t\right)=T_{wc}\left(z=0,t\right) \quad (2\text{-}9)$$

$$\left.\frac{\partial T_{wc}(z,t)}{\partial z}\right|_{z=0}=\left.\frac{\partial T_{wc}(z,t)}{\partial z}\right|_{z=L}$$

Wall layer

Energy balance:

$$\varepsilon_{ex}\rho_w C_{pw}\frac{\partial\left(T_c\right)}{\partial t}=-\frac{1}{A_{reactor}}\frac{\partial Q}{\partial z}+h_{sl}a_{ex}\left(T_{wc}-T_c\right) \quad (6)$$

SR, POX, ATR reactors were operated non-isothermally, but WGS and PrOX reactors were operated adiabatically. The reaction kinetics for each reactor was shown in Table 1-3[1]-[4]. The model of each micro-channel reactor has been verified with literature [1]-[4].

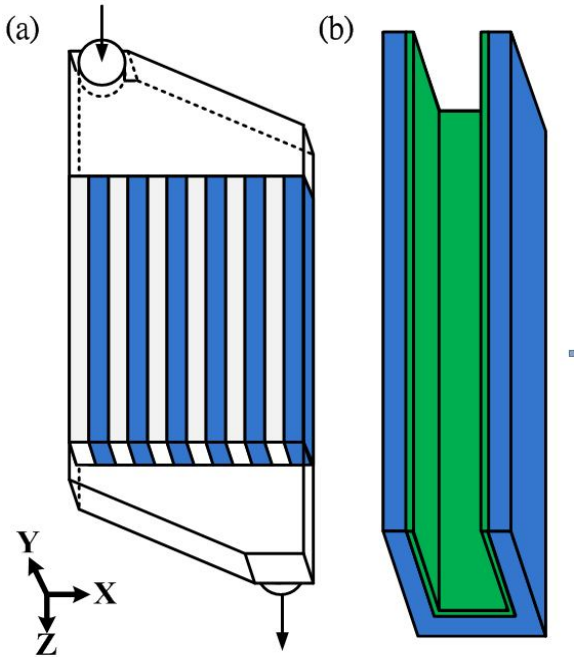


Fig. 2 Schematic illustrations of micro-channel propane reforming.

Table 1. Reaction kinetics of propane steam reforming[1]

Reactions	Kinetics (kmol/kg s)
rSR,1 $C_3H_8 + 3H_2O \leftrightarrow 3CO + 7H_2$	$r_{SR,1} = \frac{k_{SR,1} P_{C_3H_8}(1-\eta_{C_3H_8,SR})}{1+K_{CO}P_{CO}+K_{O_2}P_{O_2}} \sigma_{H_2O}$
rSR,2 $CH_4 + H_2O \leftrightarrow CO + 3H_2$	$r_{SR,2} = \frac{k_{SR,2} P_{CH_4}(1-\eta_{CH_4,SR})}{1+K_{CO}P_{CO}+K_{O_2}P_{O_2}} \sigma_{H_2O}$
rSR,3 $CO + H_2O \rightarrow CO + H_2$	$r_{SR,3} = k_{SR,3} P_{H_2O}(1-\eta_{WGS})\sigma_{CO}$
rSR,4 $CO_2 + H_2 \rightarrow CO + H_2O$	$r_{SR,4} = k_{SR,4} P_{CO_2}(1-\eta_{RWGS})\sigma_{H_2}$
rSR,5 $CO + 3H_2 \rightarrow CH_4 + H_2O$	$r_{SR,5} = k_{SR,5} P_{H_2}(1-\eta_{Met})\sigma_{CO}$

III. DESIGN ALTERNATIVES

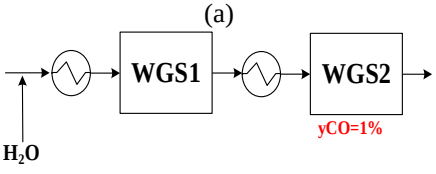
In order to remove CO from syn-gas, a typical WGS reactor was designed in series and operated adiabatically. The design configuration was shown in Fig. 3(a). Temperature profile in the WGS reactor was increased due to exothermic reaction. And the reactor with inter coolers was used. In order to meet the CO concentration target, the exiting CO concentration of second WGS reactor will approach to equilibrium conversion which is shown in Fig. 4. This means the larger WGS reactor volume must be used when the feed condition was changed. Therefore, the modified design which was a reactor with cooling jacket was shown in Fig. 3 (b). The temperature and concentration profiles in modified design were shown in Fig.5. Compare with the original design, the conversion for new design was operated away from the equilibrium conversion.

