

Modelling of a tubular solid oxide fuel cell with different designs of indirect internal reformer

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Abstract

The cell performance and temperature gradient of a tubular solid oxide fuel cell with indirect internal reformer (IIR-SOFC) fuelled by natural gas, containing a typical catalytic packed-bed reformer, a catalytic coated wall reformer, a catalytic annular reformer, and a novel catalytic annular-coated wall reformer were investigated with an aim to determine the most efficient internal reformer system. Among the four reformer designs, IIR-SOFC containing an annular-coated wall reformer exhibited the highest performance in terms of cell power density ($0.67 \text{ W} \cdot \text{cm}^{-2}$) and electrical efficiency (68%) with an acceptable temperature gradient and a moderate pressure drop across the reformer ($3.53 \times 10^{-5} \text{ kPa}$). IIR-SOFC with an annular-coated wall reformer was then studied over a range of operating conditions: inlet fuel temperature, operating pressure, steam to carbon (S : C) ratio, gas flow pattern (co-flow and counter-flow pattern), and natural gas compositions. The simulation results showed that the temperature gradient across the reformer could not be decreased using a lower fuel inlet temperature (1223 K–1173 K) and both the power density and electrical efficiency of the cell also decreased by lowering fuel inlet temperature. Operating in higher pressure mode (1–10 bar) improved the temperature gradient and cell performance. Increasing the S : C ratio from 2 : 1 to 4 : 1 could decrease the temperature drop across the reformer but also decrease the cell performance. The average temperature gradient was higher and smoother in IIR-SOFC under a co-flow pattern than that under a counter-flow pattern, leading to lower overpotential and higher cell performance. Natural gas compositions significantly affected the cell performance and temperature gradient. Natural gas containing lower methane content provided smoother temperature gradient in the system but showed lower power density and electrical efficiency.

Key words

indirect internal reforming; solid oxide fuel cell; annular-coated wall reformer; packed-bed reformer; catalytic coated wall reformer; catalytic annular reformer

1. Introduction

An indirect internal reformer solid oxide fuel cell (IIR-SOFC) is a promising technology for future energy conversion systems. The integration of an internal indirect reforming compartment to SOFC assembly enables stack thermal management and increases system efficiency. Heat generated from exothermic electrochemical reactions and ohmic losses in a SOFC can be transferred to an endothermic reforming reaction in the reformer, which is in close thermal contact with the anode side of SOFC [1–3]. Carbon deposition on the SOFC anode can also be minimized by decreasing the content of hydrocarbon directly contacting the anode. Generally, natural gas or methane is applied as the primary fuel for IIR-SOFC.

Previously, the reactivity toward natural gas steam reforming and the kinetic models of the catalyst have been reported, and most of the studies concentrated on lower C_2 and C_3 kinetics [4–9]. The work of Schadel et al. [10] developed reaction mechanisms in detail from which methane, propane, butane and natural gas (sulphur-free) steam reforming over Rh-based catalyst were evaluated by comparing the experimental results with the numerical predicted conversions. Their equations were applied in this study.

The internal reformer is typically designed as a packed-bed configuration containing a pellet or powder form of nickel (Ni)-based or noble metal-based catalysts. Typically, IIR-SOFC which contains conventional packed-bed reformer has several issues including a high pressure drop, bed redistribution and heat transfer limitation. Heat transfer is limited by

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packed-bed characteristic and external heat may not be ideally transferred to the middle of the reformer bed [11–13]. Furthermore, mismatch between the rates of endothermic and exothermic reactions in an IIR-SOFC leads to a significant local cooling effect. The previous work showed the effect of fuel type (methane, biogas, methanol, and ethanol) on the temperature gradient in tubular-packed bed internal reformer [14]. Among different primary fuels, methanol presents the smoothest temperature profile where methane shows the largest cooling spot at the first half of the reformer channel. This temperature gradient may consequently results in thermally induced mechanical stresses and reduced efficiency. The high reactivity catalyst in the packed-bed reformer was also reported to react too rapid for the reforming operation [15]. Previously, there have been several attempts to solve this problem, e.g., by applying a catalyst with lower reforming reactivity [15], by introducing some oxygen at the feed as autothermal reforming [14,16] or using a wash-coated wall reformer with the catalyst [17–21]. The wash-coated reformer was reported to provide improved heat transfer characteristics as well as a lower pressure drop across the reformer [11,12]. In addition, since the amount of catalyst per volume for the catalytic-coated wall reactor is much lower than that for the catalytic packed-bed reactor, it provides a potential benefit for IIR-SOFC application where uniform methane steam reforming activity is required [22,23]. In planar SOFC, gas flow filed can be designed to suit for the internal reformer with catalytic wash-coat application. However, in the case of tubular SOFC, a long SOFC tube is required for an internal reformer with catalytic wash-coat application, leading to an increase in ohmic loss and contact resistance between anode and current collector [24]. This is the drawback for IIR-tubular SOFC when catalytic wash-coat is used.

In this study, an alternative design of tubular IIR-SOFC containing an annular-coated wall reformer is presented. Integrating a coated wall reformer with an annular reformer, the annular-coated wall reformer involves inserting the catalytic wash-coated rod in the middle of the reformer channel and

coating the wall of the reformer channel with the catalyst. With this design, the reforming reaction occurs both at the surface of the inner reformer channel and on the surface of the catalytic annular rod. The amount of catalyst per volume is increased depending on the surface area of the annular rod and the coated wall. For this reason, the reforming activity can be greater while the pressure drop and heat transfer limitation are minimized. Furthermore, the required length of tubular SOFC can also be shortened. In detailed, the mathematical modelling was developed to predict the cell performance and temperature gradient along the cell. The behaviours of IIR-SOFCs using four categories of internal reformers were compared: a packed-bed reformer, a coated-wall reformer, an annular reformer and an annular-coated wall reformer, which were called R_1 , R_2 , R_3 and R_4 , respectively. The performance of IIR-SOFC with R_4 reformer was then studied under a range of operating conditions: inlet fuel temperature, operating pressure, steam to carbon (S : C) ratio, gas flow pattern and natural gas composition. The model code was developed on COMSOL[®] program software in two-dimensional axial code. From this study, the potential design and operating conditions of a IIR-SOFC system fuelled by natural gas were determined.

2. Model geometry and equations

Four designs of tubular SOFC integrated indirect internal reformers were compared: a packed-bed (R_1), coated-wall (R_2), annular (R_3) and annular-coated wall (R_4) reformers. The schematic diagrams of these four designs are shown in Figure 1. For all the configurations, natural gas (CH_4 86.72%, C_2H_6 8.1%, C_3H_8 2.03%, C_4H_{10} 0.44%) and steam were converted to hydrogen-rich gas in the internal reformer before being introduced into the fuel channel of tubular SOFC. Simultaneously, air was fed in the same flow direction through the air channel. All the dimensions and physical properties of SOFC system in the present work, which are summarized in Table 1, were based on the previous literatures [19,22,23].

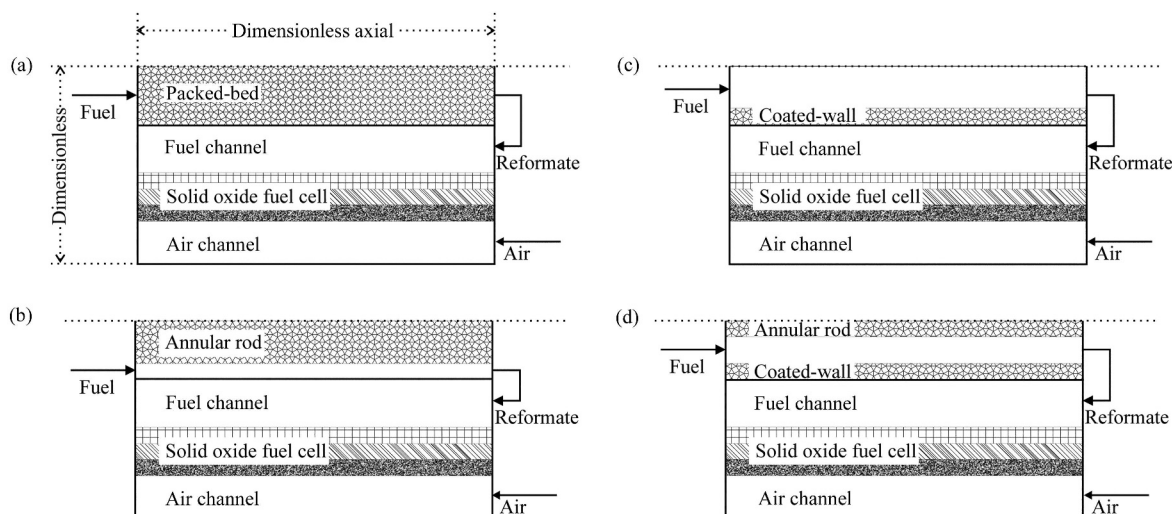


Figure 1. Schematic diagrams of tubular IIR-SOFC with (a) packed-bed reformer (R_1), (b) coated-wall reformer (R_2), (c) annular reformer (R_3) and (d) annular-coated wall reformer (R_4)