Table 2. Reaction kinetics of propane partial oxidation[1]

Reactions	Kinetics (kmol/kg s)
rPOX,1 $C_3H_8 + 5O_2 \Leftrightarrow 3CO_2 + 4H_2O$	$r_{POX,1} = \frac{k_1 P_{C_3H_8}}{1+K_{H_2O}P_{H_2O}} \sigma_{O_2}$
rPOX,2 $C_3H_8 + 3H_2O \Leftrightarrow 3CO + 7H_2$	$r_{POX,2} = \frac{k_2 P_{C_3H_8}(1-\eta_{C_3H_8,SR})}{1+K_{CO}P_{CO}+K_{O_2}P_{O_2}} \sigma_{H}$
rPOX,3 $CH_4 + 2O_2 \Leftrightarrow CO_2 + 2H_2O$	$r_{POX,3} = \frac{k_3 P_{CH_4}}{1+K_{H_2O}P_{H_2O}} \sigma_{O_2}$
rPOX,4 $CH_4 + H_2O \Leftrightarrow CO + 3H_2$	$r_{POX,4} = \frac{k_4 P_{CH_4}(1-\eta_{CH_4,SR})}{1+K_{CO}P_{CO}+K_{O_2}P_{O_2}} \sigma_{H}$
rPOX,5 $CO + H_2O \Rightarrow CO + H_2$	$r_{POX,5} = k_5 P_{H_2O}(1-\eta_{WGS})\sigma_{CO}$
rPOX,6 $CO_2 + H_2 \Rightarrow CO + H_2O$	$r_{POX,6} = k_6 P_{CO_2}(1-\eta_{RWGS})\sigma_{H_2}$
r POX,7 $CO + 3H_2 \Rightarrow CH_4 + H_2O$	$r_{POX,7} = k_7 P_{H_2}(1-\eta_{Met})\sigma_{CO}$
r POX,8 $H_2 + \frac{1}{2}O_2 \Leftrightarrow H_2O$	$r_{POX,8} = k_8 P_{H_2}\sigma_{O_2}$
r POX,9 $CO + \frac{1}{2}O_2 \Leftrightarrow CO_2$	$r_{POX,9} = k_9 P_{CO}\sigma_{O_2}$

Table 3. Reaction kinetics of auto-thermal reforming, water gas shift reaction and preferential oxidation reaction.[2]-[4]

Reactions	Kinetics
r ATR,1 $CH_4 + 2O_2 \Leftrightarrow CO_2 + 2H_2O$	$r_{ATR,1} = \frac{k_{ATR,1} K_{CH_4} P_{CH_4} K_{O_2}^{0.5} P_{O_2}^{0.5}}{\alpha^2}$
r ATR,2 $CH_4 + H_2O \Leftrightarrow CO + 3H_2$	$r_{ATR,2} = \frac{k_{ATR,2}\left(P_{CH_4} - P_{H_2}^3 P_{CO}/K_{eq,1}\right)}{k_2 \left(P_{H_2O}^{0.596}\right)}$
r ATR,3 $CO + H_2O \Leftrightarrow CO + H_2$	$r_{ATR,3} = k_{ATR,3}\left(P_{CO} - P_{CO_2}P_{H_2}K_{eq,2}\right)$
rWGS $CO + H_2O \Leftrightarrow CO_2 + H_2$	$r_{WGS} = k_{WGS} P_{CO}^{0.13} P_{H_2O}^{0.49} P_{CO_2}^{-0.12} P_{H_2}^{-0.45}(1-\beta)$
rPROX,1 $CO + \frac{1}{2}O_2 \Leftrightarrow CO_2$	$r_{PROX,1} = \frac{k_{PROX,1} P_{CO} P_{O_2}^{0.5}}{\alpha^2}$
r PROX,2 $H_2 + \frac{1}{2}O_2 \Leftrightarrow H_2O$	$r_{PROX,2} = k_{PROX,2} P_{H_2} P_{O_2}^{0.5}$
r PROX,3 $CO + H_2O \Leftrightarrow CO_2 + H_2$	$r_{PROX,3} = k_{PROX,3}\left(P_{CO_2}P_{H_2} - P_{CO}P_{H_2O}K_{eq}\right)$



(b)

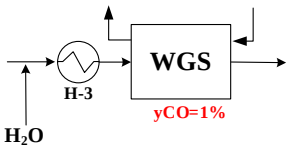


Fig. 3 Design alteratives for micro-channel water gas shift reactors.

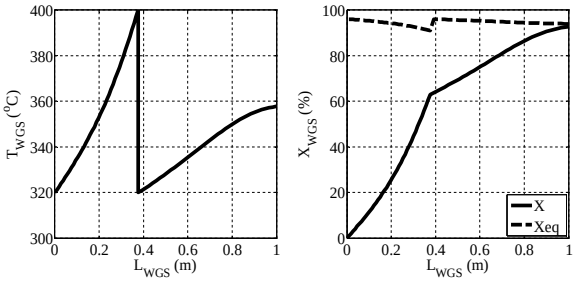


Fig. 4 Temperature and conversion profiles in the WGS reactors in series.

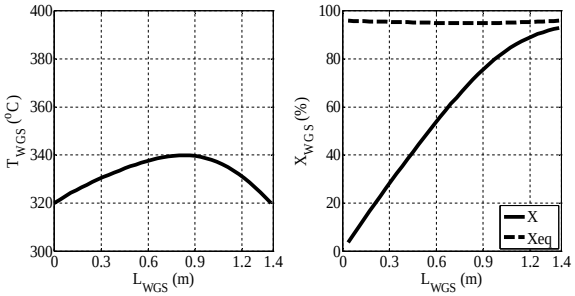


Fig. 5 Temperature and conversion profiles in the modified WGS reactor.

IV. DESIGN SPECIFICATION

The conversion of propane in the reformer was set at 99.5 %. Methane concentration in the autothermal reformer was set at 1 %. CO concentrations in the WGS and PrOX effluent were set at 1 mol% and 20 ppm, respectively. F_{H2} was set at $1.56x10^{-8}$ kmol·s^{-1}.

V. OPTIMIZATION PROBLEM

The optimization problem for micro-channel propane reforming is defined for maximizing objective function.

Objective function (Eff/Vsys)

$$= \frac{LHV(H_2)}{Q_{in} + LHV(C_3H_8)} \frac{1}{V_{sys}} \quad (7)$$

Efficiency of the propane fuel processor defined as lower heating value of hydrogen divided by lower heating value of propane and energy input. In order to meet the portable power requirement, the objective function of the process defined as E_{ff}/V_{sys}. V_{sys} denotes the total volume of the system which includes reactors and heat exchangers volume.

The optimization variables were determined from design degree of freedom. There are feed ratio O_2(or H_2O)/C_3H_8 ratio(R), reforming temperature ($T_{Reformer}$), ATR temperature (T_{ATR}), Steam injection flowrate (F_{steam}), WGS temperature (T_{WGS}), Length of preferential oxidation reactor(L_{PrOX}) and air injection in third PrOX(F_{air3}).

The process constrains are the conversion of C_3H_8 (XC_3H_8), concentration of CH_4 in ATR ($y_{CH4,ATR}$), CO concentrations in WGS and PrOX effluent($y_{CO,WGS}$, $y_{CO,PrOX}$), temperature constrain in each reactor due to catalyst operating limitation($T_{Reformer}$, T_{ATR}, T_{WGS}, T_{PrOX}).