Table 1. Constant parameter values of tubular IIR-SOFC system

Parameters	Values	References
Fuel cell length	0.60 m	Fukuhara C and Igarashi A [23]
Reformer radius	3×10^{-3} m	Fukuhara C and Igarashi A [23]
Annular catalyst rod radius	2×10^{-3} m	—
Inside radius of the cell	5.4×10^{-3} m	Fukuhara C and Igarashi A [23]
Anode thickness	1×10^{-3} m	Fukuhara C and Igarashi A [23]
Electrolyte thickness	4×10^{-5} m	Fukuhara C and Igarashi A [23]
Cathode thickness	5×10^{-5} m	Fukuhara C and Igarashi A [23]
Anode permeability	1×10^{-12}	Lee M et al. [19]
Cathode permeability	1×10^{-12}	Lee M et al. [19]
Average density of triple phase	$633.73 \text{ kg} \cdot \text{m}^{-3}$	Fukuhara C et al. [22]
Average specific heat of triple phase	$574.3 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$	Fukuhara C et al. [22]
Anode thermal conductivity	$2.7 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$	Fukuhara C et al. [22]
Cathode thermal conductivity	$9.6 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$	Fukuhara C et al. [22]
Convection coefficient in the fuel channel	$2987 \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$	Fukuhara C et al. [22]
Convection coefficient in the air channel	$1322.8 \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$	Fukuhara C et al. [22]

2.1. Gas distribution

For gas distribution, Brinkman Equation (1) was applied to calculate the distribution through the porous area (packed-bed catalyst and electrodes), while the incompressible Navier-Stokes Equation (2) was used to predict the gas flow pattern in all the gas channels [25].

$$p = -\frac{\mu}{k_p} \vec{v} + \tilde{\mu} \nabla^2 \vec{v} \quad (1)$$

$$\vec{v} \cdot (\rho \vec{v}) = -p + \tilde{\mu} \nabla^2 \vec{v} + S \quad (2)$$

where, $\vec{v}$ is the fluid velocity, ρ is the density, p is the pressure, $\tilde{\mu}$ is the effective viscosity, k_p is the permeability, and S is the source term, which is neglected since the simulation studied under steady state condition. The study was mainly focused on the diffusion of gaseous compounds through the porous reforming bed and fuel cell components.

The pressure and velocity gradient of the gas diffusion properties were taken into account by applying the molecular diffusion and binary diffusion equations, as shown in Equations (3) and (4) [26].

$$D_{i,\text{mix}} = \frac{(1 - y_i)}{\sum_{i,j \neq 1} (Y_i / D_{i,j})} \quad (3)$$

$$D_{i,j} = \frac{(0.00143) T^{1.75}}{p M_{i,j}^{1/2} [\gamma_i^{1/3} + \gamma_j^{1/3}]^2} \quad (4)$$

where, $D_{i,\text{mix}}$ and $D_{i,j}$ are the molecular diffusion and binary diffusion flux, respectively, of species i in mixed gas ($\text{m}^2 \cdot \text{s}^{-1}$), y_i is the mole fraction of species i , p is the pressure, $M_{i,j} = 2/(1/M_i + 1/M_j)$ and M_i is the molecular weight of component i , and γ is the special diffusion volume (reported by Fuller et al. [26]). The diffusion behaviour was corrected by applying porosity (ε) and tortuosity (τ) to obtain an effective diffusivity coefficient, $D_{i,\text{pmix}}^e$, as shown in Equation (5). Furthermore, gas diffusion through porous media, $D_{i,\text{pmix}}$, was explained in Equation (6) by two mechanisms of molecular diffusion ($D_{i,\text{mix}}$) and Knudsen diffusion ($D_{i,\text{ku}}$), which in turn depends on the relationship between the pore

diameter (d_p) and the mean free path of the molecular species (Equation 7).

$$D_{i,\text{pmix}}^e = \frac{\varepsilon}{\tau} D_{i,\text{pmix}} \quad (5)$$

$$\frac{1}{D_{i,\text{pmix}}} = \frac{1}{D_{i,\text{mix}}} + \frac{1}{D_{i,\text{ku}}} \quad (6)$$

$$D_{i,\text{ku}} = \frac{1}{3} d_p \sqrt{\frac{8RT}{\pi M_i}} \quad (7)$$

2.2. SOFC model

The electricity generation was calculated from the relationship between polarisation and the activated area of SOFC. Activation, concentration and ohmic polarisation are known to be major losses for SOFCs. Activation loss arises from an activation energy barrier to the electrochemical reaction at the electrode. In this work, the activation polarisation, η_{cat} , was computed with Butler-Volmer Equation (8);

$$J_i = J_0 \left[\exp \left(\frac{\alpha_a F \eta_{\text{act}}}{RT} \right) - \exp \left(\frac{-(1 - \alpha_a) F \eta_{\text{act}}}{RT} \right) \right] \quad (8)$$

where, J_i is the current density ($\text{A} \cdot \text{m}^{-2}$), J_0 is the exchange current density ($\text{A} \cdot \text{m}^{-2}$), R is the universal gas constant ($\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), and F is the Faraday constant ($\text{C} \cdot \text{mol}^{-1}$). All relevant parameters were reported by Zhu et al. [27].

The concentration polarisation occurs because of the resistance to gas diffusion through the porous media and it normally occurs at high current density and/or at high fuel utilization. Generally, gas diffusion behaviour can be predicted by mathematical models such as Fick's model, Dusty gas model (DGM), and Stefan-Maxwell model. DGM was chosen in the present work.

$$\eta_{\text{conc}} = \frac{RT}{2F} \ln \left(\frac{p_{\text{H}_2}^* p_{\text{H}_2\text{O}}}{p_{\text{H}_2} p_{\text{H}_2\text{O}}^*} \right) + \frac{RT}{2F} \ln \left(\frac{p_{\text{CO}}^* p_{\text{CO}_2}}{p_{\text{CO}} p_{\text{CO}_2}^*} \right) + \frac{RT}{4F} \ln \left(\frac{p_{\text{O}_2}^*}{p_{\text{O}_2}} \right) \quad (9)$$

Ohmic polarisation arises from ion transport across the cell, which mainly depends on the ionic and electronic conductivity of SOFC material. By applying Ohm's law, the relationship between ohmic polarisation and material resistivity can be determined. In the present work, the material properties reported by Zhu et al. [27] were used. The voltage drop was computed by the simplified equation:

$$\eta_{\text{ohm}} = JR_{\text{ohm}} \quad (10)$$

where, η_{ohm} is the voltage drop caused by ohmic losses (V); J is the current density ($\text{A}\cdot\text{m}^{-2}$), and R_{ohm} is the ohmic resistance per unit area ($\text{k}\cdot\text{m}^{-2}$). Although both H_2 and CO can be electrochemically consumed in a SOFC, the rate of electricity generated from CO is only 1/3 comparing with that of H_2 [28]; thus, the rate of CO oxidation in SOFC has been neglected in this study. At the anode|electrolyte interface, H_2 is electrochemically oxidized, whereas O_2 is consumed at the cathode|electrolyte interface. The conversion rates of H_2 , $R_{\text{elec},\text{H}_2}$, and O_2 , $R_{\text{elec},\text{O}_2}$, at the indicated boundary were simulated from Equations (11) and (12), respectively:

$$R_{\text{elec},\text{H}_2} = \frac{J_{\text{H}_2}}{2F} \quad (11)$$

$$R_{\text{elec},\text{O}_2} = \frac{J_{\text{O}_2}}{4F} \quad (12)$$

The reliability of these electrochemical equations, coded in a COMSOL® program, was validated by comparison with the experimental results of Lin et al. [29]. As shown in Figure 2, the results were in good agreement with fairly acceptable deviation (less than 10%).

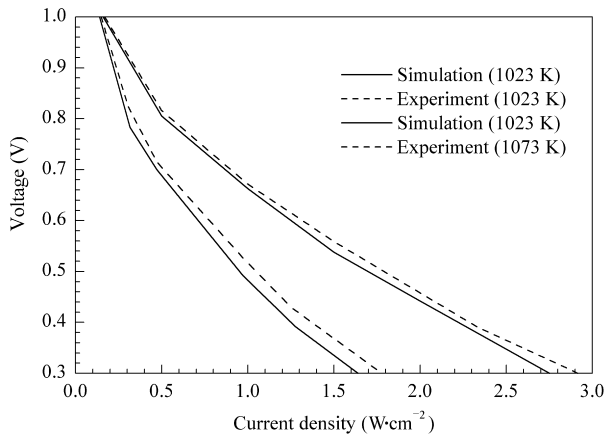


Figure 2. *I-V* curve validations between the simulation results in the present work and the experimental results (Lin et al. (2006)) [29]

2.3. Efficiency

On the basis of the assumption that most of the generated hydrogen was combusted to supply heat for the steam reforming reaction, some generated heat was used as the heat source. The thermal efficiency was defined as the amount of useful energy that can be extracted from IIR-SOFC relative to the total energy evolved by the process. The thermal efficiency,

Eff_{thermal} , of an IIR-SOFC in this section was then defined as the ratio of the heating value of hydrogen left over from combustion to that of the inlet fuel, as shown in Equation (13).

$$Eff_{\text{thermal}} = \frac{n_{\text{H}_2}^{\text{out}} LHV_{\text{H}_2, 1173 \text{ K}} - (-H_{\text{reform}})}{n_i^{\text{in}} LHV_{i, 1173 \text{ K}}} \quad (13)$$

where, n_i is the number of moles of component i and $LHV_{i, 1173 \text{ K}}$ is the lower heating value of component i at 1173 K. To investigate the electrical efficiency, the outlet reformates were fed into the fuel channel of tubular SOFC. The electrical efficiency, Eff_{elec} , was defined from the following equation.

$$Eff_{\text{elec}} = \frac{P_{\text{SOFC}} A_{\text{act}}}{\dot{n} y_i^{\text{in}} LHV_{i, 1173 \text{ K}}} \quad (14)$$

where, P_{SOFC} is the power density ($\text{J}\cdot\text{s}^{-1}\cdot\text{m}^2$), A_{cat} is the active area (m^2), $\dot{n}$ is the molar flow rate of the inlet gas, and y_i^{in} is the mole fraction of the inlet fuel.

3. Mass balance and energy balance in reformer and SOFC model

Heat transfer in this system involves conduction along stack materials. Conversion from heat flow through the system and radiation between the reformer and SOFC are concerned [30,31]. Mass and energy balances for the four configurations of internal reformer and SOFC are given in the following equations, respectively.

- Steady state 2-D dimensional model for different reformers

Packed bed reformer

$$(-D_i \cdot c_i + c_i \vec{v}) - \rho_B \cdot v_i R_{\text{reform}} = 0 \quad (15)$$

Energy balance

$$(\vec{v} \rho C_p T) - (\lambda_i \cdot T) + H_{\text{reform}} R_{\text{reform}} = 0 \quad (16)$$

Boundary

$$z = 0; r \geq 0; u_r = 0, v_r = v_{r,\text{in}}, c_{i,r} = c_{i,\text{in}}, T_r = T_{r,\text{in}}$$

$$r = r_z; z \geq 0; n \cdot (k \cdot T) = \lambda_{r,f}(T_r - T_f) + \frac{\sigma A_s (T_r^4 - T_s^4)}{\frac{1}{\varepsilon_r} + \frac{A_r}{A_s} \left(\frac{1}{\varepsilon_s} - 1 \right)}$$

Coated wall reformer

Mass balance

$$(-D_i \cdot c_i + c_i \vec{v}) = 0 \quad (17)$$

Energy balance

$$(\vec{v} \rho C_p T) - (\lambda_i \cdot T) + H_{\text{reform}} R_{\text{reform}} = 0 \quad (18)$$

Boundary

$$z = 0; r \geq 0; u_r = 0, v_r = v_{r,\text{in}}, c_{i,r} = c_{i,\text{in}}, T_r = T_{r,\text{in}}$$

$$r = r_z; z \geq 0; n \cdot N_i = \frac{1}{S_{\text{act}} A_{\text{act}}} v_i R_j$$

$$n \cdot (k \cdot T) = \lambda_{r,f}(T_r - T_f) + \frac{\sigma A_s(T_r^4 - T_s^4)}{\frac{1}{\varepsilon_r} + \frac{A_\gamma}{A_s} \left(\frac{1}{\varepsilon_s} - 1 \right)}$$

Annular reformer
Mass balance

$$(-D_i \cdot c_i + c_i \vec{v}) = 0 \quad (19)$$

Energy balance

$$(\vec{v} \rho C_p T) - (\lambda_i \cdot T) + H_{\text{reform}} R_{\text{reform}} = 0 \quad (20)$$

Boundary

$$z = 0; r \geq 0; u_r = 0, v_r = v_{r,\text{in}}, c_{i,r} = c_{r,\text{in}}, T_{\text{rod}} = T_{r,\text{in}}$$

$$r = r_z; z \geq 0; n \cdot N_i = \frac{1}{S_{\text{act}} A_{\text{act}}} v_i R_j$$

$$n \cdot (k \cdot T) = \lambda_{r,f}(T_{\text{rod}} - T_f) + \frac{\sigma A_s(T_r^4 - T_s^4)}{\frac{1}{\varepsilon_r} + \frac{A_\gamma}{A_s} \left(\frac{1}{\varepsilon_s} - 1 \right)}$$

Annular-coated wall reformer
Mass balance

$$(-D_i \cdot c_i + c_i \vec{v}) = 0 \quad (21)$$

Energy balance

$$(\vec{v} \rho C_p T) - (\lambda_i \cdot T) + H_{\text{reform}} R_{\text{reform}} = 0 \quad (22)$$

Boundary

$$z = 0; r \geq 0; u_r = 0, v_r = v_{r,\text{in}}, c_{i,r} = c_{r,\text{in}}, T_{\text{rod}} = T_{r,\text{in}},$$

$$T_r = T_{r,\text{in}}$$

$$r = r_z; z \geq 0; n \cdot N_i = \frac{1}{S_{\text{act}} A_{\text{act}}} v_i R_j$$

$$n \cdot (k \cdot T) = \lambda_{r,f}(T_{\text{rod}} - T_f) + \frac{\sigma A_s(T_r^4 - T_s^4)}{\frac{1}{\varepsilon_r} + \frac{A_\gamma}{A_s} \left(\frac{1}{\varepsilon_s} - 1 \right)}$$

$$n \cdot (k \cdot T) = \lambda_{r,f}(T_r - T_f) + \frac{\sigma A_s(T_r^4 - T_s^4)}{\frac{1}{\varepsilon_r} + \frac{A_\gamma}{A_s} \left(\frac{1}{\varepsilon_s} - 1 \right)}$$

• Steady state 2-D dimensional model for tubular SOFC
Fuel channel
Mass balance

$$(-D_i \cdot c_i + c_i \vec{v}) - \nu_i R_{\text{elec}} = 0 \quad (23)$$

Energy balance

$$(\vec{v} \rho C_p T) - (\lambda_i \cdot T) = 0 \quad (24)$$

Boundary

$$z = L; r \geq 0; u_f = u_r, v_f = v_r, p_f = p_r, c_{i,f} = c_{i,r}, T_f = T_r$$

$$r = r_r; z \geq 0; n \cdot N_{\text{H}_2, f} = -\frac{J_{\text{H}_2}}{2F}, n \cdot N_{\text{H}_2\text{O}, f} = \frac{J_{\text{H}_2}}{2F}$$

$$n \cdot N_{\text{CO}, f} = -\frac{J_{\text{CO}}}{2F}, n \cdot N_{\text{CO}_2, f} = \frac{J_{\text{CO}}}{2F}$$

$$n \cdot (k \cdot T) = h_{r,f}(T_f - T_r)$$

Solid oxide fuel cell
Energy balance

$$(\vec{v} \rho C_p T) - (\lambda_s \cdot T) + H_{\text{elec}} + \frac{\sigma A_s(T_r^4 - T_s^4)}{\frac{1}{\varepsilon_r} + \frac{A_\gamma}{A_s} \left(\frac{1}{\varepsilon_s} - 1 \right)} = 0 \quad (25)$$

Boundary anode/electrolyte interface,

$$n \cdot (k \cdot T) = H_{\text{elec}} R_{\text{elec}} + J \eta_{\text{total}}$$

$$r = r_f; z \geq 0; n \cdot (k \cdot T) = h_{f,s}(T_s - T_f)$$

$$r = r_f; z \geq 0; n \cdot (k_{\text{sa}} \cdot T) = h_{\text{sa}}(T_a - T_s)$$

Air channel
Mass balance

$$(-D_i \cdot c_i + c_i \vec{v}) = 0 \quad (26)$$

Energy balance

$$(\vec{v} \rho C_p T) - (\lambda_i \cdot T) = 0 \quad (27)$$

Boundary

$$z = 0; r \geq 0; u_a = 0, v_a = v_{a,\text{in}}, c_{i,a} = c_{a,\text{in}}, T_a = T_{\text{in}}$$

$$r = r_a; z \geq 0; n \cdot N_{\text{O}_2, f} = -\frac{J_{\text{O}_2}}{2F}$$

$$n \cdot (k \cdot T) = \lambda_{f,s}(T_s - T_f)$$

$$r = r_0; z \geq 0, n \cdot (k \cdot T) = 0$$

4. Results and discussion

As described earlier, IIR-SOFC model was studied for the four system configurations: R₁, R₂, R₃ and R₄ reformers. The model was developed as the smallest single unit cell taking into account of the effects of temperature on gas distribution, reactant conversion and charge transfer. To simplify the analysis, the following assumptions are made:

- Each section is considered to be a non-isothermal steady-state condition
- Ideal gas behaviour is applied for all the gas components
- Pressure drops in SOFC stack and coated-wall reformer are neglected
- The global fuel utilisation is maintained constantly along the cell coordinate

4.1. Modelling of IIR-SOFC as base case

IIR-SOFC model was initially simulated using constant parameters as a base case. Temperature and pressure were controlled at 1173 K and 1 bar. The mixture of natural gas and steam having a steam to carbon (S : C) ratio of 2.0 was introduced to the system. The natural gas composition of the North Sea was used as the base case (86.72% CH₄, 8.1% C₂H₆,

2.03% C_3H_8 and 0.44% C_4H_{10}). The flow rate of the inlet fuel for all the configurations was $14.2 \text{ cm}^3 \cdot \text{s}^{-1}$, while the inlet air flow rate to the cathode was $94.24 \text{ cm}^3 \cdot \text{s}^{-1}$ to maintain the oxygen utilisation at 25% in the cathode side. SOFC loading voltage of 0.7 V was applied.

Figures 3 shows the concentration profiles of methane, ethane, propane, butane, steam, hydrogen, carbon monoxide and carbon dioxide in the reformer and fuel channel of IIR-SOFC with R_1 , R_2 , R_3 and R_4 reformers, respectively. As expected, the levels of all the hydrocarbons and steam decreased along the length of the reformer, whereas those of hydrogen, carbon monoxide and carbon dioxide increased. At the end of the reformer, all of the hydrocarbons were completely converted. The gaseous products from IIR-SOFC system with R_1 internal reformer contained the highest hydrogen content (75% H_2 , 13% CO , 12% H_2O and 2% CO_2). This gaseous products then flowed backward to the fuel channel of SOFC, and an electrochemical reaction occurred to generate electricity. From the simulation, the vent gas at the outlet of fuel channel consisted of 38% H_2 , 8% CO , 50% H_2O and 14%

CO_2 . The gas compositions at the outlet of the fuel channel of IIR-SOFC were also predicted as 53% H_2 , 19% CO , 19% H_2O and 9% CO_2 for the system with R_2 reformer; 57% H_2 , 18% CO , 20% H_2O and 5% CO_2 for R_3 reformer; and 62% H_2 , 16% CO , 14% H_2O and 8% CO_2 for the system with R_4 , respectively. The hydrogen levels from IIR-SOFC with R_2 , R_3 and R_4 reformers were lower than that from IIR-SOFC with R_1 , which is mainly due to the different amount of catalyst present in the internal reformer and the different levels of water-gas shift reaction taking place in the reformer over these four configurations.

The temperature profiles at the reformer, fuel and air channels of these four IIR-SOFC systems were also predicted. Figure 4 presents the temperature profiles in reformer, fuel and air channel while Figure 5 shows the temperature gradients from COMSOL[®] program. A temperature gradient was observed for all the configurations and cooling spots were observed near the entrance of the reformers. The maximum temperature drop, 93 K, was observed for IIR-SOFC with R_1 reformer, whereas the temperature drop over IIR-SOFC

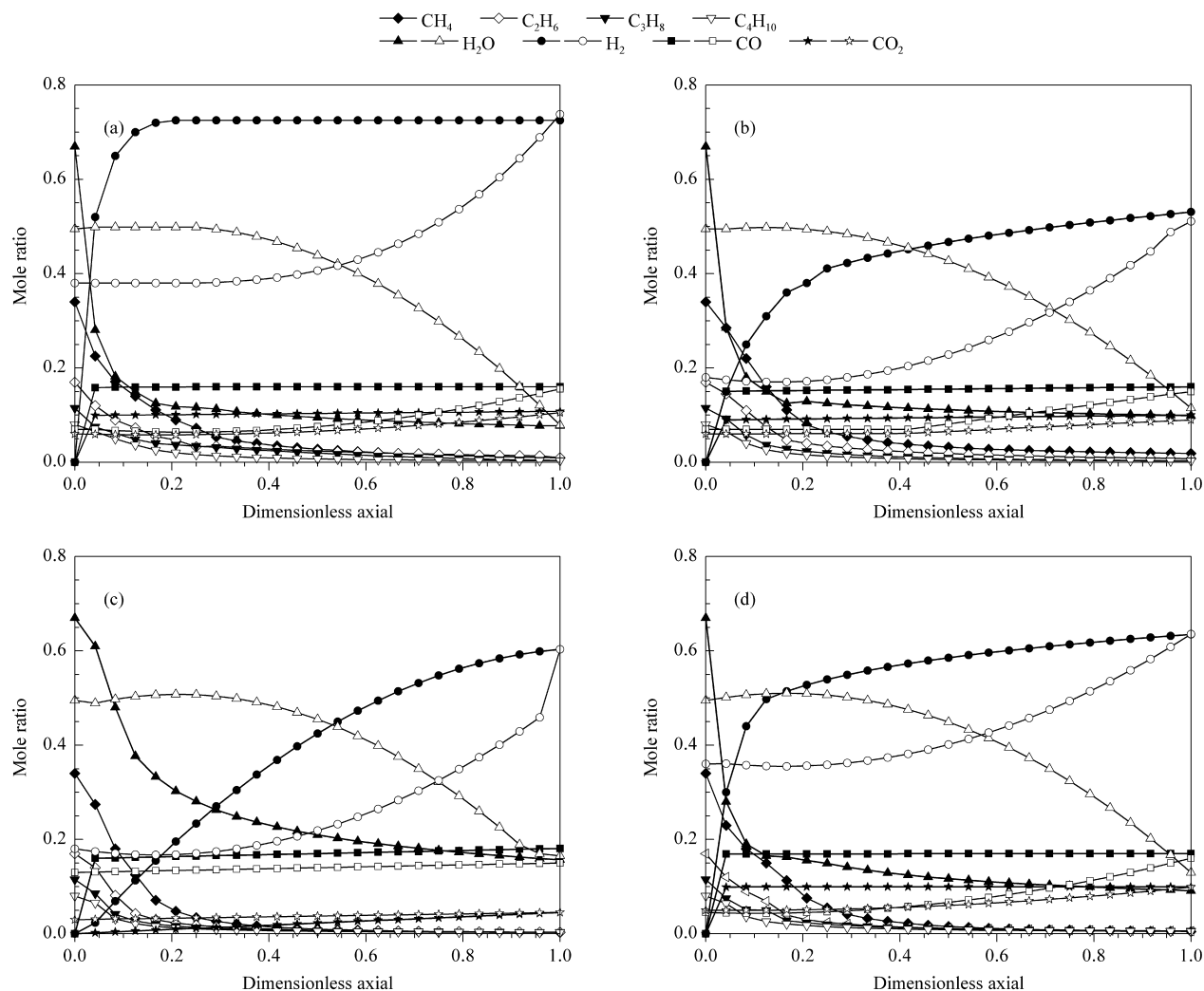


Figure 3. Concentration profiles of IIR-SOFC with (a) packed-bed reformer, (b) coated wall reformer, (c) annular reformer and (d) annular-coated wall reformer operated under constant temperature of 1173 K, pressure of 1 bar, S/C = 2, and co-flow pattern (for each species, solid symbols represent gas concentration in reformer and the rest is in fuel channel)

systems with R₂, R₃, and R₄ reformers were 3 K, 43 K and 33 K, respectively. Furthermore, the differences in the temperature distribution at the reformer, air and fuel channels for IIR-SOFC with R₁ reformer appeared to be the largest, compared with those of the other three systems. Although IIR-

SOFC with R₁ reformer can generate more H₂ content, IIR-SOFC with R₂, R₃ and R₄ reformers would be more compatible with ceramic components of SOFCs, which is subjected to the challenge of a temperature gradient for prolonged operations.