The optimization problem was formulated in following equation:

$$\underset{x\in\Omega}{\text{Maximize}}: \frac{Eff\%}{V_{System}}$$

$$\Omega = \left[R, T_{Reformer}, T_{ATR}, F_{Steam}, T_{WGS}, L_{Pr\,OX}, F_{Air\,3}\right]$$

$$\begin{aligned} &Subject\ to: \\ &x_{C_3H_8} = 99.5\%, T_{Re\ former} \le 1100^o C \\ &y_{CH_4,ATR} = 1\%, T_{ATR} \le 1000^o C \\ &y_{CO,WGS} = 1\%, T_{WGS} \le 400^o C \\ &y_{CO,Pr\,OX} = 20\,ppm, T_{Pr\,OX} \le 300^o C \end{aligned} \quad (8)$$

There are two reaction pathways which are SR and POX for propane reforming for hydrogen production. After performing (8) for each reaction pathways, the optimal stream and size results for SR and POX processes were shown in Fig. 6. The efficiencies per system volume for SR and POX process were shown in Table 4. Temperature and component molar flowrate profiles for SR and POX systems was shown in Fig. 7.

Table 4 Optimal results of diffenert reaction pathways for micro-channel propane reforming systems.

Reaction pathway	SR	POX
OP(Relatively)	74.02	62.97
Eff (%)	74.02	64.03
$F_{C3H8,in}$ (kmols)	1.995E-9	2.575E-9
H_2 (kmol·s^{-1})	1.56E-8	
H_2 m.f.(Dry%)	56	39
Q_{in} (kW)	1.034E-3	6.445E-4
V_{System} (cm^3)	1.624E-1	1.651E-1

VI. RESULTS AND DISCUSSION

For a given design specification, the optimal results of single micro-channel for SR and POX processes shows that the volumes(reactor volumes/heat exchanger volumes) of SR and POX are 0.162 (0.096/0.066) cm^3 and 0.165 (0.102/0.063) cm^3 for a fixed hydrogen production rate. However, the feed flowrate for SR and POX are $5.98x10^{-9}$ and $5.67x10^{-9}$ kmol·s^{-1}, respectively. This caused the efficiency for SR is much higher than POX. And H_2 concentration of SR and POX are 56 and 39 mol %. Therefore, the SR reactor pathway for hydrogen has more unit volume efficiency potential for a portable back-up power.

CONCLUSION

For propane reforming to produce hydrogen, this study has developed micro-channel simulation models and

has carried out the optimization analysis for SR and POX reaction pathways. The result shows that SR reactor pathway for hydrogen has more unit volume efficiency potential for a portable back-up power.

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(a)

(b)