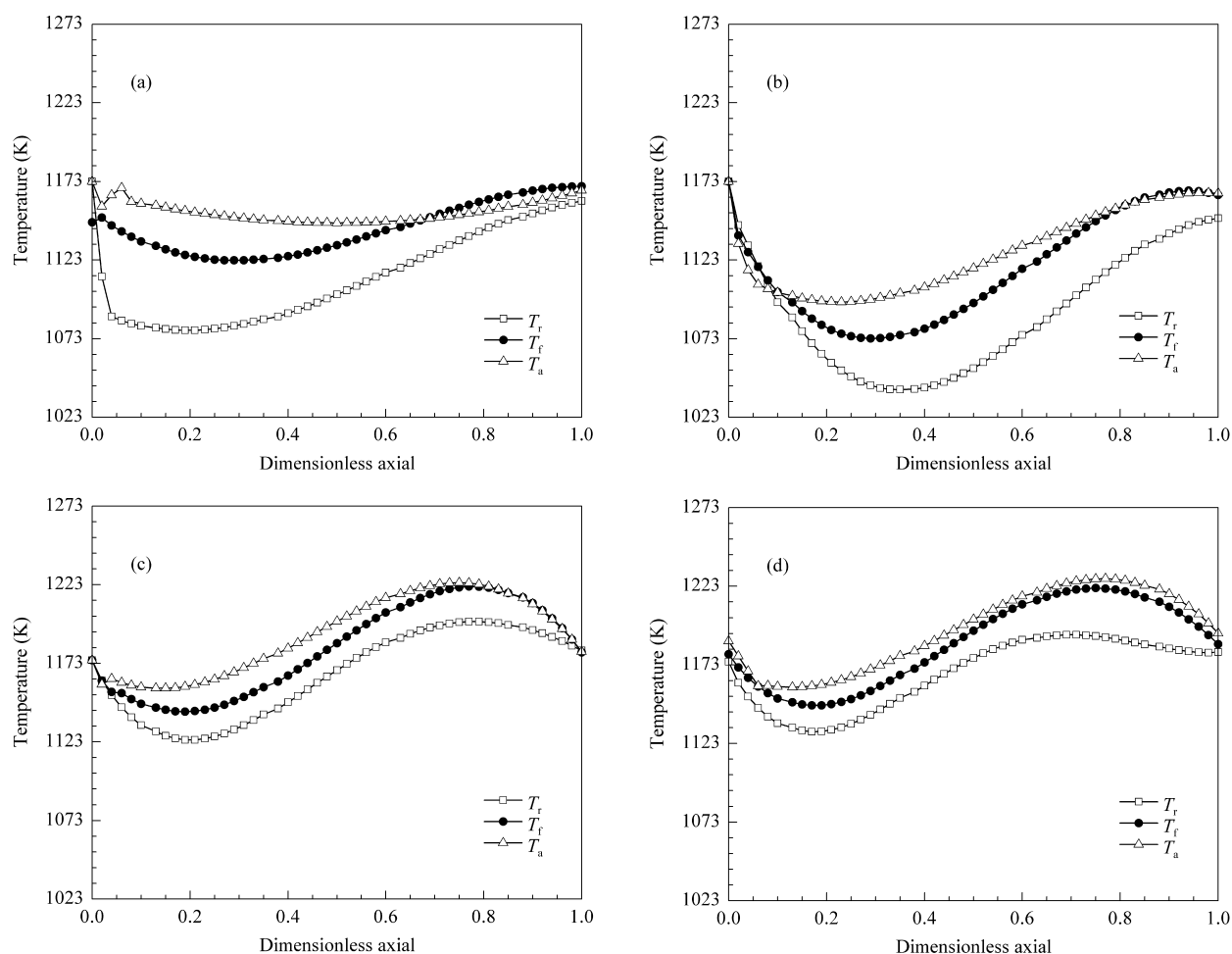


Figure 4. Temperature profiles of the reformer (T_r), fuel channels (T_f) and air channels (T_a) of IIR-SOFC with (a) packed-bed reformer, (b) coated wall reformer, (c) annular reformer and (d) annular-coated wall reformer operated under constant temperature of 1173 K, pressure of 1 bar, S/C = 2, and co-flow pattern

The performance of these four IIR-SOFC systems was then considered in terms of the power density and electrical efficiency. As shown in Figure 6, under the same operating conditions, IIR-SOFC with R₄ reformer provided the highest power density ($0.67 \text{ W} \cdot \text{cm}^{-2}$) and electrical efficiency (68%). The pressure drops across the reformer were predicted to be 2.69×10^{-4} kPa, 3.48×10^{-5} kPa, 2.57×10^{-5} kPa, and 3.53×10^{-5} kPa for IIR-SOFC with the designs R₁, R₂, R₃, and R₄, respectively.

All the simulation results above show that IIR-SOFC with the R₄ reformer can be a potential IIR-SOFC system for a natural gas feed. The system provided the highest power density and electrical efficiency and high H₂ content with acceptable temperature gradient and pressure drop across the reformer. In the next step, the effects of operating parameters on the system performance and temperature gradient were studied in

order to investigate the suitable operating conditions for this IIR-SOFC system.

4.2. Effect of fuel inlet temperature

Decreasing the reformer activity can be a way to reduce the temperature gradient across the reformer system [1,7]. Since the rate equations of methane steam reforming reaction are expressed as a function of temperature, controlling the reformer temperature affects the reforming activity. The reformer temperature can be controlled by the fuel inlet temperature. Therefore, the effects of fuel inlet temperature on the temperature gradient and cell performance were investigated by decreasing the fuel inlet temperature from 1223 K to 1123 K, while the air inlet temperature at cathode side was kept constantly.

As shown in Figure 7, the temperature gradient across the reformer could not be reduced by decreasing the fuel inlet temperature, although the temperature drop at the entrance of reformer decreased when a lower fuel inlet temperature was used. The simulation showed that the use of low fuel inlet temperature reduced the heat accumulated in the system and consequently increased the cell overpotentials and lowered the cell voltage. The lower fuel inlet temperature also affects the conversion rate in the fuel reforming process, leading to lower hydrogen production rate and then higher fuel utilization in SOFC, thus bringing an increase in concentration polarization in SOFC. The cell voltages were 0.772 V, 0.700 V and 0.647 V at 1223 K, 1173 K and 1123 K, respectively.

The inlet temperature therefore affected the power density and electrical efficiency. At 1123 K, the power density was $0.48 \text{ W}\cdot\text{cm}^{-2}$, and the electrical efficiency was 59%. At 1173 K (base case), the power density was $0.65 \text{ W}\cdot\text{cm}^{-2}$, and the electrical efficiency was 64%. At 1223 K, the power density was $0.77 \text{ W}\cdot\text{cm}^{-2}$, and the electrical efficiency was 68%.

The temperature gradient across the reformer could not be decreased using a lower fuel inlet temperature because both the power density and the electrical efficiency also decreased with lower fuel inlet temperature. Therefore, the use of a lower inlet fuel temperature is not a practical solution for IIR-SOFC with R₄ reformer.