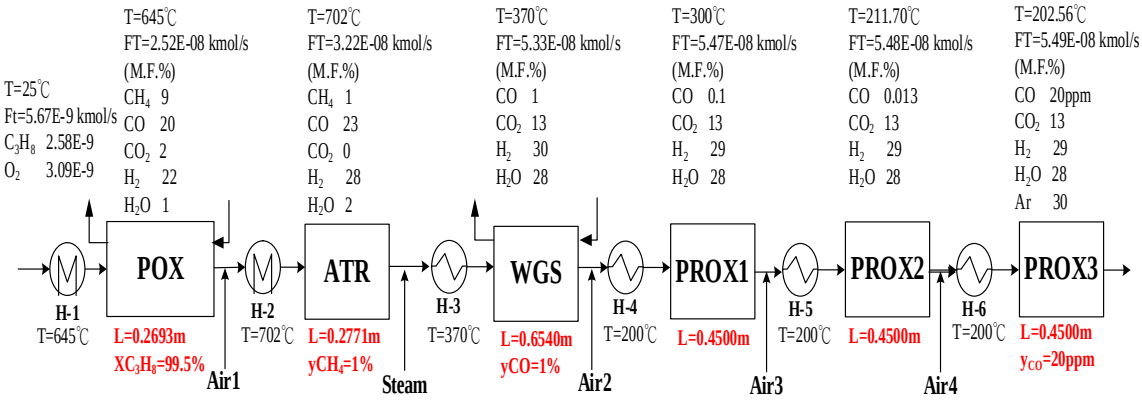
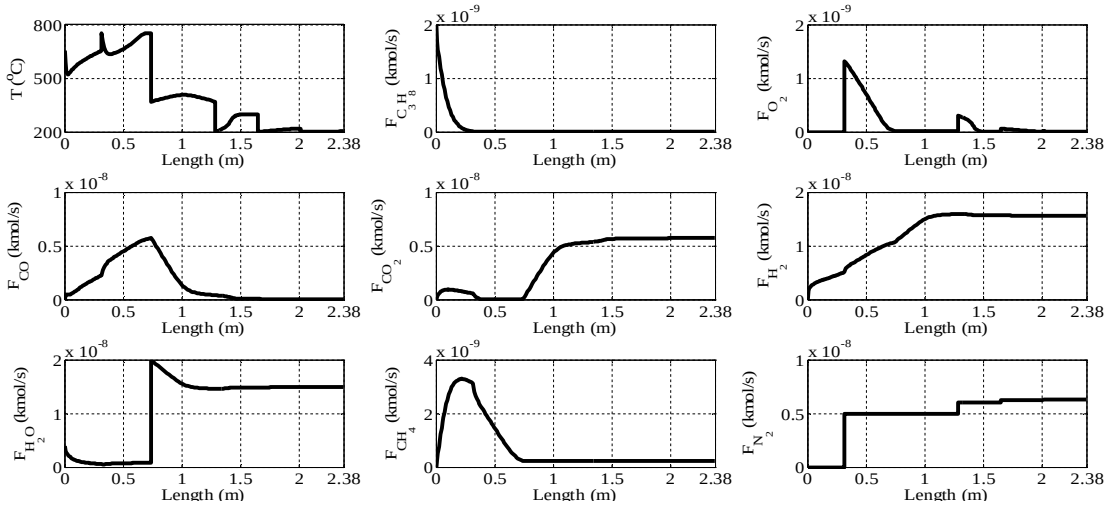


Fig. 6 Optimal designs of micro-channel propane (a) steam reforming systems, (b) partial oxidation systems.

(a)



(b)

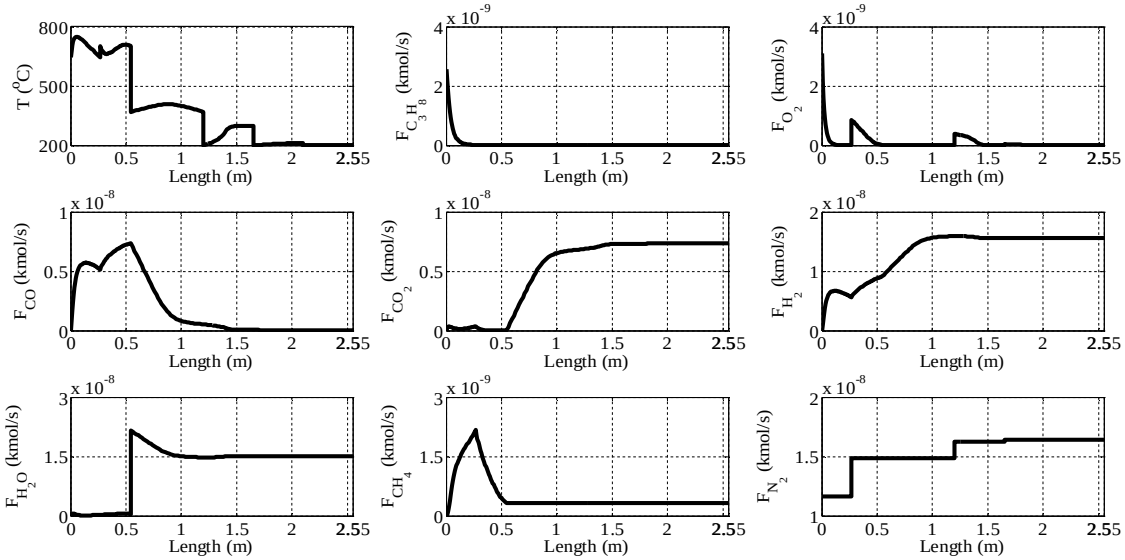


Fig. 7 Temperature and component molar flowrate profiles for (a) steam reforming systems, (b) partial oxidation systems.

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