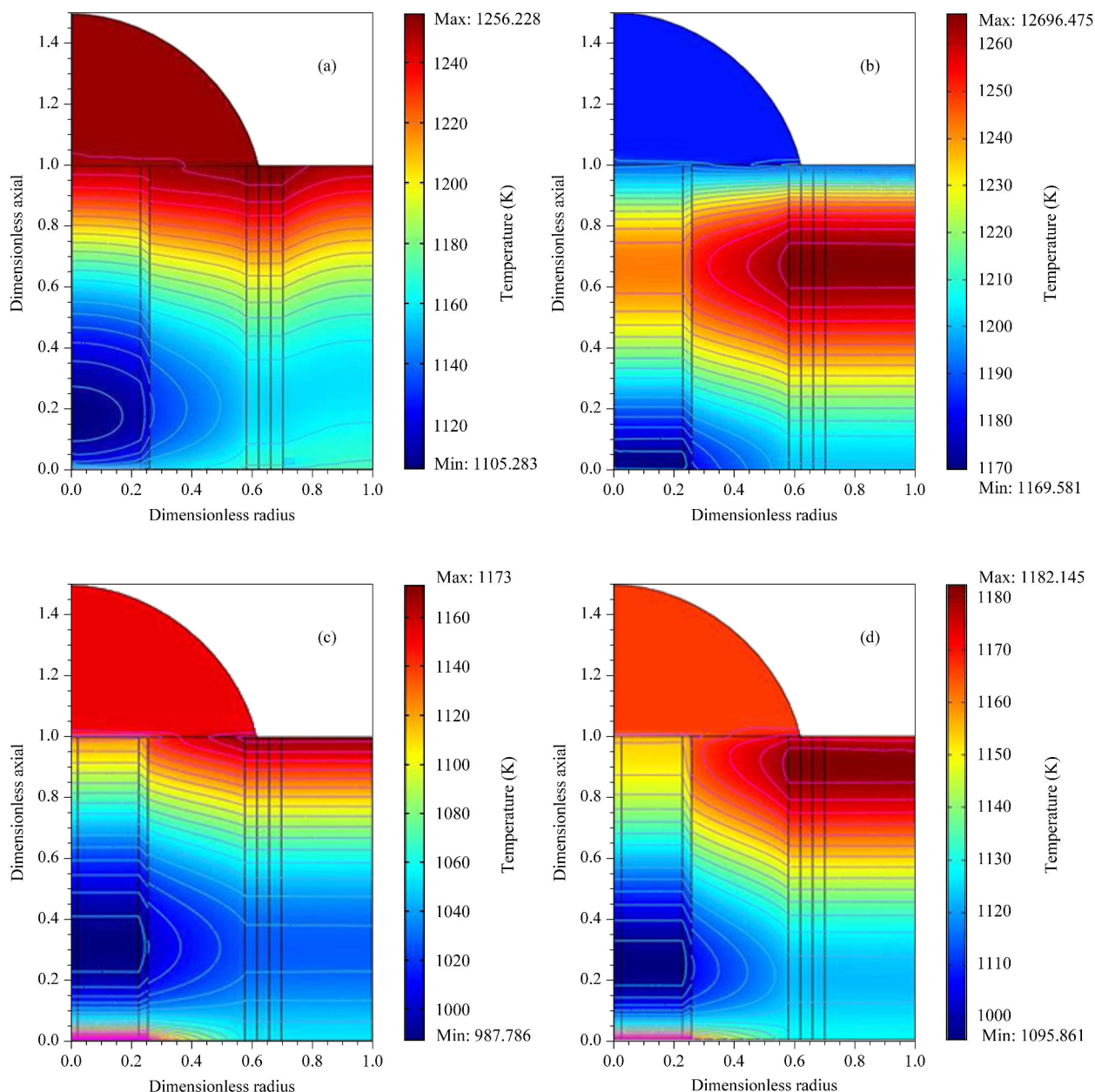


Figure 5. Temperature gradients in the reformer and fuel channel of IIR-SOFC following schematic diagrams in Figure 1: (a) packed bed, (b) coated wall, (c) annular and (d) annular-coated wall reformer (The model was coded in the COMSOL® program at constant temperature of 1173 K, pressure of 1 bar, S/C = 2, and co-flow pattern)

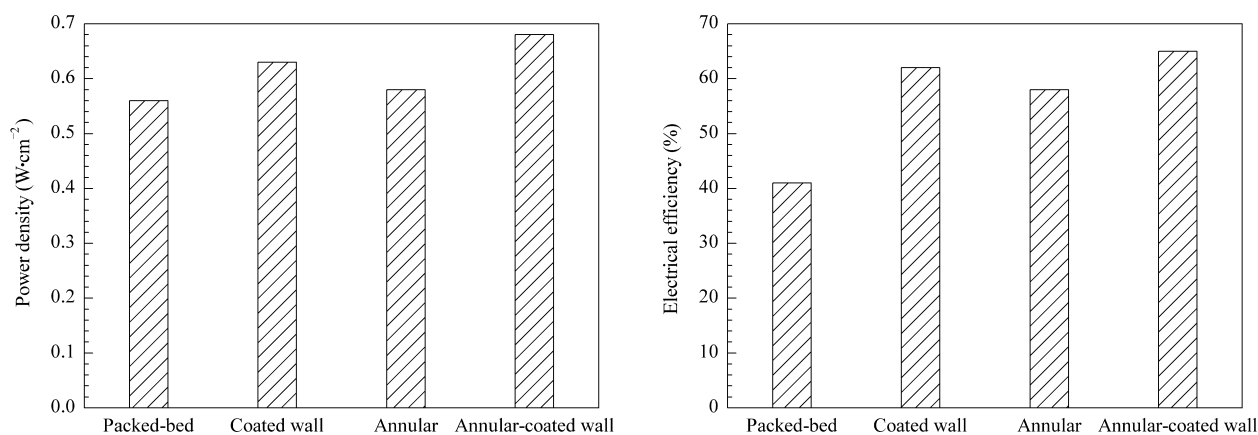


Figure 6. Comparison of power density and electrical efficiency between IIR-SOFC with packed-bed, coated wall reformer, annular and annular coated wall reformers operated under constant temperature of 1173 K, pressure of 1 bar, S/C = 2, and co-flow pattern

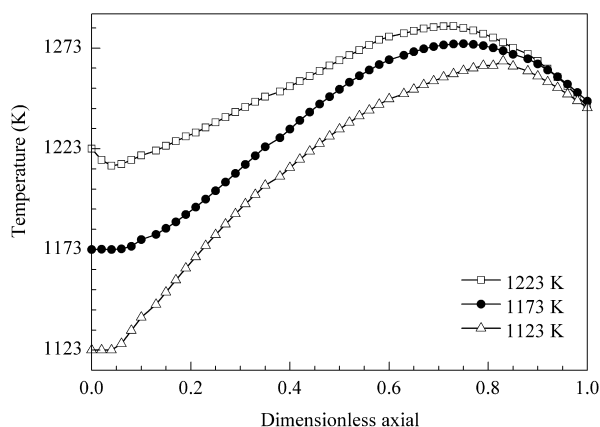


Figure 7. Effect of inlet fuel temperature on the temperature profile of reformer for IIR-SOFC with annular-coated wall reformer operated under constant pressure of 1 bar, S/C = 2, and co-flow pattern

4.3. Effect of operating pressure

The effects of operating pressure on the temperature gradient and cell performance were investigated. Figure 8 shows the influence of the operating pressure on the temperature profiles (between 1 bar and 10 bar) of IIR-SOFC with R_4 reformer when the operating temperature was maintained constantly at 1173 K and S : C was 2.0. The drop in the temperature profile significantly decreased when operating under high pressure mode. This could be caused by the change in partial pressure of gas species involving the steam reforming and electrochemical reactions, since the reaction rate can be decreased by increasing the pressure. The influence of pressure on the gas diffusion is also a possible reason for the decrease in temperature drop.

The power density and electrical efficiency obtained from IIR-SOFC operated at 10 bar ($0.67 \text{ W}\cdot\text{cm}^{-2}$ power density, 66% electrical efficiency) were also slightly higher than those operated at 1 bar ($0.65 \text{ W}\cdot\text{cm}^{-2}$ power density, 64% electrical efficiency). Furthermore, higher open-circuit potential and

lower overpotentials were obtained when IIR-SOFC with R_4 reformer was operated under high pressure mode (10 bar), which in turns leads to higher cell voltages. The cell voltage increased to 0.783 V for the system operated at 10 bar pressure, while that was 0.700 V for the same system operated at 1 bar pressure. Therefore, increasing the operating pressure can not only reduce the temperature gradient across IIR-SOFC with R_4 reformer but also increase the cell performance.

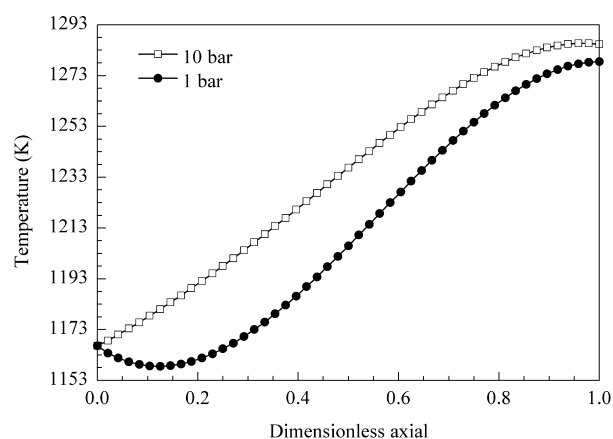


Figure 8. Effect of operating pressure on the temperature profile of reformer for IIR-SOFC with annular-coated wall which operated under constant temperature of 1173 K, S/C = 2, and co-flow pattern

4.4. Effect of steam to carbon ratio

The effects of inlet steam content on the temperature gradient along the system and on the system performance were investigated by varying the inlet steam to carbon (S : C) ratio from 2.0 to 4.0. Figure 9 shows the effect of inlet S : C ratio on the temperature profile of IIR-SOFC with R_4 reformer. When S : C was increased, the temperature gradient in the reformer, fuel and air channels decreased. This decrease could be due to the accumulated heat in the system since excess steam fed to the system could be further used in endothermic reactions in

the reformer. However, the use of a high inlet S : C ratio significantly reduced the electrical efficiency from 67% to 35% when S : C was 2.0 and 4.0, respectively. This was caused by fuel dilution.

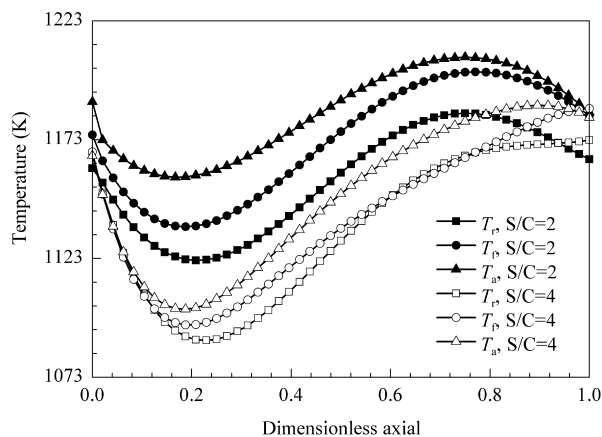


Figure 9. Effect of S : C ratio on temperature profile of IIR-SOFC with annular-coated wall reformer operated under constant temperature of 1173 K, pressure of 1 bar, and co-flow pattern

4.5. Effect of flow direction

The comparison of counter-flow pattern and co-flow pattern (shown in previous section) was done. Figure 10 shows the temperature profiles in the reformer, air and fuel channels of IIR-SOFC with R₄ reformer operated under a counter-flow pattern. By comparing the temperature gradients across the system for R₄ reformer under a co-flow pattern (Figure 4d), it can be seen that flow pattern significantly affected the temperature gradient. The temperature gradient at the entrance of the reformer over R₄ reformer with the counter-flow pattern was higher than that with the co-flow pattern. Under the counter-flow pattern, the significant temperature increase along the air flow channel could be due to the heat accumulation along SOFC. For the co-flow system, heat was firstly generated at

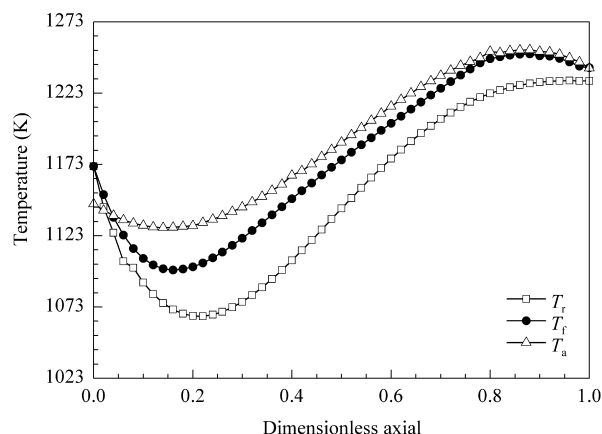


Figure 10. Temperature profiles of the reformer (T_r), fuel channels (T_f), and air channels (T_a) of IIR-SOFC with annular-coated wall reformer operated under counter-flow pattern

the end of the channel ($z = 1$) and then accumulated along the air and steam until reaching the entrance of reformer ($z = 0$); thus, the temperature gradient became smoother. The average temperature in IIR-SOFC with the co-flow pattern was higher than that with the counter-flow pattern, leading to a greater mean cell temperature and lower overpotential. The power density and electrical efficiency of R₄ reformer operated under a counter-flow pattern were $0.62 \text{ W}\cdot\text{cm}^{-2}$ and 61%, respectively, which were lower than those ($0.62 \text{ W}\cdot\text{cm}^{-2}$ and 68%) conducted under a co-flow pattern.

4.6. Effect of natural gas composition

The effect of natural gas composition on IIR-SOFC performance (temperature profile, power density and electrical efficiency) was investigated. Table 2 shows pure methane and three different compositions of natural gas that were used: the base case (North Sea source), raw and sale natural gases from the Gulf of Thailand.

Table 2. Composition of natural gas in base case, raw and sale natural gas from Thailand gulf

	Compositions (vol%)				
	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	CO ₂
The North Sea (base case)	86.72	8.10	2.03	0.44	—
Raw natural gas from Thailand gulf	67.39	9.33	5.15	2.22	14.26
Sale natural gas from Thailand gulf	72.31	7.24	2.19	0.93	14.70

The thermodynamic properties of these different compositions of natural gas were identified in terms of lower heating value (LHV) and thermal efficiency. The LHV value and thermal efficiency of fuel are shown in Figure 11. Although the base case had the highest LHV value, pure methane had the highest thermal efficiency.

Figure 12 shows the temperature gradients in the reformer, fuel and air channels of IIR-SOFC fuelled by natural gas from different sources. As shown in this figure, the composition of the natural gas significantly affected the temperature profile, i.e., IIR-SOFC fuelled by raw natural gas and sale natural gas showed smoother temperature gradients than those of base case and pure methane. There were also temperature drops at the inlet of the reactor channel in every category. Pure methane exhibited a temperature drop in the reactor channel from 1173 K to 1020 K, while the temperature dropped to 1070 K, 1071 K and 1098 K for base case, raw gas and sale gas, respectively. The average temperature for IIR-SOFC with R₄ reformer tube, which was fuelled by pure methane and the North Sea natural gas, was higher compared with those of raw and sale natural gases, likely because of the content of methane in the feedstocks. The higher content of methane in the base case resulted in a stronger endothermic steam reforming reaction at the entrance of the reformer section, which consequently resulted in a larger temperature drop over this area.

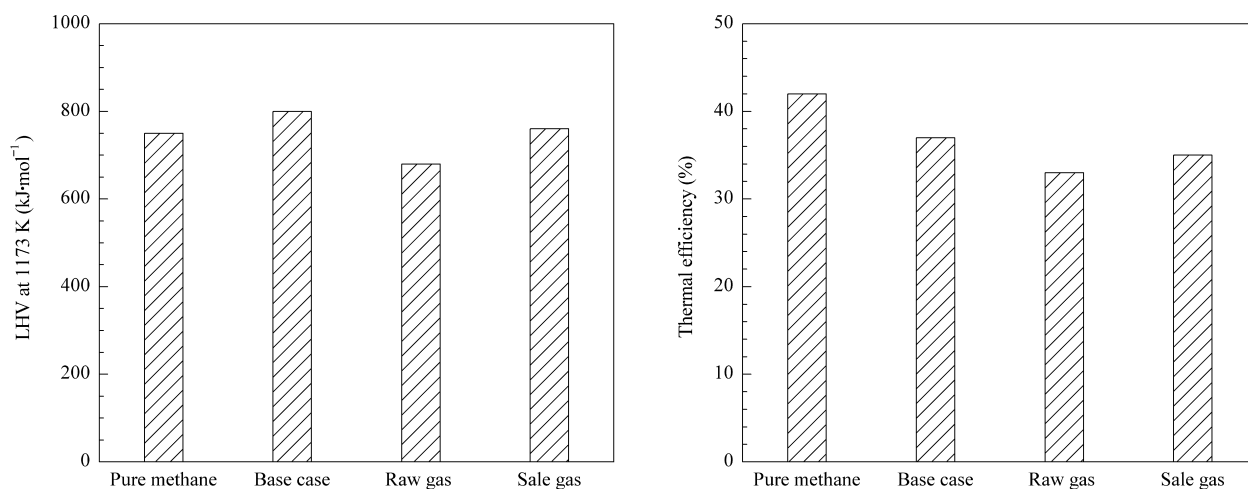


Figure 11. Thermal properties (LHV and thermal efficiency) of each fuel under isothermal condition (1173 K and 1 bar)

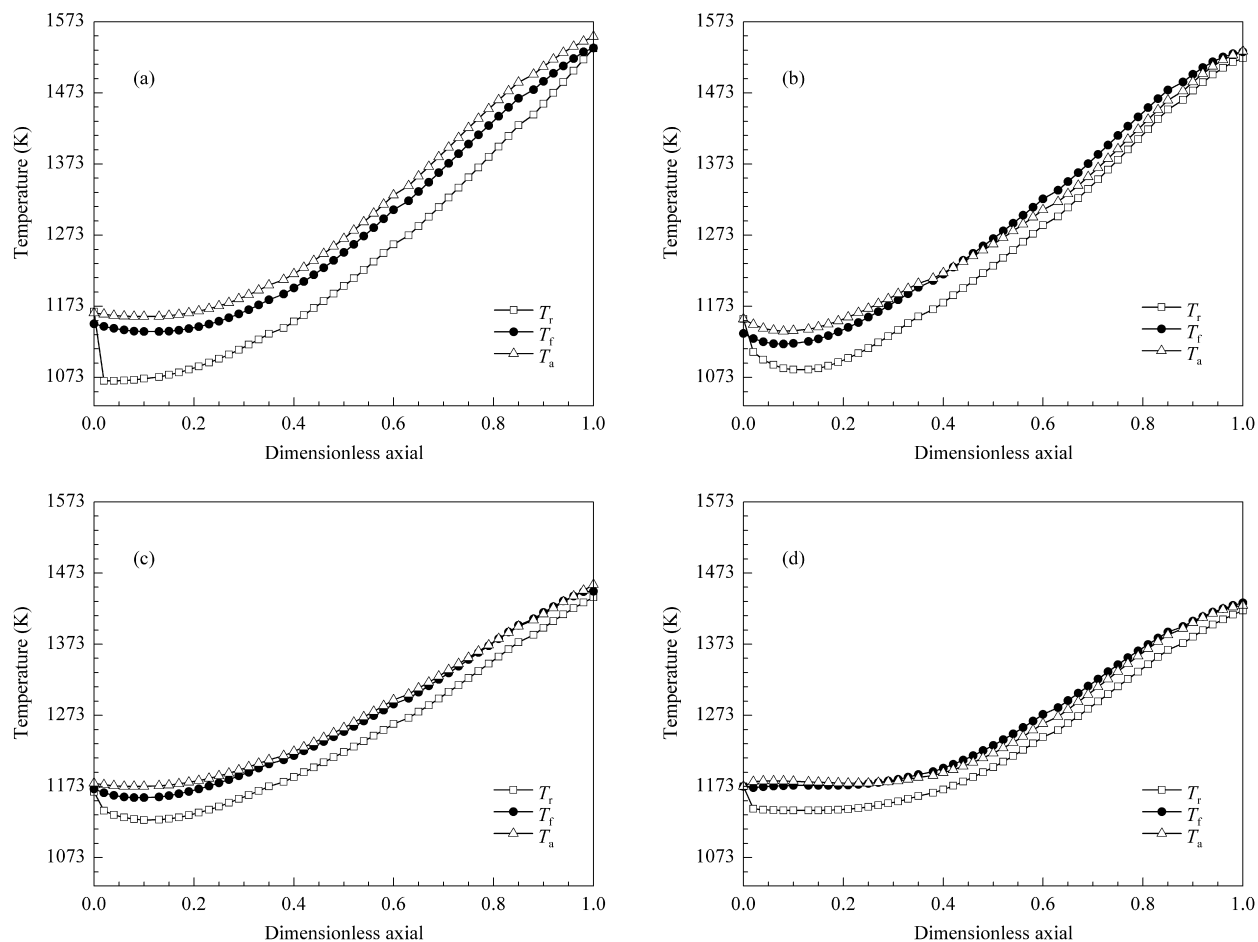


Figure 12. Effect of natural gas composition on temperature profile operated under co-flow pattern at 1173 K. (a) Pure methane, (b) Base case, (c) Raw natural gas from Gulf of Thailand, (d) Sale natural gas (raw natural gas after treated)

The natural gas composition also affects the electrical efficiency and power density. As shown in Figure 13, the power densities for pure methane, base case, raw natural gas and sale natural gas were $0.6 \text{ W}\cdot\text{cm}^{-2}$, $0.52 \text{ W}\cdot\text{cm}^{-2}$, $0.45 \text{ W}\cdot\text{cm}^{-2}$ and $0.48 \text{ W}\cdot\text{cm}^{-2}$, respectively. The electrical

efficiencies for pure methane, base case, raw natural gas and sale natural gas were 45%, 41%, 37% and 39%, respectively. Thus, the electrical efficiency and power density increased with the increasing methane content in the feedstocks.

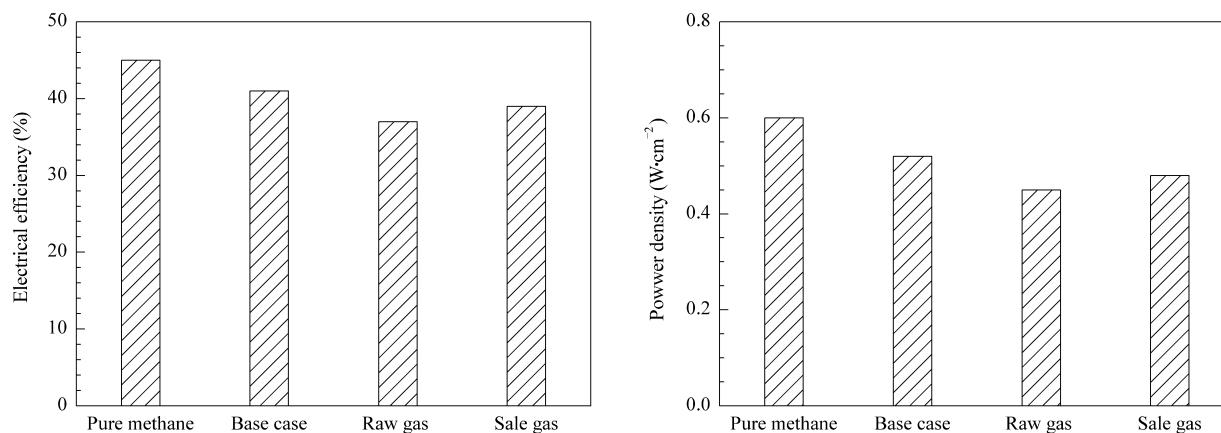


Figure 13. Electrical efficiency and power density achieved by IIR-SOFC fuelled by different composition of natural gas, required volumetric flow rate of each fuel operated at 1173 K, 1 bar and under co-flow pattern

5. Conclusions

The simulations of a IIR-SOFC fuelled by natural gas with a conventional R_1 reformer indicated that all the hydrocarbons in natural gas (i.e., methane, ethane, propane and butane) were rapidly consumed by the reformer. Hence, the temperature appeared to drop sharply at the entrance of the reformer, and this drop was mainly related to the mismatch between the rapid endothermic steam reforming reaction rate and the amount of heat supplied from the electrochemical reaction. On the other hand, IIR-SOFC with the internal R_2 , R_3 and R_4 reformers provided smoother natural gas conversion and a low temperature drop at the entrance of the internal reformer, which are more compatible to SOFC material. In addition, a significantly higher power density and electrical efficiency as well as lower pressure drop can be achieved, particularly in the case of IIR-SOFC with R_4 reformer.

A sensitivity analysis of selected parameters was then performed for IIR-SOFC with R_4 reformer. IIR-SOFC with a co-flow (of fuel and air) pattern provided a higher voltage and smoother temperature gradient along the system than that with a counter-flow pattern. The reduction of fuel inlet temperature resulted in a smoother temperature profile at the entrance of the reformer but also led to an increase in cell overpotentials and consequently reduced the cell voltage. Increasing the operating pressure resulted in an increased system efficiency and a reduced temperature drop at the entrance of the internal reformer. The use of a high inlet steam to carbon (S : C) ratio also reduced the temperature drops as well as the electrical efficiency.

Lastly, it was observed that the composition of natural gas also played an important role in the thermal and electrical performance of IIR-SOFC. Comparing natural gas from the North Sea to natural gas from Thailand (i.e., the raw gas from the Gulf of Thailand, and the sale natural gas after processing), Thai natural gas had lower methane content and provided a smoother temperature gradient along SOFC system but achieved a lower power density and electrical efficiency.

Acknowledgements

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Nomenclatures

A_{act}	Active surface area (m ²)
IIR-SOFC	Indirect internal reformer solid oxide fuel cell
k_p	Permeability
$D_{i,j}$	Binary diffusion flux (m ² ·s ⁻¹)
$D_{i,mix}$	Molecular diffusivity of component i in mixed gas (m ² ·s ⁻¹)
$D_{i,pmix}^e$	Effective diffusivity coefficient (m ² ·s ⁻¹)
$D_{i,pmix}$	Gas diffusion through porous media (m ² ·s ⁻¹)
$D_{i,ku}$	Knudsen diffusivity coefficient (m ² ·s ⁻¹)
Eff_{elec}	Electrical efficiency (%)
$Eff_{thermal}$	Thermal efficiency (%)
F	Faraday constant (9.6495 × 10 ⁴ C·mol ⁻¹)
J_0	Exchange current density (A·m ⁻²)
J_i	Current density (A·m ⁻²)
$LHV_{i,1173\text{ K}}$	Lower heating value of component i at 1173 K
M_i	Molecular weight of component i (g·mol ⁻¹)
n_i	Moles of component i (mol)
$\dot{n}$	Molar flow rate of the inlet gas
P_{SOFC}	Power density (J·s ⁻¹ ·m ⁻²)
p	Pressure (bar)
R	Universal gas constant (8.3145 J·mol ⁻¹ ·K ⁻¹)
R_{elec, H_2}	Conversion rate of H ₂
R_{elec, O_2}	Conversion rate of O ₂
R_{ohm}	Ohmic resistance per unit area (k ⁻¹ ·m ⁻²)
T	Temperature (K)
y_i	Mole fraction of species i

Greeks letters

ε	Porosity
η_{act}	Activation loss (V)
η_{conc}	Concentration loss (V)
η_{ohm}	Ohmic loss (V)

- ρ Fluid phase density ($\text{kg}\cdot\text{m}^{-3}$)
 $\vec{\mu}$ Effective viscosity ($\text{Pa}\cdot\text{s}$)
 $\vec{v}$ Fluid velocity ($\text{m}\cdot\text{s}^{-1}$)
 γ Special diffusion volume reported by Fuller et al. (1966) [26]

Subscripts and superscripts

- a Anode
 c Cathode
 H₂ Hydrogen
 H₂O Steam
 O₂ Oxygen
 CO Carbon monoxide
 CO₂ Carbon dioxide
 in Inlet fuel

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